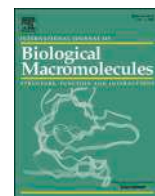


Portofoliu lucrări relevante în domeniul tezei

- 1) **Stanciu M.D.**, Teodorescu H.D., Vlase S., Mihalica M., Cosnită M., Savin A, Multiscale assessment of artificial aging treatment of polysaccharides from tonewood species, *Int. J. Biol. Macromol.*, Volume 274, Part 1, 2024, 133310, <https://doi.org/10.1016/j.ijbiomac.2024.133310>.
<https://www.sciencedirect.com/science/article/pii/S0141813024041151>
- 2) Gurău, L.; Timar, M.C.; Coşereanu, C.; Cosnita, M.; **Stanciu, M.D. (autor corespondent)**, Aging of Wood for Musical Instruments: Analysis of Changes in Color, Surface Morphology, Chemical, and Physical-Acoustical Properties during UV and Thermal Exposure. *Polymers* 2023, 15, 1794. <https://doi.org/10.3390/polym15071794>
- 3) **Stanciu, M.D.**; Cosnita, M.; Gliga, G.V.; Gurau, L.; Timar, C.M.; Guiman, M.V.; Năstac, S.M.; Roşca, I.C.; Bucur, V.; Dinulică, F. Tunable Acoustic Properties Using Different Coating Systems on Resonance Spruce Wood. *Adv. Mat. Interfaces* 2024, 1, 2300781, <https://onlinelibrary.wiley.com/doi/10.1002/admi.202300781>
- 4) **Stanciu, M.D.**; Timar, M.C.; Mihalica, M.; Cosnita, M.; Dinulică, F. Comparisons of the Effects of Polymer and Alcohol Varnishes on Norway Spruce Wood Surface Modifications. *Polymers* 2025, 17, 2131. <https://doi.org/10.3390/polym17152131>
- 5) **Stanciu, M.D.**; Guiman, M.V.; Năstac, S.M. (2025e) New Challenges in Assessment of the Acoustic Properties of Coating Polymers. *Polymers* 2025, 17, 1418. <https://doi.org/10.3390/polym17101418>
- 6) Faktorová, D.; **Stanciu, M.D. (autor corespondent)**; Krbata, M.; Savin, A.; Kohutiar, M.; Chlada, M.; Năstac, S.M. Analysis of the Anisotropy of Sound Propagation Velocity in Thin Wooden Plates Using Lamb Waves. *Polymers* 2024, 16, 753. <https://doi.org/10.3390/polym16060753>
- 7) **Stanciu, M.D.**; Teodorescu, H.D.; Vlase, S. (2020) Degradation of Mechanical Properties of Pine Wood Under Symmetric Axial Cyclic Loading Parallel to Grain. *Polymers* 2020, 12, 2176. <https://doi.org/10.3390/polym12102176>
- 8) **Stanciu M.D.**, Ardeleanu A.F., Teodorescu Draghicescu H, Reverse engineering in finite element analysis of the behaviour of lignocellulosic materials subjected to cyclic stresses, in *Procedia Manufacturing* 22 (2018), pp 65-72, 11th International Conference Interdisciplinarity in Engineering, INTER-ENG 2017, 5-6 October 2017, Tirgu Mures, Romania. <https://www.sciencedirect.com/science/article/pii/S2351978918303056>
- 9) **Stanciu M.D.**, Bucur V., Valcea C. S., Savin A., Sturm R., (2018) Oak particles size effects on viscous-elastic properties of wood polyester resin composite submitted to ultraviolet radiation, *Wood Sci Technol* 52 (2): 365-382. <https://link.springer.com/article/10.1007/s00226-017-0971-0>
- 10) **Stanciu M.D.**, Teodorescu D. H., Tămaş F., Terciu O.M. Mechanical and Rheological Behaviour of Composites Reinforced with Natural Fibres, *Polymers* 2020, 12 (6), 1402, <https://www.mdpi.com/2073-4360/12/6/1402>



Multiscale assessment of artificial aging treatment of polysaccharides from tonewood species

Mariana Domnica Stanciu^{a,*}, Horatiu Draghicescu Teodorescu^a, Sorin Vlase^a,
Mircea Mihalca^a, Mihaela Cosnita^b, Adriana Savin^{a,c}

^a Faculty of Mechanical Engineering, Transilvania University of Brasov, 29 Eroilor, 500036, Brasov, Romania

^b Department of Product Design Mechatronics and Environment, Transilvania University of Brasov, 29 Eroilor, 500036, Brasov, Romania

^c Institute of Research and Development for Technical Physics, B-dul Mangeron 47, 700050, Iasi, Romania

ARTICLE INFO

Keywords:

Aging
Acoustic
Mechanical properties
Photo-degradation
Crystallinity

ABSTRACT

In the acoustics of musical instruments with a resonator body, the aging of the wood leads to the improvement of the acoustic properties due to increasing the crystallinity of wood. This phenomenon could be explained by the fact that wood is a complex product based on three-dimensional polymer chains of carbohydrates, its aging being closely related to covalent cross-linking and scission of polymer chains. The aim of this study was to evaluate at a multiscale the changes produced artificial aging of tone wood by measuring the acoustic, mechanical and chemical parameters. The spruce and maple wood samples were investigated before and after exposure to ultraviolet (UV) radiation, through the tensile test, the time-of-flight method (TOF), the analysis of the wood color and the determination of the chemical fingerprint through Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD). The obtained results showed that the effects of artificial aging are manifested at the chemical level where the crystallinity increases up to the acoustic level, depending on the wood species and their quality class. These results are relevant for musical instrument manufacturers to find treatments that lead to superior acoustic properties.

1. Introduction

In the acoustics of musical instruments with a resonator body, it has been assumed that the aging of wood leads to improved acoustic properties. To understand how wood aging contributes to the acoustic qualities of musical instruments, it is essential to analyze detailed and accurate information about the architecture and properties of the resonance wood at different scales [1–3]. The improvement of the acoustic quality of the soundboard through aging starts from the chemical level, by increasing the degree of crystallinity of the cellulose and decreasing the content of amorphous carbohydrates. Analyzing the phenomenon of artificial aging from the macroscale to the nanoscale, it can be considered that the chemical changes produced by artificial aging are manifested by breaking the covalent bonds in the organic compounds of wood, reducing the mass, increasing the stability to humidity variations, and decreasing the lignin content. Even if the chemical changes are not quantitatively at the mechanical/elastic level, nevertheless, at the acoustic level they increase the sound propagation speed. The aging of

wood, both through photo-degradation processes and through thermal oxidation, produces changes in the structure of the wood, visible on X-ray radiographs through the difference in the density of the woody compared to that of unaged wood [3–6]. From the point of view of the chemical architecture of wood, it is a complex natural carbohydrate product based on three-dimensional polymer chains of carbohydrates, namely cellulose, hemicellulose and lignin, with minor amounts of extractives and inorganic compounds. In the case of wood for musical instruments, i.e. spruce (*Picea abies* Karst. L.) and maple (*Acer pseudo-platanus* L.), cellulose is found in a proportion of approximately 50.69–50.90 %, being a linear homopolysaccharide, composed of β -D-glucopyranos units, with β -1,4-glycosides covalent bonds, having the role of strengthening the cell walls (Fig. 1a) [7–9]. According to [7–12], hemicelluloses are amorphous polymers, acting as binders in cell walls and ensuring their flexibility. Hemicelluloses have also been found to be essential for the formation of the cellulose microfibril structure during the deposition of cellulose in the cell wall. Hemicelluloses represent a large group of branched heteropolymers, composed of several

* Corresponding author.

E-mail addresses: mariana.stanciu@unitbv.ro (M.D. Stanciu), draghicescu.teodorescu@unitbv.ro (H.D. Teodorescu), svlase@unitbv.ro (S. Vlase), mihalca.mircea@unitbv.ro (M. Mihalca), mihaela.cosnita@unitbv.ro (M. Cosnita), asavin@phys-iasi.ro (A. Savin).

<https://doi.org/10.1016/j.ijbiomac.2024.133310>

Received 30 October 2023; Received in revised form 23 May 2024; Accepted 12 June 2024

Available online 21 June 2024

0141-8130/© 2024 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

monomeric units, of which, studies have shown that in softwood such as spruce, xyloglucans have a structural role in the primary cell walls forming, together with cellulose, a load-bearing network that prevents cell breakage under mechanical stress. Fig. 1b shows the structure of xyloglucans. Lignin constitutes a group of branched aromatic biopolymers, being an amorphous carbohydrate, made up of hydroxyphenyl propane units, in a three-dimensional structure. Studies have shown that the main compounds of native lignin are the monolignols known as p-cumaryl alcohol, coniferyl alcohol and sinapyl alcohol (Fig. 1c). Lignin is predominantly found in the secondary cell wall, ensuring the compression resistance of the fibers but also a hydrophobic surface of the fibers, necessary for the transport of water [11–13]. The chemical structure of wood is presented in numerous studies, with details of the chemical compounds and their location in the architecture of the cellular walls of the wood, in both spruce and maple wood.

Cellulose, hemicellulose and lignin chains are found in different proportions and the way the cell walls are formed depends on the genetic information of the wood species. Thus, in spruce wood, the cells with the role of resistance and water transport are the tracheids, and in maple wood, the axial system is made up of fibers and vessels. In musical instruments, in the dry state of the wood, these formations are responsible for the transmission of sounds and vibrations in the longitudinal direction. The effect of wood aging on physical and mechanical properties has been studied, but the literature is quite poor in terms of studies on light photodegradation and thermal oxidation treatments in order to increase the acoustic performance of wood. The aging of the wood can be visually observed by the change in the color of the wood, the color change being large at the beginning of the aging, after which it decreases over time.

According to [14–16], artificial aging methods, such as the light-fastness test with a UVA 351 lamp or heat treatment, have proven to be adequate to simulate color changes due to natural aging. On the other hand, aging by applying a thermal oxidation process leads to the degradation of hemicelluloses, an effect reported by many authors [17–19]. Simultaneous exposure to UV radiation and mild thermal treatment produces color changes and changes in mechanical and durability properties [19–21]. As the hydroxyl content of hemicelluloses decreases, the wood becomes less hydrophilic, resulting in lower equilibrium moisture content (EMC) and better dimensional stability [3,22–24]. This was explained by [8] by the fact that lignin is associated

with hemicelluloses, so that lignin carbohydrate complexes are formed, which are resistant to hydrolysis. The weight loss observed during heat treatment by [3,19], is considered also caused by the degradation of hemicelluloses. [25] highlights the fact that artificial aging can change (usually increase) the specific modulus (specific dynamic Young's modulus) E'/ρ of wood without changing the value of the damping ($\tan \delta$). Thus, to increase the specific dynamic Young's modulus, the dry mass loss should be a maximum of 2–3 % by applying a heat treatment at 100 °C and 63 % RH for 30 days, which could lead to wood characteristics corresponding to 500 years of aging. Analyzing the mechanical behavior of modern and aged hinoki wood in the radial (R) and longitudinal (L) directions, [25] found that the difference in behavior between the L and R directions can be explained by the different structural organization of the wood fibers, the post-linear (?) being influenced by the age of the wood.

Thus, the aged wood was brittle, results that correlate with chemical analyzes and thermo-mechanical tests performed in parallel, showing a decrease in hemicellulose content, as well as an increase in lignin crosslinking [25]. Studying the vibrational properties of aged wood (approx. 300 years) compared to those of new wood (8 years old), [26] observed that the wood presented a higher longitudinal and transverse stiffness, a higher speed of sound in the longitudinal direction and a lower damping in the longitudinal direction than the current wood. There are still many controversies concerning the effect of aging on elastic, acoustic and chemical properties. Contrary to the results highlighted by [26], the studies [27–28] show that there are no significant differences from a chemical point of view, between the wood of the old Cremonese violins and the new wood.

Since there are so many controversies related to the effect of artificial aging of wood on its acoustic properties, the main objective of the present paper was to investigate the effect of artificial aging on the physical, elastic, acoustic and chemical properties of the wood to be used for musical instruments. The novelty of the study consists in the multiscale evaluation of the chemical, mechanical and acoustic changes produced by the artificial aging of the current resonance wood in relation to the anatomical structure of the tonewood. Exposing the wood to UV radiation that penetrates the surface of the wood with a maximum depth of 2.5 mm, thickness close to the thickness of the violin boards [29] can be a method to improve the acoustic performance of tone wood, before the final manufacture of the violin.

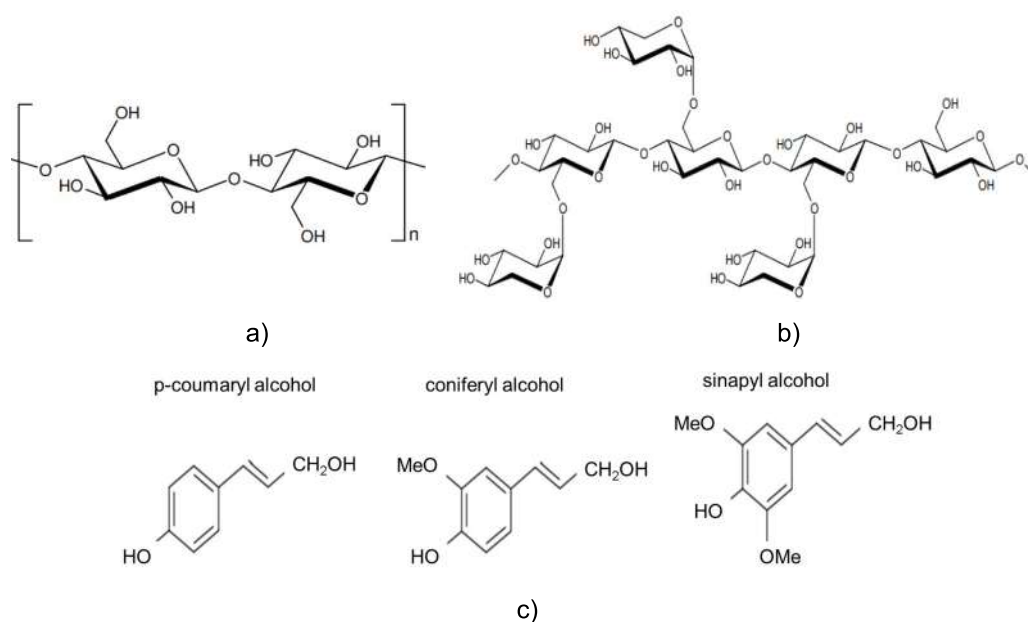


Fig. 1. The main structural polymers from wood: a) β -D-glucopyranose unit from cellulose chain; b) the structure of xyloglucans (hemicellulose); c) the main compounds of native lignin.

2. Materials and methods

2.1. Sample preparation

The wood samples were made of two wood species used for the construction of violins: spruce (*Picea abies* (L), Karst) and maple (*Acer pseudoplatanus*, L). Two sets of samples were prepared: one as control, and the other to be aged. The wood samples were provided by a musical instrument factory. The set of control samples was tensile tested, and the other samples were exposed to artificial aging for 1000 h. After exposure, the samples were investigated for the determination of mass, color and chemical composition, as well as for the comparative processing of the results with the initial data and those of the control samples. Fig. 2 shows the shape and dimensions used both for the tensile test and the velocity of sound measurement (TOF method). The samples were extracted from boards dried naturally for 3 years and mechanically processed under identical conditions. Then, the boards were conditioned to reach a moisture content of 6–8 %. Within each set of samples there were four categories of samples: those from spruce wood, anatomical class A, coded Spruce A, respectively anatomical class D, coded Spruce D, as well as those from maple wood, anatomical class A, coded Maple A, respectively anatomical class D, coded Maple D, according to the description of these categories indicated in previous studies [30–31]. The samples were prepared according to the SR EN 408:2004 standard, obtaining dog-bone type samples, specific to the tensile test (Fig. 2) and samples for the ultrasonic test (US) based on time of flight method (TOF) [32–35]. Table 1 shows the mean values of physical characteristics and sample sizes.

2.2. Methods

2.2.1. Artificial aging of wood

The wood samples were introduced into a photocatalytic reactor being exposed to the ultra-violet (UV) radiation produced by the 3 UV tubes (Philips, TL-D BLB 18 W/108) and 4 VIS light tubes (Philips, TL-D Super 80 18 W/ 865), for a period of 1000 h. The radiation emitted by

the UV tubes had wavelengths between 340 and 400 nm, with wavelength $\lambda_{\max}$ (emission) = 365 nm, and the average value of UV radiation measured with a Delta-T pyranometer, type BF3 was 3 W/m^2 [32,36,37]. Periodically, the samples were controlled, rotated so that there was a uniform exposure on all surfaces. The distance between the samples and the lamps inside the reactor during irradiation was 20 cm, and the temperature inside the irradiation chamber was 50°C .

2.2.2. Tensile test

To evaluate the changes produced by artificial aging from the mechanical point of view, the elastic characteristics of the wood samples were subjected to the static tensile test also presented in previous works [38–39]. The tests were carried out on the LS100 Lloyd's Instrument universal testing machine belonging to the Mechanical Engineering Department of Transilvania University in Braşov. The samples were loaded at a constant rate of 1 mm/min until failure. Elongation was measured simultaneously with loading using the extension device. Nexygen Plus software was used for data acquisition. Following the tensile tests, the stress-strain curves, the strain (ϵ), the longitudinal elastic modulus (denoted $E_{L,static}$), the specific modulus ($E_{L,static}/\rho$), the tensile stress (σ), and the stiffness of each category of samples (S), were determined before and after aging.

2.2.3. Determination of sound velocity in wood based on time of flight method (TOF)

The measurement of the velocity of sound propagation in wood in the longitudinal direction (denoted V_L) was carried out using a portable ultrasound device, LUCCHIMETTER, Cremona Italy. The samples, on which the US measurements were performed, were obtained from the same material as the samples used for the tensile test and exposed to the same aging conditions. The determination of sound velocity is based on the time of flight method, which measures the travel time of the wave between two sensors that are inserted into the sample [30,35,40–42]. Delaying the signal over a known distance between the transmitter and the receiver of the US equipment allows the stress wave speed to be calculated. The measurements were carried out under laboratory

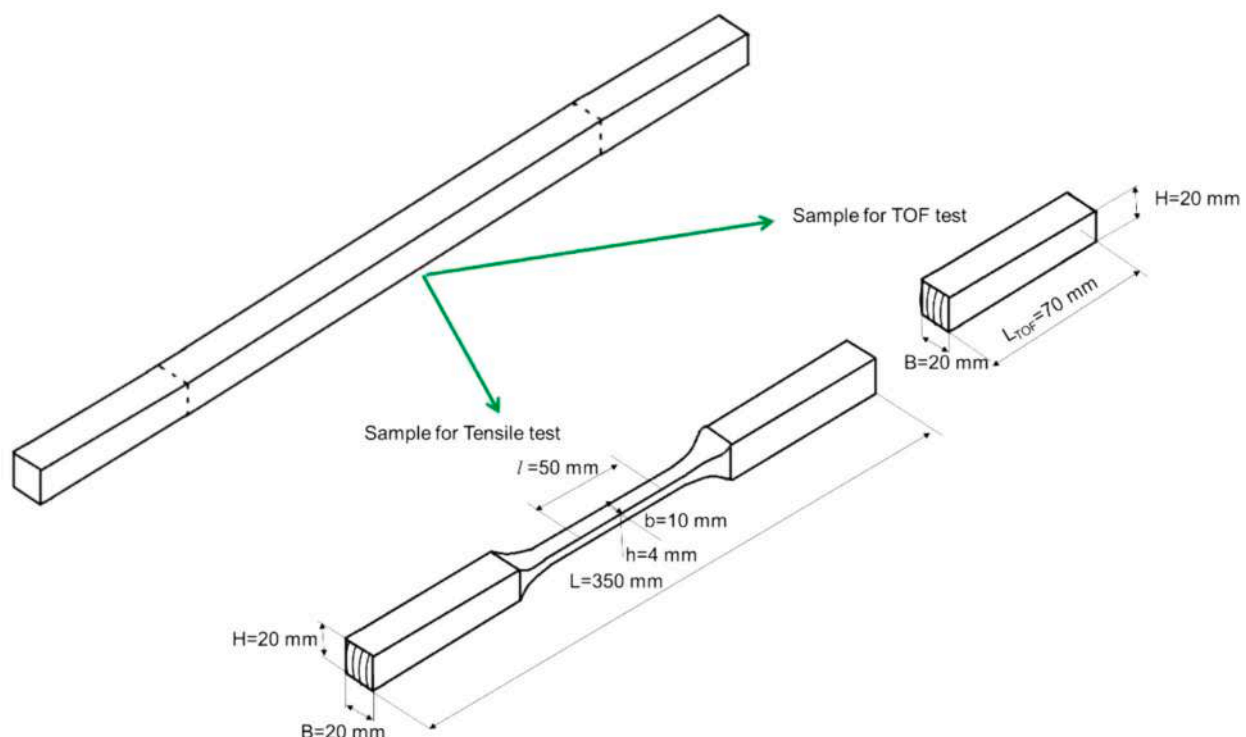


Fig. 2. The geometry of the samples prepared for the experimental investigations.

Table 1

Mean values and standard deviation of the physical characteristics of the tested samples.

Type of samples	Tensile test				TOF test			No of samples
	MC (%)	Width b (mm)	Thickness h (mm)	Gauge length l (mm)	Length L_{TOF}	Mass (g)	Density (g/cm ³)	
Spruce A	6.50 (0.8)	9.99 (0.11)	3.98 (0.43)	50	70	11.729 (0.298)	0.397 (13)	12
Spruce D	7.01 (0.5)	10.03 (0.10)	4.43 (0.33)	50	70	13.255 (0.900)	0.447 (24)	12
Maple A	7.26 (0.6)	10.09 (0.08)	3.97 (0.14)	50	70	18.683 (0.840)	0.627 (31)	12
Maple D	6.96 (0.5)	10.40 (0.29)	4.23 (0.23)	50	70	17.485 (1.271)	0.577 (38)	12

conditions (at a temperature of 20 ± 4 °C and a humidity of 60 ± 5 %).

Wood density (ρ) of each sample was also determined based on the ratio of mass to volume of the samples measured at each stage of the experiment (before and after UV exposure). First, the dynamic modulus of elasticity (denoted $E_{L,dyn}$) was calculated as a function of ultrasonic velocity (V_L) and density, according to eq. (1) [30,31,35,40–42].

$$E_{L,dyn} = V_L^{2*} \rho \quad (1)$$

Taking into account the existence of an incremental velocity that develops in small samples, it is necessary to eliminate the effect of the rapid incremental propagation velocity and to take into account the slowest speed of the developing plane wave [33,35,43]. Thus, for calculating the longitudinal modulus of elasticity, [33,35,43] propose the introduction of a correction factor k in order to obtain the correct data from the TOF instruments, eq. (1) becoming eq. (2):

$$E_{L,dyn}^* = \left(\frac{V_L}{k}\right)^2 \rho \quad (2)$$

According to [33,35,43], for an orthotropic medium such as wood, the Kelvin-Christoffel equation gives k which is calculated as a function of the Poisson's ratio of the wood (see eq. 3):

$$k = \sqrt{\frac{1 - \nu_{RT}\nu_{TR}}{1 - \nu_{RT}\nu_{TR} - \alpha}} \quad (3)$$

where α is:

$$\alpha = 2\nu_{RL}\nu_{TR}\nu_{LT} + \nu_{TL}\nu_{LT} + \nu_{RL}\nu_{LR} \quad (4)$$

where ν_{RL} , ν_{LR} , ν_{RT} , ν_{TR} , ν_{TL} , ν_{LT} are the Poisson's ratios of wood.

In this study, based on the experimental values obtained by the tensile test ($E_{L,static}$) and the measurement of the sound propagation speed in the longitudinal direction, the authors calculated the value of the correction factor k for spruce and maple samples, before and after artificial aging for 1000 h, using eq. (5):

$$k = V_L \sqrt{\frac{\rho}{E_{L,static}}} \quad (5)$$

Mean values (MV) and standard deviation (SD) of the measured parameters were recorded before and during temperature and UV exposure. The measurements were performed at a temperature of 24 °C and a humidity of 65 %.

2.2.4. Color modification

According to the procedures presented in previous studies [32,37,44], the change in wood color denoted ΔE^* induced by UV and mild heating upon long-term exposure, was calculated based on eq. (6). Color parameters such as lightness L^* , redness a^* , and yellowness b^* were determined experimentally before and after artificial aging, using the Konica Minolta CR-400 chromometer.

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}, \quad (6)$$

where ΔL^* – the lightness difference between lightness after 1000 h UV exposure ($L_{UV1000h}^*$) and initial lightness (L_0^*); Δa^* – redness difference between redness after 1000 h UV exposure ($a_{UV1000h}^*$) and initial redness (a_0^*) and Δb^* – yellowness difference between yellowness after 1000 h UV exposure ($b_{UV1000h}^*$) and initial yellowness (b_0^*) of wood samples.

The intensity of color or chroma (denoted C^*) is calculated based on eq. (7) [45]:

$$C^* = \sqrt{a^{*2} + b^{*2}}, \quad (7)$$

2.2.5. Fourier transforms infrared spectroscopy (FTIR)

The chemical changes produced by UV and thermal exposure were investigated using a FTIR spectrometer (VERTEX70, Bruker, Ettlingen, Germany) with ATR (Attenuated Total Reflectance) module. The spectra were recorded in the range 4500–500 cm⁻¹, with a resolution of 4 cm⁻¹ and 16 scans per sample. Recorded spectra were further processed for baseline correction and smoothing, and average spectra were calculated for each sample category before and after aging using OPUS software (version 7.2, Bruker, Ettlingen, Germany). The working method was adopted according to [32,46,47].

2.2.6. X-ray diffraction (XRD)

Crystallinity data were collected in the 2θ angle range between 10° and 80° in fixed time mode, with a step interval of 0.01° to 25°, using a Bruker Advanced D8 diffractometer (CuK α 1 radiation, with a wavelength of 1.5406 Å, at 40 kV and 20 mA) [9].

3. Results and discussion

3.1. Mechanical and acoustic properties modification due to aging

3.1.1. Mechanical properties from tensile test

The stress-strain curves for the spruce and maple wood samples from the two anatomical quality classes, A and D, before and after artificial aging are shown in Fig. 3. It can be seen, as a general trend, that the aged spruce samples appeared stiffer (with higher E) and stronger (higher σ) than before exposure. Similar observations were reported for hinoki wood [25]. The differences in the stress-strain curves are smaller in the case of maple wood samples (maple is a deciduous wood with anatomical characteristics different from those of softwood). The $E_{L,static}$ values for aged spruce wood are slightly higher than those for spruce wood samples before 1000 h of UV exposure, by 2.6 % (class A) and 9.3 % (class D). In the case of maple wood samples, a slight increase in $E_{L,static}$ can be observed by 1.38 % for class D, after aging. Class A maple samples showed a slightly decrease in $E_{L,static}$ after 1000 h of UV exposure (3 %). The artificial aging process led to an increase in the stiffness of the samples as a result of the degradation of the main chemical compounds

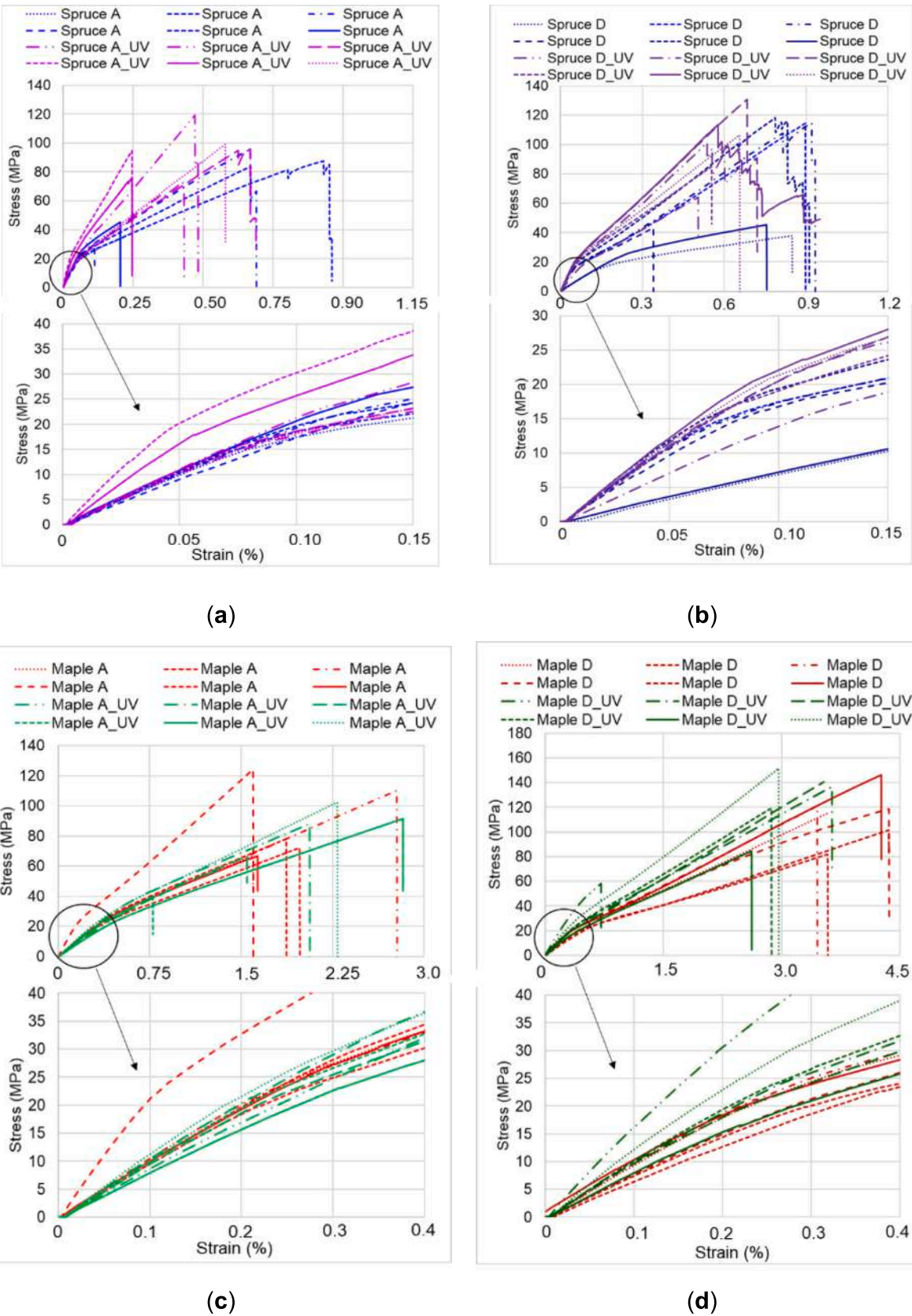


Fig. 3. The stress-strain curves: (a) Spruce wood sample class A; (b) Spruce wood sample class D; (c) Maple wood sample class A; (d) Maple wood sample class D.

of the wood.

The way wood breaks is closely related to the orientation of the anatomical elements in relation to the stress axis. According to [40,41], the initiation of tensile failure occurs either inside the cell wall where its layers are subjected to shear and, subsequently, irreversible elongation absorbs the energy without loss of strength [48–49], or between cells, when they have thin walls [50–52]. Fig. 4 shows the tensile failure of the samples, in the case of spruce wood, there are visible differences between the control samples and those subjected to artificial aging for 1000 h. The failure pattern of spruce before UV exposure is chip type, while in the aged spruce samples the mode is pure tension failure.

Fig. 5 shows the regression curves between the static modulus of elasticity and density for the two categories of wood species analyzed (spruce and maple). Due to the anatomical characteristics of maple, the regression curves differ before and after photo-degradation compared to spruce wood. From Fig. 6a it can be seen that only the unaged D spruce wood samples show a regression model that explains 66 % of the stiffness variability with respect to the specific modulus. For maple wood, the R2 value greater than 0.6, as in the case of Maple A, Maple A_UV and

Maple D samples, indicates a higher variability explained by the regression model (Fig. 6b).

3.1.2. Acoustic and elastic properties from TOF test

Fig. 7 a,b shows the density stratification of the spruce and maple wood samples, before and after aging. It can be seen that the aging treatments are different depending on the wood species: the spruce wood samples do not undergo considerable changes in density, while, in the case of the maple wood samples, those of class A register a decrease in density with approx. 3 %. On the other hand, UV exposure for 1000 h led to an increase in the speed of sound propagation in spruce wood (by 4.7 % for Spruce A and 5.9 % for Spruce D), compared to maple wood samples, where the propagation speed increased by 2 % for Maple A (Fig. 7c), while the Maple D samples did not show any increase (Fig. 7d).

Table 2 contains the average values of the main mechanical and acoustic properties determined. In Table 2, the correction factors k_L for each sample category vary according to the species and the effect of different photodegradation on the material structure and implicitly by the different values of Poisson's ratio, as highlighted in [24,43].

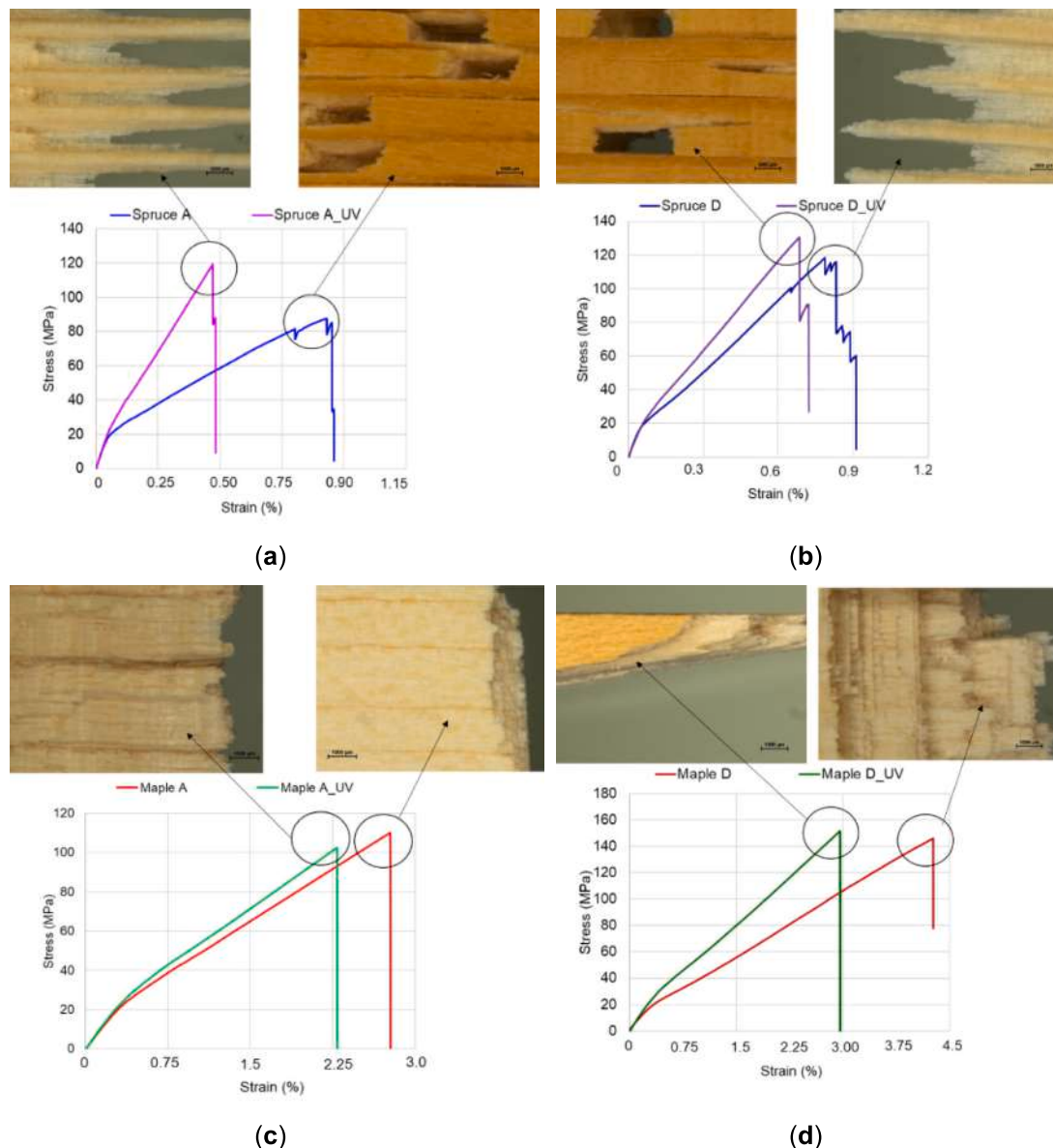


Fig. 4. Failure patterns obtained in destructive tests: (a) Spruce wood sample class A; (b) Spruce wood sample class D; (c) Maple wood sample class A; (d) Maple wood sample class D.

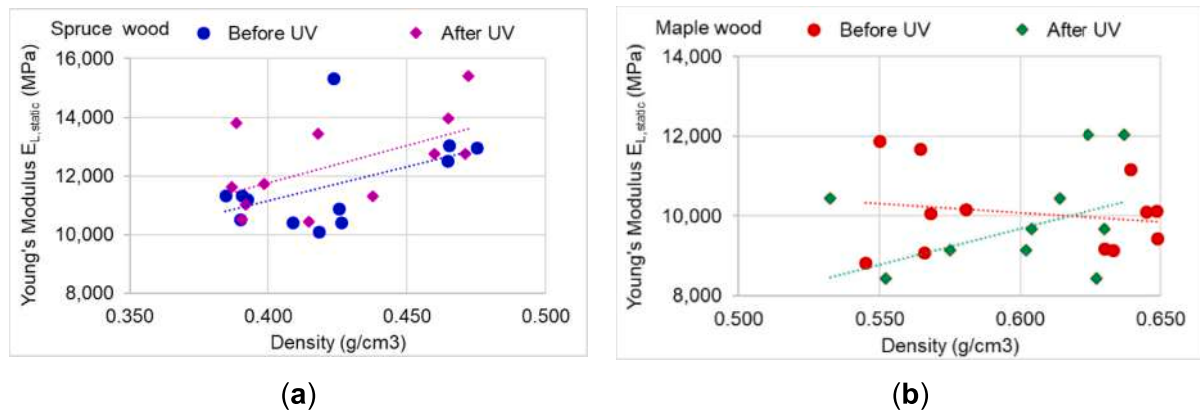


Fig. 5. Scatter plot $E_{L,static}$ over density for wood before and after 1000 h exposure to artificial aging: (a) spruce wood samples; (b) maple wood sample.

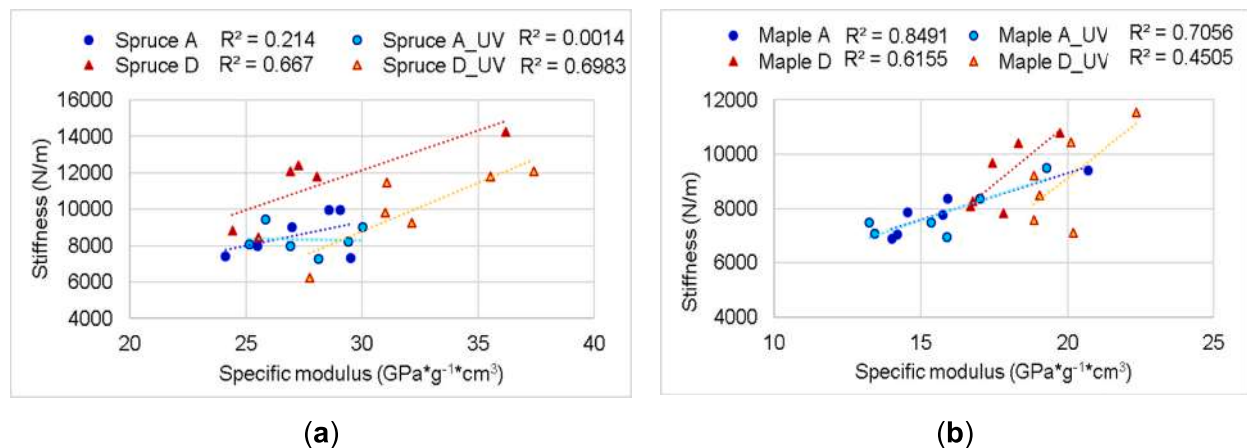


Fig. 6. Relationship between stiffness and specific modulus ($E_{L,static}/\rho$) for wood before and after 1000 h exposure to artificial aging: (a) spruce wood samples; (b) maple wood sample.

Contrary to [43] who reports k_L values of 0.97 for spruce wood, in the current study, k_L is 1.098 for class A spruce, 1.142 for A_UV spruce and for D spruce; the value of the correction factor remains constant before and after aging, respectively the value of 1.065. In the case of maple wood samples, k_L is higher, being 1.185 (as an average value) for both unaged and aged samples. Although the simplified equation can be used for comparisons, it should be noted that differences in Poisson's ratios are not taken into account in this case, introducing uncertainty into the comparison, as mentioned by [33,35,36,43].

3.2. Changes in color properties

The color changes of the aged wood samples after the exposure for 1000 h can be observed with the naked eye, as highlighted in Fig. 8. Measuring the color parameters with specialized equipment and calculating the color difference based on eq. (6), showed that the color changes are more pronounced in spruce than in maple, and within each species, in spruce, class A more than class D, probably due to the higher lignin content. In the case of maple wood samples, the ratio is the reversed - samples from class D showed a more pronounced change in color compared to those from class A (Table 3). In terms of color intensity, the parameter C has the same value for spruce, regardless of the quality class, while for maple wood it varies, the color being more intense after artificial aging, especially for maple wood samples, class D maple. Wood exposed to direct sunlight undergoes chemical degradation caused by UV radiation.

According to [46,47], lignin contributes 80–95 %, carbohydrates 5–20 %, and extractives about 2 % to the total absorption coefficient of

wood. Thus, lignin is the cell wall component most sensitive to UV light, it transfers UV light to the cellulose, which also leads to cellulose degradation according to the study described in [53]. In addition to photo-degradation, wood modification must also be considered, as the samples were also subjected to mild heating at a temperature of 50 °C, which may lead to the degradation of wood biopolymers. The more the wood changes its color in the direction of decreasing brightness, the more the surface temperature of the externally irradiated wood increases, reaching 60–90 °C, according to the research from [54,55]. Comparing the results obtained in this study with those highlighted by [56] who analyzed the color change of the samples after 600 h of exposure to artificial light, the recorded spruce wood ΔE^* is 19, and for the maple wood ΔE^* is 12; it was found that photodegradation for 1000 h led to ΔE^* varying between 23 and 25 for spruce wood, and ΔE^* varying between 14 and 19 for maple wood, respectively. The color variation is mainly due to changes in the degree of yellow and red as a result of aging, visible in the magnitude of the difference in Chroma ΔC^* . The yellowing of wood samples after exposure to UV light reflects that they have undergone chemical changes as a consequence of the development of chromophoric compounds during lignin photodegradation [57–60].

3.3. Fourier transforms infrared spectroscopy (FTIR)

Due to their different structures of the two species, but also the way in which the anatomical elements are formed in the radial longitudinal section, the characteristic degradation processes, as well as their sensitivity to degradation, differ greatly. While photo-degradation of wood is

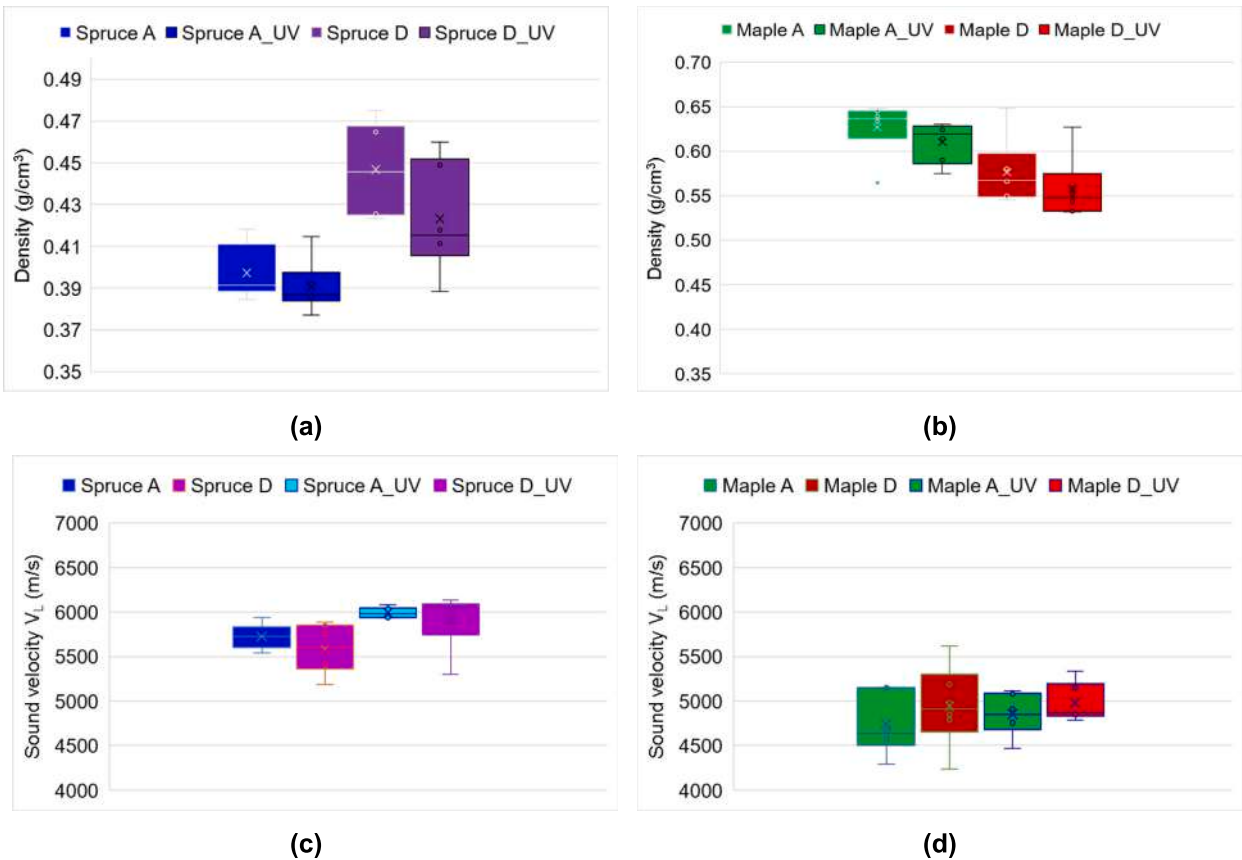


Fig. 7. Density variation of samples before and after aging in the case of spruce wood (a); Density variation of samples before and after aging in the case of maple wood (b); Sound velocity in longitudinal direction of spruce wood samples before and after aging (c); Sound velocity in longitudinal direction of maple wood samples before and after aging (d).

Table 2
Mean values and standard deviation of mechanical and acoustic properties of tested samples. Legend: MV – mean value; SD – standard deviation; ρ – density; $E_{L,dyn}$ – the dynamic elasticity modulus in longitudinal direction; $E_{L,static}$ – the modulus of elasticity in longitudinal direction obtained by static test; k_L – correction factor; $E_{L,dyn}^k/\rho$ – the specific modulus obtained from TOF test; $E_{L,static}^k/\rho$ – the specific modulus obtained by tensile test; S – the stiffness by tensile test; σ – tensile strength; ϵ – percentage strain at break.

Sample		ρ (kg/m ³)	$E_{L,dyn}$ (MPa)	$E_{L,static}$ (MPa)	k_L	$E_{L,dyn}^k/\rho$ (GPa*g ⁻¹ *cm ³)	$E_{L,static}^k/\rho$ (GPa*g ⁻¹ *cm ³)	S (kN/m)	σ (MPa)	ϵ (%)
Spruce A	MV	397	13,031	10,822	1.098	33	27	8606	72	0.97
	SD	13	803	544	0.059	1.6	2.1	1206	24	0.77
Spruce A_UV	MV	391	14,480	11,102	1.142	35	28	8338	93	0.85
	SD	19	688	546	0.034	0.7	1.9	785	17	0.17
Spruce D	MV	447	14,006	12,519	1.060	31	28	11,304	105	0.82
	SD	24	1747	1759	0.054	3.1	4.1	2238	15	0.35
Spruce D_UV	MV	423	14,918	13,687	1.071	35	32	10,112	106	0.77
	SD	35	2228	987	0.102	3.5	3.2	2220	15	0.05
Maple A	MV	627	14,091	9873	1.196	22	15	7888	86	1.28
	SD	31	1684	1028	0.076	3.2	2.5	930	25	0.73
Maple A_UV	MV	610	14,400	9587	1.230	23	15	7816	80	0.89
	SD	23	1544	1509	0.070	2.3	2.3	965	17	0.28
Maple D	MV	577	14,246	10,267	1.175	24	17	9170	116	2.07
	SD	38	3115	1088	0.126	4.5	1.1	1286	23	0.94
Maple D_UV	MV	558	13,887	10,109	1.116	24	18	9060	124	1.12
	SD	40	2130	2099	0.039	2.2	1.6	1694	24	0.34

considered a surface-related process due to limited penetration of light into wood [1,32,56], the mild heating on long-term exposure can affect the entire cross-section. Fig. 9 and Fig. 10 compare the FTIR spectra for spruce and maple samples, respectively, in the 2200–600 cm⁻¹ footprint region.

3.3.1. FT-IR spectral analysis of spruce wood

Fig. 9 shows the FT-IR spectra for the spruce samples A and D after UV exposure, as well as for the control samples. The peak near 1730 cm⁻¹ (non-conjugated carbonyl), corresponding to the C=O stretching vibration in the O-C=OH group of the glucuronic acid (GlcA) according to [61], shows an intensification in the treated samples as a result of

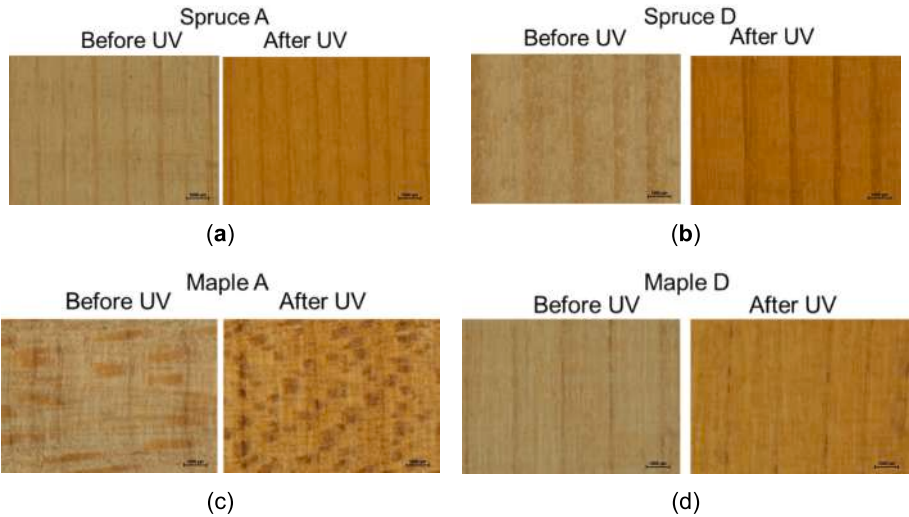


Fig. 8. Comparisons of the color of the samples before and after artificial aging: (a) Spruce wood sample class A; (b) Spruce wood sample class D; (c) Maple wood sample class A; (d) Maple wood sample class D.

Table 3
The mean values and SD for color parameters.

Sample		L*	a*	b*	E*	C*	ΔE^*	ΔC^*
Spruce A	MV	85.006	1.925	18.928	87.109	19.026	25.095	22.900
	SD	0.644	0.235	1.040	1.029	0.548		
Spruce A_UV	MV	74.736	7.526	41.130	85.638	41.813	23.817	22.21
	SD	1.418	0.919	1.437	1.508	1.087		
Spruce D	MV	83.546	2.448	19.651	85.861	19.803	13.801	12.97
	SD	1.243	0.468	1.769	1.790	1.127		
Spruce D_UV	MV	74.941	7.312	41.320	85.890	41.962	18.866	16.04
	SD	1.383	0.825	1.234	1.272	1.087		
Maple A	MV	78.973	4.280	16.937	80.882	17.469	13.801	12.97
	SD	4.161	1.035	0.851	1.023	3.924		
Maple A_UV	MV	74.254	5.612	29.838	80.221	30.361	18.866	16.04
	SD	2.773	0.764	2.390	2.365	3.227		
Maple D	MV	84.968	2.410	16.513	86.591	16.687	18.866	16.04
	SD	1.836	0.636	0.669	0.713	1.721		
Maple D_UV	MV	75.043	5.514	32.254	81.867	32.722	18.866	16.04
	SD	2.125	0.574	1.777	1.802	2.232		

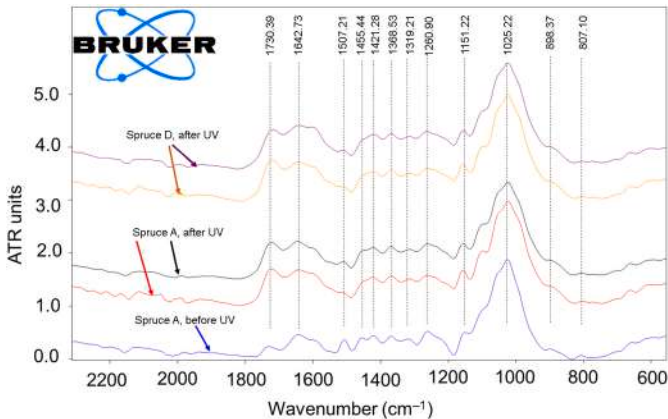


Fig. 9. Comparative FT-IR spectra for spruce wood before and after 1000 h of exposure to UV radiation.

some oxidation processes. The decrease of absorptions from 1507 cm^{-1} (vibration of the aromatic skeleton of lignin) is clearly observed. Analyzing the characteristic peaks of cellulose, the O–H bending vibration of water sorption at 1645 cm^{-1} , the C–H bending vibrations at

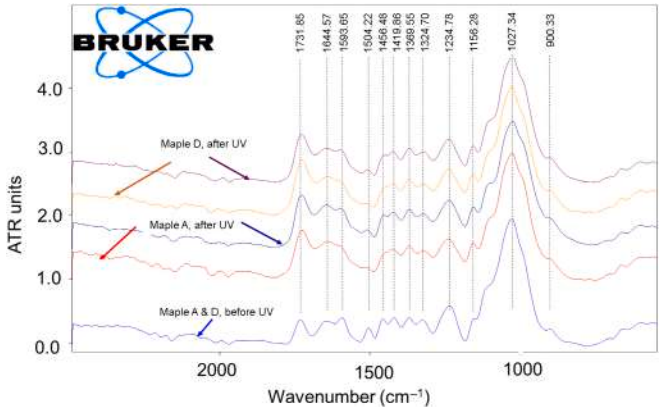


Fig. 10. Comparative FTIR spectra for maple wood samples before and after 1000 h of exposure to UV radiation.

1370 cm^{-1} and the stretching vibration of the glucose ring at 1115 cm^{-1} , it was found that after UV exposure, the spruce wood shows an intensification of the absorptions from 1370 cm^{-1} and 1151 cm^{-1} , specific to the structural elements of polysaccharides, correlating with the partial degradation of lignin. Lignin degradation after UV exposure of spruce

samples is evidenced by changes in the following bands: the aromatic skeletal vibration at 1507 cm^{-1} , the C—O stretching of the guaiacyl unit at 1260 cm^{-1} and the syringyl ring vibration, together with the C—O stretching at 1210 cm^{-1} . Similar results were reported by [61], for Chinese fir wood subjected to different heat treatment temperatures. An equally significant degradation is also observed for the 1455 cm^{-1} absorption band attributed to C—H deformation groups—lignin, carbohydrates: cellulose, hemicelluloses; CH₂ bending—cellulose, according to [32,61–65].

3.3.2. FT- IR spectral analysis of maple wood

In the case of maple wood, the chemical degradation of the main chemical components of the wood is similar to that of spruce wood (Fig. 10). An interesting phenomenon in maple wood is the intensification of the absorption band at 1732 cm^{-1} , after exposure to UV radiation for 1000 h, which is characteristic to non-conjugated carbonyl groups. These changes highlight the degradation of lignin and the formation of chromophore compounds with carbonyl groups (aldehydes, ketones, acids and esters), results that are in good agreement with the specialized literature [32,62–66]. The absorption at 1645 cm^{-1} (conjugated carbonyl, aromatic ketones, quinones) remains clearly distinct and apparently slightly enhanced upon aging treatment (it may be associated with new chromophoric groups with conjugated carbonyl groups, including quinone-type structures). The decrease in absorptions attributed to lignin can be clearly seen from 1504 cm^{-1} (lignin aromatic skeleton vibration) and 1594 cm^{-1} (aromatic core). Thus, the absorption at 1594 cm^{-1} is no longer clearly distinct but becomes a shoulder in a wider band (approx. $1550\text{--}1700\text{ cm}^{-1}$). The absorptions at 1370 cm^{-1} and 1156 cm^{-1} which are assigned to some structural elements of polysaccharides (cellulose, hemicelluloses) stand out better (intensification 1370 cm^{-1} , clear highlighting 1156 cm^{-1}) for aged samples and this observation can be correlated with the partial degradation of lignin.

According to [26,62–66], when cellulosic materials are exposed to an alternating wet-dry cycle, their mechanical flexibility and water accessibility are irreversibly reduced by the formation of irreversible intermolecular hydrogen bonds, which leads to the restriction of the mobility of amorphous carbohydrates. This phenomenon could explain both the increase in the rigidity of the wood and the speed of sound propagation in wood after aging. Similar studies have revealed that the most prone to photooxidation reactions is lignin, which decomposes approx. 80–95 % of UV light due to aromatic compounds, while cellulose and hemicellulose absorb only 5–20 % of UV light, according to [50,67–69]. The most significant peaks of the wood samples and their assignment in the FTIR spectra are shown in Table 4.

3.4. The crystallinity content

Wood crystallinity is defined as the weight fraction of crystalline cellulose. The increases in crystallinity affect the mechanical and acoustic properties, such as sound speed in the longitudinal direction, Young's modulus and stiffness increase, flexibility decreases with increasing crystallinity. Spruce wood shows a more homogeneous structure and reduced crystallinity dispersion depending on the quality class and specific modulus, unlike maple wood which is characterized by a higher anisotropy, less crystalline cellulose content before aging artificial but with greater sensitivity to the aging treatment. As can be seen from Fig. 11, the crystal diffraction peaks appear near 17° and 22.5° of the X-ray diffraction angle (2θ) which represents the crystal diffraction intensity of wood cellulose as reported in [70–73]. The diffraction patterns obtained on samples before and after UV exposure differ considerably both from one species to another and from one anatomical structure organization to another (class A spruce and maple, and class D spruce and maple, respectively).

The diffraction patterns obtained on the samples before and after UV exposure differ considerably from one species to another as well as from one anatomical structure organization to another (class A spruce and

Table 4
Peaks of wood samples and their assignments in FTIR spectra.

Peak assignments	Compound	Wavenumber (cm^{-1})			
		Spruce		Maple	
		Before UV	After UV	Before UV	After UV
C=O stretching in ketone and carbonyl groups	Hemicellulose	1730	1730↑	1732	1732↑
C=O stretching	Lignin	1642	1642↓	1645	1645↓
C=C stretching of the aromatic ring	Lignin	–	–	1594	1594↓
C=C stretching of the aromatic ring	Lignin	1507	1507↓	1504	1504↓
CH ₂ stretching	Lignin and hemicellulose	1455	1455↓	1456	1456↓
C–H bending	Cellulose and hemicellulose	1368	1368↑	1369	1369↑
C–H and O–H vibration	Polysaccharides (hemicellulose and hollocellulose)	1260	1260↓	1234	1234↓
C–O–C asymmetric stretching	Cellulose and hemicellulose	1151	1151↑	1156	1156↑
C–O stretching	Cellulose	1025	1025	1027	1027
C–H deformation	Cellulose	898	898↓	900	900↓

maple, and class D spruce and maple, respectively). This is caused by the differences in the crystallinity of the samples, determined both by the proportion of early wood - late wood, the width of the annual rings, the regularity of the annual rings, the degree of fiber waviness (in the case of maple samples), the age of the tree/annual ring and not in the last row of angle microfibrils that reflect different crystallinity [72]. It is observed that the class A spruce and class D maple samples show an increase in crystallinity after exposure to UV radiation, compared to the other categories (class D spruce and class A maple) where the crystallinity decreases after UV exposure. The crystallinity index for class D spruce wood is 17 % lower after UV exposure, and for class A spruce wood, the crystallinity index increases by 2.8 %. The largest increases are for D class maple wood, with the crystallinity index being 17 % higher after exposure. For class A maple wood, the crystallinity index decreases by 2.8 %. Similar values regarding the crystallinity index for common spruce wood were also reported in [70–73]. Over 900 h of wood aging, the crystalline structure underwent negative changes with a decrease in the percentage of crystallinity determined mainly by cellulose depolymerization after long UV aging. The crystallinity of spruce wood is higher than that of maple wood by approx. 30 % as can be seen in Fig. 12, comparing the crystallinity before the applied treatment.

4. Conclusions

This study is a multiscale analysis of the effect of artificial wood aging for musical instruments through physical, mechanical, acoustic and chemical measurements of spruce and maple wood samples. The paper demonstrated that artificial aging for 1000 h of exposure leads to chemical changes with more effect on sound speed than mechanical properties. Thus, the parameters most affected by artificial aging were the speed of sound propagation, which was significantly higher in the class A spruce wood samples and the longitudinal modulus of elasticity in the class A maple wood samples. These results are correlated with the increase in the crystallinity index. An improvement in acoustic and mechanical properties after UV exposure was noticed for maple class D, where both stiffness and crystallinity index increased. The results highlighted the heterogeneous nature of wood, even within the same

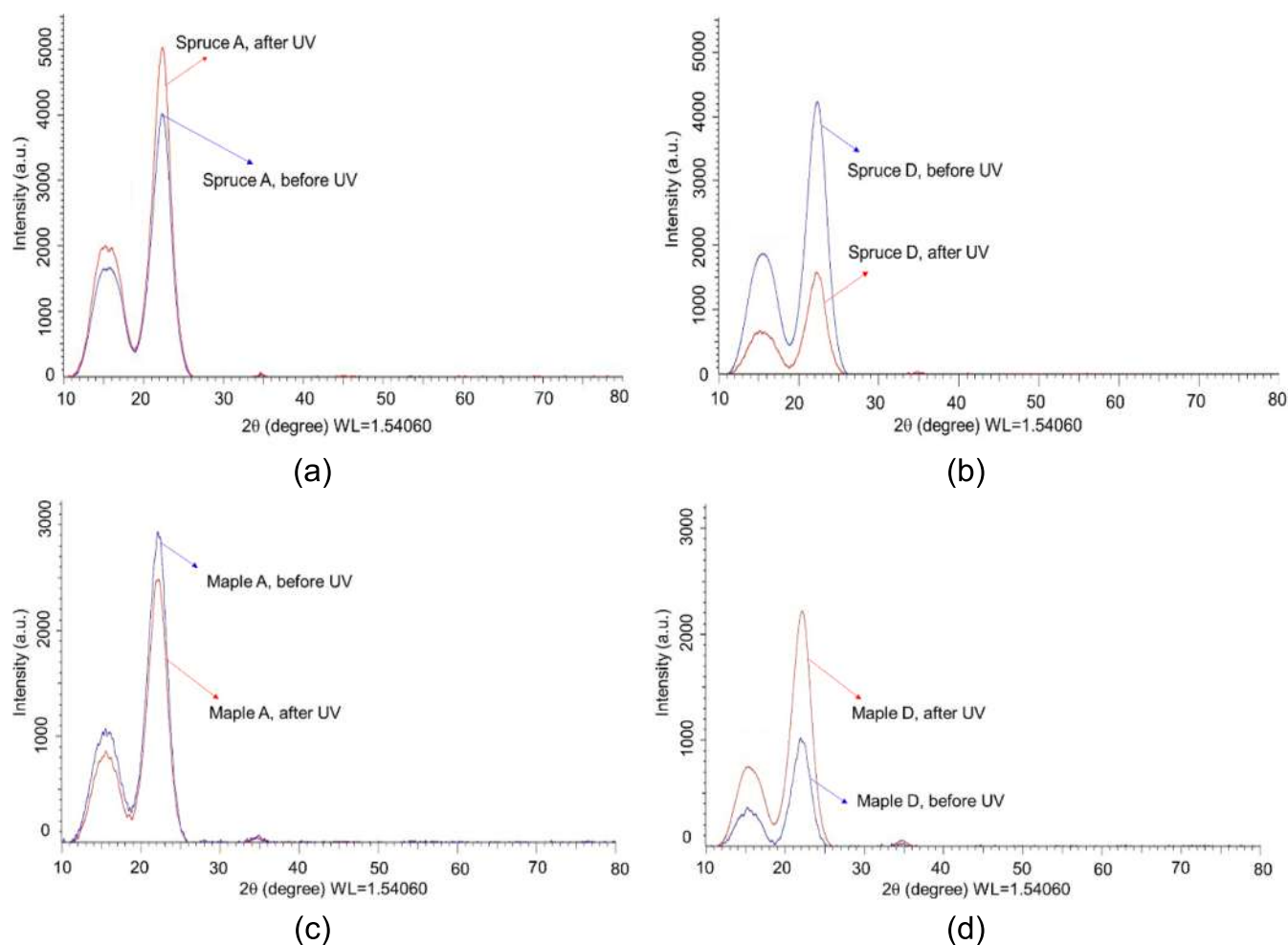


Fig. 11. XRD patterns of the control and aged wood: a) spruce wood grade A; b) spruce wood grade D; c) maple wood grade A; d) maple wood grade D.

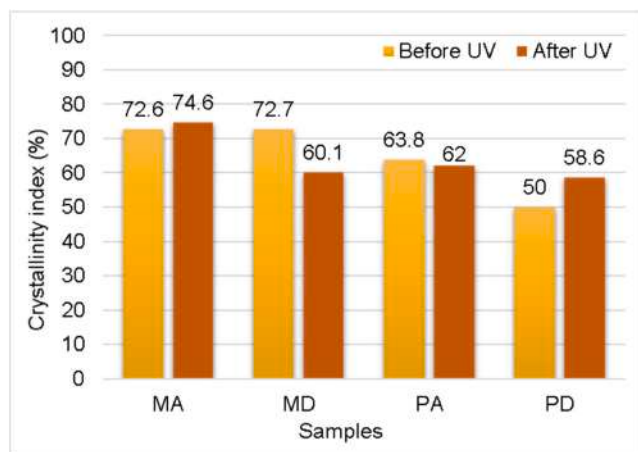


Fig. 12. Crystallinity index comparisons.

species, where the proportion of early wood - late wood, the amount of polysaccharides and the anatomical architecture of the wood lead to different chemical, acoustic and mechanical changes, under the same conditions of UV irradiation.

The physical and chemical changes produced by artificial aging, manifested by the breaking of covalent bonds in organic polymers, the reduction of mass, the increase of surface roughness, the increase of

hydrophobicity and stability to humidity variations, the decrease of the lignin content in the soundboard can lead to the improvement of the acoustic properties (speed of sound propagation and acoustic radiation) of the wood used in musical instruments. Applying a light photo-degradation treatment, before assembling the plates in the violin body, could result in an increase in the acoustic performance of the instrument, similar to old, naturally aged instruments.

CRediT authorship contribution statement

Mariana Domnica Stanciu: Writing – original draft, Software, Resources, Project administration, Investigation, Funding acquisition, Formal analysis, Conceptualization. **Horatiu Draghicescu Teodorescu:** Software, Methodology, Investigation, Formal analysis, Data curation. **Sorin Vlase:** Writing – review & editing, Supervision, Methodology, Investigation. **Mircea Mihalcica:** Writing – original draft, Visualization, Validation, Data curation, Conceptualization. **Mihaela Cosnită:** Writing – original draft, Software, Methodology, Formal analysis, Data curation. **Adriana Savin:** Writing – review & editing, Validation, Data curation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgments

This research was supported by a grant from the Ministry of Research, Innovation and Digitization, CNCS/CCCDI—UEFISCDI, project number 61PCE/2022, PN-III-P4-PCE2021-0885, ACADIA—Qualitative, dynamic and acoustic analysis of anisotropic systems with modified interfaces. The authors acknowledge the structural funds project PRO-DD (POS-CCE, O.2.2.1., ID 123, SMIS 2637, No. 11/2009) for providing the infrastructure used in this research. We are grateful to the technical staff of Gliga Musical Instruments, Reghin, a Romanian manufacturer of musical string instruments, for supplying the specimens. We would like to thank Prof. Timar Cristina from the Transilvania University of Brasov for the support given in carrying out the FTIR analyses.

References

- [1] Y. Kataoka, M. Kiguchi, R.S. Williams, P.D. Evans, Violet light causes photodegradation of wood beyond the zone affected by ultraviolet radiation, *Holzforschung* 61 (1) (2007) 23–27.
- [2] E.A. Salca, T. Krystofiak, B. Lis, S., Hiziroglu glossiness evaluation of coated wood surfaces as function of varnish type and exposure to different conditions, *Coatings* 11 (2021) 558.
- [3] B.F. Tjeerdma, M. Boonstra, A. Pizzi, P. Tekely, H. Militz, Characterisation of thermally modified wood: molecular reasons for wood performance improvement, *Holz Roh Werkst.* 56 (3) (1998) 149–153.
- [4] M.D. Stanciu, M. Mihălică, F. Dinulică, A.M. Nauncef, R. Purdoi, R. Lăcătuș, G. V. Gliga, X-ray imaging and computed tomography for the identification of geometry and construction elements in the structure of old violins, *Materials* 14 (2021) 5926.
- [5] B.C. Stoel, T.M. Borman, A comparison of wood density between classical Cremonese and modern violins, *PLoS One* 3 (7) (2008) e2554.
- [6] N. Sodini, D. Dreossi, R. Chen, M. Fioravanti, Non-invasive microstructural analysis of bowed stringed instruments with synchrotron radiation X-ray microtomography, *J. Cult. Herit.* 13 (2012) 44–49.
- [7] A.S. Srdovic, Interactions between Wood Polymers in Wood Cell Walls and Cellulose/Hemicellulose Biocomposites, Thesis for The Degree Of Doctor Of Philosophy, Department of Chemical and Biological Engineering, Chalmers University of Technology, Göteborg, Sweden, 2011 (accessed on 28.08.2023).
- [8] N. Španić, V. Jambrečević, M. Klarić, Basic chemical composition of wood as a parameter in raw material selection for biocomposite production, *Cellul. Chem. Technol.* 52 (3–4) (2018) 163–169.
- [9] M. Cosnita, C. Cazan, M.A. Pop, D. Cristea, Aging resistance under short time ultraviolet (UV) radiations of polymer wood composites entirely based on wastes, *Environ. Technol. Innov.* 31 (2023). Article 103208.
- [10] F.F.P. Kollmann, A. Wilfred, J. Côté, Principles of Wood Science and Technology I, Springer-Verlag, New York Inc., New York, 1968, pp. 1–54.
- [11] D. Fengel, Ultrastructural behaviour of cell wall polysaccharides, *TAPPI J.* 53 (3) (1970) 497–503.
- [12] A.J. Kerr, D.A.I. Goring, The ultrastructural arrangement of the wood cell wall, *Cellul. Chem. Technol.* 9 (6) (1975) 563–573.
- [13] K.L. Kato, R.E. Cameron, A review of the relationship between thermally-accelerated ageing of paper and hornification, *Cellulose* 6 (1999) 23–40.
- [14] H.T. Chang, T.F. Yeh, S.T. Chang, Comparisons of chemical characteristic variations for photodegraded softwood and hardwood with/without polyurethane clear coatings, *Polym. Degrad. Stab.* 77 (1) (2002) 129–135.
- [15] T.C. Chang, H.T. Chang, C.L. Wu, S.T. Chang, Influences of extractives on the photodegradation of wood, *Polym. Degrad. Stab.* 95 (2010) 516–521.
- [16] S.A. Sebnem, D.T. Eylem, A.E. Mahmut, I. Yildirim, Natural weathering of sixteen wood species: changes on surface properties, *Polym. Degrad. Stab.* 183 (2021) 109415.
- [17] S. Yildiz, E.D. Gezer, U.C. Yildiz, Mechanical and chemical behavior of spruce wood modified by heat, *Build. Environ.* 41 (12) (2006) 1762–1766.
- [18] C. Gomri, M. Cretin, M. Semsarilar, Recent progress on chemical modification of cellulose nanocrystal (CNC) and its application in nanocomposite films and membranes—a comprehensive review, *Carbohydr. Polym.* 294 (2022) (Article 119790).
- [19] P. Niemz, T. Hofmann, T. Rétfalvi, Investigation of chemical changes in the structure of thermally modified wood, *Maderas-Ciencia Y Tecnologia* 12 (2) (2010) 69–78.
- [20] J. Bourgois, G. Janin, R. Guyonnet, The color measurement - a fast method to study and to optimize the chemical-transformations under - gone in the thermally treated wood, *Holzforschung* 45 (5) (1991) 377–382.
- [21] M. Hakku, M. Petrissans, P. Gerardin, A., Zoulalian investigations of the reasons for fungal durability of heat-treated beech wood, *Polym. Degrad. Stab.* 91 (2) (2006) 393–397.
- [22] J.J. Weiland, R. Guyonnet, Study of chemical modifications and fungi degradation of thermally modified wood using DRIFT spectroscopy, *Holz Roh Werkst.* 61 (3) (2003) 216–220.
- [23] K. Kränitz, *Effect of natural aging on wood*. PhD Thesis ETH Zurich (2014), accessed on 01.08.2023.
- [24] N. Zeniya, E. Obataya, K. Endo-Ujiie, M. Matsuo-Ueda, Changes in vibrational properties and colour of spruce wood by hygrothermally accelerated aging at 95–140 °C and different relative humidity levels, *SN. Appl. Sci.* 1 (2019) 7.
- [25] M. Yokoyama, J. Gril, M. Matsuo, H. Yano, et al., Mechanical characteristics of aged Hinoki (*Chamaecyparis obtusa* Endl.) wood from Japanese historical buildings, in: International Conference on Wooden Cultural Heritage, Evaluation of Deterioration and Management of Change, 2009, 8p fihal-00795997.
- [26] T. Noguchi, E. Obataya, K. Ando, Effects of aging on the vibrational properties of wood, *J. Cult. Herit.* 13 (3) (2012) 21–25.
- [27] K. Kränitz, M. Deublein, P. Niemz, Determination of dynamic elastic moduli and shear moduli of aged wood by means of ultrasonic devices, *Mater. Struct.* 47 (6) (2014) 925–936.
- [28] C.K. Su, S.Y. Chen, J.H. Chung, G.C. Li, B. Brandmair, et al., Materials engineering of violin soundboards by Stradivari and Guarneri, *Angew. Chem. Int. Ed. Eng.* 60 (35) (2021) 19144–19154, <https://doi.org/10.1002/anie.202105252> (Epub 2021 Jun 27. PMID: 34062043; PMCID: PMC8457145).
- [29] W.C. Feist, D.N.-S. Hon, Chemistry of weathering and protection, in: R. Rowell (Ed.), *The Chemistry of Solid Wood*, Advances in Chemistry Series, vol. 207, American Chemical Society (ACS), Washington DC, 1984, pp. 401–454.
- [30] F. Dinulică, M.D. Stanciu, A. Savin, Correlation between anatomical grading and acoustic-elastic properties of resonant spruce wood used for musical instruments, *Forests* 12 (2021) 1122.
- [31] F. Dinulică, A. Savin, M.D. Stanciu, Physical and acoustical properties of wavy grain sycamore maple (*Acer pseudoplatanus* L.) used for musical instruments, *Forests* 14 (2023) (Article 197).
- [32] L. Gurău, M.C. Timar, C. Coşoreanu, M. Cosnita, M.D. Stanciu, Aging of wood for musical instruments: analysis of changes in color, surface morphology, chemical, and physical-acoustical properties during UV and thermal exposure, *Polymers* 15 (2023) (Article 1794).
- [33] M.K. Andrews, Which acoustic speed?, in: Proceedings of the 13th International Symposium on Non-destructive Testing of Wood, University of California, Berkeley Campus California, USA, 19–21, August, 2002.
- [34] M.K. Andrews, Wood quality measurement, *Son et Lumiere*, N. Z. J. For. 47 (2002) 19–21.
- [35] M. Legg, S. Bradley, Measurement of stiffness of standing trees and felled logs using acoustics: a review, *J. Acoust. Soc. Am.* 139 (2) (2016) 588–604.
- [36] H. Hansen, Acoustic Studies on Wood, Master Thesis, University of Canterbury New Zealand, 2006. accessed on 20 August 2023.
- [37] R. Gall, M.D. Stanciu, E. Filimon, M. Cosnita, V.G. Gliga, The influence of artificial aging on resonance wood on its physical characteristics, in: Proceedings of the 9th International Conference on Advanced Composite Materials Engineering, 2022, pp. 73–81.
- [38] M.D. Stanciu, H.D. Teodorescu, S. Vlase, Degradation of mechanical properties of pine wood under symmetric axial cyclic loading parallel to grain, *Polymers* 12 (2020) 2176.
- [39] M.D. Stanciu, H.D. Teodorescu, I.C. Roşca, Mechanical properties of GFRPs exposed to tensile, compression and tensile–tensile cyclic tests, *Polymers* 13 (2021) 898.
- [40] V. Bucur, R.R. Archer, Elastic constants for wood by an ultrasonic method, *Wood Sci. Technol.* 18 (4) (1984) 255–265.
- [41] V. Bucur, Acoustics of Wood, 2nd ed, Springer, Berlin, Germany, 2006, pp. 173–196.
- [42] R. Gonçalves, A.J. Trinca, Comparison of elastic constants of wood determined by ultrasonic wave propagation and static compression testing, *Wood Fiber Sci.* 43 (1) (2011) 64–75.
- [43] P. Niemz, D. Caduff, Research into determination of the Poisson ratio of spruce wood, *Holz Roh Werkst.* 66 (1) (2008) 1–4.
- [44] M.D. Stanciu, D. Sova, A. Savin, N. Ilias, G.A. Gorbacheva, Physical and mechanical properties of ammonia-treated black locust wood, *Polymers* 12 (2020) 377.
- [45] P. Bekhta, T. Krystofiak, B. Lis, N. Bekhta, The impact of sanding and thermal compression of wood, varnish type and artificial aging in indoor conditions on the varnished surface color, *Forests* 13 (2022) 300.
- [46] H. Norrstrom, Light absorbing properties of pulp and pulp components. 1. Method, *Svensk Papperstidning-Nordisk Cellulosa* 72 (2) (1969) 25–31.
- [47] M.L. Kuo, N.H. Hu, Ultrastructural changes of photodegradation of wood surfaces exposed to UV, *Holzforschung* 45 (5) (1991) 347–353.
- [48] J. Keckes, I. Burgert, K. Frühmann, M. Müller, K. Kölln, et al., Cell-wall recovery after irreversible deformation of wood, *Nat. Mater.* 2 (2003) 810–814.
- [49] C.M. Altaner, M.C. Jarvis, Modelling polymer interactions of the 'molecular Velcro' type in wood under mechanical stress, *J. Theor. Biol.* 253 (2008) 434–445.
- [50] M.F. Ashby, K.E. Easterling, R. Harrysson, S.K. Maiti, The fracture and toughness of woods, *Proc. R. Soc. London, Ser. A* 398 (1985) 261–280.
- [51] C. Lanvermann, P. Hass, F.K. Wittel, P. Niemz, Mechanical properties of Norway spruce: intra-ring variation and generic behavior of earlywood and latewood until failure, *Bioresources* 9 (2014) 105–119.
- [52] A.L. Christoforo, T.H. Panzera, F.A.R. Lahr, Estimation of tensile strength parallel to grain of wood species, *Engenharia Agrícola* 39 (4) (2019) 533–536.
- [53] M.N. Yildirim, B. Uysal, A. Özçifci, A.H. Ertas, Determination of fatigue and static strength of Scots pine and beech wood, *Wood Research* 60 (4) (2015) 679–686.
- [54] T. Yoshimoto, Photochemical analysis of wood and related substances, *J. Japan Wood Res Soc.* 18 (1) (1972) 45–49.

- [55] L. Tolvaj, S. Molnár, Photodegradation and thermal degradation of outdoor wood, in: Joseph Gril (Ed.), *Wood Science for Conservation of Cultural Heritage –Braga 2008: Proceedings of the International Conference Held by COST Action IE0601 (Braga - Portugal, 5–7 November), 2008*, pp. 67–72.
- [56] U. Müller, M. Rätzsch, M. Schwanninger, M. Steiner, H. Zobl, Yellowing and IR-changes of spruce wood as result of UV-irradiation, *J. Photochem. Photobiol. B Biol.* 69 (2003) 97–105.
- [57] L. Oltean, A. Teischinger, C. Hausmann, Wood surface discolouration due to simulated indoor sunlight exposure, *Holz Roh Werkst.* 66 (1) (2008) 51–56.
- [58] H. Wikberg, S.L. Maunu, Characterisation of thermally modified hard- and softwoods by C-13 CPMAS NMR, *Carbohydr. Polym.* 58 (4) (2004) 461–466.
- [59] J. Geffertová, A. Geffert, E. Výboňová, The effect of UV irradiation on the colour change of the spruce wood, *Acta Facultatis Xylologiae Zvolen* 60 (1) (2018) 41–50.
- [60] E. Karami, I. Brémaud, S. Bardet, T. Almeras, D. Guibal, P. Langbour, K. Pourtahmas, J. Gril, Reversible and irreversible effects of mild thermal treatment on the properties of wood used for making musical instruments: comparing mulberry to spruce, *iForest* 15 (2022) 256–264, <https://doi.org/10.3832/for4074-015>.
- [61] S. Cheng, A. Huang, S. Wang, Q. Zhang, Effect of different heat treatment temperatures on the chemical composition and structure of Chinese fir wood, *BioRes* 11 (2) (2016) 4006–4016.
- [62] M.C. Timar, A.M. Varodi, L. Gurau, Comparative study of photodegradation of six wood species after short-time UV exposure, *Wood Sci. Technol.* 50 (2016) 135–163.
- [63] X.Y. Liu, M.C. Timar, A.M. Varodi, An investigation of accelerated temperature-induced aging of four wood species: colour and FTIR, *Wood Sci. Technol.* 51 (2017) 357–378.
- [64] X.Y. Liu, M.C. Timar, A.M. Varodi, R. Nedelcu, M. Torcătoru, Colour and surface chemistry changes of wood surfaces coated with two types of waxes after seven years exposure to natural light in indoor conditions, *Coatings* 12 (2022) 1689.
- [65] C. Boeriu, D. Bravo, R. Gosselink, J. Dam, Characterisation of structure-dependent functional properties of lignin with infrared spectroscopy, *Ind. Crop. Prod.* 20 (2004) 205–218.
- [66] R. Javier-Astete, J. Melo, J. Jimenez-Davalos, et al., Classification of Amazonian fast-growing tree species and wood chemical determination by FTIR and multivariate analysis (PLS-DA, PLS), *Sci. Rep.* 13 (2023) 7827, <https://doi.org/10.1038/s41598-023-35107-6>.
- [67] K. Kránitz, W. Sonderegger, C.T. Bues, P. Niemz, Effects of aging on wood: a literature review, *Wood Sci. Technol.* 50 (1) (2016) 7–22.
- [68] M. Báder, R. Németh, J. Sandak, et al., FTIR analysis of chemical changes in wood induced by steaming and longitudinal compression, *Cellulose* 27 (2020) 6811–6829.
- [69] D. Wang, L. Lin, F. Fu, et al., The fracture mechanism of softwood via hierarchical modelling analysis, *J. Wood Sci.* 65 (58) (2019) 1–11.
- [70] R.S. Davidson, The photodegradation of some naturally occurring polymers, *J. Photochem. Photobiol. B Biol.* 33 (1996) 3–25.
- [71] F. Lionetto, R. Del Sole, D. Cannoletta, G. Vasapollo, A. Maffezzoli, Monitoring wood degradation during weathering by cellulose crystallinity, *Materials* 5 (2012) 1910–1922.
- [72] S. Andersson, R. Serimaa, T. Paakkari, P. Saranpää, E. Pesonen, Crystallinity of wood and the size of cellulose crystallites in Norway spruce (*Picea abies*), *J. Wood Sci.* 49 (2003) 531–537.
- [73] A. Cogulet, P. Blanchet, V. Landry, Wood degradation under UV irradiation: A lignin characterization, *J. Photochem. Photobiol. B Biol.* 158 (2016) 184–191.

Article

Aging of Wood for Musical Instruments: Analysis of Changes in Color, Surface Morphology, Chemical, and Physical-Acoustical Properties during UV and Thermal Exposure

Lidia Gurău ¹, Maria Cristina Timar ¹, Camelia Coșereanu ¹, Mihaela Cosnita ^{2,*}
and Mariana Domnica Stanciu ^{3,*}

¹ Faculty of Furniture Design and Wood Engineering, Transilvania University of Brasov, 500036 Brasov, Romania

² Department of Product Design Mechatronics and Environment, Transilvania University of Brasov, 29 Eroilor, 500036 Brasov, Romania

³ Faculty of Mechanical Engineering, Transilvania University of Braşov, B-dul Eroilor 29, 500360 Brasov, Romania

* Correspondence: mihaela.cosnita@unitbv.ro (M.C.); mariana.stanciu@unitbv.ro (M.D.S.)

Abstract: The acoustic features of old resonance wood in violins exhibit a superior quality when compared to those from new resonance wood. This study focuses on an assessment of the sound quality of two types of wood for musical instruments, spruce and maple (class A and D), before and after aging via thermal and UV exposure. The samples were characterized before and after UV aging in terms of color change (using a Chroma meter), surface morphology (using a MarSurf XT20 instrument), chemical changes (monitored by FTIR spectroscopy), and sound propagation speed (using an ultrasound device). After UV treatment, the wavier surface increased the area of exposure and degradation. Also, the color changes were found to be more accentuated in the case of spruce compared to sycamore maple. The FTIR results indicated more advanced aging processes for spruce when compared to maple under the same experimental conditions. This difference resulted mostly from the increased formation of carbonyl-containing chromophores via oxidative processes in spruce rather than in maple, which is in agreement with the color change findings. Exposure of both species to thermal and UV radiation led to an increase in sound propagation speed, both longitudinally and radially, and to a greater extent in wood quality class A when compared to quality class D.

Keywords: resonance wood; acoustic quality; sound propagation; UV aging; color changes; chemical changes; surface morphology



Citation: Gurău, L.; Timar, M.C.; Coșereanu, C.; Cosnita, M.; Stanciu, M.D. Aging of Wood for Musical Instruments: Analysis of Changes in Color, Surface Morphology, Chemical, and Physical-Acoustical Properties during UV and Thermal Exposure. *Polymers* **2023**, *15*, 1794. <https://doi.org/10.3390/polym15071794>

Academic Editor: Vlatka Jirouš-Rajković

Received: 26 February 2023

Revised: 28 March 2023

Accepted: 3 April 2023

Published: 5 April 2023



Copyright: © 2023 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 (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

The acoustic quality of old violins has aroused the interest of researchers to explore the causes that lead to higher sound quality when comparing geometrically identical violins that have been manufactured from recently made resonance wood. According to some researchers, the natural aging of wood is responsible for increasing the acoustic quality of violins. Thus, ref. [1,2] highlight the occurrence of significant differences in the wood density of old violins compared to the wood of new violins. The decrease in density by 33% in spruce boards and 10% in maple boards caused changes in the stiffness distribution, which can have a direct impact on vibration effectiveness or can indirectly change sound radiation due to the modified damping characteristics. On the other hand, Su et al. 2021 [3] examined the effects of natural aging on Cremonese spruce using C13 solid-state nuclear magnetic resonance, noting that there was little sign of degradation, which was in contrast to Cremonese sycamore wood that showed significant hemicellulose degradation and the demethoxylation of lignin. Such distinctions may be caused by fundamental differences in the chemical compositions of wood. However, aging can also mean the formation of new

substances and stabilization, which can, in some cases, be a desirable effect [4]. The critical wavelengths to break the most important chemical bonds in wood polymers are 346, 334, and 289 nm. These wavelengths are found in the UV component of solar radiation and affect carbon-carbon, carbon-oxygen, and carbon-hydrogen bonds, respectively [5].

In addition to photodegradation, surface thermal degradation must also be considered because the surface temperature of outdoor irradiated wood can reach 60–90 °C, depending on its color [6]. Wood aging also leads to changes in the size of micropores, considering that extended aging time makes the wood microstructure more stable, resulting in a decrease in the number of micropores [7]. All investigations into naturally or artificially aged wood have highlighted both chemical and physical changes, with these being connected to each other. Thus, the color changes of wood as a result of natural aging are related to specific chemical changes involving both the main and secondary chemical components of wood [8,9] that are associated with the modification of other physical properties, such as surface roughness [10,11] or wetting properties and adhesion capacity [12,13]. Changes in chemical and mechanical properties are not limited to the wood surface. Mechanical properties can also be affected by aging wood under variable conditions of temperature and relative humidity [14–17]. It is certain that the aging process of wood differs depending on the environmental conditions (outdoors or indoors). When wood is exposed to direct sunlight, severe damage is induced by UV radiation [9,10,18,19]. In the situation of objects stored indoors, as is the case of stringed musical instruments, the sunlight spectrum is mostly filtered by window panes, resulting in a decrease in the intensity of UV radiation. In addition, in indoor environments, artificial light sources are also present. Due to different light spectrums, the photodegradation processes of indoor wood are not the same as those for outdoor wood. The studies carried out by artificial aging procedures on different wood species have shown that the color changes are rapid in the first 12 h of exposure for hardwoods and for the first 24 h for softwoods [9,20–22]. A continuation of the exposure time beyond these limits has shown a decrease in the fading speed. Most wood species recorded almost no further color change until the end of the irradiation period.

Several studies have addressed the problem of the photodegradation of wooden surfaces due to UV and thermal radiation, but very few of them have analyzed the acoustic and physical changes produced in the resonance wood used for musical instruments [17,23–27]. Noguch et al. 2012 [17] and Obataya 2017 [24] observed an increase in the stiffness of naturally aged wood by approximately 38% in 121-year-old wood, after which a decrease was observed with increasing aging time. The speed of sound was 14% higher for the 276-year-old wood compared to the 8-year-old wood. Similar results were also obtained by Kranitz et al. [16], who observed an increase in the dynamic modulus of elasticity in the longitudinal direction with tree age.

The main objective of this work is to study whether the effect of artificial aging through thermal and UV exposure can improve the acoustic parameters of two wood species that are commonly used for musical instruments: spruce and sycamore maple. The novelty of the paper consists of a holistic research approach, in which the aging effect is regarded not only upon acoustics solely but in combination with other changes, such as on surface color, surface morphology, and chemical modifications, in order to provide a better understanding of the aging process.

2. Materials and Methods

2.1. Materials

The wood samples selected for this study belong to the two most used wood species for the construction of violins: spruce (*Picea abies* (L.) Karst.) and sycamore maple (*Acer pseudoplatanus*, L.). Two quality class samples were prepared, depending on their anatomical characteristics: class A and class D, selected according to the anatomical classification from previous studies [28,29]. Spruce wood samples were coded MA (class A) and MD (class D), respectively, and differed in the number and width of the annual rings, with the finest structure attributed to class A. Sycamore maple wood samples were coded PA

(class A with a curly grain) and PD (class D with a straight grain). The sample code used after exposure to ultraviolet radiation was the UV suffix, for example, MAUV (spruce, quality A, and exposure to UV). The wood was harvested from the forests of the Carpathian Mountains. It was cut and naturally dried for 3 years (class D) and 10 years (class A) to obtain the semi-finished products necessary for the manufacturing of stringed musical instruments. The samples were processed in the form of plates with dimensions of 240 mm × 80 mm × 4 mm, respecting the main directions of wood (length (longitudinal direction) × width (radial direction) × thickness (tangential direction)). All plates were sanded with 220-grit sandpaper. Three replicates were studied for each sample category, as shown in Figure 1.

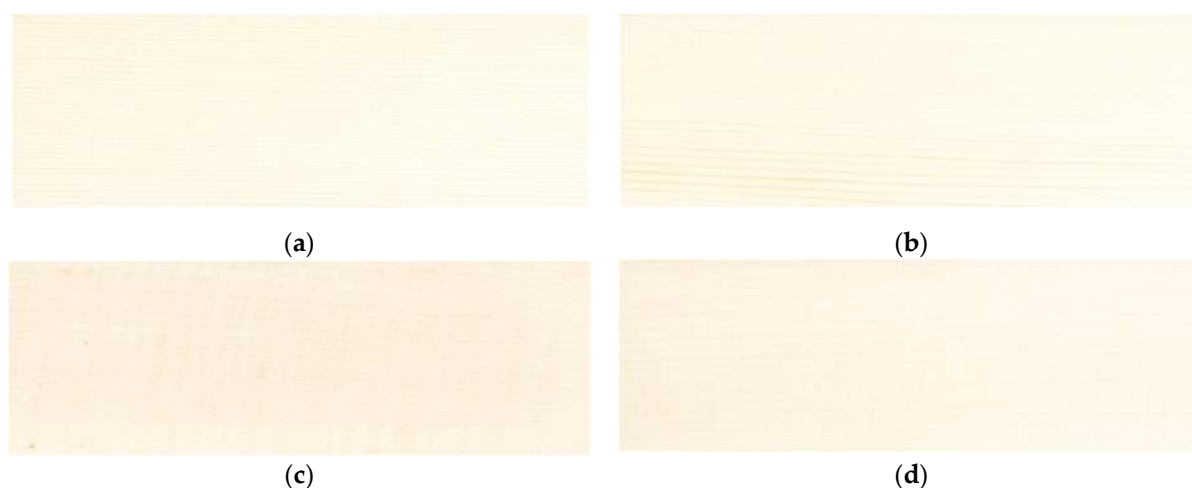


Figure 1. The types of samples studied: (a) spruce samples, grade A; (b) spruce samples, grade D; (c) sycamore maple samples, grade A; (d) sycamore maple samples, grade D.

2.2. Methods

2.2.1. UV and Thermal Exposure

The samples were introduced into a photocatalytic reactor ICD – Transilvania University of Braşov, Braşov, Romania, equipped with 2 UV tubes (Philips, TL-D BLB 18 W/108) and 5 VIS light tubes (Philips, TL-D Super 80 18 W/865). Each tube emits radiation in the UV range, with wavelengths between 340–400 nm and wavelength λ_{max} (emission) = 365 nm; the average value of UV irradiation was measured with a Delta-T pyranometer, type BF3, with 3 W/m² [30]. Wood samples were exposed to UV for 360 h [31]. The distance between the samples and the lamp during irradiation was 20 cm, and the temperature inside the irradiation chamber was 50 °C. Physical and acoustic properties were periodically evaluated and measured. The moisture content was monitored using a Merlin HM8-WS1 moisture meter (Merlin Technology Inc. 1441 E. Business Center Dr., Mount Prospect, Illinois, USA), and the mass was measured with a Kern and Sohn Weighing Balance, EWJ 600-2SM (Mechanikus Gottlieb KERN, Balingen, Germany).

2.2.2. Wood Color Change Measurements

The degree of change in the wood color as a result of the progressive exposure to UV and to thermal radiation was determined by monitoring the color parameters with a chroma meter CR-400 Konica Minolta. Thus, the (L^*) lightness values were obtained, as well as the chromatic co-ordinates on the green-red axes (the degree of green/red), a^* , the degree of blue/yellow, b^* , and the total color change, denoted ΔE_{ab}^* . The latter was calculated with Equation (1), according to [22,32,33]:

$$\Delta E_{ab}^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (1)$$

where ΔL^* —the lightness difference, Δa^* —the redness difference, and Δb^* —the yellowness difference between wood before and after exposure to UV radiation.

The color was measured in three points on the plate, which were positioned according to the schematic representation in Figure 2. The guide marks served to maintain the same location when monitoring the color before and during UV exposure.

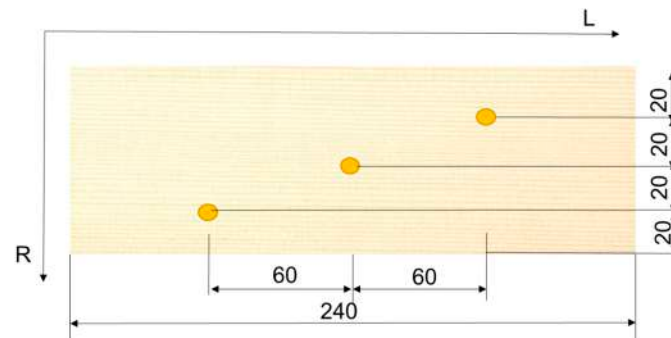


Figure 2. The color measurement location.

2.2.3. Surface Quality Measurements

The equipment used for the evaluation of the surface morphology comprised a MarSurf XT20 instrument manufactured by MAHR Gottingen GMBH (Göttingen, Germany), fitted with an MFW 250 scanning head, with a tracing arm in the range of $\pm 750 \mu\text{m}$, and a stylus with a $2 \mu\text{m}$ tip radius and a 90° tip angle. The stylus moved at a speed of 0.5 mm/s and exerted a low scanning force of 0.7 mN at a lateral resolution of $5 \mu\text{m}$. Three measurements per specimen were recorded by following an identical trace, before and after exposure to UV, according to the measurement principles from Figure 3. The scanned profiles were processed with MARWIN XR20 software provided by the instrument supplier (Göttingen, Germany). The measured profiles contain a superposition of deviations from the nominal flat surface, surface waviness, and surface roughness [34]. By removing the form deviations, a primary profile was obtained, which contained the waviness and roughness together. A special filtering procedure using a cut-off value separated the roughness profile from the primary profile. A robust Gaussian regression filter with a cut-off length of 2.5 mm was used in this research [34]. Mean value parameters were calculated, such as R_a (arithmetical mean deviation of the roughness profile), R_t (total height of profile), and W_a (arithmetical mean deviation of the waviness profile) (from ISO 4287:2009) [35]. Other parameters included the Abbot-curve parameters: R_k (the core roughness depth), R_{pk} (the reduced peak height), and R_{vk} (the reduced valley depth) from ISO 13565-2:1998 [36], explained in detail in [37]. The parameter R_k is closely related to “processing roughness” or “core roughness” [37], being the most stable parameter (small standard deviation) and the least influenced by the presence of isolated protrusions or valleys of the profile. R_{pk} is useful in assessing the surface fuzziness in a profile, while R_{vk} is sensitive to surface deep cavities occurring below the core roughness.

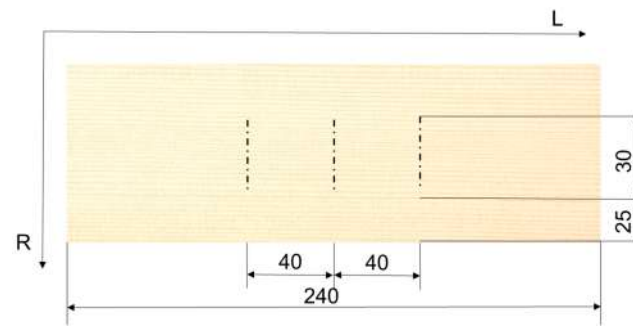


Figure 3. The measuring principle for the surface morphology of the samples. Values in mm.

2.2.4. FTIR Analysis of Chemical Changes on Wood Surfaces

The chemical changes produced by UV and thermal exposure were investigated using an FTIR spectrometer (ALPHA, Bruker, Ettlingen, Germany) with an ATR (attenuated total reflectance) module. The spectra were recorded in the range $4000\text{--}600\text{ cm}^{-1}$ at a resolution of 4 cm^{-1} and 24 scans per sample. Spectra were recorded in 3 areas for each sample. The recorded spectra were further processed for baseline correction and smoothing, and average spectra were computed for each category of sample/treatment using the OPUS software (version 7.2, Bruker, Ettlingen, Germany). Average spectra were further normalized (min-max normalization) and compared to highlight any chemical changes due to aging. The working method was adopted according to [9,10].

Furthermore, the normalized average spectra were integrated, and the ratios of the areas of some relevant absorption bands of the main chemical components of wood were calculated to better highlight the chemical changes brought about by aging. The selected absorption bands were those at around $1506\text{--}1507\text{ cm}^{-1}$, assigned to aromatic skeletal vibration of lignin, $1730\text{--}1740\text{ cm}^{-1}$, assigned to unconjugated carbonyl groups, and about 1370 cm^{-1} , assigned to holocellulose and considered as an internal reference [38]. The calculated ratios were: A_{1506}/A_{1370} , A_{1730}/A_{1370} , and A_{1730}/A_{1506} , as in previously reported research [9].

2.2.5. Sound Velocity Measurements

The measurement of the sound propagation speed in wood in the longitudinal (VLL) and radial (VRR) direction was carried out using a LUCCHIMETTER portable ultrasound device, Cremona, Italy. The principle of the ultrasound (US) measurements is presented in Figure 4 [17]. The density of each plate was also determined in each stage of the experiment, and the longitudinal and radial modulus of elasticity was calculated in accordance with the calculation relationship mentioned by [26]. The mean (MV) and standard deviation (SD) values of the measured parameters were recorded before and during exposure to temperature and UV. The rate of change of Young's modulus with exposure time was calculated as a percentage difference in the values measured at successive exposure durations.

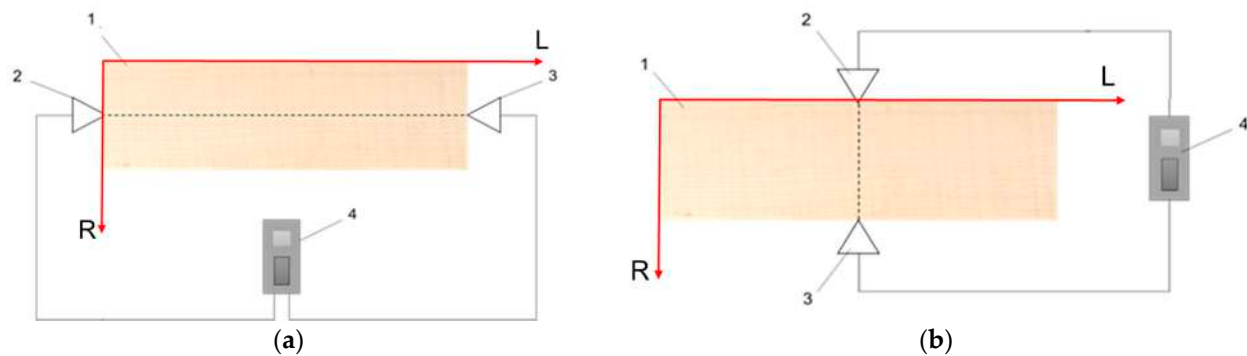


Figure 4. Measuring the sound velocity in wood: (a) in the longitudinal direction; (b) in the radial direction. Legend: 1—sample; 2—transmitter; 3—receiver; 4—US transmitter; acquisition and displayed data device.

3. Results and Discussions

3.1. Changes in Color Parameters

Table 1 presents the mean values and the standard deviations of the L^* , a^* , and b^* co-ordinates for all studied samples before and after UV exposure. The ΔE^* and ΔL^* total variations were also calculated and recorded. The color changes differed between the two species—spruce and sycamore maple—but the differences were minor between the two quality classes A and D within the same species, as can be seen in Figure 5 and in the color differences from Table 1. Exposure to UV caused a change in brightness (by decreasing the value of this parameter), with the speed of change reaching the maximum value in the first 72 h of exposure. Thus, after the first 72 h of exposure to the UV radiation, the wood surface darkened by 3.43% in the PA samples, 4.76% in the PD samples, 4.36% in the MA spruce samples, and 4.35% in the MD samples.

Table 1. Color co-ordinates L^* , a^* , and b^* , measured before and after exposure to UV.

Wood Samples		Before UV			After UV			Total Variation		Moisture Content (%)	
		L^*	a^*	b^*	L^*	a^*	b^*	ΔE^*	ΔL^*	Before UV	After UV
MA	MV	85.63	1.67	20.34	79.12	3.77	32.07	14.75	−7.64	7.73	5.93
	SD	0.21	0.14	0.88	0.13	0.06	0.77			0.25	0.12
MD	MV	86.02	1.67	20.07	79.34	3.67	31.71	15.18	−7.49	7.63	5.57
	SD	1.02	0.47	0.31	0.64	0.22	0.62			0.12	0.4
PA	MV	81.37	3.78	17.23	75.92	4.05	24.71	9.26	−5.45	7.03	4.43
	SD	0.14	0.10	0.30	0.34	0.17	0.48			0.35	0.32
PD	MV	82.03	3.01	16.82	75.68	4.28	25.10	10.50	−6.34	6.60	4.03
	SD	3.35	0.26	0.66	0.98	0.87	0.47			0.85	0.25

The spruce darkened more compared to the sycamore maple samples, recording a total color variation of around 15 when compared to the sycamore maple, whose total color variation was around 10, as can be seen in Table 1. The results obtained are in agreement with those reported by [21,39,40], where the change in color for spruce was the largest among all the investigated species. Some researchers [10] found that the sycamore maple that was subjected to a long simulated natural aging process indoors suffered from a dramatic decrease in brightness after 4–5 months of exposure. After this time interval, the process was reversed so that the degree of brightness partially recovered (approximately 45%) after 12 months of natural aging simulation [10]. When sycamore maple was exposed for longer (84 months), the color darkened again. It is worth mentioning that time 0 from the graphs in Figure 5 represents the values of the parameters measured before exposure to UV in the initial stage. Figure 6 shows the difference in color between the initial samples and the accelerated aging ones, at the end of the exposure.

3.2. Study on the Surface Morphology

3.2.1. Surface Morphology Parameters for Spruce and Maple, before and after the UV Treatment

Among the surface parameters evaluated, Table 2 contains the ones which proved to be the most sensitive to UV exposure. They will be analyzed in the following subsections in combination with the measured profiles. The R_k parameter is a measure of the central area of the profile, where most of the profile data are concentrated, and is the most indicated parameter for quality assessment, being an expression of the majority of measured points on a surface [34]. The R_k mean values before and after the UV treatment are depicted for both species and quality classes in Figure 7.

3.2.2. The Effect of UV Treatment on Spruce Wood

Since the same measuring trace was followed before and after the UV treatment, this allowed not only for a reliable comparison between the roughness parameters but also for a visual comparison of the profiles. A first observation was that the spruce samples bulged after the UV treatment, which can be seen in Figure 8, showing a measured spruce profile (MA quality) before and after the UV treatment. The green arrow indicates an accentuation of the deviation from flatness of approx. 100 microns in amplitude. Another observation was that the sanded spruce surfaces contain a specific wavy aspect which is related to the sequence of earlywood–latewood, and their frequency depends on the frequency of the annual rings (number of occurrences on a given length). This seems to be a typical reaction of spruce wood after sanding. Deep gaps occur at the beginning of a new annual ring, corresponding to the first earlywood tissue; then, the wood forms a bump covering the earlywood–latewood sequence until the next annual growth border, where a new gap is formed. This “anatomical waviness” is accentuated by the UV treatment, and this behavior can be observed by the naked eye and by touch, as well as by the evidence in Figure 9, where the primary profiles of spruce MA and spruce MD are shown. For example, the surface waviness, expressed by W_a , increased more than three times in the case of MA spruce treated with UV (Table 2). This phenomenon was also observed by [41,42] in the case of the photodegradation of wood combined with thermal oxidation.

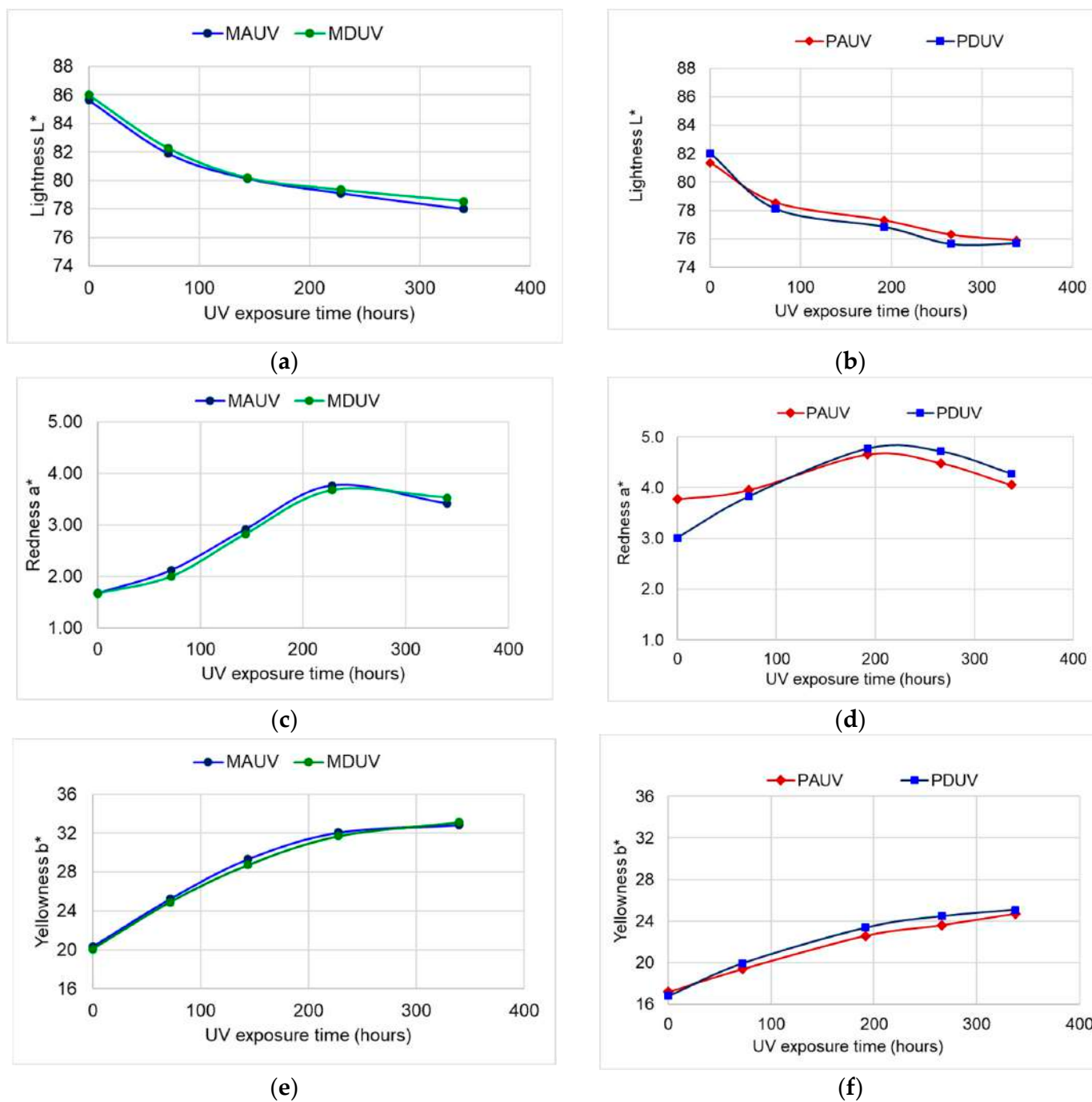


Figure 5. The variation of color parameters with an increase in UV exposure time: (a) lightness of spruce samples; (b) lightness of sycamore maple samples; (c) redness of spruce samples; (d) redness of sycamore maple samples; (e) yellowness of spruce samples; (f) yellowness of sycamore maple samples.

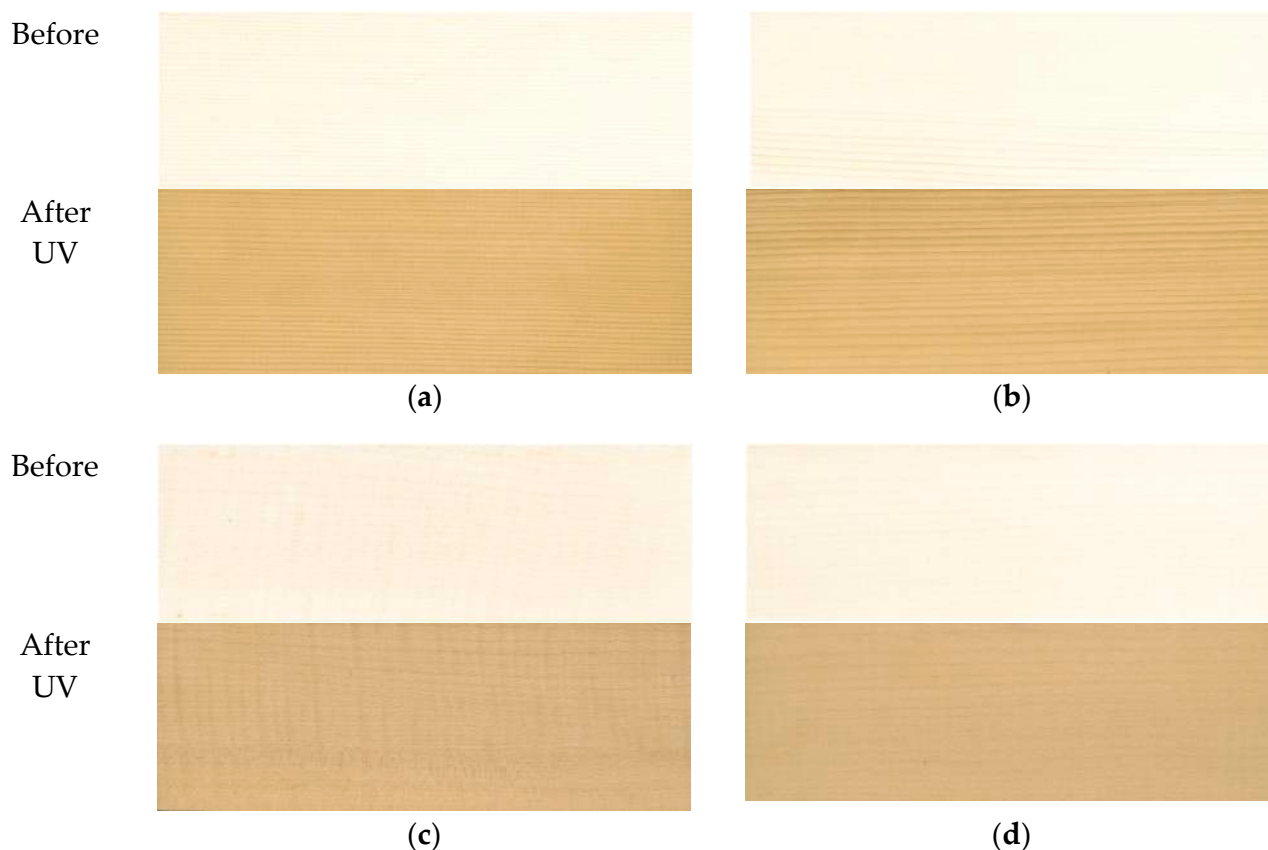


Figure 6. Color comparison between wood samples before and after artificial aging: (a) spruce samples, grade A; (b) spruce samples, grade D; (c) sycamore maple samples, grade A; (d) sycamore maple samples, grade D.

Table 2. The average values (MV) of the roughness parameters (in microns) and their standard deviations (SD), as measured before and after exposure to UV.

Wood Samples		Ra	Rk	Rpk	Rvk	Rk + Rpk + Rvk	Rt	Wa
MA	MV	4.61	15.37	4.37	6.02	25.75	41.23	5.61
Before UV	SD	0.35	1.24	0.42	1.11	2.12	4.64	1.11
MA	MV	5.62	18.76	4.56	7.28	30.60	48.75	18.85
After UV	SD	0.46	2.31	0.50	1.72	2.51	10.48	3.48
MD	MV	4.37	13.61	3.20	7.43	24.24	39.53	3.64
Before UV	SD	0.44	1.30	0.52	0.51	2.32	1.05	0.19
MD	MV	4.47	13.78	3.45	7.37	24.60	40.03	4.46
After UV	SD	0.43	0.93	0.03	0.94	1.89	3.13	0.12
PA	MV	3.40	8.93	4.36	8.08	21.37	39.76	0.53
Before UV	SD	0.60	1.27	1.58	2.16	4.42	4.57	5.42
PA	MV	3.34	8.40	4.80	9.03	22.23	44.53	4.44
After UV	SD	0.46	1.61	1.89	0.77	3.19	5.24	15.22
PD	MV	4.69	13.44	4.52	9.71	27.66	49.49	4.72
Before UV	SD	0.37	1.34	0.90	0.62	1.40	5.99	6.66
PD	MV	4.48	12.52	4.20	10.57	27.29	45.22	3.36
After UV	SD	0.37	1.08	0.78	0.66	0.95	2.90	13.19

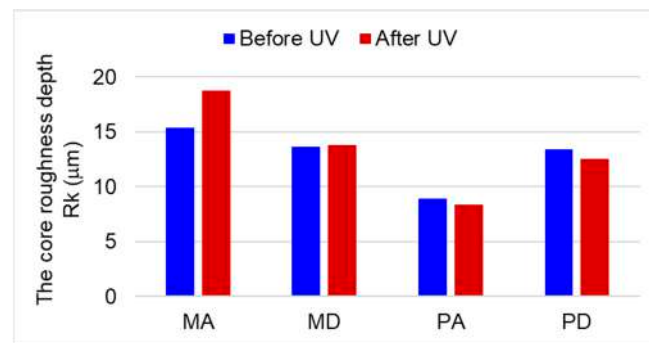


Figure 7. Quantitative analysis of the core roughness depth (Rk) before and after UV treatment.

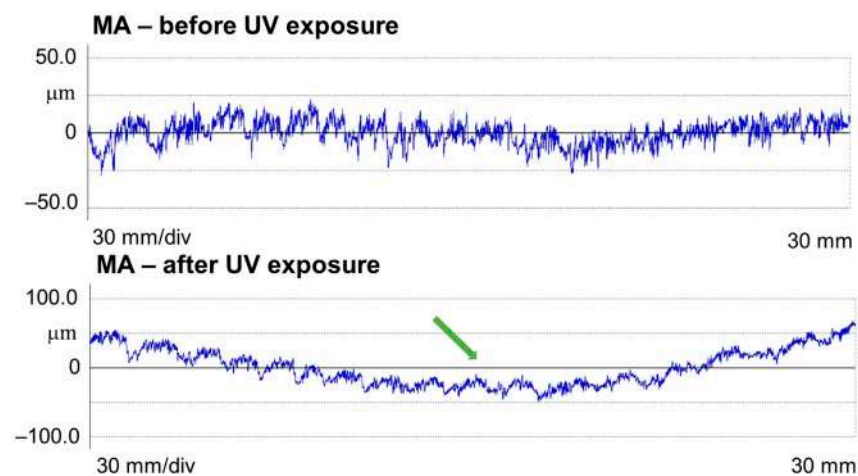


Figure 8. Measured profile of MA spruce samples before and after UV treatment (legend: the deformation/bulging of the piece is marked with the green arrow).

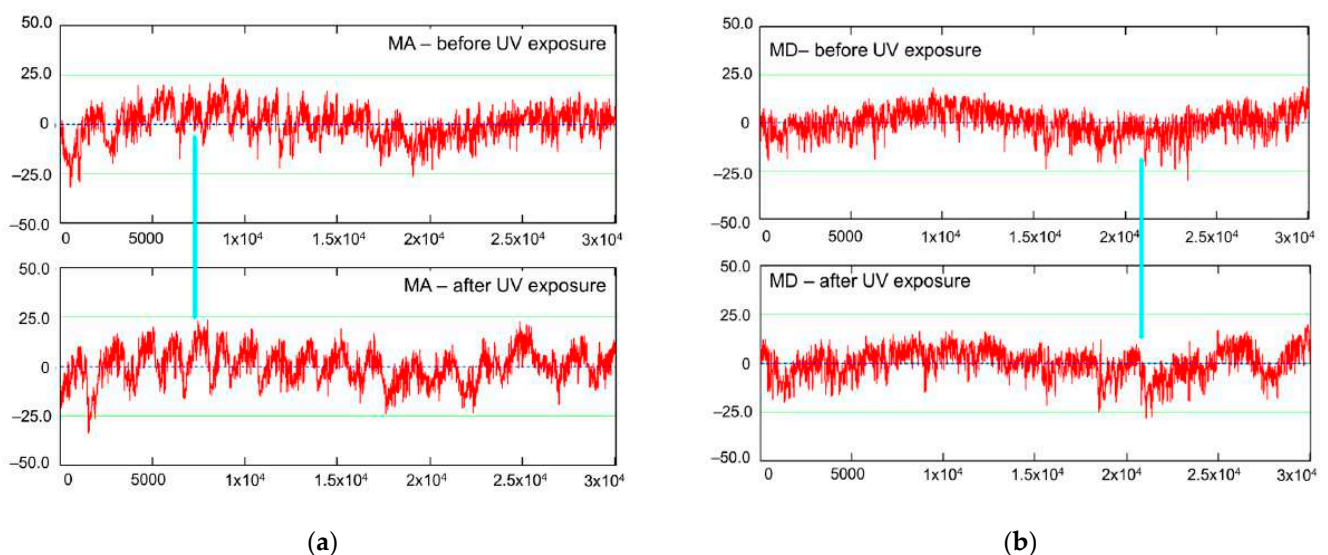


Figure 9. Comparisons of the primary profiles in the case of the MA and MD spruce boards, before (above) and after UV exposure (below): (a) sample grade MA; (b) sample grade MD (legend: the blue arrow highlights the differences in the roughness profiles).

The anatomical waviness of the MA spruce class, characterized by narrower annual rings, gave birth to a higher frequency anatomical waviness when compared to the spruce MD class, where the annual rings were wider (Figure 9).

The separation of roughness irregularities from waviness is made by selecting a filter cut-off. The value that is recommended for wood surfaces, namely 2.5 mm, in accordance with [34], can retain the high-frequency waviness (anatomical waviness) in the roughness profile, which was mainly the case for the spruce MA class (Figure 10) and less for MD. An increase in magnitude for the anatomical waviness is clearly visible (the blue profile) after UV exposure.

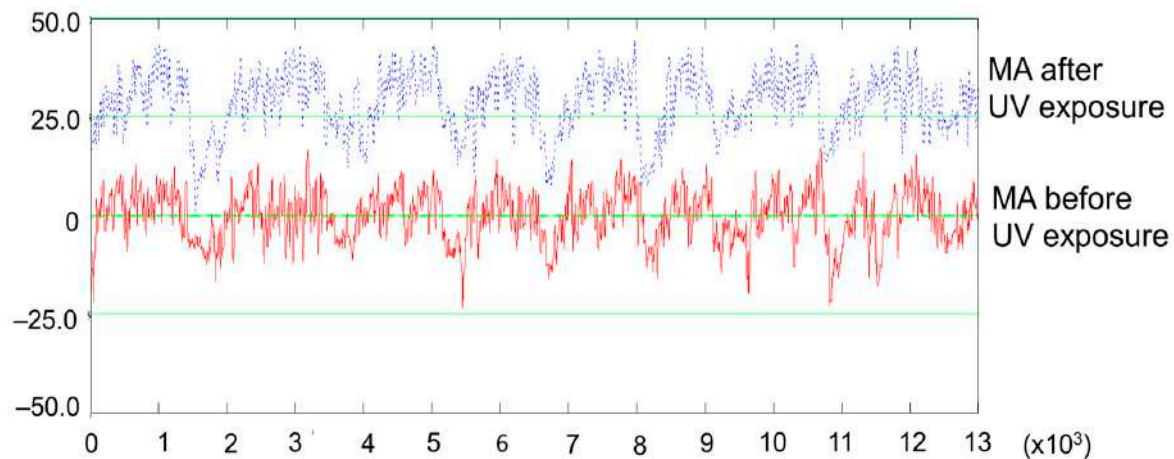


Figure 10. Details of the roughness profiles measured on the MA samples (shown offset and covering a length of 13 mm). Red—before treatment; blue—after UV treatment.

A wavier surface means an increased area of exposure to UV and temperature modification and, thus, a higher likelihood for surface chemical degradation, which will be discussed in Section 3.3. Retaining the anatomical waviness in the roughness profile had an impact on the assessment of the roughness of the MA quality spruce. The central roughness (R_k) of the profile and also the average roughness (R_a) were higher after UV treatment by approx. 22% (Table 2, Figure 7). In the case of the MD quality spruce, the roughness changes produced by the UV treatment were negligible, approx. 1% in the case of R_k and 2% in the case of R_a . Even if the anatomical waviness increased slightly after exposure to UV radiation, the impact on the roughness was reduced.

3.2.3. The Effect of UV Treatment on the Surface Morphology of Sycamore Maple Wood

As in the case of spruce, the exposure of maple to UV light caused surface bulging (Figure 11), and this behavior was present for both qualities of wood. Another observation was that the UV treatment accentuated the surface waviness of the curly maple, where the W_a increased by app. three times (Table 2). As in the case of spruce, an increase in surface waviness causes more area exposure to the modification agent. From Table 2 and Figure 7, it can be observed that before and also after UV treatment, the core roughness (R_k) of the curly maple was smaller than that of the straight-grain maple. The slightly higher density of curly maple (659 kg/m^3) in comparison to straight grain maple (626 kg/m^3), together with different local hardnesses caused by the variation in grain orientation in the curly maple (from along to almost across the grain), might have been responsible for a smoother sanded surface for the curly maple. The effect of the UV treatment on maple wood can be seen in Table 2 and Figure 7 via the discrete decrease in the central roughness of the profile, R_k , by approx. 6–7%, which may be a consequence of a shrinkage phenomenon, narrowing the initial wood cavities and so reducing the ability of the stylus to penetrate.

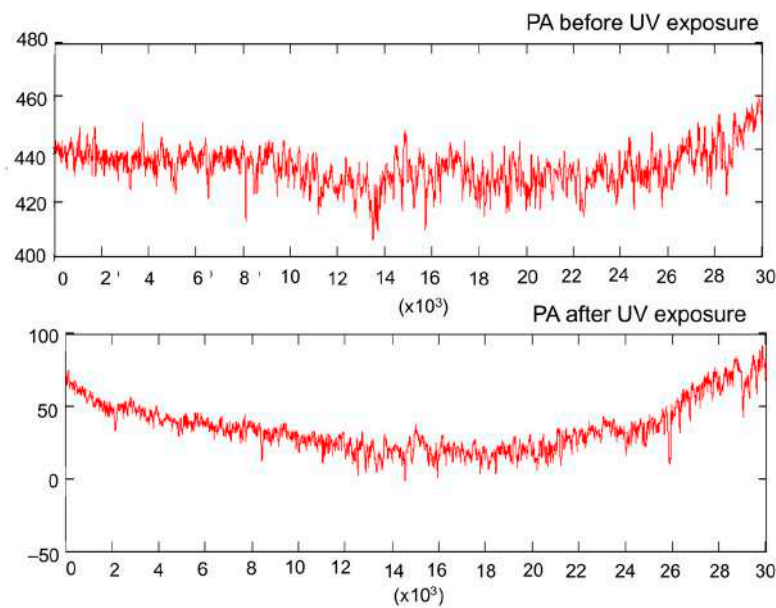


Figure 11. Measured profile of PA sycamore maple samples before and after UV treatment.

The profile comparisons in Figure 12a for curly maple show a discrete shrinkage phenomenon occurring after the treatment, where some of the features have slightly changed their initial location. Another observation in the comparative profiles of Figure 12 was that some of the deepest features (possible earlywood pores) deepened further, which was perhaps due to a cracking effect under treatment. This caused an increase in the Rvk parameter by approx. 11% in PA quality and approx. 9% in PD quality (Table 2).

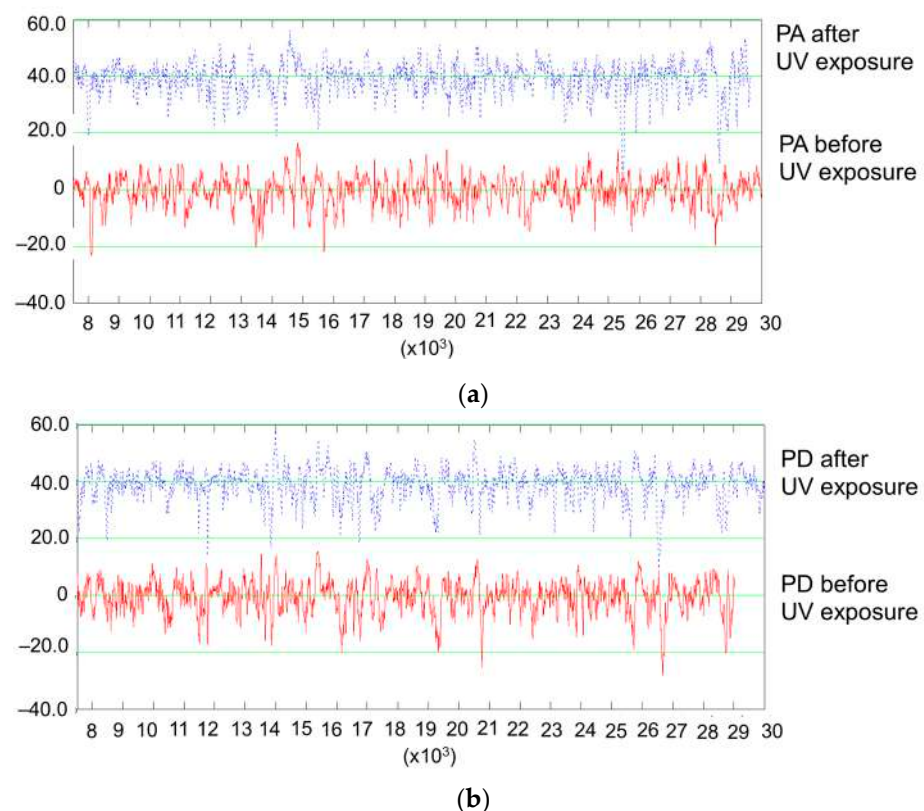


Figure 12. Comparisons of roughness profiles in the case of the PA and PD sycamore maple samples before and after UV exposure: (a) sample grade: PA; (b) sample grade: PD.

It can be concluded that the UV treatment has accentuated the shape deviations from a flat surface and has enlarged the area exposure by accentuating the surface waviness. This phenomenon was more pronounced for quality class A in both species. The surface roughness evaluated by the parameter R_k has a tendency to increase after exposure to UV in the case of spruce samples regardless of the class, and this is mainly attributed to an increase in high-frequency anatomical waviness being retained in the roughness profiles. A slight decrease in the core roughness (R_k) for sycamore maple wood may be attributed to surface shrinkage.

3.3. FTIR Spectroscopy

The comparative spectra for spruce and sycamore maple (Figure 13), as well as the data in Table 3, illustrate the common chemical characteristics of the two wood species as well as some of the differentiating features, such as an increased absorption intensity at 1730 cm^{-1} , which is assigned to unconjugated carbonyl groups that were observed for sycamore maple wood when compared to spruce wood. This can be associated with a higher content of acetyl groups that are mainly present in hemicelluloses of a pentosan type (e.g., xylan), which are found in higher percentages in hardwoods compared to softwoods [43,44].

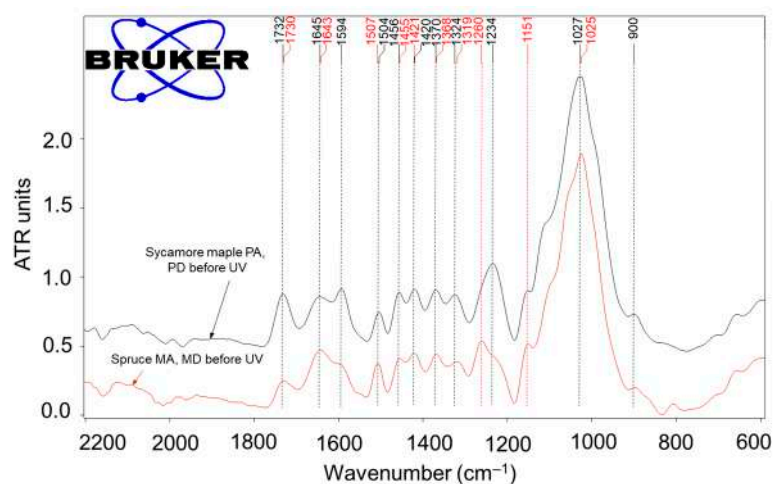


Figure 13. Comparative FTIR spectra for spruce wood and sycamore maple wood samples for the narrow range of $1800\text{--}600\text{ cm}^{-1}$ encompassing the fingerprint region.

Table 3. Chemical differences between spruce and sycamore maple wood before UV exposure.

Samples	The Ratio of the Areas Corresponding to the Wave Number		
	A1730/A1370 Nonconjugated Carbonyl/(Cel + H Cel)	A1504-1507/A1370 Lignin/(Cel + H Cel)	A1730/A1504-1507 Nonconjugated Carbonyl/Lignin
MA before UV	1.87	1.96	0.95
MA after UV	3.91	1.47	2.65
MA after UV/MA before	2.09	0.75	2.78
MD before	1.51	1.99	0.76
MD after UV	3.56	1.38	2.58
MD after UV /MD before	2.36	0.69	3.41
PA before	3.91	1.11	3.52
PA after UV	5.01	0.91	5.50
PA after UV /PA before	1.28	0.82	1.56
PD before UV	3.93	1.37	2.85
PD after UV	4.67	0.84	5.54
PD after UV /PD before	1.19	0.61	1.94

The FTIR analysis also highlighted differences in the characteristic absorptions of lignins; for spruce, an absorption at 1261 cm^{-1} , which is assigned to guaiacyl (G) ring breathing (characteristic for the guaiacyl type lignin (GL) in softwoods), was identified, while for the maple samples, well-defined absorptions at 1325 cm^{-1} and 1235 cm^{-1} , which are assigned to syringyl (S) rings and C-O stretching in lignin and xylan (with contributions from the syringyl ring, respectively), were identified due to the different nature of hardwood lignins, which are of a syringyl-guaiacyl nature (SGL). Additionally, the absorption of the aromatic skeleton vibration of lignin was recorded at 1507 cm^{-1} for spruce and at 1504 cm^{-1} for sycamore maple due to the same structural differences [9,38,44–46]. On the other hand, the absorption of the aromatic nucleus at approximately 1593 cm^{-1} appeared only as a shoulder in the spruce wood spectrum, whereas it was clearly distinct in the maple wood spectrum.

The calculated ratios of the areas of the relevant absorption peaks A1730/A1370 (unconjugated carbonyls/holocellulose) and A1504–1507/A1370 (lignin/holocellulose) (centralized in Table 3) highlighted the differences between the two studied species. Thus, the calculated ratios A1730/A1370 for sycamore maple wood in its initial state (before UV treatment) were 3.91–3.93, which is higher than those calculated for spruce wood: 1.51–1.87 due to a larger amount of acetyl groups in the hemicelluloses (mostly pentosans) that were reported in the global holocellulose content (cellulose and hemicelluloses). On the other hand, the calculated ratios A1504–A1507/A1370 of 1.96–1.99 for spruce compared to 1.11–1.37 for maple are in accordance with the higher content of lignin reported in holocellulose for softwoods compared to hardwoods [43].

The comparative spectra recorded for the sycamore maple and spruce wood before and after UV exposure indicated chemical changes that affected lignin, which is the main UV absorber in wood structures. A decrease in the most characteristic absorption band of lignin ($1504\text{--}1507\text{ cm}^{-1}$) was clearly observed, as well as the intensification of the absorption band at 1730 cm^{-1} , which is characteristic of nonconjugated carbonyl groups. These changes highlight the degradation of lignin and the formation of chromophore compounds with carbonyl groups (Figure 14a,b), which is in good accordance with the literature [8–10,12,38,45–47].

The results of the semi-quantitative evaluation of the chemical change after UV exposure via the calculated absolute and relative ratios of the selected relevant absorptions are contained in Table 3.

The relative ratios were calculated by reporting the absolute ratios after UV exposure to their initial values, allowing for an overview of the processes occurring during the experimental aging procedure and a comparative evaluation of the behavior of the two species. Thus, the decrease in the ratios between lignin and holocellulose (A1510/A1370), resulting in relative ratios lower than 1.0 (0.75–0.69 for spruce; 0.82–0.61 for sycamore maple) highlighted the degradation of lignin regardless of species and quality class, while the increase in the ratios of nonconjugated carbonyl to holocellulose (A1730/A1370), resulting in relative ratios higher than 1.0 (2.09–2.36 for spruce; 1.19–1.28 for sycamore maple) highlighted oxidative processes, with the formation of carbonyl-containing chromophores.

Based on this relative semi-quantitative evaluation, lignin degradation was almost similar for the two species under study, with some variations for both species depending on the quality class of the wood. Lignin degradation appeared to be slightly more intense for the samples in quality class A, both in the case of spruce (8.67%) and sycamore maple (34%), but no conclusion should be drawn based only on this type of evaluation.

The relative ratios of A1730/A1370 clearly suggest more advanced oxidative processes in the case of the spruce wood samples than in the case of maple wood. The generation of carbonyl groups as a result of lignin photo-oxidation was found to be much higher in softwoods when compared to hardwoods by other researchers [38,45]. Based on the relative FTIR ratios calculated in this research, some small differences appeared between the quality classes for both wood species. For the spruce wood class A samples, the formation of carbonyl chromophores seemed to be 13% lower than for the D class samples,

while for the sycamore maple class A samples, the oxidative process seemed more intense, at approximately 7.8% higher than for the class D samples. The two chemical processes occurring in parallel during the UV-induced photo-oxidation of wood (lignin degradation and the oxidation of lignin degradation products, forming colored compounds containing carbonyl chromophores) are cumulatively illustrated by the increase in the ratios of nonconjugated carbonyl/lignin (A_{1730}/A_{1510}), with their relative values higher than 1.0 after UV exposure (Table 3). Values of 2.78–3.41 for the spruce samples (classes A and D) and 1.56–1.64 for the sycamore maple samples (classes A and D) indicate more advanced aging processes for spruce compared to sycamore maple under the experimental conditions employed in this research. This difference resulted mostly from the higher formation of carbonyl-containing chromophores via oxidative processes, which is in good accordance with the greater color changes measured in the spruce samples ($\Delta E = 14.74$ – 15.17) when compared to sycamore maple samples ($\Delta E = 9.26$ – 10.50) presented in Table 1.

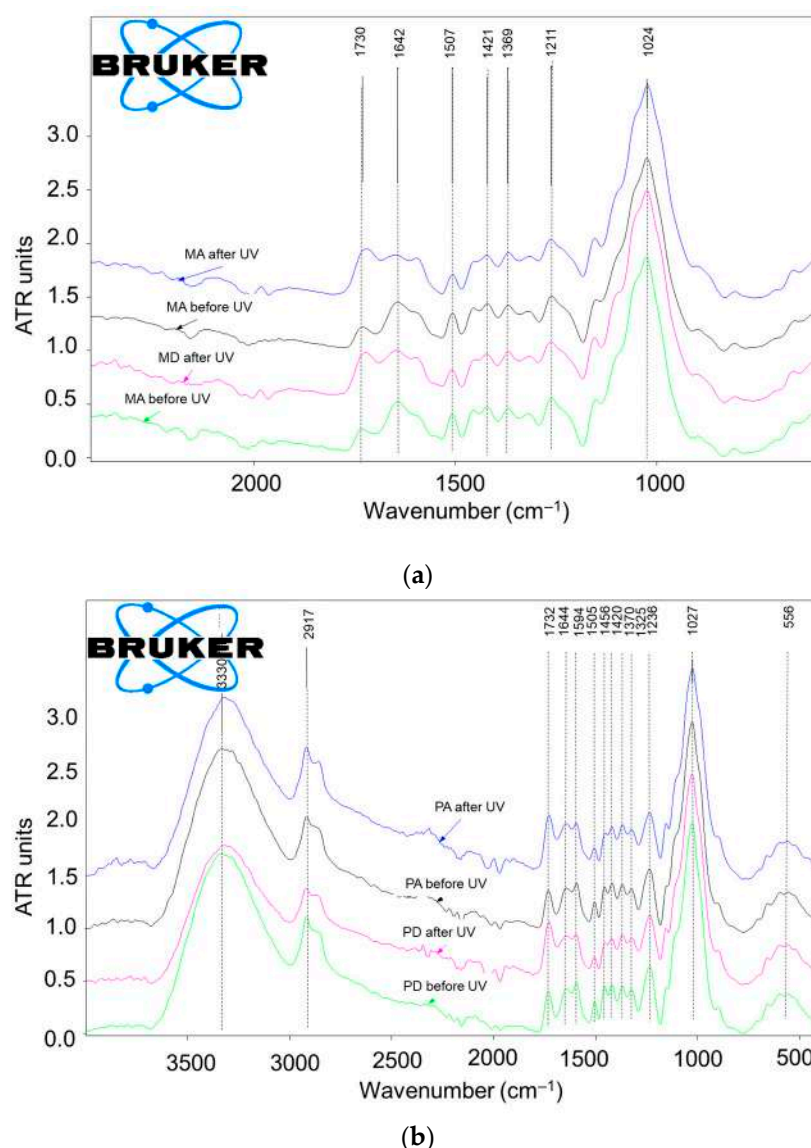


Figure 14. Comparative FTIR spectra (normalized averages) in a narrow range: 2000 – 600 cm^{-1} : (a) samples of spruce wood qualities MA and MD before and after UV exposure; (b) samples of sycamore maple wood qualities PA and PD before and after UV exposure.

3.4. Changes in Acoustic Properties

After thermal and UV aging, all the wood samples used for the construction of musical instruments registered a decrease in density; approximately 19% for the spruce wood samples and approximately 10% for the maple samples (Figure 15a,b). Exposure to UV radiation had the effect of increasing the speed of sound propagation in the wood, both longitudinally and radially, in both species. It was found that the changes produced by the lignin degradation processes (highlighted in Section 3.3.) led to an increase in the sound propagation speed by 5–6% in the longitudinal direction in both the spruce wood and sycamore maple wood. In the radial direction, the increase in the sound speed reached up to 15%, with the anatomical quality class being an indicator of differentiation. Thus, in the case of the quality class A samples, the sound velocity in the radial direction increased after the UV treatment by 14.5% for spruce and 15.5% for sycamore maple when compared to the values obtained for the class D samples (9.7% spruce; 11.5% maple) (Figure 15c–f). The Young's modulus values in the longitudinal direction, for which the calculation is based on the product of the speed squared and the density, recorded an increase after exposure to UV radiation, with 3% for the PA samples, 6% for the PD samples, 3.1% for the MA samples, and 3.5% for the MD samples. The most notable changes were registered in the radial direction, where the modulus of elasticity had the largest increase in the class D samples for both spruce and maple (Figure 15g–j).

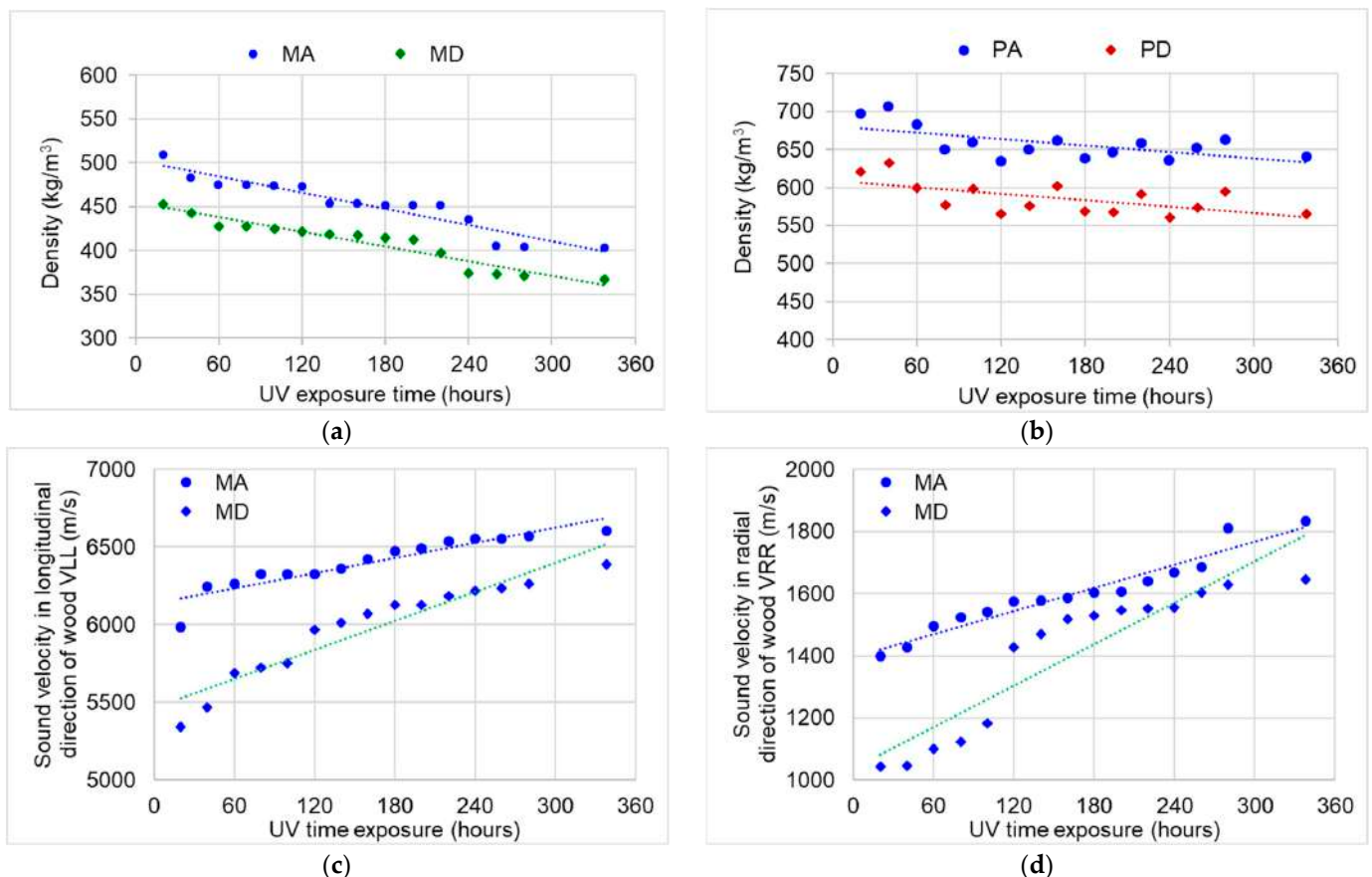


Figure 15. Cont.

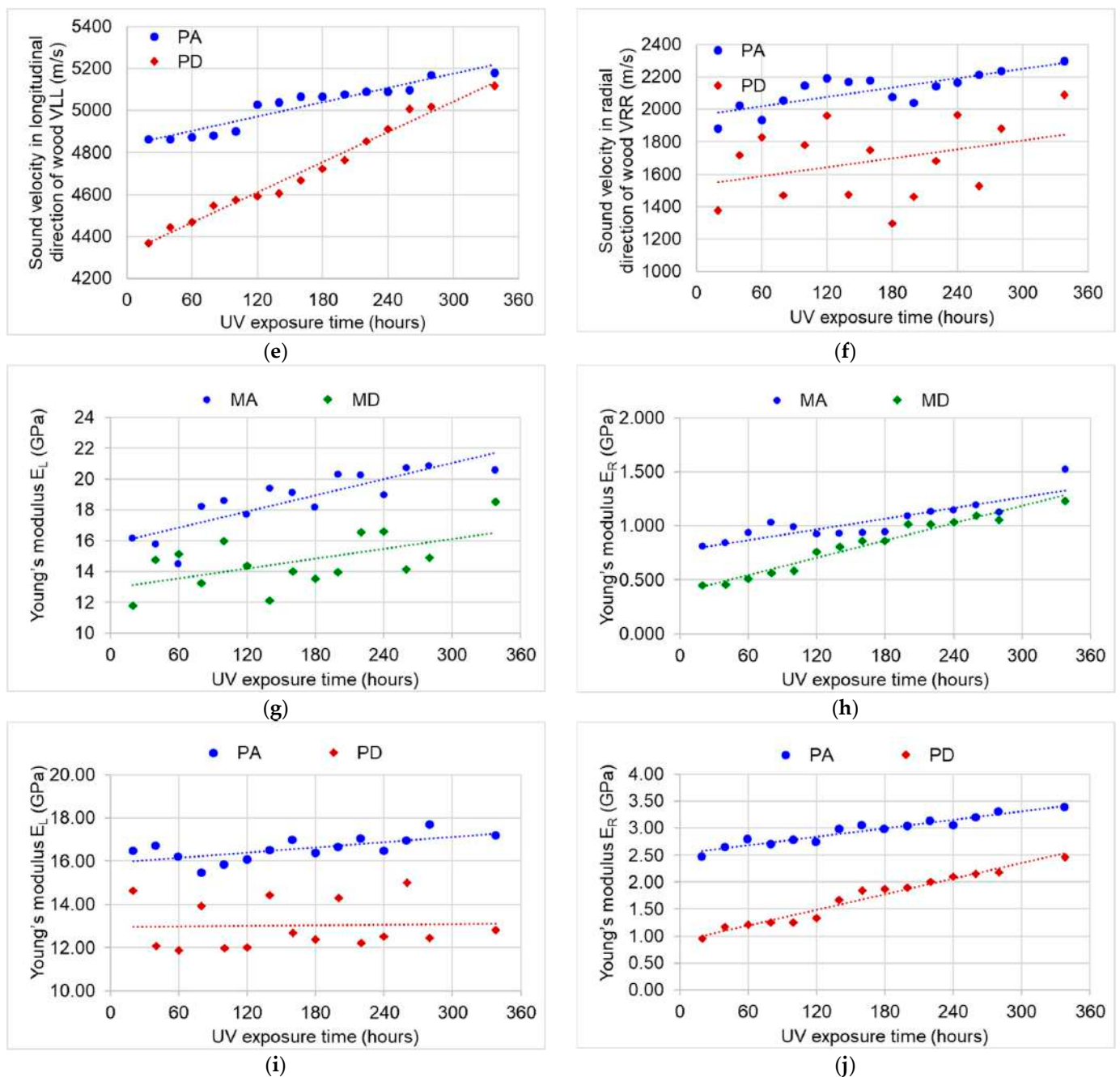


Figure 15. The variation in the physical, acoustic, and elastic parameters with aging duration: (a) density variation in the spruce samples; (b) density variation in the maple samples; (c) variation in sound velocity in spruce wood in the longitudinal direction; (d) variation in the sound velocity in the spruce samples in the radial direction; (e) variation in the sound velocity in the sycamore maple samples in the longitudinal direction; (f) variation if the sound velocity in the sycamore maple samples in the radial direction; (g) variation in the Young's modulus in the spruce samples in the longitudinal direction; (h) variation in the Young's modulus in the spruce samples in the radial direction; (i) variation in the Young's modulus in the sycamore maple samples in the longitudinal direction; (j) variation in the Young's modulus in the sycamore maple samples in the radial direction.

Table 4 summarizes the acoustic and elastic parameters measured during exposure to thermal and UV treatment. It can be observed that the only property that registered a decrease in value was the density of both species and qualities.

Table 4. Summary of acoustic and elastic parameters determined before and during exposure to UV. Legend: ρ —density (kg/m^3); V_{LL} —sound velocity in wood in the longitudinal direction, (m/s); V_{RR} —sound velocity in wood in the radial direction, (m/s); E_L —elasticity modulus in the longitudinal direction (GPa); E_R —elasticity modulus in the radial direction (GPa); MD—mean value; SD—standard deviation.

		Spruce MA					Spruce MD				
		Initial	72 h	192 h	266 h	300 h	Initial	72 h	192 h	266 h	300 h
ρ ($\text{kg}\cdot\text{m}^{-3}$)	MV	476	459	444	443	442	431	406	405	404	399
	SD	37	13	35	35	36	30	29	30	28	29
		$y = -0.1634x + 479.6$					$y = -0.0563x + 418.62$				
V_{LL} (m/s)	MV	6187	6387	6458	6474	6513	5776	5958	5963	6075	6091
	SD	180	108	117	127	134	374	423	238	303	320
		$y = 1.7366x + 6125.9$					$y = 3.3054x + 5443.7$				
V_{RR} (m/s)	MV	1529	1538	1602	1643	1704	1329	1377	1400	1426	1459
	SD	42	113	90	59	113	251	286	263	272	243
		$y = 44.6x + 1452.6$					$y = 30.733x + 1306.1$				
E_L (GPa)	MV	18.27	18.53	18.63	18.74	18.85	14.50	14.51	14.56	14.94	15.00
	SD	2.33	0.94	2.02	2.15	2.23	2.74	2.92	2.17	2.43	2.48
		$y = -0.0016x + 18.86$					$y = 0.006x + 13.72$				
E_R (GPa)	MV	0.79	1.02	1.08	1.13	1.20	0.81	0.83	0.86	0.88	1.30
	SD	0.12	0.17	0.09	0.10	0.26	0.32	0.35	0.34	0.34	0.33
		$y = 0.0016x + 0.77$					$y = 0.0027x + 0.39$				
		Sycamore maple (PA)					Maple PD				
ρ ($\text{kg}\cdot\text{m}^{-3}$)	MV	695	651	649	648	646	618	582	581	578	573
	SD	12	12	12	11	10	16	17	18	16	15
		$y = -0.1428x + 681.13$					$y = -0.1408x + 609.17$				
V_{LL} (m/s)	MV	4866	4937	5057	5084	5149	4557	4662	4755	4763	4818
	SD	5.20	80.30	15.59	6.35	45.31	260.29	225.16	221.52	238.53	275.65
		$y = 0.6465x + 4605.9$					$y = 0.6465x + 4605.9$				
V_{RR} (m/s)	MV	1947	2115	2141	2130	2249	1506	1641	1701	1737	1831
	SD	70.77	70.38	55.99	65.59	43.97	237.23	249.30	226.70	252.63	283.52
		$y = 0.9598x + 1960.4$					$y = 0.9191x + 1533.9$				
E_L (GPa)	MV	15.78	16.33	16.53	16.87	17.30	11.94	12.23	12.55	13.68	14.69
	SD	2.92	1.37	0.92	1.48	3.47	0.08	0.16	0.13	0.77	0.30
		$y = 0.004x + 15.92$					$y = 0.0005x + 12.94$				
E_R (GPa)	MV	2.64	2.89	2.94	2.98	3.29	1.11	1.28	1.79	2.00	2.27
	SD	0.136	0.052	0.108	0.103	0.17	0.14	0.05	0.11	0.10	0.17
		$y = 0.0026x + 2.5215$					$y = 0.0048x + 0.9083$				

The other properties (sound velocity, as well as the modulus of elasticity in the longitudinal and radial direction) increased after repeated exposure to UV. Their highest increase was obtained in the radial direction regardless of the species. From a qualitative point of view, it can be concluded that the UV and thermal treatment led to an improvement in the acoustic and elastic parameters of the wood selected for musical instruments, as characterized by the relatively low thickness (maximum 4 mm) studied in this paper. In agreement with the above findings, the literature data [17,24,25,28,48–53] confirm that the ultrasound velocity and dynamic elastic modulus of the aged wood shift to higher values when compared to that of recently produced wood.

In Figure 16, the stiffness rate of change for all samples is represented, which is calculated as a percentage difference between the values at successive exposure durations. It can be observed that the samples from class A, both spruce and sycamore maple, show the same trend for the elasticity modulus in both the longitudinal and radial directions. The most important changes occur at the beginning of the exposure (after 72 h), and then a decrease in the rate of change is recorded. After 300 h, in the case of the sycamore maple samples, the rate of change of the analyzed parameter increases again. In the class D

samples, the most important changes in the longitudinal direction occur from 200 h of aging onwards.

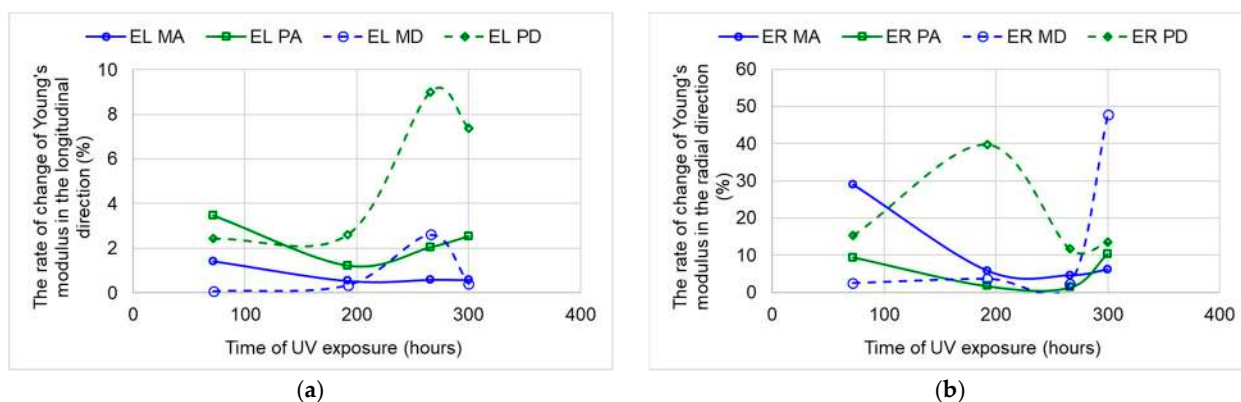


Figure 16. The rate of change in the Young's modulus with exposure time: (a) in the longitudinal direction; (b) in the radial direction.

4. Conclusions

The aim of this paper was to analyze the changes induced via exposure to UV radiation and temperature on the physical, chemical, and acoustic properties of two quality classes (A and D) of spruce and sycamore maple wood. The main results are summarized as follows:

- The UV treatment induced an increase in the total color change, which was more accentuated in spruce compared to sycamore maple. However, the differences in the color change between the two quality classes (A and D) were insignificant;
- The FTIR results indicated a more advanced aging process for spruce compared to maple under the same experimental conditions. This difference resulted mostly from the formation of more carbonyl-containing chromophores by oxidative processes, which is in good accordance with the greater color changes measured in the spruce samples compared to the sycamore maple samples;
- A wavier surface after the UV treatment increased the area of exposure and degradation, and this was more pronounced for quality class A;
- For both species, the sound speed increased after the UV treatment in the longitudinal as well as in the radial direction. UV exposure improved the sound speed to the greatest extent for quality class A (of the two species) and for radial direction sound propagation. The quality class A samples registered a sound speed increase in the radial direction of 14.5% (spruce) and 15.5% (maple) when compared to class D (9.7% spruce; 11.5% sycamore maple). The sound velocity increased by approx. 5–6% in the longitudinal direction;
- The most important changes in the stiffness of the class A boards (spruce and sycamore maple) occurred in the first 72 h of exposure to thermal and UV radiation and after 200 h for the class D samples.

Author Contributions: Conceptualization, M.D.S. and C.C.; methodology, L.G., M.C., M.C.T. and M.D.S.; software, L.G., M.C.T. and M.D.S.; validation, C.C. and M.C.; formal analysis, L.G., M.C.T. and M.D.S.; investigation, L.G., M.C.T., M.D.S. and M.C.; resources, M.D.S.; data curation, L.G., M.C.T. and C.C.; writing—original draft preparation, M.D.S. and C.C.; writing—review and editing, L.G., M.C. and M.C.T.; visualization, M.D.S.; supervision, L.G. and M.C.T.; project administration, M.D.S.; funding acquisition, M.D.S. All authors have read and agreed to the published version of the manuscript.

Funding: This research was supported by a grant from the Ministry of Research, Innovation and Digitization, CNCS/CCCDI—UEFISCDI, project number 61PCE/2022, PN-III-P4- PCE2021-0885, ACADIA—Qualitative, dynamic and acoustic analysis of anisotropic systems with modified interfaces.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: <https://acadia.unitbv.ro/index.php>.

Acknowledgments: We hereby acknowledge the structural funds project PRO-DD (POS-CCE,O.2.2.1., ID 123, SMIS 2637, No. 11/2009) for providing the infrastructure used in this work. We are grateful to the technical staff of Gliga Musical Instruments, Reghin, a Romanian manufacturer of musical string instruments, for supplying the specimens.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Stoel, B.C.; Borman, T.M. A Comparison of Wood Density between Classical Cremonese and Modern Violins. *PLoS ONE* **2008**, *3*, e2554. [CrossRef]
2. Stanciu, M.D.; Mihălcică, M.; Dinulică, F.; Nauncef, A.M.; Purdoi, R.; Lăcătuș, R.; Gliga, G.V. X-ray Imaging and Computed Tomography for the Identification of Geometry and Construction Elements in the Structure of Old Violins. *Materials* **2021**, *14*, 5926. [CrossRef]
3. Su, C.K.; Chen, S.Y.; Chung, J.H.; Li, G.C.; Brandmair, B.; Huthwelker, T.; Fulton, J.L.; Borca, C.N.; Huang, S.J.; Nagyvary, J.; et al. Materials Engineering of Violin Soundboards by Stradivari and Guarneri. *Angew. Chem. Int. Ed. Engl.* **2021**, *60*, 19144–19154. [CrossRef] [PubMed]
4. Smidt, E.; Schwanninger, M.; Tintner, J.; Böhm, K. Ageing and Deterioration of Materials in the Environment—Application of Multivariate Data Analysis. In *Multivariate Analysis in Management, Engineering and Science*; IntechOpen: London, UK, 2013. [CrossRef]
5. Hernandez, V.A.; Romero, R.; Sagredo, N.; Contreras, D.; Evans, P.D. Studies of the Photoprotection of Radiata Pine Wood Using Photocatalytic Nanoparticles. *Forests* **2022**, *13*, 1922. [CrossRef]
6. Tolvaj, L.; Molnár, S. Photodegradation and thermal degradation of outdoor wood. In Proceedings of the Wood Science for Preservation of Cultural Heritage: Mechanical and Biological Factors, Braga, Portugal, 5–7 November 2008; pp. 67–72.
7. Kojiro, K.; Furuta, Y.; Ohkoshi, M.; Ishimaru, Y.; Yokoyama, M.; Sugiyama, J.; Kawai, S.; Mitsutani, T.; Ozaki, H.; Sakamoto, M.; et al. Changes in micropores in dry wood with elapsed time in the environment. *J. Wood Sci.* **2008**, *54*, 515–519. [CrossRef]
8. Tolvaj, L.; Molnár, Z.; Németh, R. Photodegradation of wood at elevated temperature: Infrared spectroscopic study. *J. Photochem. Photobiol. B Biol.* **2013**, *121*, 32–36. [CrossRef]
9. Timar, M.C.; Varodi, A.M.; Gurau, L. Comparative study of photodegradation of six wood species after short-time UV exposure. *Wood Sci. Technol.* **2016**, *50*, 135–163. [CrossRef]
10. Liu, X.Y.; Timar, M.C.; Varodi, A.M.; Sawyer, G. An investigation of accelerated temperature-induced ageing of four wood species: Colour and FTIR. *Wood Sci. Technol.* **2016**, *51*, 357–378. [CrossRef]
11. Liu, X.; Timar, M.C.; Varodi, A.M.; Nedelcu, R.; Torcătoru, M.-J. Colour and Surface Chemistry Changes of Wood Surfaces Coated with Two Types of Waxes after Seven Years Exposure to Natural Light in Indoor Conditions. *Coatings* **2022**, *12*, 1689. [CrossRef]
12. Tolvaj, L.; Molnar, Z.; Magoss, E. Measurement of photodegradation-caused roughness of wood using a new optical method. *J. Photochem. Photobiol. B Biol.* **2014**, *134*, 23–26. [CrossRef] [PubMed]
13. Jirouš-Rajković, V.; Miklečić, J. Enhancing Weathering Resistance of Wood—A Review. *Polymers* **2021**, *13*, 1980. [CrossRef] [PubMed]
14. Kuo, M.-L.; Hu, N. Ultrastructural Changes of Photodegradation of Wood Surfaces Exposed to UV. *Holzforschung* **1991**, *45*, 347–353. [CrossRef]
15. Froidevaux, J.; Volkmer, T.; Ganne-Chédeville, C.; Gril, J.; Navi, P. Viscoelastic behavior of aged and non-aged spruce wood in the radial direction. *Wood Mater. Sci. Eng.* **2012**, *7*, 1–12. [CrossRef]
16. Kránitz, K.; Deublein, M.; Niemz, P. Determination of dynamic elastic moduli and shear moduli of aged wood by means of ultrasonic devices. *Mater. Struct.* **2013**, *47*, 925–936. [CrossRef]
17. Noguchi, T.; Obataya, E.; Ando, K. Effects of aging on the vibrational properties of wood. *J. Cult. Heritage* **2012**, *13*, S21–S25. [CrossRef]
18. Gall, R.; Stanciu, M.D.; Filimon, E.; Cosnita, M.; Gliga, V.G. The influence of artificial aging on resonance wood on its physical characteristics. In Proceedings of the 9th International Conference on Advanced Composite Materials Engineering, Brasov, Romania, 17–18 October 2022; pp. 73–81.
19. Van Blokland, J.; Adamopoulos, S.; Ahmed, S.A. Performance of Thermally Modified Spruce Timber in Outdoor Above-Ground Conditions: Checking, Dynamic Stiffness and Static Bending Properties. *Appl. Sci.* **2020**, *10*, 3975. [CrossRef]
20. Chédeville, C.G.; Jääskeläinen, A.S.; Froidevaux, J.; Hughes, M.; Navi, P. Natural and artificial ageing of spruce wood as observed by FTIR-ATR and UVR spectroscopy. *Holzforschung* **2012**, *66*, 163–170. [CrossRef]
21. Cirule, D.; Kuka, E.; Andersone, I.; Andersons, B. Wood discoloration patterns depending on the light source. *Heritage Sci.* **2022**, *10*, 158. [CrossRef]

22. Oltean, L.; Teischinger, A.; Hansmann, C. Wood surface discolouration due to simulated indoor sunlight exposure. *Holz Als Roh-Und Werkst.* **2008**, *66*, 51–56. [[CrossRef](#)]
23. Zeniya, N.; Obataya, E.; Endo-Ujii, K.; Matsuo-Ueda, M. Changes in vibrational properties and colour of spruce wood by hygrothermally accelerated ageing at 95–140 °C and different relative humidity levels. *SN Appl. Sci.* **2018**, *1*, 7. [[CrossRef](#)]
24. Obataya, E. Effects of natural and artificial ageing on the physical and acoustic properties of wood in musical instruments. *J. Cult. Herit.* **2017**, *27*, S63–S69. [[CrossRef](#)]
25. Ono, T. Frequency responses of wood for musical instruments in relation to the vibrational properties. *Acoust. Sci. Technol.* **1996**, *17*, 183–193. [[CrossRef](#)]
26. Danihelová, A.; Vidholdová, Z.; Gergel, T.; Kružlicová, L.S.; Pástor, M. Thermal Modification of Spruce and Maple Wood for Special Wood Products. *Polymers* **2022**, *14*, 2813. [[CrossRef](#)]
27. Mania, P.; Gasiorek, M. Acoustic Properties of Resonant Spruce Wood Modified Using Oil-Heat Treatment (OHT). *Materials* **2020**, *13*, 1962. [[CrossRef](#)] [[PubMed](#)]
28. Dinulică, F.; Stanciu, M.D.; Savin, A. Correlation between Anatomical Grading and Acoustic–Elastic Properties of Resonant Spruce Wood Used for Musical Instruments. *Forests* **2021**, *12*, 1122. [[CrossRef](#)]
29. Dinulică, F.; Savin, A.; Stanciu, M.D. Physical and Acoustical Properties of Wavy Grain Sycamore Maple (*Acer pseudoplatanus* L.) Used for Musical Instruments. *Forests* **2023**, *14*, 197. [[CrossRef](#)]
30. Tismanar, I.; Obreja, A.C.; Buiu, O.; Duta, A. VIS-active TiO₂—graphene oxide composite thin films for photocatalytic applications. *Appl. Surf. Sci.* **2020**, *538*, 147833. [[CrossRef](#)]
31. Yin, H.; Moghaddam, M.S.; Tuominen, M.; Dédinaite, A.; Wälinder, M.; Swerin, A. Wettability performance and physicochemical properties of UV exposed superhydrophobized birch wood. *Appl. Surf. Sci.* **2022**, *584*, 152528. [[CrossRef](#)]
32. Sahin, H.T.; Mantanis, G.I. Colour changes in wood surfaces modified by a nanoparticulate based treatment. *Wood Res.* **2011**, *56*, 525–532.
33. Stanciu, M.D.; Sova, D.; Savin, A.; Ilias, N.; Gorbacheva, G.A. Physical and Mechanical Properties of Ammonia-Treated Black Locust Wood. *Polymers* **2020**, *12*, 377. [[CrossRef](#)]
34. Gurau, L.; Irle, M. Surface Roughness Evaluation Methods for Wood Products: A Review. *Curr. For. Rep.* **2017**, *3*, 119–131. [[CrossRef](#)]
35. ISO 4287:2009; Geometrical Product Specifications (GPS). Surface Texture: Profile Method. Terms. Definitions and Surface Texture Parameters. International Organization for Standardization: London, UK, 2009.
36. ISO 13565-2:1998; Geometrical Product Specifications (GPS)—Surface Texture: Profile Method. Surfaces Having Stratified Functional Properties. Part 2: Height Characterisation Using the Linear Material Ratio Curve. International Organization for Standardization: London, UK, 1998.
37. Gurau, L. The Roughness of Sanded Wood Surfaces. Ph.D. Thesis, Brunel University, London, UK, 2004.
38. Pandey, K.K.; Vuorinen, T. Comparative study of photodegradation of wood by a UV laser and a xenon light source. *Polym. Degrad. Stab.* **2008**, *93*, 2138–2146. [[CrossRef](#)]
39. Müller, U.; Rätzsch, M.; Schwanninger, M.; Steiner, M.; Zöbl, H. Yellowing and IR-changes of spruce wood as result of UV-irradiation. *J. Photochem. Photobiol. B Biol.* **2003**, *69*, 97–105. [[CrossRef](#)] [[PubMed](#)]
40. Kránitz, K.; Sonderegger, W.; Bues, C.-T.; Niemz, P. Effects of aging on wood: A literature review. *Wood Sci. Technol.* **2015**, *50*, 7–22. [[CrossRef](#)]
41. Kataoka, Y.; Kiguchi, M.; Williams, R.S.; Evans, P.D. Violet light causes photodegradation of wood beyond the zone affected by ultraviolet radiation. *Holzforschung* **2007**, *61*, 23–27. [[CrossRef](#)]
42. Kataoka, Y. Photodegradation of Wood and Depth Profile Analysis. *Mokuzai Gakkaishi* **2008**, *54*, 165–173. [[CrossRef](#)]
43. Fengel, D.; Wegener, G. *Wood—Chemistry, Ultrastructure, Reactions*; Walter de Gruyter: Berlin, Germany; New York, NY, USA, 1984.
44. Wagenführ, R. *Holzatlas (Wood Atlas)*; Hanser Fachbuchverlag: Leipzig, Germany, 2000. (In German)
45. Chang, H.-T.; Yeh, T.-F.; Chang, S.-T. Comparisons of chemical characteristic variations for photodegraded softwood and hardwood with/without polyurethane clear coatings. *Polym. Degrad. Stab.* **2002**, *77*, 129–135. [[CrossRef](#)]
46. Chang, T.-C.; Chang, H.-T.; Wu, C.-L.; Chang, S.-T. Influences of extractives on the photodegradation of wood. *Polym. Degrad. Stab.* **2010**, *95*, 516–521. [[CrossRef](#)]
47. Agresti, G.; Bonifazi, G.; Calienno, L.; Capobianco, G.; Lo Monaco, A.; Pelosi, C.; Picchio, R.; Serranti, S. Surface Investigation of Photo-Degraded Wood by Colour Monitoring, Infrared Spectroscopy, and Hyperspectral Imaging. *J. Spectrosc.* **2013**, *2013*, 380536. [[CrossRef](#)]
48. Crețu, N.; Roșca, I.C.; Stanciu, M.D.; Gliga, V.G.; Cerbu, C. Evaluation of Wave Velocity in Orthotropic Media Based on Intrinsic Transfer Matrix. *Exp. Mech.* **2022**, *62*, 1595–1602. [[CrossRef](#)]
49. Danihelová, A.; Spisiak, D.; Halachan, P.; Gergel, T.; Kružlikova, L. Physico-acoustical characteristics of usual and unusual wood species. *Akustika* **2015**, *35*, 22–27.
50. Kúdela, J.; Kunštár, M. Physical-acoustical characteristics of maple wood with wavy structure. *Ann. Warsaw Univ. Life Sci.—SGGW For. Wood Technol.* **2011**, *75*, 12–18.
51. Yoshikawa, S.; Waltham, C. Woods for Wooden Musical Instruments. In Proceedings of the International Symposium on Musical Acoustics (ISMA) 2014, Le Mans, France, 7–12 July 2014.

52. Brémaud, I. Acoustical properties of wood in string instruments soundboards and tuned idiophones: Biological and cultural diversity. *J. Acoust. Soc. Am.* **2012**, *131*, 807–818. [[CrossRef](#)] [[PubMed](#)]
53. Straže, A.; Jerman, J.; Brus, R.; Merela, M.; Gorisek, Z.; Krajnc, L. Selected structural, physical and acoustic properties of sycamore maple wood with fiddleback figure. In Proceedings of the 9th Hardwood Conference, An underutilized resource: Hardwood Oriented Research, Sopron, Hungary, 24–25 June 2021; pp. 261–266.

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.

Tunable Acoustic Properties Using Different Coating Systems on Resonance Spruce Wood

Mariana Domnica Stanciu,* Mihaela Coșniță, Ghiorghe Vasile Gliga, Lidia Gurau,* Maria Cristina Timar, Maria Violeta Guiman, Silviu Marian Năstac, Ioan Călin Roșca, Voichita Bucur, and Florin Dinulică

The study investigates the effect of the type of varnish and the number of layers on some acoustic properties of the resonance spruce in combination with the changes produced in some physical, morphological, and chemical properties of wood. In addition to color changes and surface chemistry, the surface roughness and morphology are modified by the thickness of the varnish film, 10 layers being optimal from this point of view, as well as the oil-based finish. The sound absorption coefficient increases with the number of varnish layers and varies with the sound frequency range, varnish type, and wood quality, all contributing to the acoustic tunability. For example, for a sound frequency of 1.5 kHz, it is observed that the oil-based varnish with 5 and 10 layers contributes to a full sound, while the alcohol varnish, due to a lower absorption coefficient for this frequency, can lead to some nasal sounds. Applying more than 10 layers of varnish does not improve the sound performance as it will soften the sound in an oil-based finish and make the sound too sharp in the case of alcohol-varnished wood.

violin correlated with the constructive form, and the applied varnishing system. The acoustic quality of the resonance wood has been the subject of numerous studies relating this quality with the physical, elastic, and acoustic properties of wood. Some studies classified the acoustic quality of wood according to its anatomical characteristics such as, for example, the proportion of early wood–late wood and the width of the annual rings.^[1–4] With regard to the construction of the historical as well as of the nowadays violins precious information was gathered by means of various imaging methods that now constitute valuable 3D digital models and help luthiers and researchers to understand the technology of violin-making. The dynamics and acoustics of violins, with an emphasis on dynamic signature modes, have

been highlighted in studies that shed light on properties such as resonance frequencies, the acoustic radiation of violins, and the frequency spectrum.^[5–7] Some studies have compared the acoustic parameters of varnished and unvarnished violins as it has been proven that the applied varnish system changes the dynamic response of the instruments, at least until the evaporation of the solvent at the wood–varnish interface.^[8–11] Some studies outlined the acoustic differences between the contemporary violins manufactured with the same shape, geometry, and wood material as the historical violins, which hypothetically could be attributed to the differences in the finishing system (varnish).^[12–14] Although the varnish plays the role of protecting the wood (musical instrument) against environmental humidity fluctuations, but also an aesthetic role, the amorphous structure of the varnish produces changes at the vibrational and acoustic level. Thus, the research carried out by refs. [13–16] highlighted that both: the type of varnish (resin type) and especially the number of layers (film thickness) are responsible for the change in the acoustic quality of a violin, either ennobling or affecting the quality it had before being varnished. The argument of these researchers is related to the surface and mechanical changes that occur as a result of applying the varnish films, and on the other hand, the changes in the porosity and surface roughness of wood, as well as the increase in mass, stiffness and internal friction of the new system (varnish film and wood). According to refs. [12–15] the

1. Introduction

Studies on the acoustic quality of violins have highlighted the three determining factors: factors related to the wood material (species, the quality of the anatomical structure), the size of the

M. D. Stanciu, M. Coșniță, G. V. Gliga, L. Gurau, M. C. Timar, M. V. Guiman, S. Marian Năstac, I. Călin Roșca, F. Dinulică
Transilvania University of Brasov
29 Eroilor, Brasov 500036, Romania
E-mail: mariana.stanciu@unitbv.ro; lidiagurau@unitbv.ro
S. Marian Năstac
Engineering and Agronomy Faculty in Braila
“Dunarea de Jos” University of Galati
Calarasilor 29, Braila 810017, Romania
V. Bucur
School of Science
RMIT University
GPO Box 2476, Melbourne, VIC 3001, Australia

The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/admi.202300781>

© 2024 The Authors. Advanced Materials Interfaces published by Wiley-VCH GmbH. This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

DOI: 10.1002/admi.202300781

application of varnish leads to an instant decrease in the resonant frequency of the plate due to the increase in mass, but the stiffness effects develop gradually as a result of the rheological phenomena that occur during the process of hardening the varnish film, with effects different on the two main directions of the violin plates (longitudinal and radial). These processes continued even after the drying of the varnish was complete.

Interdisciplinary research on the chemical content of the varnishes of old violins performed in order to identify the chemical elements responsible for the acoustic quality has highlighted the existence of some mineral particles used as pore-filling material.^[17] However, in the literature, there are controversies on the chemical fingerprints of old varnishes, especially regarding the preparation of recipes. Although some researchers consider that the varnish system is responsible for the acoustic quality of antique violins, Cai et al.^[18] proposes the analysis of cellulose rearrangement patterns as a result of both wood aging and long-term exposure of musical instruments to vibrations. It is certain that, regardless of the varnish used, the film thickness (number of applied layers) and the wood–varnish interface lead to changes in the elastic and vibrational properties of the resonance wood used as a support. Wood varnishing is generating a new, asymmetrical layered system, influencing not only the longitudinal (E_L) and radial (E_R) modulus of elasticity but also the shear modulus in the longitudinal-radial plane (G_{LR}).^[19–21]

To simplify calculations and comparisons with other materials, some researchers^[5] introduced the equivalent elastic and acoustic values that depend on the wood's main directions and the quality class of the musical instruments. For violins, E_R and G_{LR} have a predominant influence on the acoustic sound propagation and the acoustic radiation in comparison with E_L . The equivalent quality factor shows that, for instruments in the guitar category, the damping properties along the longitudinal directions tend to predominate, while for instruments in the violin family, the damping properties in the radial direction are more important. Taking into account the typical elastic and damping properties of spruce boards, i.e., long and narrow boards, they are intrinsically more damped than short and wide boards. Although the soundboard is appreciated for the high speed of sound propagation in the longitudinal direction, the ability of wood to dampen sounds plays an important role in the acoustic quality of the musical instrument. In this respect, the influence of the thickness of the polyurethane finishing layers on the acoustic absorption coefficient of the resonance wood used in piano construction was highlighted by some authors.^[22] They found that an increase in the varnish layer thickness leads to an increase in the acoustic absorption coefficient for frequencies higher than 2500 Hz, while, at frequencies between 1000–2000 Hz, the values of the absorption coefficient decrease. The wood species influences the values of the absorption coefficient. Similar studies on the acoustic absorption of wood from different wood species were also reported.^[23–28] Thus, the wood–varnish system found in the construction of musical instruments presents distinct acoustic properties compared to the wood material itself. The asymmetry of the system structure as a result of applying the varnish film only on one surface (the face of the instrument), produces a difference in the acoustic behavior of the plate in contact with the sound waves. Knowing that the stiffness of the varnished boards is different from the stiffness of unvarnished ones, based on ex-

perimental research, some authors^[29] developed a mathematical model for calculating the modulus of elasticity of the asymmetric varnishing system containing wood and lacquer film. In conclusion, most studies carried out on wood used for musical instruments have theoretically and experimentally approached the wood acoustic properties by determining the sound propagation speed, the resonance frequencies, the damping, and the quality factor.

To complement the previous studies, the research presented in this paper aims to characterize the performance of spruce resonance wood when covered with different varnishing systems, focusing on the reflection and sound absorption of the wood–lacquer system.

The novelty of the article consists of a comprehensive approach, in which the effect of the varnishing systems (varnish type, number of layers applied) on the selected acoustic parameters is analyzed in combination with the effect they produce on the physical, morphological, and the chemical properties of resonance spruce wood. The statistical analysis provides the correlation between those different factors. Knowing the acoustic characteristics, such as the sound absorption coefficient of the soundboard, is important in predicting the amount of sound absorbed by the violin's soundboard.

2. Experimental Section

2.1. Sample Preparation

A number of 36 spruce wood samples (*Picea abies* L. Karst) belonging to anatomical quality classes A (coded MA) and D (coded MD) with a moisture content of 6–8%, with dimensions of $240 \times 80 \times 4 \text{ mm}^3$ ($L \times R \times T$) were prepared from timber selected for violins (Figure 1). The classification of the samples into the two classes of anatomical quality was carried out based on the criteria presented in previous studies (width of annual rings, proportion of early wood, proportion of latewood).^[2] The samples' surfaces were calibrated and sanded at a local musical instruments producer, by following the factory technology, common for preparing violin surfaces before varnishing. The average values of the initial mass, wood density (coded WD), and dimensions of the wood samples before varnishing are presented in Table S1 (Supporting Information). The characteristics of samples before varnishing were kept in control: their mass, density, surface color, surface roughness, chemical composition, and acoustic properties. Then, both quality samples (MA, MD) were subjected to varnishing on one side: 18 samples with oil-based varnish (coded LU), and the other 18 samples with alcohol varnish (coded LS). Three types of varnish applications were made for each varnishing material, differing in the number of layers applied: 5, 10, 15 and consequently differing in the resulting coating thickness (Figure 1). For each varnish thickness (number of layers NL), there were three replicates prepared. Figure 2 shows a representation of the varnished samples with an indication of the thickness values of the layered structures: the spruce wood substrate (thickness $h_w = 4 \pm 0.2 \text{ mm}$); the wood–varnish interface (thickness $h_{(w-v)} = 30 \pm 10 \mu\text{m}$) and the varnish film (thickness $h_v = 60 \div 100 \mu\text{m}$). The samples were obtained by applying successive varnish layers, drying, and sanding any intermediary layer with 320-grit paper.

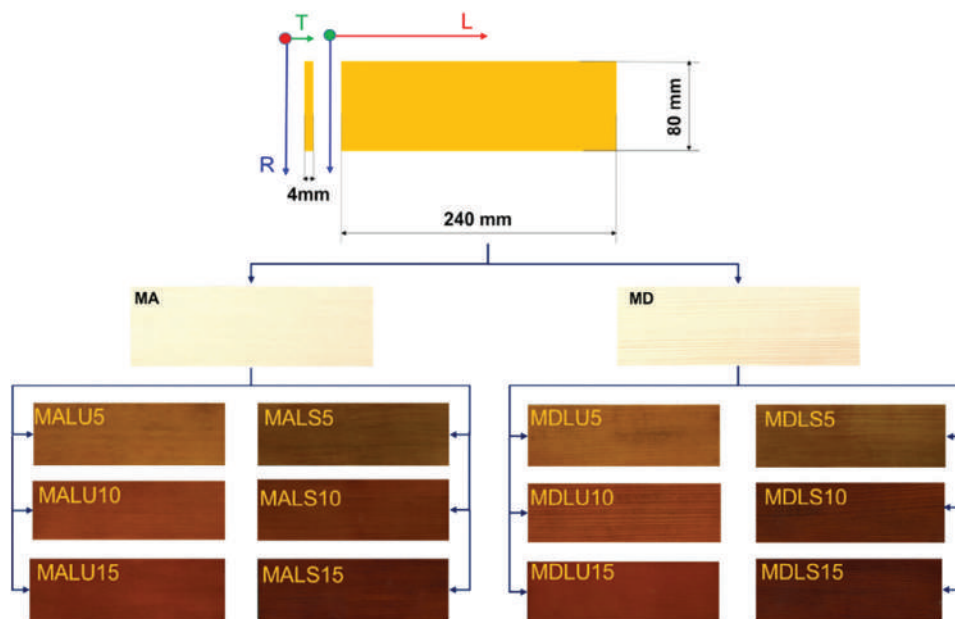


Figure 1. Types of prepared specimens.

According to ref. [15] the mass change of the spruce samples after applying the coating was evaluated as an areal mass loading (AM) induced by the varnish system (Equation 1):

$$AM = \frac{m_{vs} - m_w}{b * l} \quad ((1))$$

where AM is the areal mass loading induced by the varnish system (g m^{-2}) [15]; m_{vs} —the final mass of the varnished wood, m_w —the initial mass of the wooden sample, b —the sample width; l —the sample length.

The application of varnish was carried out by a professional luthier, and the coating systems (oil-based varnish, alcohol varnish) were made according to the recipe of the violin maker.

2.2. Methods

2.2.1. Color Measurement

Color measurements in the CIE Lab system were performed with a Konica Minolta CR-400 chroma meter. Color coordinates, lightness (L^*), redness (a^*), and yellowness (b^*), were measured, on all wood samples, both initially and after each layer applied. The color measurements were made in three points (see Figure S1,

Supporting Information), selected to be representative of the natural nonuniformity of the wood color.^[30–32] Color differences denoted ΔE^* between the total color of the control samples and the color values measured, in the same locations, after varnishing were determined with Equation 2:

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

where ΔL^* is the lightness difference between the lightness after varnishing and the initial lightness, Δa^* is the difference in the redness between the value after varnishing and the initial value, and Δb^* is the difference in yellowness between the value recorded after varnishing and the initial value.

2.2.2. Determination of Surface Energy

The evaluation of the surface energy (denoted SE) of the wood samples was carried out by the contact angle method. The value of the contact angle (denoted CA) depends on three factors: the morphology of the substrate expressed by the surface tension between the solid and gas medium (mN m^{-1}); the nature of the liquid expressed by the superficial liquid and gas tension (mN m^{-1}); the nature of liquid and substrate

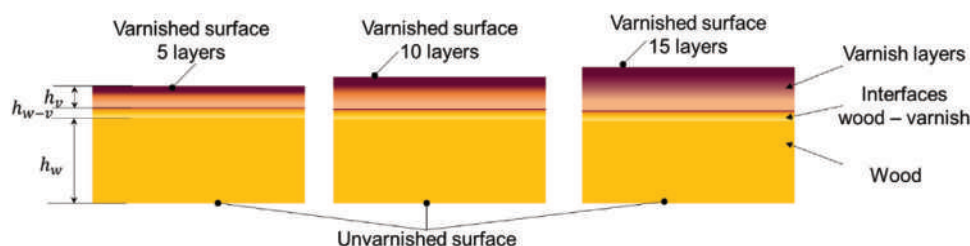


Figure 2. The coating system consists of the wood substrate, the wood–varnish interface, and the varnish film obtained by applying successive layers.

interactions expressed by the surface tension between the solid–liquid medium (mN m^{-1}).^[32,33] The CA was determined with the System OCA-20 equipment, using successively distilled water and glycerin, for the drop, with a volume of 10 μL . Thus, the values of the contact angle for water (noted CAW) and for glycerin (CAG) were measured.^[33,34] The measurements were performed at room temperature and under normal humidity conditions ($T = 22.7^\circ\text{C}$ and $\text{RH} = 65\%$). Three measurements per sample were made in the same areas, before and after varnishing. (Figure S1, Supporting Information).

2.2.3. Surface Quality Measurements

The surface quality of the samples before and after finishing was investigated using the MarSurf XT20 instrument, equipped with a stylus with a tip radius of 2 μm . The scanned profiles were further processed with the MARWIN XR20 software. The measurements were made on the same trace, before and after varnishing, the 30 mm profiles being scanned perpendicular to the fiber direction, with a lateral resolution of 5 μm (according to the scheme in Figure S1, Supporting Information). After removing the shape errors, a special filtering procedure was applied to the primary profile obtained, by using a robust Gaussian regression filter with a threshold value of 2.5 mm. This threshold separated the roughness profile from the waviness profile according to the procedure described in refs. [32,35–37]. The mean values of the following parameters were calculated: R_a (the arithmetic mean deviation of the roughness profile) from ISO 4287:2009, R_k (the core roughness depth of the roughness profile), R_{pk} (the reduced peak height of the roughness profile) and R_{vk} (the reduced valley depth of the roughness profile) from ISO 13565-2:1998^[36] and explained in detail in ref. [37].

2.2.4. Chemical Analysis with the Fourier Transformed Infrared Spectroscopy

Fourier transformed infrared spectroscopy (FTIR) was employed to analyze and compare the surface chemical features of the bare wood substrate and of the wood surfaces after coating with the two types of varnishes, applied in 5, 10, and 15 layers, respectively, resulting in three different thicknesses of the coating film. An Alpha Bruker spectrometer equipped with an attenuated total reflectance (ATR) unit was employed. The FTIR spectra were recorded in the range $4000\text{--}600\text{ cm}^{-1}$, at a resolution of 4 cm^{-1} , 24 scans per spectrum, while a minimum of three spectra were recorded for each sample. OPUS 7.2 software was employed for the further processing of the recorded spectra obtaining the min–max normalized average spectra for all the investigated samples.^[32,38–41]

2.2.5. Evaluation of Noise Insulation Characteristics

The analysis in the impedance tube was performed in relation to the standard procedure based on the two-microphone transfer function method (TFM) according to ISO 10534–2 and ASTM E1050–12 international standards.^[42–44] Hereby, the TFM was

used in order to evaluate the acoustic impedance and sound reflection coefficient at normal impedance. The general setup used for the evaluation of the sound absorption/reflection coefficient is schematically presented in Figure S2a (Supporting Information). The procedure consisted of cutting round shape samples, with 29 mm diameter, out from the varnished specimens according to the diagram in Figure S2b (Supporting Information). Each sample (1) was inserted into the sample holder of the impedance tube (2), type 4206, Brüel&Kjær (Nærum, Denmark), and acoustic signals with the frequency range 100 Hz–6.4 kHz were generated inside the tube using the loudspeaker (3); the signals provided by microphones (4) were acquired by a conditioner–DAQ board system (5), and finally were transmitted to a computer system (6)—see the schematic diagram in the Figure S2a,c (Supporting Information).^[45–48] The samples were investigated on both: the unvarnished (denoted “a”) and the varnished (denoted “b”) sides, in order to identify the differences between sound absorption/reflection coefficients caused by the varnish layers (Figure S2a,c, Supporting Information).

Based on experimental evaluation of the sound absorption coefficient (denoted SAC), the noise reduction coefficient (NRC) was calculated as the arithmetic average of the sound absorption coefficients at specific mid-range frequencies of the octave bands (250, 500, 1000, and 2000 Hz; see Equation 3).^[23,49]

$$\text{NRC} = \frac{\text{SAC}_{250} + \text{SAC}_{500} + \text{SAC}_{1000} + \text{SAC}_{2000}}{4} \quad (3)$$

In addition, the normal incidence sound reflection coefficient and the specific acoustic impedance were analyzed with respect to the frequency range of the impedance tube. The amount of reflection was provided by the sound reflection coefficient (usually denoted SRC), which depends on the material surface profile, the frequency of the traveling wave, and the incident angle which is the angle between the wavefront and the normal direction to the surface.^[45–49] The impedance tube provided the conditions of normal incidence investigations (null angle), with the controlled frequency band of the incident waves.

2.2.6. Statistical Analysis

From a statistical point of view, due to a considerable amount of data, this was grouped as follows: the wood characteristics studied in this paper were treated as alternative nominal variables (quality class), binary variables (varnished/unvarnished), nominal variables (wood varnishing systems), discrete quantitative variables (number of layers applied), and continuous quantitative variables (wood density, AM, color parameters, roughness parameters, contact angle, surface energy, NRC and absorption coefficient). The quantitative variables were first described with descriptive statistics (mean, minimum, maximum values, and coefficient of variation). In order to choose the most suitable test for identifying the differences between variables, the normality of the distribution of the variables was checked, with the Shapiro–Wilk test.^[50] The effect of independent variables was studied with analysis of variance or nonparametric tests (Mann–Whitney, Kruskal–Wallis), as appropriate. The way of association of the variables was explored by means of principal component analysis (noted PCA). The significance and strength of associations

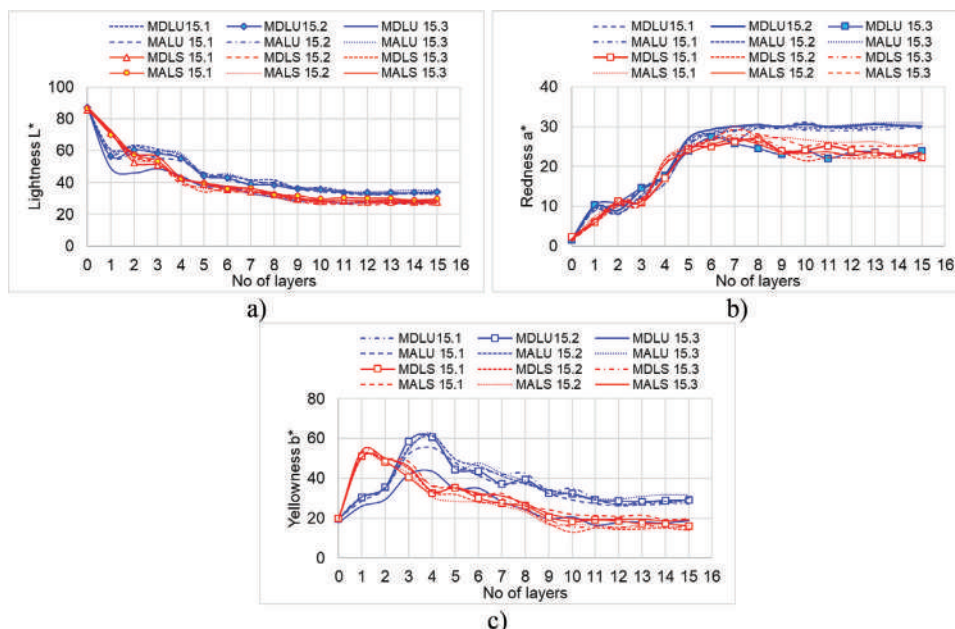


Figure 3. Color changes during the varnishing process: a) lightness; b) redness; and c) yellowness.

between variables were examined using simple correlation.^[51] Statistical data processing was performed with STATISTICA 8.0 (2007) software.

3. Results and Discussion

3.1. The Effect of Varnishing Systems on the Physical Parameters

3.1.1. Change in the Wood Color

The varnish and the number of varnish layers substantially changed the color of the samples. The alcohol varnish had a more pronounced effect on lightness, darkening the samples more than the oil-based varnish. After varnishing, the redness and yellowness changed substantially (p from the Kruskal–Wallis test < 0.001 for Δa^* and Δb^*). Both parameters a^* and b^* increased significantly more in oil-based varnish samples compared to samples finished with alcohol varnish. Thus, with each layer of varnish, the lightness decreased on average by 0.8% (**Figure 3**). The degree of red increased continuously until 10 layers were applied, after which it remained constant. The degree of yellowness decreased with the number of layers, on average by 1.4 units after each varnish film. The evolution of color changes during the varnishing process is shown in **Figure 3**, for each color parameter. The evolution of changes in color parameters is divided into three levels: between layers 1 and 5, the greatest change in all color parameters is observed; between layers 6 and 10 the second level is recorded, where the speed of change is considerably reduced, and between layers 11 and 15 a stabilization of the parameters is observed. Of course, this development depends on the formulation of the coating system, the pigments used, and the sanding between coats. The quality of the wood samples (MA, MD) did not influence the color parameters of the varnishing (p from the

Mann–Whitney test = 0.60 for ΔL^* , 0.83 for Δa^* , 0.62 for Δb^* , 0.24 for ΔE^*).

The total color difference ΔE was higher for the LS varnish in comparison with LU varnish for both wood quality classes (MA, MD) and increased with the number of varnish layers. (**Figure S3**, Supporting Information).

3.1.2. Surface Morphology

In the case of the MA quality of the resonance spruce, which is characterized by narrow and dense annual rings, it was noted the presence of specific anatomical undulations corresponding to the succession of early wood and latewood zones. These undulations are generated by sanding zones with different densities. Having a high frequency, these undulations are not eliminated by filtering and remain captured in the roughness profiles. The presence of anatomical undulations is clearly visible after the roughness profiles (before and after finishing) were superimposed, for the MA material quality and both types of finishing (see **Figure S4**, Supporting Information). Even if the finishing covers the anatomical cavities and it reduces the raised fiber, the anatomical undulation is still visible. It can be noticed that in the case of the oil-based finish, LU, the increase in the number of layers produced a reduction in the surface roughness, reducing even the anatomical undulations (**Figure S4a**, Supporting Information). This is due to the fact that this type of finish fills the wood pores well and has a good surface covering power. In the case of finishing with solvent-based varnish, LS, the finish reduces the surface irregularities, but to a lesser extent than in the case of the LU finish. However, the anatomical undulation persists or becomes even more accentuated after varnishing, being sensed also by touch. The anatomical undulation retained in the roughness profiles depends on the initial undulation existing on

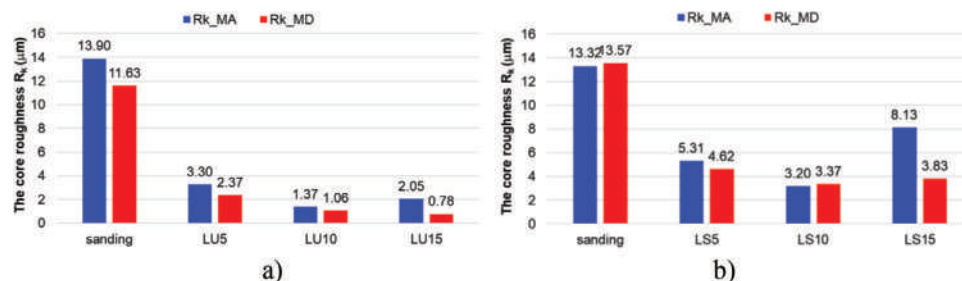


Figure 4. The core roughness R_k , for spruce qualities MA and MD: a) LU finished; b) LS finished.

the surface of the unfinished samples and influences the roughness values both before and after finishing. This explains why the MA quality surface finished with 15 layers of LS varnish appears wavier than in the case of samples with a lower number of layers (Figure S4b, Supporting Information). The core roughness, R_k , decreased after 5 layers of LU finishing, by 76% for MA and 80% for MD, and after 10 layers it decreased by $\approx 90\%$ for both qualities of spruce wood (Figure 4a). After 5 layers of LS lacquer, R_k decreased by 60% for MA and by 65% for MD, and after 10 layers, R_k decreased by 75% for both spruce qualities (Figure 4b). The decrease in roughness after finishing with 5, respectively 10 layers compared to the unfinished support was significant following the single factor ANOVA test with a significance level $p < 0.05$. Also, by increasing the number of layers to 10 compared to 5, it produced a significant improvement in the central roughness R_k , for both types of finishing. Increasing the number of layers to 15 did not produce significant changes in the surface quality expressed by R_k , except for the case of LS finishing at MA quality, where the roughness actually increased, most likely due to the surface undulation caused by the early wood–latewood alternation. Moreover, with the increase in the number of layers to 15, the surfaces became more sensitive to scratches or the inclusion of dust particles, which did not improve the quality of the surfaces. The most responsive parameters to the presence of such defects on the surface were R_{pk} and R_{vk} , which marked a slight increase in the case of the 15-layer finish. Therefore, the best quality of the finished wood was recorded for a maximum number of 10 layers. R_{vk} , in the case of sanded wood and before finishing, is an expression of the depth of the cavities due to the cellular voids that exceed in size the traces produced by the abrasive grains in the wood (for example, tracheids from earlywood, resin canals). By applying the finish, a filling of these cavities is expected, which will reduce the values of the R_{vk} parameter. Similarly, R_{pk} is a measure of the peaks of isolated irregularities, such as fibers raised after sanding and covered by finishing. The ANOVA test indicated significant differences between the R_{vk} values of the two types of finishes, with significantly lower values in the case of oil-based varnish. This also confirms the fact that the oil-based varnish (LU) covers the cavities better than the solvent-based lacquer (LS), in the case of spruce and for both material qualities.

3.1.3. Surface Energy

In the first stage, the values of the contact angle were determined for the two fluids (distilled water and glycerin), whose variation is

shown in (Figure S5, Supporting Information). It was observed that regardless of the fluid used, the contact angle was higher in the case of samples varnished with LU, for both wood quality classes. In contrast to the varnished samples, the control samples have a higher degree of crystallinity (Figure 5). So, the varnish film, regardless of the nature of the varnish, leads to a decrease in crystallinity, and the two components of the surface energy (polar and dispersive) give information about the polarity of the surface. The surface energy is closely related to the acoustic properties of the samples. The lower the surface energy, the lower the porosity of the surface and the lower the capacity of sound absorption, meaning that the surface becomes acoustically reflective.

3.2. The Influence of the Varnishing System on the Surface Chemical Features

The spectra from Figure 8 show, in the IR range $3500\text{--}1700\text{ cm}^{-1}$ absorptions, some common functional groups/chemical bonds: H-bonded —OH groups ($3500\text{--}3331\text{ cm}^{-1}$ O–H stretch); characteristic double absorption of methylene and methyl groups (aliphatic) at $2926\text{--}2858\text{ cm}^{-1}$ (for LU varnished samples); $2927\text{--}2858\text{ cm}^{-1}$ (for LS varnished samples); $2919\text{--}2860$ (for unvarnished wood); unconjugated carbonyl groups (C=O stretch) assignable to aldehydes, ketones, esters or free acids at 1724 cm^{-1} (for LU varnished samples); 1708 cm^{-1} (for LS varnished samples); 1730 cm^{-1} (for unvarnished wood). For the wood substrate, the absorption at 1730 cm^{-1} is due mostly to the acetyl ester groups in the structure of hemicelluloses. The absorption at 1724 cm^{-1} in the spectra of LU film may be assigned to the unconjugated CO in ester groups from the structure of oils (glycerol–fatty acids), while the absorption at lower wavenumber 1708 cm^{-1} in the spectrum of LS film may indicate the presence of unconjugated CO mainly in free acid carboxyl groups. Also, FTIR spectra indicate a higher amount of —OH groups in the structure of LS compared to LU by the higher and better-highlighted absorption at 3360 cm^{-1} .

In the fingerprint region ($1700\text{--}600\text{ cm}^{-1}$), the FTIR spectra of the uncoated spruce wood are totally different from those of the wood samples coated with the two types of lacquers, regardless of the number of coating layers (5, 10, 15). Though some absorptions assigned to basic chemical bonds and/or structural features of organic chemical compounds, such as methylene or methyl groups, respectively C—O , C—O—C , O—H chemical bonds, with absorptions at $1455\text{--}1458\text{ cm}^{-1}$, respectively $1240\text{--}1260\text{ cm}^{-1}$ and

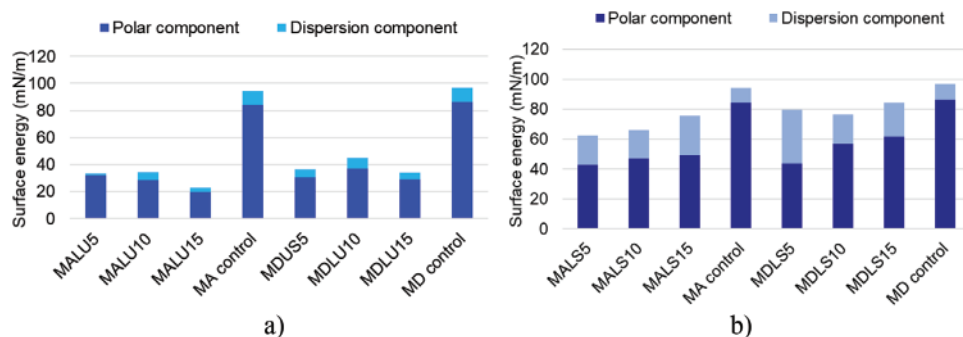


Figure 5. Comparisons of surface energy (average values): a) samples finished with oil-based varnish; b) samples finished with alcoholic varnish.

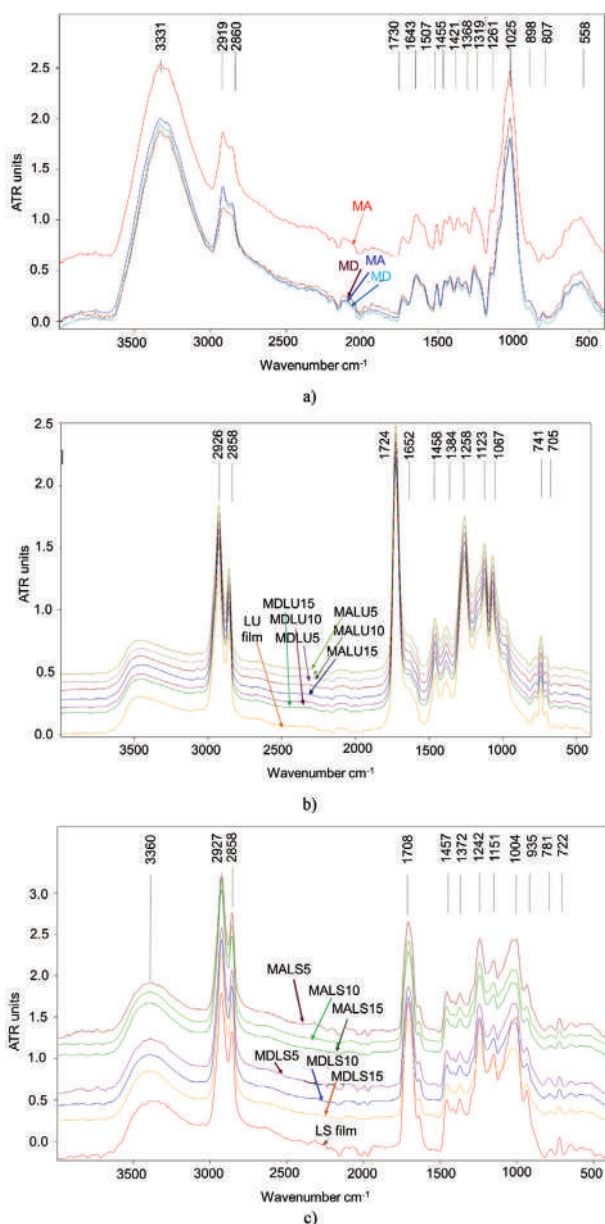


Figure 6. FTIR spectra of wood samples: a) unvarnished spruce wood; b) LU varnished; c) LS varnished.

1100–1000 cm⁻¹ may be present in all the spectra (Figure 6), there are notable differences in terms of the relative intensity of those bands and their actual position (wavenumber). Differences in the spectra of the unvarnished wood and those of the varnished samples are clearly visible starting from the absorption at 1460 cm⁻¹, as centralized in Table S2 (Supporting Information). The wood characteristic absorptions in the fingerprint region, namely the lignin-related bands at 1507, 1600, 1319, 1261 cm⁻¹ and those due to hollo cellulose (cellulose, hemicelluloses) at 1369, 1155–1151, 1025, and 898 cm⁻¹ are clearly visible in the uncoated wood samples, but there were totally obscured in the spectra of the coated samples, for all the three thicknesses of the coating films. It can be concluded, that, for all coated samples, the recorded FTIR spectra represent, exclusively, the chemical components of the coating film.

3.3. The Effect of Varnishing Systems on the Acoustic Parameters

3.3.1. Sound Absorption Coefficient

Figures 7 and 8 show the average values of the acoustic absorption coefficients (SAC) measured on the unvarnished side (index “a”) and the varnished side (“b”) of samples. The anatomical structure of the unvarnished wood, respectively the wood quality class, influence the absorption characteristics. Thus, the absorption coefficient for the MA quality samples had peak values between 0.4 and 0.6 for the alcoholic varnish, LS, and 0.2–0.4 for the oil-based varnish, LU. (Figures 7a and 8a). Also, in comparison with the unvarnished side, for the MA category samples, the varnished side presents a distinct behavior with respect to the finishing system with notable differences, mainly when LS finishing was applied. For the LS samples, the maximum absorption appears in the range of 4–5 kHz, with SAC_{max} = 0.45 for the MALS10 sample and SAC_{max} = 0.25 for the MDLS10 sample respectively (Figures 7b and 8b). For MALU samples, the maximum absorption appears in the range of 3–4 kHz, with SAC_{max} = 0.30 for the MALU15 sample and, respectively, in the range of 2.0–3.5 kHz for MDLU samples, with SAC_{max} = 0.30–0.40. In the case of wood from the MD quality class, there were no significant differences between the sound absorption coefficients for the two analyzed surfaces (with and without varnish layers). Both LS and LU samples present local modulations of the absorption coefficient ≈2.3, 4.0, and 5.7 kHz frequency values.

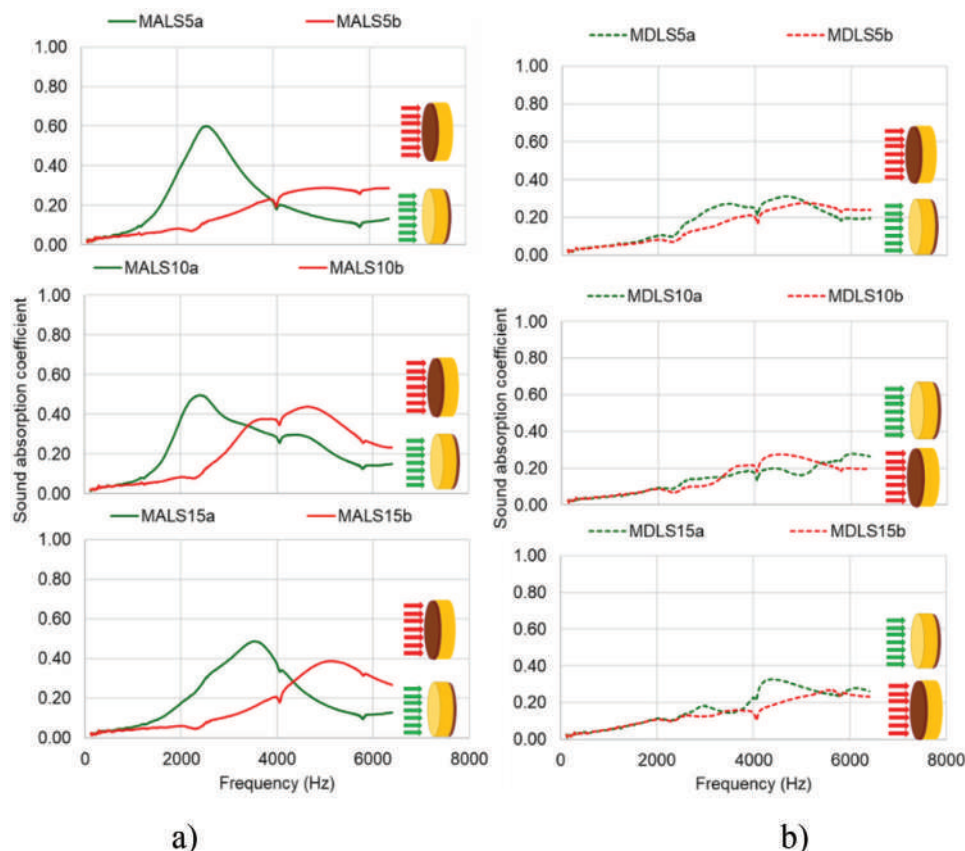


Figure 7. The sound absorption coefficient for LS varnished samples in relation to the sound frequency: a) spruce MA quality class; b) spruce MD quality class.

Correlating the results obtained in the acoustic impedance tube test with those highlighted by refs. [23,52] it can be concluded that the alcoholic varnish, LS, has a more pronounced effect on the acoustic parameters than the oil-based one. A thick layer of varnish (15 layers) does not improve the sound quality, regardless of the type of varnishing system, because it will either lead to a soft, dark sound, in the case of oil-based varnish, or too sharp, harsh sound, in the case of alcohol varnish. The acoustic behavior is related to the material mass, stiffness, and porosity. According to ref. [11] the impedance magnitude is determined by the square root of the material stiffness multiplied by its mass, both factors increasing as a result of the application of the lacquer films. In the samples varnished with alcohol varnish, LS, the mass is lower but the stiffness is increased as a result of the chemical recipe of the varnish, while in the samples varnished with oil-based varnish, the mass is higher, but the stiffness is lower.

Taking into account that the analysis was comparatively performed for varnished versus unvarnished sides of all samples, it was observed that the maximum absorption was recorded between 1–4 kHz for the unvarnished side of the MA quality class samples (with an absolute maximum ≈ 2 kHz). At the same time, for the varnished sides, the maximum absorption was recorded for frequencies greater than 2 kHz, even beyond 4 kHz, with an absolute maximum ≈ 2.5 kHz for the MD quality class samples, and ≈ 4.2 kHz

for the MA quality class samples (Figure S6, Supporting Information).

The undesirable qualities of a musical instrument (violins), respectively having a “shrill” or “hoarse” sound, seem to be associated with an excessive high-frequency content or too little low-frequency content and with little damping of some frequencies.^[53] The authors have proposed a classification of the sound quality by five adjectives: bright, harsh, nasal, clear, or good sound, corresponding to five frequency intervals namely: 190–380, 380–760, 760–1520, 1520–3040, and 3040–6080 Hz. According to ref. [54] the frequency ranges of 1.300–4.200 kHz should be responsible for the brightness, the effective radiation, and the evenness of the tone, while the range of 4.200–6.400 kHz should be relatively low to create a clear sound (damped sounds). From here it follows that for a warm sound, the damping should be higher in the range of 1500–3040 kHz, an idea also supported by ref. [55]

From Figure 9a,b it follows that the samples varnished with oil-based varnish show the highest values of the sound damping coefficient for the frequency of 1.5 kHz. It appears that the oil-based varnish with 5 and 10 layers contributes to obtaining a full sound, while the alcoholic varnish can lead to obtaining some nasal sounds. For the frequency of 3 kHz, Figure 9c,d, it can be seen that again, the oil-based varnish with 15 layers has the highest sound absorption coefficient (0.35–0.45), followed by a group of samples with 5 and 10 layers of LU, with a SAC between

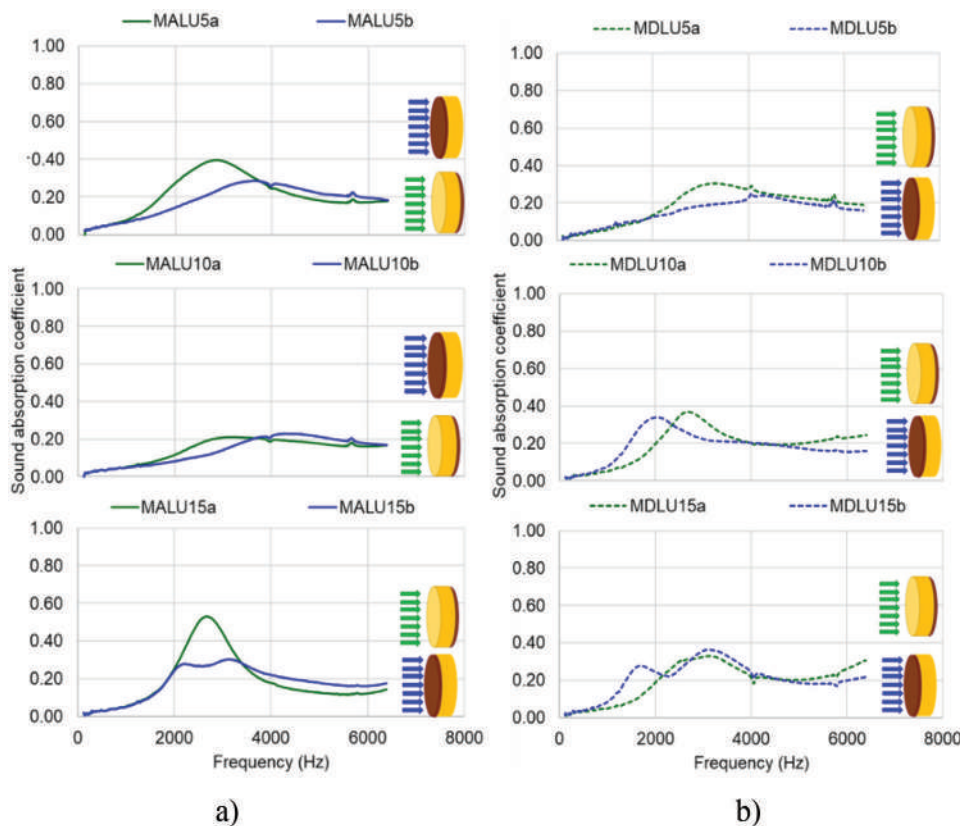


Figure 8. The sound absorption coefficient for LU varnished samples in relation to the sound frequency: a) spruce MA quality class; b) spruce MD quality class.

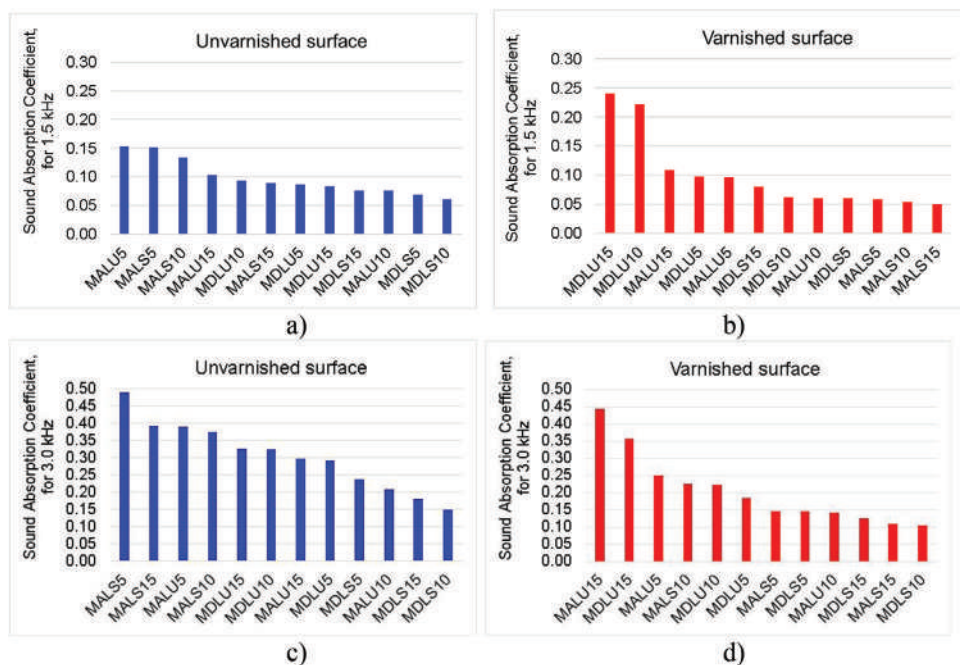


Figure 9. Sound absorption coefficient for 1.5 kHz, unvarnished, (a) and varnished (b) samples and 3 kHz, unvarnished (c) and varnished (d).

Table 1. The descriptive statistics of the studied properties.

Dependent variable	No. of samples	Minim	Mean	Maxim	Coefficient of variation [%]	Normality ^{a)}
WD [g cm ⁻³]	36	0.370	0.436	0.517	8.99	Yes
AM [g m ⁻²]	36	55.36	138.24	243.49	41.83	No
L* [%]	198	20.69	62.42	88.39	43.12	No
a*	198	1.05	11.95	31.79	97.93	No
b*	198	12.54	24.31	92.74	40.43	No
Ra	72	0.24	2.78	5.34	56.11	No
Rk	72	0.63	8.19	18.31	64.79	No
Rpk	72	0.30	3.72	8.85	48.31	No
Rvk	72	0.63	5.17	11.02	46.93	No
CAW (deg)	90	24.75	70.68	100.60	26.61	No
CAC (deg)	90	31.25	72.42	99.40	25.30	No
SE [mN m ⁻¹]	90	16.21	64.80	328.28	80.78	No
PC [mN m ⁻¹]	90	0.01	47.99	245.56	97.97	No
DC [mN m ⁻¹]	90	0	16.38	94.57	143.02	No
NRC	94	0.03	0.07	0.24	60.03	No

^{a)} The normality hypothesis cannot be rejected (YES) respectively cannot be accepted (NO)

0.20–0.25. The last category of samples, with the SAC coefficient between 0.15–0.1 was specific to samples varnished with alcoholic varnish with 5, 10, and 15 layers.

3.3.2. Sound Reflection Coefficient

The variation of the sound reflection coefficient with the sound frequency for the unvarnished and varnished samples shows a similar graphical trend in relation to the sound frequency (Figure S7, Supporting Information). However, the reflection coefficient recorded greater values in the case of the varnished surfaces (0.75–1.00) in comparison with the unvarnished ones. It is worth mentioning that for the spruce samples of the MA quality class, when the sound absorption coefficient acquires a maximum value ≈ 2.3 kHz, the sound reflection coefficient indicates the lowest values, down to 0.6, at the same frequency. In addition, it can be noticed that for the MD quality class, there was no difference in terms of sound absorption/reflection coefficients between the varnished and unvarnished sides.

3.3.3. Noise Reduction Coefficient

NRC represents an important indicator of noise absorption for a certain material (established by ASTM C423 Regulation). This parameter was evaluated for both, the varnished and the unvarnished sides of all samples. The results are presented in Table S3 (Supporting Information). The alcohol varnish considerably reduced both the magnitude and the amplitude of the NRC variation. In contrast, the oil-based varnish applied to the soundboard does not change the NRC. The absorption coefficient decreases significantly ($p = 0.0008$) after varnishing with alcohol varnish and decreases insignificantly ($p = 0.08$) when varnishing with oil-based varnish. The number of layers has no contribution to the reduction of the NRC, but it affects the absorption coefficient,

the size of which increases with the number of added layers, especially when it reaches 15 layers.

3.4. Statistical Panoramic Overview

The statistical analysis of the studied parameters highlighted the fact that the type of varnishing system and the number of layers are the most influential independent variables, along with the wood density, which varies with the wood quality class (MA or MD). Between the two quality classes of wood, the differences in the physical properties (color, morphology, and surface energy) become insignificant after applying the varnish films. Table 1 shows the range of variation of the studied properties.

The statistical significance from the ANOVA F test, the Mann–Whitney test, or the Kruskal–Wallis test can be found in Table 2. Thus, the samples treated with oil-based varnish have a significantly higher areal mass loading (AM) induced by the varnish system (by 50 g m⁻²) than the samples treated with alcohol varnish. Obviously, the AM increases directly proportional to the number of layers of varnish applied—on average by 10–14 g m⁻² for each layer of added varnish. If the quality of wood class does not influence the color of the finish, however, the type of varnishing system has different effects on the color: the oil-based varnish had a lightness 50% higher than the alcoholic varnish, and the redness and yellowness changed substantially with the number of varnish layers (p from Kruskal–Wallis test < 0.001 for Δa^* and Δb^*). Both the degree of redness (a^*) and the degree of yellowness (b^*) increased significantly, more in the oil-based samples compared to the alcohol-based samples. Both the type of varnish and the number of layers substantially changed the samples color.

Thus, with each layer of varnish the lightness decreased by 0.8%, on average. The degree of red increased continuously until the application of 10 layers, after which it remained constant. The degree of yellowness decreased with the number of layers,

Table 2. The results of the statistical tests (p-value), checking the differences between groups.

Dependent variable	Wood quality class	Unvarnished/ varnished	Type of the varnish system	No. of layers
WD [g cm^{-3}]	0.17 ^{a)}	0.59 ^{a)}	0.59 ^{a)}	0.23 ^{a)}
AM [g m^{-2}]	0.68 ^{b)}	–	0.40 ^{b)}	<0.001 ^{c)}
L^* (%)	0.83 ^{b)}	<0.001 ^{b)}	0.33 ^{b)}	<0.001 ^{c)}
a^*	0.20 ^{b)}	<0.001 ^{b)}	<0.001 ^{b)}	<0.001 ^{c)}
b^*	0.10 ^{b)}	<0.001 ^{b)}	<0.001 ^{b)}	<0.001 ^{c)}
Ra	0.48 ^{b)}	<0.001 ^{b)}	<0.001 ^{b)}	0.10 ^{c)}
Rk	0.30 ^{b)}	<0.001 ^{b)}	<0.001 ^{b)}	0.06 ^{c)}
Rpk	0.73 ^{b)}	0.004 ^{b)}	0.002 ^{b)}	0.02 ^{c)}
Rvk	0.51 ^{b)}	<0.001 ^{b)}	<0.001 ^{b)}	0.48 ^{c)}
CAW (deg)	0.56 ^{b)}	<0.001 ^{b)}	<0.001 ^{b)}	0.31 ^{c)}
CAG (deg)	0.97 ^{b)}	<0.001 ^{b)}	<0.001 ^{b)}	0.91 ^{c)}
SE [mN m^{-1}]	0.68 ^{b)}	<0.001 ^{b)}	<0.001 ^{b)}	0.75 ^{c)}
PC [mN m^{-1}]	0.29 ^{b)}	0.004 ^{b)}	0.01 ^{b)}	0.07 ^{c)}
DC [mN m^{-1}]	0.63 ^{b)}	0.46 ^{b)}	<0.001 ^{b)}	0.67 ^{c)}
NRC	0.85 ^{b)}	0.06 ^{b)}	<0.001 ^{b)}	0.31 ^{c)}

^{a)} p from ANOVA F test; ^{b)} p from Mann–Whitney test; ^{c)} p from Kruskal–Wallis test, (for a 0.05 level of significance)

on average by 1.4 units after each varnish film. The effect of varnishing manifested on all parameters related to the surface morphology (R_a , R_k , R_{pk} , and R_{vk}), the reduction being greater in the case of the oil-based varnish than the alcoholic varnish, but without statistical confirmation (p from Kruskal–Wallis test = 0.06, 0.07, 0.10, and 0.13 respectively).

The number of layers applied had a significant influence on R_{pk} (Table 2), whose magnitude decreased with an increase in their number, especially from 5 to 10 layers. In contrast, the number of layers did not significantly affect the values of R_a , R_k , and R_{vk} (Table 2). The varnishing system produced a more pronounced decrease in surface energy in the case of oil-based varnish and almost insignificant in the case of alcoholic varnish. The dispersive component was not significantly affected by the varnish; it increased slightly and insignificantly with the alcohol varnish but decreased slightly with the oil varnish. The number of layers applied had no statistically detectable effect on these physical parameters (Table 2). The sound absorption in samples varnished with the alcohol varnish was significantly reduced compared to the oil-based varnish, an observation highlighted statistically by the size and amplitude of the NRC and the absorption coefficient (SAC) ($p = 0.0008$). The acoustic absorption coefficient increased with the increase in the number of layers, regardless of the type of varnish.

Based on the Factor Analysis, four principal components were selected, the first two, together, explaining 53% of the total variance. The first main component is the roughness parameters, which vary with the varnish system, together with the contact angle and the degree of redness. The second component is described by the lightness and the degree of yellowness and, at the antipode, by the number of varnish layers (Figure 10). It is observed that the roughness parameters vary with the dispersive component of the surface energy. The coating system is closely related to the contact angle and NRC. The color components (L ,

a , b) projected on different axes, suggest a different behavior in relation to the other properties examined.

4. Conclusion

The study investigated the effect of the varnish type and the number of layers on some acoustic properties of the resonance spruce analyzed in combination with the changes produced in some physical, morphological, and chemical wood properties.

The alcohol varnish has darkened the wood color more than the oil-based varnish and the most important color changes occurred up to 10 layers. No important color change and no surface quality improvement occur if more than 10 layers of lacquer are applied. The surface chemical analysis of the varnished samples confirmed a complete varnish surface coverage, the oil-based lacquer proving a superior surface quality in comparison with the alcoholic varnish.

The application of varnish has increased the sound reflection coefficient and it was significantly higher in the case of samples varnished with alcohol varnish compared to those covered with oil-based varnish. The sound absorption coefficient increased with the number of varnish layers and varied with the range of sound frequencies, with the type of varnish, and with the wood quality, all contributing to the acoustic tunability.

For example, for a sound frequency of 1.5 kHz, it appeared that the oil-based varnish with 5 and 10 layers contributes to obtaining a full sound, while the alcoholic varnish can lead to some

Projection of the variables on the factor-plane (1 x 2)

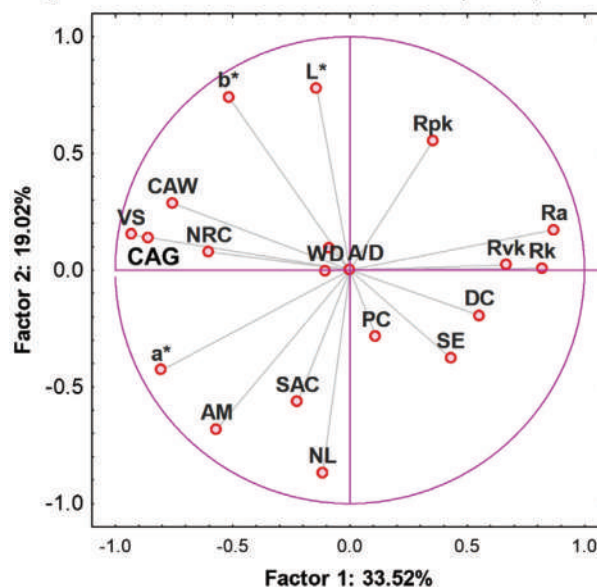


Figure 10. Physical and acoustical parameters in the 1,2 plane of the PCA legend: a^* : color redness, A/D quality class of wood, AM: areal mass loading, b^* : color yellowness, CAE: contact angle in water, CAW: contact angle in ethylene glycol, DC: dispersion component of SE, L^* : color lightness, NL: no of layers, PC: polar component of SE, R_a : the arithmetic mean deviation of the roughness profile, R_k : the core roughness depth of the roughness profile, R_{pk} : the reduced peak height of the roughness profile, R_{vk} : the reduced valley depth of the roughness profile, SAC: sound absorption coefficient, SE: surface energy, VS: varnish system, WD: wood density.

nasal sounds. Applying 15 layers of lacquer does not improve the sound performance, because it will soften the sound when finishing with oil-based varnish and will generate a too sharp sound in case of alcoholic varnish. A maximum number of 10 layers seems to be a reasonable choice.

There are some limitations that keep us away from establishing which type of varnish is more advantageous from the point of view of the acoustic quality of the violins as a result of the fact that the investigations presented in this study were carried out on rectangular plates of constant thickness, and not on violin plates, the studies will continue with the analysis of the sound propagation speeds in the longitudinal and radial direction, as well as with the analysis of the viscous–elastic behavior of the varnished samples.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

This research was supported by a grant from the Ministry of Research, Innovation, and Digitization, CNCS/CCCDI—UEFISCDI, project number 61PCE/2022, PN-III-P4-PCE2021-0885, ACADIA—Qualitative, dynamic and acoustic analysis of anisotropic systems with modified interfaces. The authors acknowledge the structural funds project PRO-DD (POS-CCE, O.2.2.1., ID 123, SMIS 2637, No. 11/2009) for providing the infrastructure used in this research. The authors are also grateful to the technical staff of Gliga Musical Instruments, Reghin, a Romanian manufacturer of musical string instruments, for supplying the specimens.

Author Contributions

S.M.D. performed the conceptualization, formal analysis, and investigation, worked with the software, gathered resources, acquired funds, wrote and prepared the original draft, and administered the project. C.M. performed the conceptualization, supervision, validation, and data curation, and also wrote, reviewed, and edited the final manuscript. G.V.G. developed the methodology, performed validation, and investigation, and gathered resources. G.L. developed the methodology, worked with software, performed formal analysis, investigation, data curation, and supervision, and wrote, reviewed, and edited the final manuscript. T. C. developed the methodology, worked with software, formal analysis, investigation, and data curation, and wrote, reviewed, and edited the final manuscript. G.V. developed the methodology, worked with software, and performed formal analysis, investigation, and data curation. N.S.M. developed the methodology, worked with software, performed validation, and data curation, and wrote, reviewed, and edited the final manuscript. R.I.C. developed the methodology, performed validation and supervision, gathered resources, and wrote, reviewed, and edited the final manuscript. B.V. developed the methodology, performed supervision, and wrote, reviewed, and edited the final manuscript. D.F. developed the methodology, worked with software, performed formal analysis, and wrote, reviewed, and edited the final manuscript. All authors have read and agreed to the published version of the manuscript.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords

chemical changes, color changes, noise reduction coefficient, resonance spruce wood, sound absorption coefficient, surface energy, surface roughness, varnishing system

Received: September 22, 2023
Revised: December 10, 2023
Published online: January 19, 2024

- [1] a) V. Bucur, *Handbook of Materials for String Musical Instruments*, Springer, Berlin, Germany **2016**, Ch 3; b) V. Bucur, *Handbook of Materials for String Musical Instruments*, Springer, Berlin, Germany **2016**, Ch 8.
- [2] F. Dinulica, M. D. Stanciu, A. Savin, *Forests* **2021**, 12, 1122.
- [3] R. Viala, V. Placet, S. Cogan, *J. Cult. Herit.* **2020**, 42, 108.
- [4] M. Spycher, F. W. M. R. Schwarze, R. Steiger, *Wood Sci Technol*; **2008**, 42, 325.
- [5] M. Quintavalla, F. Gabrielli, C. Canevari, *Appl. Acoust.* **2022**, 187, 108521.
- [6] T. Watanabe, T. Matsumoto, N. Kinoshita, H. Hayashi, *J. Jpn. Wood Res. Soc.* **1967**, 13, 177.
- [7] H.-C. Tai, Y.-P. Shen, J.-H. Lin, D.-T. Chung, *Proc. Natl. Acad. Sci. USA* **2018**, 115, 5926.
- [8] M. Mihălcică, M. D. Stanciu, S. M. Nastac, F. Dinulică, A. M. Nauncef, I. C. Roșca, A. Savin, *Appl. Sci.* **2021**, 11, 11297.
- [9] M. D. Stanciu, M. Mihalica, F. Dinulica, A. M. Nauncef, R. Purdoi, R. Lacatu, G. V. Gliga, *Materials* **2021**, 14, 5926.
- [10] M. D. Stanciu, F. Dinulica, V. Bucur, V. G. Gliga, S. M. Nastac, M. Câmpian, *Thin-Walled Struct.* **2022**, 174, 109042.
- [11] J. C. Schelleng, *J. Acoust. Soc. Am.* **1968**, 44, 1175.
- [12] M. Schleske, *Catgut Acoust. Soc. J.* **2002**, 4, 50.
- [13] M. Sedighi Gilani, J. Pflaum, S. Hartmann, R. Kaufmann, M. Baumgartner, F. W. M. R. Schwarze, *Appl. Phys. A* **2016**, 122, 260.
- [14] S. L. Lämmlein, D. Mannes, F. W. M. Schwarze, I. Burgert, M. Sedighi Gilani, in *Model Validation and Uncertainty Quantification*, (Eds.: R. Barthorpe, R. Platz, I. Lopez, B. Moaveni, C. Papadimitriou), Conference Proceedings of the Society for Experimental Mechanics Series Vol. 3, Springer, Cham **2017**.
- [15] S. L. Lämmlein, B. Van Damme, D. Mannes, F. W. M. R. Schwarze, I. Burgert, *Holzforschung* **2020**, 74, 765.
- [16] M. Odlyha, J. J. Lucejko, A. Lluveras-Tenorio, F. di Girolamo, S. Hudziak, A. Strange, A. Bridaroli, L. Bozec, M. P. Colombini, *Molecules* **2022**, 27, 6378.
- [17] J. Nagyvary, R. N. Guillemette, C. H. Spiegelman, *PLoS One* **2009**, 4, e4245.
- [18] W. Cai, H.-C. Tai, *AsiaChem* **2020**, 11, 10.
- [19] O. E. Rodgers, *J. Catgut. Acoust. Soc.* **1988**, 1, 2.
- [20] W. Y. Chung, *Korea Furnit Soc* **2000**, 11, 45.
- [21] E. B. Skrodzka, B. J. B. Linde, A. Krupa, *Arch. Acoust.* **2013**, 38, 75.
- [22] W. Xu, X. Fang, J. Han, Z. Wu, J. Zhang, *Wood Fiber Sci.* **2020**, 52, 28.
- [23] J. Smardzewski, W. Batko, T. Kamisinski, A. Flach, A. Pilch, D. Dziurka, R. Mirski, E. Roszyk, A. Majewski, *Holzforschung* **2014**, 68, 467.
- [24] J. Shen, *Front. Forest. China* **2006**, 1, 431.
- [25] Z.-H. Jiang, R.-J. Zhao, B.-H. Fei, *J. For. Res.* **2004**, 15, 207.
- [26] S. A. Ahmed, S. Adamopoulos, *Appl. Acoust.* **2018**, 140, 92.
- [27] H. Kolya, C. Won Kang, *Appl. Acoust.* **2020**, 169, 107475.

- [28] E.-S. Jang, C.-W. Kang, *Holzforschung* **2021**, 75, 1115.
- [29] J. McLennan, *J Aust Assoc Musical Instrum Mak. XIX* **2000**, 1, 16.
- [30] M. D. Stanciu, D. Sova, A. Savin, N. Ilias, G. A. Gorbacheva, *Polymers* **2020**, 12, 377.
- [31] E.-A. Salca, T. Krystofiak, B. Lis, S. Hiziroglu, *Coatings* **2021**, 11, 558.
- [32] L. Gurau, M. C. Timar, C. Cosereanu, M. Cosnita, M. D. Stanciu, *Polymers* **2023**, 15, 1794.
- [33] E. A. Papp, C. Csiha, *Surf. Interfaces* **2017**, 8, 54.
- [34] M. D. Stanciu, A. Savin, S. M. Nastac, *J. Mechan. Eng.* **2018**, 64, 698.
- [35] L. Gurau, M. Irle, *Curr. For. Rep.* **2017**, 3, 119.
- [36] ISO1920-2:2021. Geometrical product specifications (GPS) – Surface texture: Profile . Part 2: Terms, definitions and surface texture parameters
- [37] L. Gurau, *The roughness of sanded wood surfaces, Doctoral thesis*, Forest Products Research Centre, Buckinghamshire Chilterns University College, Brunel University, London, **2004**.
- [38] X. Y. Liu, M. C. Timar, A. M. Varodi, G. Sawyer, *Wood Sci. Technol.* **2017**, 51, 357.
- [39] X. Liu, M. C. Timar, A. M. Varodi, R. Nedelcu, M.-J. Torcatoru, *Coatings* **2022**, 12, 1689.
- [40] I. Sandu, P. O. Tanasa, I. C. A. Sandu, I. C. Negru, A. V. Sandu, V. Vasilache, *Appl. Sci.* **2020**, 10, 306.
- [41] I. M. Cortea, R. Cristache, I. Sandu, *Rom. Rep. Phys.* **2016**, 68, 615.
- [42] ISO 11654 :1997. In: Rating of sound absorption. International Organization for Standardization (ISO) Geneva, Switzerland.
- [43] ISO10534-2:2023. Acoustics – determination of acoustic properties in impedance tubes: Part 2: Two microphone technique for normal sound absorption coefficient and normal surface impedance.
- [44] ASTM E1050:98 Standard Test Method for Impedance and Absorption of Acoustical Materials Using a Tube, Two Microphones and a Digital Frequency Analysis System, **1998**.
- [45] I. Curtu, M. D. Stanciu, C. Cosereanu, O. Vasile, *Mat. Plast.* **2012**, 49, 68.
- [46] S. A. Nitu, N. Sporea, N. Iatan, I. Durbaca, I. O. Vasile, G. C. Ciocoiu, *Mat. Plast.* **2022**, 59, 131.
- [47] C. Debeleac, P. Nechita, S. Nastac, *Polymers* **2019**, 11, 1223.
- [48] Y. Cherradi, I. C. Rosca, C. Cerbu, H. Kebir, A. Guendouz, M. Benyoucef, *Appl. Acoust.* **2021**, 174, 107759.
- [49] Y. Takahashi, T. Otsuru, R. Tomiku, *Appl. Acoust.* **2005**, 66, 845.
- [50] D. J. Sheskin, *Handbook of Parametric and Nonparametric Statistical Procedures*, 3rd ed., Chapman & Hall/CRC, Boca Raton, FL, USA **2004**.
- [51] J. H. Zar, *Biostatistical Analysis*, Prentice-Hall Inc., Englewood Cliffs, NJ, USA, **1974** p. 620.
- [52] M. V. Guiman, M. D. Stanciu, I. C. Roşca, S. V. Georgescu, S. M. Nastac, M. Câmpian, *Materials* **2023**, 16, 5998.
- [53] C. Fritz, I. Cross, B. C. J. Moore, J. Woodhouse, *J. Acoust. Soc. Am.* **2007**, 122, 3640.
- [54] H. Dünnwald, *Catgut Acoust. Soc. J. (Series II)* **1991**, 1, 1.
- [55] H. Meinel, *J. Acoust. Soc. Am.* **1957**, 29, 817.

Article

Comparisons of the Effects of Polymer and Alcohol Varnishes on Norway Spruce Wood Surface Modifications

Mariana Domnica Stanciu ^{1,2,3,4,*} , Maria Cristina Timar ⁵ , Mircea Mihalca ¹, Mihaela Cosnita ⁶  and Florin Dinulică ⁷ 

¹ Department of Mechanical Engineering, Transilvania University of Braşov, B-dul Eroilor 29, 500036 Braşov, Romania; mihalca.mircea@unitbv.ro

² Romanian Society of Rheology, Petru Poni Institute of Macromolecular Chemistry, Room 119, 41-A, Grigore Ghica Voda Alley, 700487 Iasi, Romania

³ Romanian Society of Theoretical and Applied Mechanics, 266 Pantelimon, 2 Sector, Office 4, 021652 Bucureşti, Romania

⁴ Romanian Society of Acoustics, 266 Pantelimon, 2 Sector, Office 4, 021652 Bucureşti, Romania

⁵ Faculty of Furniture Design and Wood Engineering, Transilvania University of Braşov, 500036 Braşov, Romania; cristinatimar@unitbv.ro

⁶ Department of Product Design Mechatronics and Environment, Transilvania University of Braşov, 29 Eroilor, 500036 Braşov, Romania; mihaela.cosnita@unitbv.ro

⁷ Faculty of Silviculture and Forest Engineering, Transilvania University of Braşov, 1 Sirul Bethoven, 500123 Braşov, Romania; dinulica@unitbv.ro

* Correspondence: mariana.stanciu@unitbv.ro

Abstract

Spruce wood is a natural polymeric material, consisting of cellulose, lignin, hemicelluloses and other secondary components, which gives it a unique chemical footprint and architecture. Varnishes are used in musical instruments to protect the wood against humidity variations, wood being a hygroscopic material, but also to protect the wood from dirt. The varnishes used both to protect the wood from resonance and to ensure a special aesthetic appearance are either polymeric varnishes (nitrocellulose, oil-based) or volatile solvents (spirit). In this study, the color changes, the surface morphology and the chemical spectrum produced by three types of varnishes, applied in 5, 10 and 15 layers, on resonance spruce plates were analyzed. The results revealed significant changes in the color parameters: the lightness decreased by approximately 17% after the first layer, by 50% after 5 layers, by 65% after 10 layers and by 70% after 15 layers. The color parameters are most influenced by the anatomical quality of spruce wood (annual ring width and earlywood/latewood ratio) in the case of oil-based varnishes and least influenced in the case of nitrocellulose varnishes. The chemical fingerprint was determined by FTIR spectrum analysis, which revealed that the most pronounced absorptions were the double band 2926–2858 cm^{−1}, corresponding to aliphatic methylene and methyl groups (asymmetric and symmetrical C-H stretch), and the bands at 1724 cm^{−1} (oil-based varnish), 1722 cm^{−1} (nitrocellulose varnish) and 1708 cm^{−1} (spirit varnish), all assigned to non-conjugated carbonyl groups in either carboxylic acids, esters aldehydes or ketones. The novelty of the study lies in the comparative analysis of three types of varnishes used in the musical instrument industry, applied to samples of spruce resonance wood with different macroscopic characteristics in three different layer thicknesses.

Keywords: polymeric varnish for musical instruments; overall color change; surface morphology; Fourier transformed infra-red



Academic Editor: Mariaenrica Frigione

Received: 5 July 2025

Revised: 30 July 2025

Accepted: 31 July 2025

Published: 1 August 2025

Citation: Stanciu, M.D.; Timar, M.C.; Mihalca, M.; Cosnita, M.; Dinulică, F. Comparisons of the Effects of Polymer and Alcohol Varnishes on Norway Spruce Wood Surface Modifications. *Polymers* **2025**, *17*, 2131. <https://doi.org/10.3390/polym17152131>

Copyright: © 2025 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

(<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Norway spruce wood (*Picea abies* Karst. L.) is a natural polymer that, from the point of view of chemical architecture, contains three-dimensional polymer chains of carbohydrates, namely cellulose (50.69–50.90%), hemicellulose (pentoses (7.18–11.20%) and hexoses) and lignin (26.68–33.25%), as well as extractable substances and inorganic compounds [1–4]. The moisture absorption capacity of wood depends on the hydrophilic properties of the polymer chains of the main chemical constituents of wood, as well as on the accessibility of water to the polymer chains [5]. According to [5], the hydroxyl groups in hemicelluloses and lignin are easily accessible to water molecules due to their branched structure. Since wood is a hygroscopic material and exposed to dirt, various protective coatings have been used over time to ensure its aesthetic appearance and protect it from moisture. Researchers have long studied the chemical composition of varnishes used for historical musical instruments, with the aim of identifying the organic and inorganic compounds that could be responsible for the acoustic quality of musical instruments [6–8]. The results highlighted that the varnishes used are complex mixtures of organic (oils and resins) and inorganic (pigments, fillers, etc.) compounds, with different solvents/additives, such as essential oils, alcohol and oil-based varnishes [6–8]. According to the analysis made [7], the varnishes used for varnishing musical instruments, as coating substances that are applied in one or more layers, can be classified according to the solvent they contain in three categories: spirit-based; drying oil-based; essential oil-based. In the case of oil varnishes, the oil is vegetable oil; the most used are linseed oil, walnut oil and castor oil. Spirit varnishes are based on a mixture of resins dissolved in alcohol; that is why they are also called alcoholic varnishes. Resins are natural or artificial polymers having the property of softening or melting when the temperature gradually increases and can then be spread on support surfaces. Researchers classify natural resins produced by trees into two main groups: diterpenes (based on organic compounds of two terpene units $C_{20}H_{32}$) and triterpene resins (with three $C_{30}H_{48}$ terpenic units). Examples of diterpene resins include sandarac—the resin of the *Juniperus communis* tree (northern Africa, Morocco), rosin—the resin of the species of the Pinaceae family, and copal—tree product from *Protium copal* (Burseraceae) (Mexico, Central America). Triterpene resins include dammar—*Canarium strictum* (India), mastic—*Pistacia lentiscus* tree (Greece), and elemi—produced by the *Canarium luzonicum* tree (Philippines). Besides these resins, fossil resins (amber), as well as resins produced by insects (shellac), gums, proteins, waxes and natural dyes, were also identified [7]. The varnishes were used to protect the wood against dirt, mechanical damage and humidity variations in the environment, as well as for the aesthetic values that the instrument acquired through color and gloss. Most studies have focused on the study of the chemical analysis of the different types of finishes used on historical instruments, color being one of the additional properties correlated with inorganic compounds [9–11]. Ref. [10] studied the nanomechanical properties of finishing samples using traditional violin varnish recipes applied to maple wood. The alcohol varnish, having a higher stiffness, penetrated the wood less than the oil-based varnish, and quantitative nanomechanical mapping demonstrated a difference in adhesion values between the oil-based and alcohol-based samples. Most studies have analyzed the relationship between the type of finish and the dynamic and acoustic properties induced by the stiffness of the new varnish–wood system, both immediately after the application and curing of the varnish [11–14] and after the application of aging treatments [15–19]. The physical properties that the lacquer for musical instruments must possess are gloss, transparency, color, wear, dirt resistance and adhesion to the wood, and among the mechanical properties, elasticity and the ability to improve the tone of the instrument. Varnishing soundboards with polymeric finishes or volatile solvents leads to changes in the rigidity and mass of the wood board, producing changes in its vibrational and acoustic properties [17]. Elasticity is

the most important property of the lacquer since it must not affect the vibration mode of the lacquered instrument. Refs. [12,16,17,20–24] have demonstrated that varnishes increase the damping of wood along and perpendicular to the grain directions. The varnishes reduce sound radiation along the fiber but increase it in the perpendicular direction. However, there are few studies that analyze the modification of color parameters as a result of applying different types of varnishes to the resonance spruce wood. This paper aims to comparatively analyze the effect of varnish film thickness on the color parameters, surface morphology and chemical fingerprint of resonance spruce wood. The analysis was performed both before and after the application of each varnish layer, investigating three types of varnishes: spirit, oil-based and nitrocellulose. The novelty of the study lies in the quantitative and qualitative analysis of the color, surface morphology and chemical fingerprint of wood varnished with the varnishes used in the construction of stringed musical instruments.

2. Materials and Methods

2.1. Sample Preparation

The wood samples in the form of rectangular plates with dimensions of 200 mmx80 mmx4 mm were made of Norway spruce wood (*Picea abies* (L.) Karst.) harvested from the Romanian Carpathian mountains. The spruce trees were harvested from the Moldovița Forest District (Suceava—Bucovina), Romania, known for its resonant Norway spruce stands. The tree diameters were 600–650 mm, and the 4/4 violin blanks were extracted by quarter cutting at a base distance of approximately 3 m, as can be seen in Figure 1. The samples come from the raw material warehouse of the musical instrument factory, being prepared from semi-finished products for violins that have been naturally dried for 5–8 years, reaching a moisture content of 8–10%. The main technological operations involved in the preparation and obtaining of the samples, as mentioned in [25], are schematically presented in Figure 2.

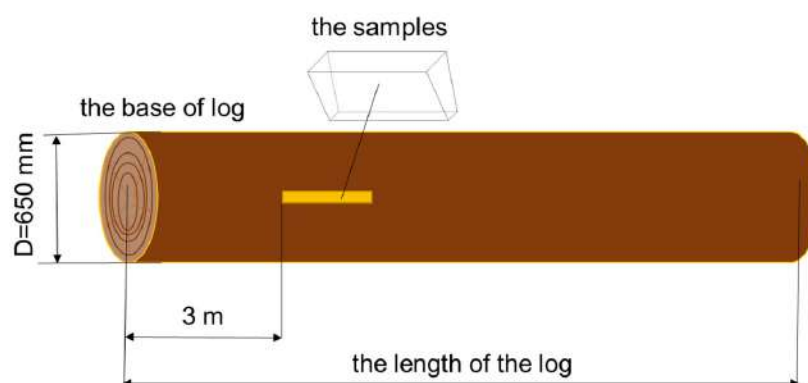


Figure 1. The position of the wooden blanks in the spruce logs.

Unlike the classification in STAS 10824-76 (Romanian standard) [26], where only two quality classes are mentioned for the faces/backs of musical instruments (A and B), each of which is divided into three subgroups, in this study, two types of sounding spruce wood used for violin faces are analyzed, having extreme anatomical characteristics. Class A designates the best quality of wood, and class D refers to the worst quality of wood used for musical instruments. The samples were grouped into two quality classes depending on the anatomical parameters, such as the width of the annual rings, the proportion of late wood/early wood, presence/absence of anatomical defects and regularity of annual rings. Grade A represents the samples with narrow annual ring widths, below 1 mm, regular, $74.97 \pm 1.6\%$ early wood proportion and $25.03 \pm 1.5\%$ late wood proportion and

grade D represents the samples with annual ring widths greater than 2.5 mm, irregular, $76.36 \pm 1.32\%$ early wood proportion and $23.64 \pm 1.13\%$ late wood proportion [27,28]. Detailed information about the anatomical quality classes of sounding wood is detailed in the study previously presented in [27,28].

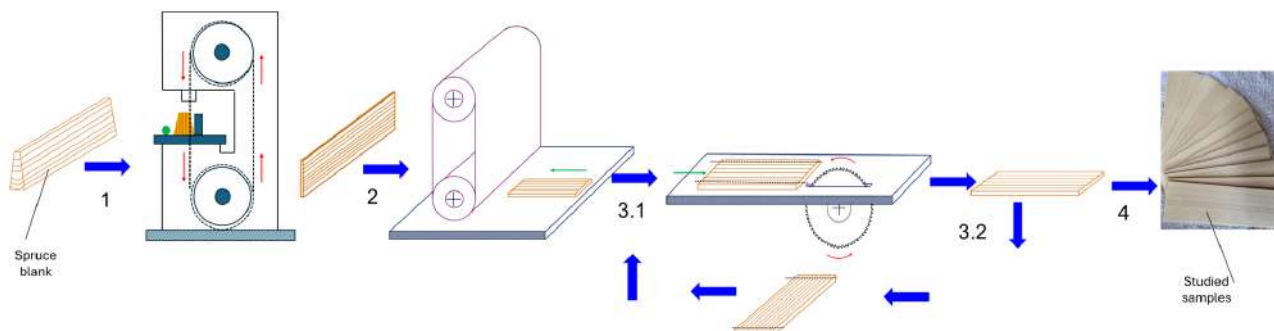


Figure 2. The main operations for sample preparation. Legend: 1—slitting of the blank on a band saw; 2—calibration of the faces on a sanding calibrating machine (four passes with different grits of the sanding roller); 3.1—straightening the edges for basing; 3.2—cutting (sectioning) to length; 4—the samples at the final dimensions. (Arrow legend and color code: Technological flow—blue arrow; part advance—green arrow; machine tool feed—red arrow).

Figure 3 presents the two categories of spruce wood samples (coded with S). A total of 54 samples were prepared (27 from each quality class, 3 samples from each varnishing category). The marks positioned at 50, 100 and 150 mm represent the position of the wood color measurement points.

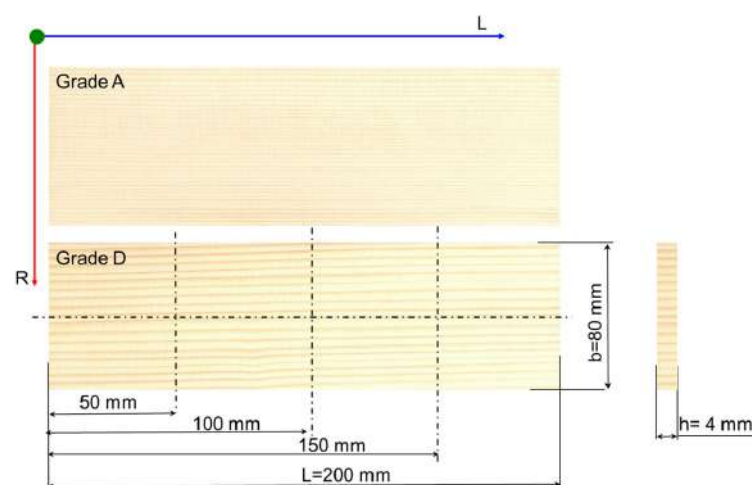


Figure 3. The aspect and sizes of samples from A and D quality grades of spruce wood (Legend: L—longitudinal direction of wood; R—radial direction of wood; L—length; b—width; h—thickness; 50 mm, 100 mm and 150 mm are the positions used for color measurement).

The whiteboards were subsequently grouped according to the type of varnish applied. These were grouped into three subcategories depending on the type of varnish, namely oil-based varnish coded LU, alcohol varnish coded LS and nitrocellulose varnish coded NC. All varnishes are commercial products, as can be seen in Table 1. Oil-based varnish (LU) contains a mixture of natural and synthetic resins dissolved in turpentine and linseed oil. Curing is based on the oxidative polymerization of oil. Nitrocellulose varnish (NC) is also an artificial polymeric product obtained from the treatment of natural polymeric cellulose with nitric acid, part of the hydroxyl groups in cellulose being replaced by nitrate groups. The solvent used contains ethyl acetate and butyl acetate, ketones such as acetone

and methyl ethyl ketone, and aromatic hydrocarbons. Spirit varnish mainly uses ethyl alcohol (ethanol), which dissolves the resin, with shellac being used in the past. Currently, for musical instruments, various resins are used that have properties like shellac.

Table 1. Materials for finishing.

Type of Material (Code)	Trade Name	Producer	Website
Varnishes			
Oil-based varnish (LU)	Joha Oil Varnish Standard	Hammerl GmbH & Co. KG	https://www.hammerl.com/en/varnishes.html (accessed on 27 July 2025)
Alcohol varnish (LS)	Joha Spirit varnish standard	Hammerl GmbH & Co. KG	https://www.hammerl.com/en/varnishes.html (accessed on 27 July 2025)
Nitrocellulose varnish (NC)			
Coloring materials			
Color extracts for varnishes (CEV)	Joha red (2903) Joha yellow (2901) Joha brown (2904)	Hammerl GmbH & Co. KG	https://www.hammerl.com/en/varnishes.html (accessed on 27 July 2025)
Water stains * (WS)	169 red brown 125 pure yellow 104 nut brown dark	Hammerl GmbH & Co. KG	https://www.hammerl.com/en/varnishes.html (accessed on 27 July 2025)
Kalium dichromate ** (KD)	-	International Laboratory SRL, Cluj Napoca, Romania	

Notes: * WS-R recipe: nut brown dark 5 g, pure yellow 2.5 g, and red brown 2.5 g in 1000 mL water for samples varnished with LU; ** employed as water solution: Kalium dichromate 53.5 g/1000 mL water.

For each type of varnish, regardless of the substrate type A or D, three varnish thicknesses quantified from the point of view of the varnishing process were established depending on the total number of layers of finishing materials applied: 5, 10 and 15. It has to be specified that the technologies included a first phase of coloring with a water-based solution (layer 1 or layers 1–2), generally continued with application of several colored varnish layers, and ended with 3–5 layers of colorless varnish (without any coloring extract). As an exception, for NC finished samples, after the initial coloring, only colorless varnish was employed (layers 4–15). Also, the technologies were particularized for each type of varnish by the musical instrument manufacturer (Gliga Musical Instruments Factory), respecting the recipes and conditions related to the finishing of violins, as can be seen in Table 2.

Table 2. Outlook of the finishing technology with 15 layers for the three types of varnishes (Legend: KD—Kalium dichromate; WS—Water stains; WS-R—Water stains recipe; CEV—Color extracts for varnishes).

Layers	Spirit Varnish (LS)	Nitrocellulose Varnish (NC)	Oil-Based Varnish (LU)
1	KD	WS-125 yellow	WS-R
2	LS+CEV2901	WS-104 nut brown	LU
3	LS+CEV2901	NC base coat	LU+CEV2901
4	LS+CEV2903	NC	LU+CEV2901
5	LS+CEV2901+CEV2903	NC	LU+CEV2903
6	LS+CEV2901+CEV2903	NC	LU+CEV2903
7	LS+CEV2901+CEV2903	NC	LU+CEV2904

Table 2. Cont.

Layers	Spirit Varnish (LS)	Nitrocellulose Varnish (NC)	Oil-Based Varnish (LU)
8	LS+CEV2904	NC	LU+CEV2904
9	LS+CEV2904	NC	LU+CEV2904
10	LS+CEV2904	NC	LU+CEV2904
11	LS	NC	LU+CEV2904
12	LS	NC	LU+CEV2904
13	LS	NC	LU
14	LS	NC	LU
15	LS	NC	LU

The general aspect of the various types of varnished samples can be viewed in Figure 4.

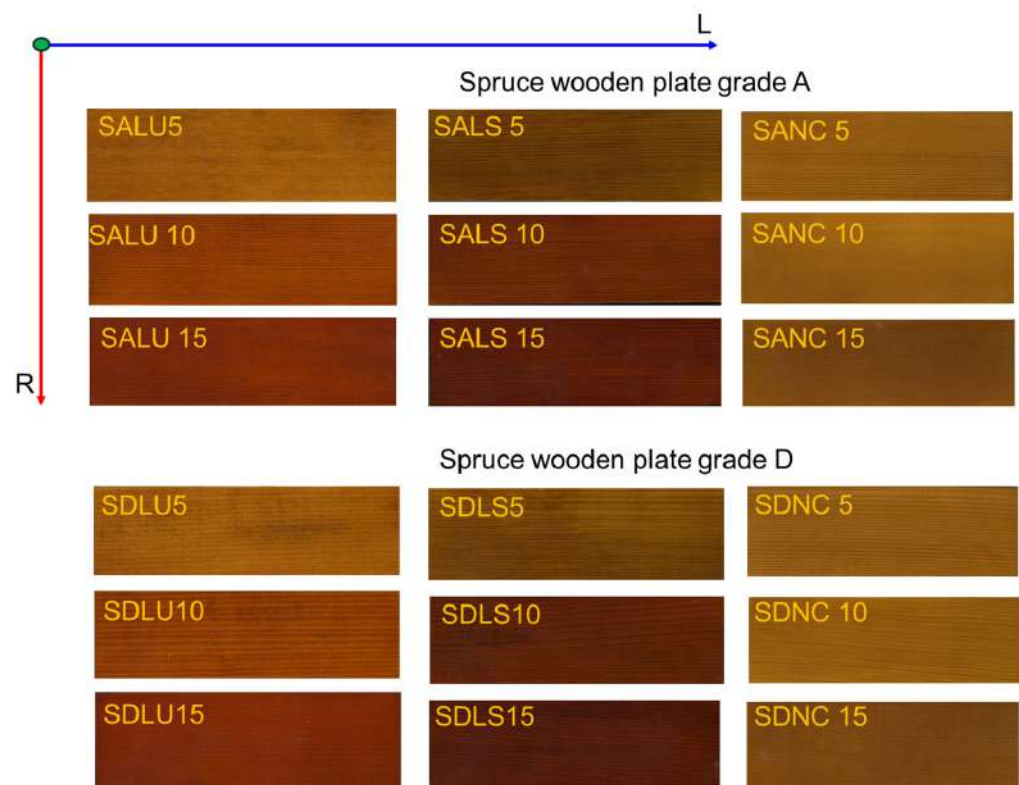


Figure 4. The varnished samples (Legend: SALU5—spruce wood grade A, varnished with oil-based varnish, 5 layers; SALS5—spruce wood grade A, varnished with spirit varnish, 5 layers; SANC5—spruce wood grade A, varnished with nitrocellulose varnish, 5 layers; SALU10—spruce wood grade A, varnished with oil-based varnish, 10 layers; SALS10—spruce wood grade A, varnished with spirit varnish, 10 layers; SANC10—spruce wood grade A, varnished with nitrocellulose varnish, 10 layers; SALU15—spruce wood grade A, varnished with oil-based varnish, 15 layers; SALS15—spruce wood grade A, varnished with spirit varnish, 15 layers; SANC15—spruce wood grade A, varnished with nitrocellulose varnish, 15 layers).

2.2. Methods

2.2.1. Thickness of Varnishes' Film

According to [12,14,29,30], to allow for a direct comparison between the mass changes of spruce boards varnished with different types of varnishes and with different film thicknesses, the changes were evaluated as an areal mass loading (denoted AML) induced by the coating system using relation (1).

$$AML = \frac{m_v - m_i}{b * L}, \quad (1)$$

where m_v is the mass of varnished sample; m_i is the mass of sample before varnish; b and L are the sizes of the sample. The mass was measured with a Kern DLB160-3A analytical balance (Kern&Sohn GmbH, Balingen, Germany).

To analyze the areal mass loading increase ΔAML of the samples because of the increase in the thickness of the varnish film, relationship (2) was applied:

$$\Delta AML = \left(\frac{AML_{n+5} - AML_n}{AML_n} \right) * 100, \quad (2)$$

where AML_n is the AML value of samples with superior number of layers ($n = 5; 10$).

2.2.2. Color Measurement

The first color measurements were performed before the varnishing process on all class A and D spruce wood samples, following the measurement scheme in Figure 3. The color parameters L^* (lightness), a^* (redness) and b^* (yellowness) were measured with the colorimeter, using the CIE- $L^*a^*b^*$ color measurement system (according to CIE Commission Internationale de l'Eclairage), and based on them, E^* was calculated [14,27,29–31]. The overall color change ΔE^* was calculated with the following Equation (3):

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}, \quad (3)$$

where ΔL^* , Δa^* and Δb^* are the differences between coordinates of the values L^* , a^* and b^* of the varnished surface and before varnishing.

2.2.3. The Contact Angle Method

The evaluation of the surface energy of the wood samples was carried out by the contact angle (CA) method. The value of the contact angle depends on three factors: the morphology of the substrate, expressed by the surface tension between the solid and gas medium (mN/m); the nature of the liquid, expressed by the superficial liquid and gas tension (mN/m); the nature of liquid and substrate interactions, expressed by the surface tension between the solid–liquid medium (mN/m) [32–35]. A liquid placed on a solid surface, in the absence of gravitational forces, will take the shape corresponding to the minimum energy of the system [36–39]. The CAs were determined with the System OCA-20 equipment (Data Physics Instruments, L7 Laboratory—ICD Transilvania University of Brasov) using successively distilled water and glycerin for the drop with a volume of 10 μ L. Thus, the values of the contact angle for water and for glycerin were measured. The measurements were performed at room temperature and under normal humidity conditions ($T = 22.7^\circ\text{C}$ and $RH = 65\%$). Three measurements per sample were made in the same areas presented in the previous methods (Figure 5). Based on the images recorded every second, the dynamic studies of the contact angle changes allow the evaluation of the absorption/adsorption capacity of the samples. The CA can take values between 0 and 180° . If the $CA < 90^\circ$, the analyzed surface is polar, i.e., the material is hydrophilic (absorbs liquid), and if $CA > 90^\circ$, the surface is dispersive, i.e., the material has a hydrophobic character (does not absorb liquid). The type of interaction between that surface and the liquid used in the analysis can be estimated from the CA angle [37–40]. Surface energy is a quantity that characterizes the morphology of the surface, in its turn being responsible for the ability to absorb or reflect acoustic waves. The measurements were performed at the same points presented in Figure 3, positioned at 50, 100 and 150 mm from edge sample.

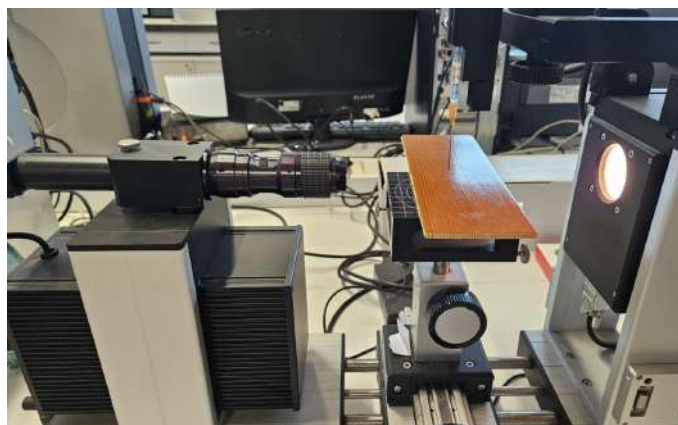


Figure 5. The testing of samples with System OCA-20 equipment.

2.2.4. Fourier Transformed Infrared (FTIR) Spectroscopy

Fourier transform infrared spectroscopy (FTIR) was used to analyze and compare the chemical characteristics of the untreated wood surface and the wood surfaces after coating with the three types of varnishes, applied in 5, 10 and 15 layers. FTIR analysis was performed with an Alpha Bruker spectrometer equipped with an attenuated total reflectance (ATR) unit. FTIR spectra were recorded in the range $4000\text{--}600\text{ cm}^{-1}$, at a resolution of 4 cm^{-1} , 24 scans per spectrum, and processed with OPUS 7.2 software [33–35].

2.2.5. Statistical Analysis

The statistical analysis consisted of data processing with STATISTICA 8.0 (StatSoft 2007) [36]. In the first stage, the sources of variation were probed, using the hypothesis of normal distribution of variables with the Shapiro–Wilk test; the significance or statistical relationship between variables was determined using Mann–Whitney U test and Kruskal–Wallis test, with p -values determining statistical significance. Subsequently, to rank the influence of various factors, such as the quality class of the wood used as substrate (denoted by SS), the type of varnish (TL) and the number of varnish layers (NL) on the studied properties, principal component analysis (PCA) was used. Finally, a multifactorial discriminant analysis of the measured properties, in relation to the variables mentioned above, was performed.

3. Results and Discussion

3.1. Variation in Areal Mass Loading

Figure 6 shows the variation in areal mass loading with increasing thickness of the varnish film. Thus, after the application and drying of the first layer of stain, it is sanded with 280 grit abrasive paper, and after the successive application and drying of the varnish films, they are sanded with 320 grit abrasive paper. The highest varnish consumption is recorded for spirit varnish (LS), approximately 2.4 times more than the surface consumption of oil-based varnish (LU), for five layers, for both class A and class D spruce wood. The lowest consumption is observed for the nitrocellulose varnish (NC), approximately 1.9 times less than the oil-based varnish (LU). With an increasing number of layers, areal mass loading increases regardless of the type of varnish, as can be seen in Table 3. The consumption of nitrocellulose lacquer is almost identical regardless of the quality of the wood. The lowest consumption of lacquer among the three categories of samples was recorded in the case of alcohol lacquer.

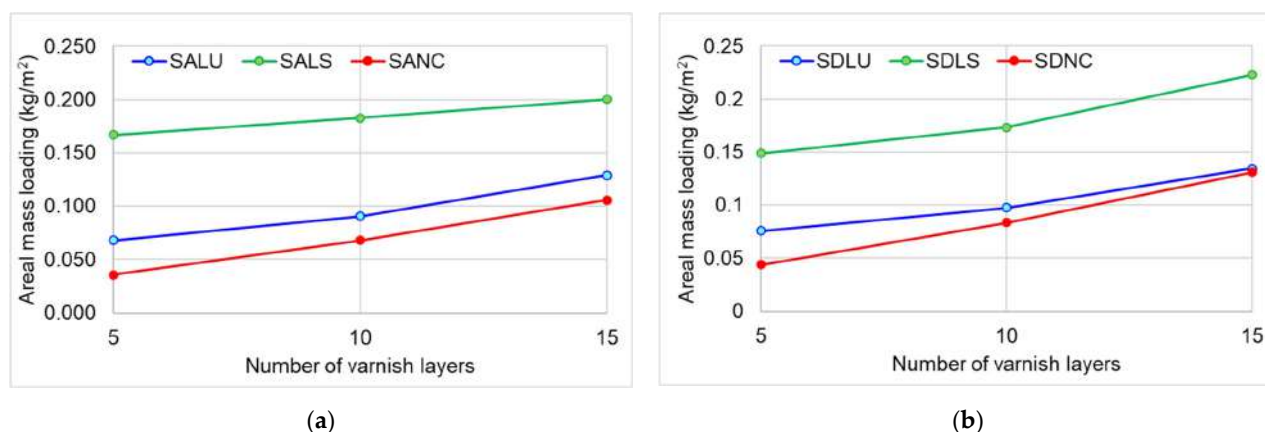


Figure 6. Variation in areal mass loading with type of varnish: (a) Grade A samples; (b) Grade D samples.

Table 3. The average values of AML and the increase.

Samples	AML (kg/m ²)	ΔAML (%)
SALU5	0.068	-
SALU10	0.090	33.052
SALU15	0.129	42.580
SALS5	0.167	-
SALS10	0.183	9.606
SALS15	0.200	9.409
SANC5	0.036	-
SANC10	0.068	90.322
SANC15	0.106	55.205
SDLU5	0.076	-
SDLU10	0.097	28.732
SDLU15	0.134	37.949
SDLS5	0.149	-
SDLS10	0.173	16.624
SDLS15	0.223	28.498
SDNC5	0.044	-
SDNC10	0.084	90.844
SDNC15	0.131	56.573

3.2. Variation in Color Parameters

3.2.1. Changes in Color Parameters During the Varnishing Process

Figure 7 shows the evolution of the color parameters during the finishing process for the samples with 15 layers, for the three types of varnishes. In Figure 7, the layer marked with zero represents the initial wood substrate before varnishing, and the following corresponds to the successive layers of finishing materials, the color parameters being measured after the drying of each applied layer. In general, it is observed that the lightness decreased for all the samples after the staining phase, though the values differed as a function of the staining materials and the actual technology. For SALU15 and SDLU15 stained with WS-R (a mixture of red brown, pure yellow and nut brown dark), the decrease in lightness was 31–35% (layer 1). For the samples SALS15 and SDLS15 stained with KD, the decrease was only 16%. For samples SANC15 and SDNC15, with staining in two layers, the decrease was around 16% after layer 1 (WS-125 yellow) and reached about 40% after layer 2 (WS-104 nut brown) (Figure 7a,b). Further lacquering of these samples brought about a decrease in lightness only after the first applied layer, followed by stabilization throughout the rest of the finishing technology. For the samples SALS15 and SDLS15,

as well as SALU15 and SDLU15, there was a wavy decrease of lightness up to layer 9 (varnishes colored with the darkest color extract), followed by stabilization. The evolution curves for the chromatic color parameters, redness (a^*) and yellowness (b^*), presented in Figure 7c–f are specific to the technology presented in Table 2. The most pronounced changes occur in the case of redness and yellowness, the parameters that increase by 300% (redness) and 600% (yellowness) after the application of the first layer. In Figure 8, an increase of 30–40% in the overall color can be noticed compared to the initial color of wood in white. The greatest overall color difference was obtained after applying the first layer of nitrocellulose varnish ($\Delta E^* = 50 \div 60$) compared to the LU and LS varnish, where ($\Delta E^* = 30 \div 40$). Starting with the fifth layer, the color difference remains approximately constant for all types of finishes analyzed, regardless of the quality of the substrate or the macrostructural particularities of the spruce wood.

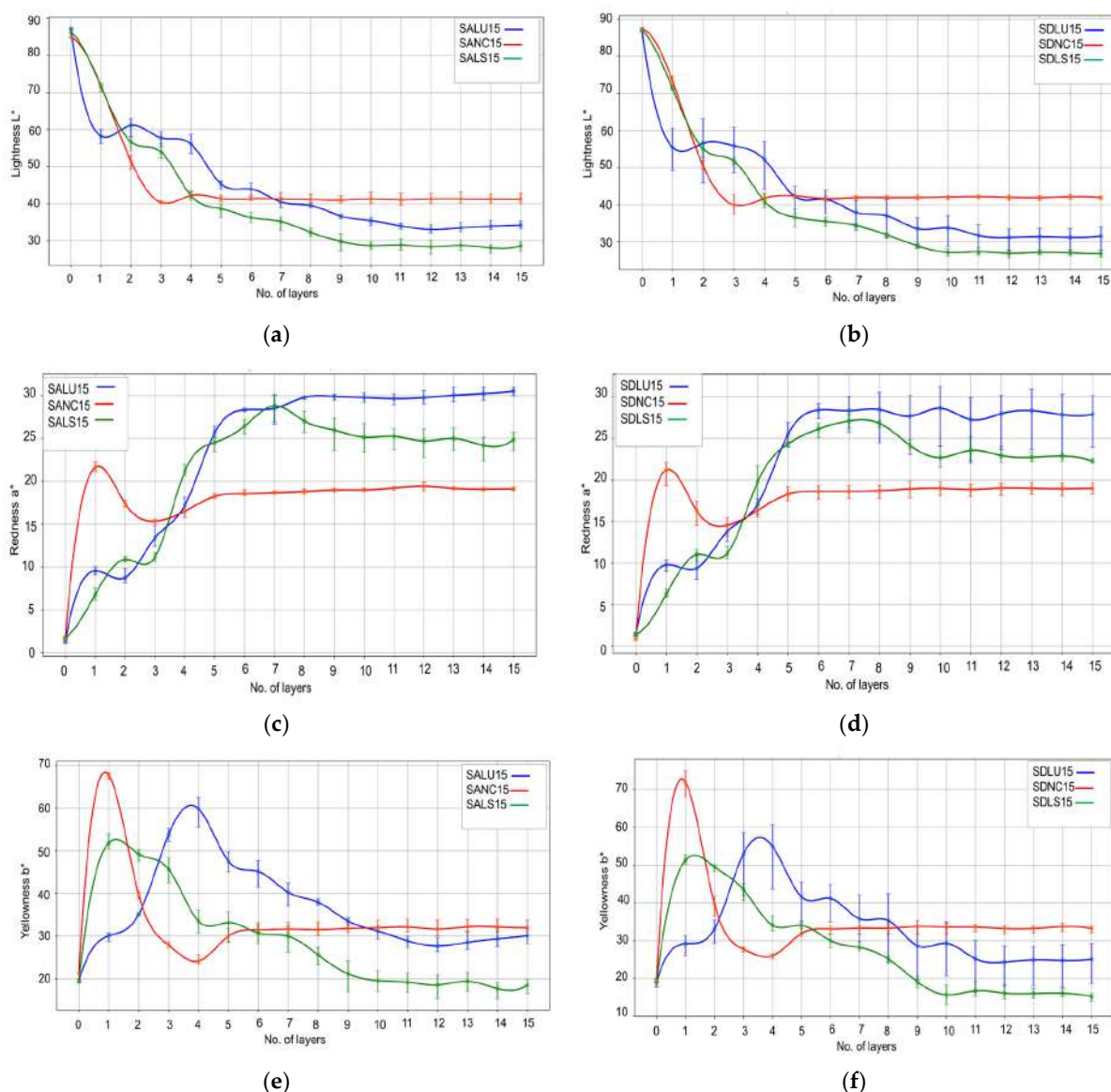


Figure 7. Changes in color parameters: (a) lightness L^* for spruce wood grade A; (b) lightness L^* for spruce wood grade D; (c) redness a^* for spruce wood grade A; (d) redness a^* for spruce wood grade D; (e) yellowness b^* for spruce wood grade A; (f) yellowness b^* for spruce wood grade D. Legend: SALU15, SDLU15—spruce wood grade A/D, varnished with oil-based varnish, 15 layers; SALS15, SDLS15—spruce wood grade A/D, varnished with spirit varnish, 15 layers; SANC15, SDNC15—spruce wood grade A/D, varnished with nitrocellulose varnish, 15 layers.

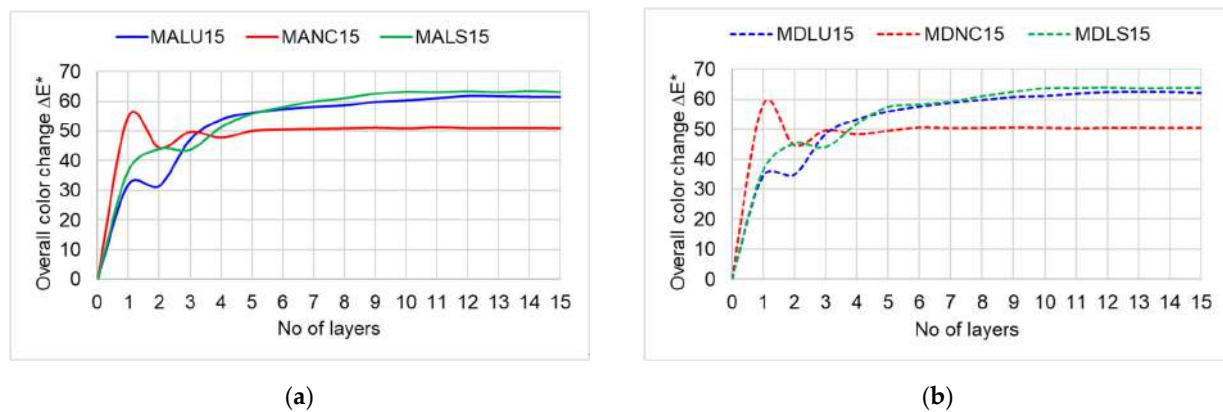


Figure 8. Overall changes in total color ΔE^* . (a) for spruce wood grade A and (b) for spruce wood grade D. (Legend: SALU15, SDLU15—spruce wood grade A/D, varnished with oil-based varnish, 15 layers; SALS15, SDLS15—spruce wood grade A/D, varnished with spirit varnish, 15 layers; SANC15, SDNC15—spruce wood grade A/D, varnished with nitrocellulose varnish, 15 layers).

3.2.2. Changes in Color Parameters in Accordance with the Thickness of Varnish

Before and after varnishing, the samples were positioned in the 3D CIEL color space, according to Figure 9. It was found that the unvarnished samples form a cluster in terms of color parameters, regardless of the quality class of the spruce wood. After varnishing, the clusters formed depend on the type of varnish applied and the thickness of the layers. The largest dispersion of the clusters was visible for 15 layers of varnish (Figure 9c). The lowest values of lightness, redness and yellowness were in the case of samples varnished with spirit varnish, and the highest values of the color parameters are recorded for the samples varnished with nitrocellulose varnish, regardless of the film thickness (Figure 9). The proportion of late wood and the width of annual rings, according to which the quality class of spruce wood was established, were reflected in the color of the finish, regardless of the thickness of the applied layers. Of all the color parameters measured, the most consistent change was shown by redness, which increases on average from 1.57 to 23.73. Table 4 summarizes the average values of the color parameters. The mean and standard deviation were calculated for nine values from each sample category.

Table 4. The average and standard deviation values of color parameters.

Samples	Before Varnish			After Varnish			ΔE^*
	L^*	a^*	b^*	L^*	a^*	b^*	
SALU5	85.49 (0.86)	2.06 (0.50)	19.46 (0.62)	48.37 (3.44)	24.03 (1.76)	49.13 (2.39)	52.34
SALU10	86.13 (0.17)	1.74 (0.22)	20.02 (0.64)	39.43 (4.62)	29.43 (0.54)	38.06 (7.35)	46.19
SALU15	87.12 (0.25)	1.29 (0.17)	19.54 (0.47)	35.86 (2.02)	30.38 (0.47)	32.39 (3.05)	60.32
SALS5	86.40 (0.42)	1.58 (0.07)	19.33 (0.40)	38.42 (1.21)	21.08 (3.76)	33.79 (2.23)	53.77
SALS10	86.11 (1.14)	1.96 (0.46)	19.61 (0.69)	31.35 (2.63)	25.43 (0.90)	23.55 (4.33)	59.90
SALS15	85.99 (0.22)	1.83 (0.10)	19.51 (0.25)	29.02 (0.41)	25.44 (0.59)	19.92 (1.24)	61.68
SANC5	85.01 (0.62)	1.64 (0.36)	21.14 (0.50)	49.78 (0.85)	20.80 (0.20)	44.57 (1.42)	46.45
SANC10	84.72 (1.11)	1.77 (0.97)	21.15 (0.91)	49.92 (1.41)	20.54 (0.40)	43.20 (1.43)	45.27
SANC15	84.94 (0.30)	1.64 (0.27)	21.27 (0.76)	41.85 (1.08)	19.80 (0.53)	33.13 (1.29)	48.24
SDLU5	87.38 (0.63)	1.38 (0.27)	18.70 (0.90)	46.74 (3.66)	23.92 (1.40)	46.57 (5.39)	54.19
SDLU10	86.34 (1.16)	1.68 (0.33)	18.96 (1.59)	38.75 (3.77)	28.66 (3.43)	36.97 (6.72)	55.63
SDLU15	87.16 (0.28)	1.40 (0.15)	19.06 (1.10)	35.44 (4.71)	29.80 (3.04)	31.31 (7.69)	60.26
SDLS5	87.22 (0.29)	1.48 (0.25)	18.08 (1.27)	39.08 (3.20)	21.47 (3.16)	36.40 (3.26)	55.26

Table 4. Cont.

Samples	Before Varnish			After Varnish			ΔE^*
	L*	a*	b*	L*	a*	b*	
SDLS10	87.06 (0.31)	1.54 (0.13)	18.93 (0.69)	29.44 (2.55)	23.58 (1.39)	20.24 (5.35)	61.71
SDLS15	87.05 (0.28)	1.41 (0.15)	19.07 (0.26)	27.74 (1.23)	23.93 (2.03)	17.92 (3.26)	63.45
SDNC5	86.68 (0.42)	1.15 (0.65)	19.79 (1.27)	51.80 (1.22)	19.63 (0.58)	44.83 (3.34)	46.75
SDNC10	87.85 (1.24)	0.71 (0.54)	18.10 (0.55)	54.61 (2.83)	19.61 (0.77)	48.22 (1.43)	48.68
SDNC15	87.24 (0.62)	0.86 (0.32)	19.76 (0.90)	43.36 (1.03)	19.71 (0.68)	35.02 (1.88)	50.14

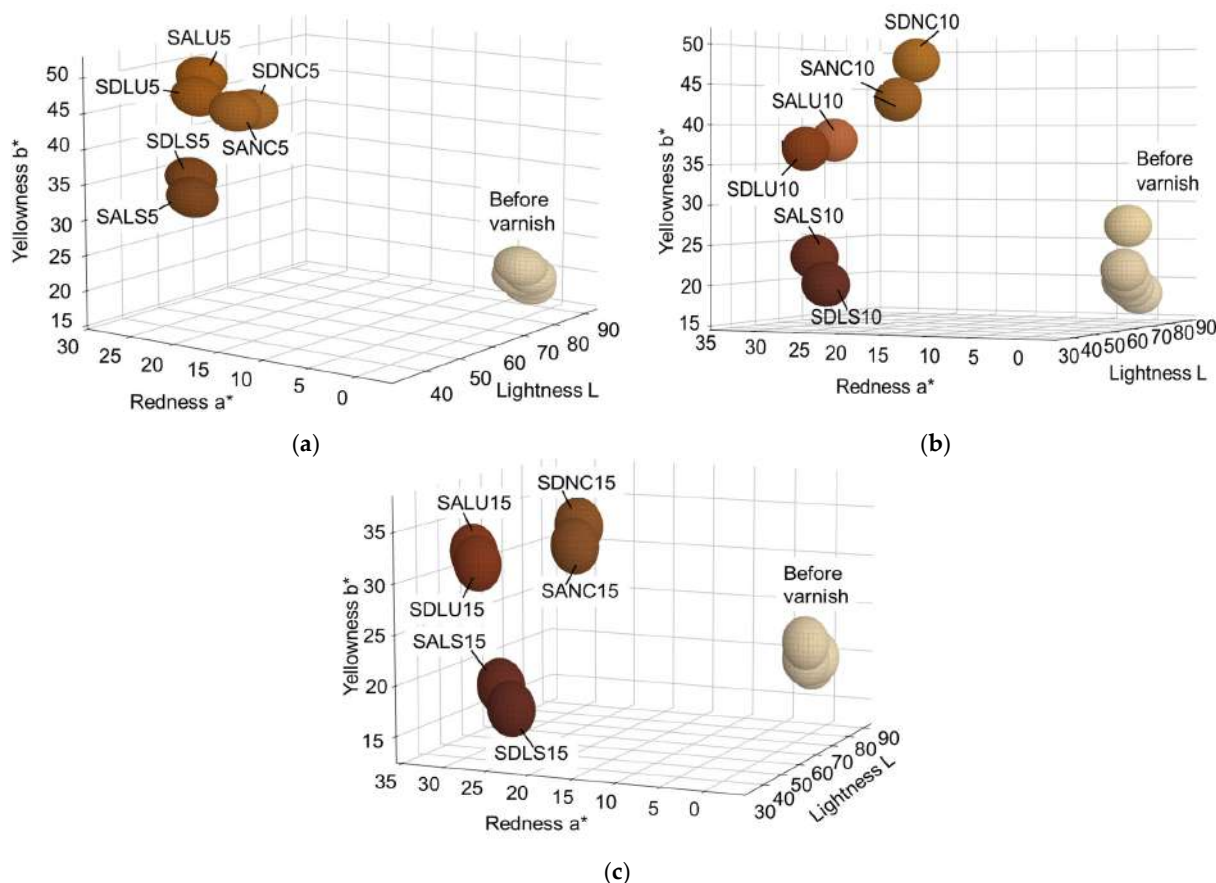


Figure 9. Distribution of varnished samples in the 3D CIE-Lab color space: (a) samples varnished with 5 layers; (b) samples varnished with 10 layers; (c) samples varnished with 15 layers.

In Figure 10, the color correspondence of the measured parameters is presented, i.e., from the CIE-L color space L^* , a^* and b^* in the RGB color space (Red, Green and Blue), using a free application for conversion. In Table 5, the RGB values of the color parameters are summarized.

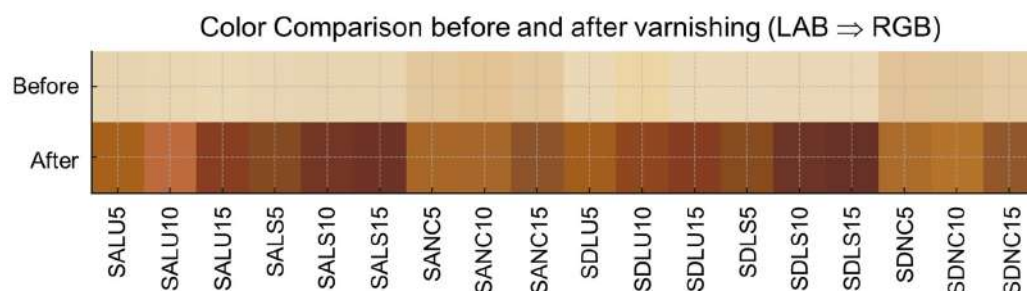


Figure 10. The color of samples in RGB space.

Table 5. The RGB color parameters.

Samples	Before Varnish			After Varnish		
	Red	Green	Blue	Red	Green	Blue
SALU5	232	211	177	169	97	27
SALU10	234	213	178	148	71	30
SALU15	235	216	181	138	62	33
SALS5	234	214	180	134	76	35
SALS10	234	213	179	118	56	38
SALS15	233	213	178	111	51	34
SANC5	231	210	173	168	103	40
SANC10	230	209	172	168	104	44
SANC15	231	210	172	142	85	44
SDLU5	236	217	184	164	93	29
SDLU10	233	214	180	145	70	31
SDLU15	235	216	182	136	61	34
SDLS5	235	216	184	137	77	32
SDLS10	235	216	182	110	53	39
SDLS15	235	216	182	105	49	39
SDNC5	234	215	180	172	109	45
SDNC10	235	219	186	181	116	44
SDNC15	235	217	181	146	89	44

3.3. Surface Morphology of Varnished Wood Samples

In Figure 11, the average values of the surface energy of the polar component and of the dispersive component for the three types of varnishes, applied with different thicknesses, are presented comparatively. Unlike the varnished samples, the unvarnished spruce wood samples, denoted SA (wood grade A) and SD (wood grade D), have a higher degree of crystallinity, which leads to high values of the surface energy, compared to the energy of the varnished surfaces (Figure 11a). Of the three types of varnishes, the most hydrophobic varnished surface was that of oil-based varnish compared to nitrocellulose and alcohol varnishes. The surface energy is higher for wood samples of grade D, with a higher proportion of early wood. Analyzing the variation in surface energy only between the varnished samples, it is found that the lowest surface energy is presented by the oil-based varnish, approximately 30% lower than that of the NC and LS varnished samples (Figure 11a).

Also, the dispersion of the surface energy values was higher for the unvarnished wood because of the different anatomical characteristics and heterogeneity of the wood structure in comparison with the samples covered with varnish films. The two components of the surface energy (polar (Figure 11b) and dispersive (Figure 11c)) provide information about the polarity of the surface. Thus, the unvarnished wood presents a large polar component, larger than the dispersive one, indicating a polar (hydrophilic) surface. This hydrophilic behavior is also observed for the varnished samples, but the polarity of the surfaces was lower than for the unvarnished wood, regardless of the grade. With increasing varnishing film thickness, the polar energy decreases for the NC and LU varnishes, while for the LS varnished samples, the polarity increases by approximately 30%; this is in good agreement with the variation in AML, which registered the highest value for LS varnished samples attributable to its polar nature and large polar interactions throughout the hydrophilic bare wood surface. The dispersive component presented in Figure 11c was the result of physical dispersion forces; the polar one comes from stronger interactions between the component particles—chemical interactions, dipole–dipole and ion–dipole. The highest dispersive component is recorded for the samples coated with five layers of nitrocellulose varnish, and it decreases with the increasing number of layers. At the opposite pole, the lowest

values of dispersive energy are recorded in samples varnished with oil-based varnish. The quality class of the wood covered with varnishes does not produce major changes in terms of the morphology of the varnished surfaces, as was highlighted by [33,37,38].

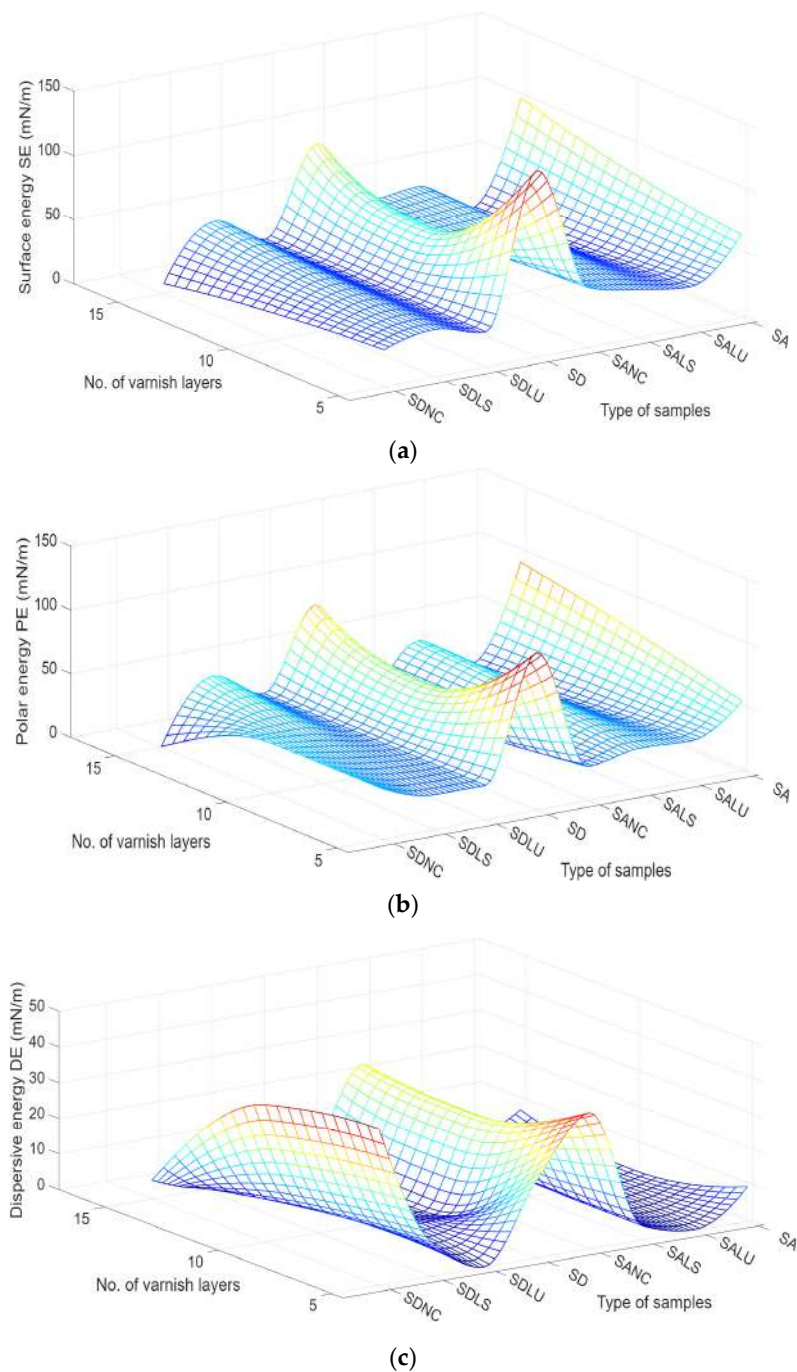


Figure 11. Variation in surface morphology in terms of (a) surface energy; (b) polar energy; and (c) dispersive energy. Legend: SA—unvarnished spruce wood grade A; SD—unvarnished spruce wood grade D.

Celluloses are mainly responsible for the dissipative energy, while the matrix (lignin and hemicelluloses) is more sensitive to humidity variations and contributes to the viscoelasticity and swelling of the wood; therefore, it presents higher polar energy. Microfibrils and matrix are linked by hydrogen bonds and covalent cross-links, which impose hygroscopicity and dimensional instability in the material in general [10,39–44].

3.4. Correlation Between Color and Surface Parameters Based on Statistical Analysis

The following variables were used in the statistical analysis: type of wood substrate (denoted SS); type of varnish (TV); number of varnish layers (NL); areal mass loading (AML); color parameters before varnishing (lightness denoted LBF; redness aBF; yellowness bBF) and after varnishing (lightness denoted LAV; redness aAV; yellowness bAV); color difference (DE); surface energy (SE); polar component (PC); and dispersive component (DC). In the first stage, the influence of the three types of factors (wood quality class, varnish type and number of layers) on the determined physical and morphological properties was determined, the results being summarized in Table 6. With the exception of some color parameters (LBF, bBF, aAV and DE), most of the variables show a high level of variability (coefficients of variation: 20–139%), which implies the existence of sources for this variability. PC and DC are the properties with the highest dispersion of values around the mean (Table 6). None of the variables are normally distributed, so the course of non-parametric statistics was followed (Table 6).

Table 6. Sources of variation in the properties of studied samples.

Sample Properties	Mean	Standard Deviation	Normality *	The Significance of Differences Between		
				SS **	TV ***	NL ***
AML	0.126	0.05	NO	0.6800	<0.001	<0.001
LBF	84.903	2.63	NO	0.0020	-	
aBF	2.492	1.42	NO	0.0300	-	
bBF	21.151	3.01	NO	0.0010		
LAV	40.039	8.11	NO	0.5000	<0.001	<0.001
aAV	23.946	3.93	NO	0.3700	<0.001	<0.001
bAV	34.691	9.90	NO	0.6500	<0.001	<0.001
DE	52.752	9.04	NO	0.1900	<0.001	<0.001
SE	51.263	39.38	NO	0.6800	<0.001	0.87
PC	35.075	35.96	NO	0.0200	0.28	0.13
DC	16.234	22.63	NO	0.1300	<0.001	0.4

* The hypothesis of normality of the distribution of variables was verified with the Shapiro–Wilk test: YES—the hypothesis of normality cannot be rejected/NO—the hypothesis of normality cannot be accepted. ** *p* from Mann–Whitney U test. *** *p* from Kruskal–Wallis test. Values highlighted in italics are significant for the statistical test used.

AML, the color of the wood after varnishing, DC and SE are not influenced by the type of wood material (A, D). The color before varnishing varies depending on the type of wood (Table 6). PC also depends significantly on the type of wood. PC is the only property that is not influenced by the type of varnish used (Table 6). The multiple comparison matrix associated with the nonparametric significance test shows that the color differences before and after varnishing are significant only for nitrocellulose varnishes ($p < 0.001$; $p = 0.26$ for the other varnishes). Also, the differences in SE are due to the LU and NC varnishes ($p < 0.03$), and the differences in DC magnitude are only due to the LU varnish ($p < 0.001$). Among the properties studied, the number of varnish layers (NL) leaves its mark only on AML and the color of the wood after varnishing (Table 6). In contrast, SE, PC and DC have no relationship with the number of varnish layers applied. The change in the degree of redness of the color occurs only at five varnish layers, as shown by the multiple comparison matrix attached to the Kruskal–Wallis test. But the overall color differences (ΔE) change at each of the varnish layers. With PCA, five principal components were extracted, the first two together explaining 62% of the total variance, as can be seen in Figure 12. The first principal component, which explains 44% of the total variance, is oriented in the direction of the color difference ΔE (factor loadings = -0.99), which varies in tandem with the brightness of the color before varnishing. So, the lighter the wood, the more pronounced

the effect of varnishing on the color. The second component is partly explained by the type of varnish (factor loadings = +0.63), which varies in tandem with DC and SE. The type of substrate is a non-influential variable.

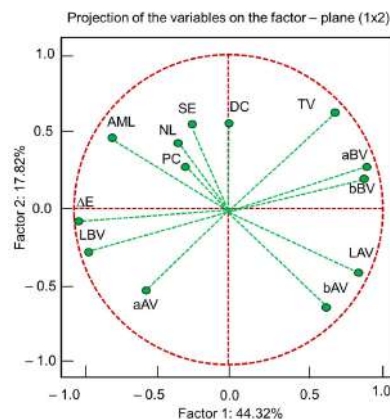


Figure 12. Principal component analysis (PCA).

According to the PCA, only the type of varnish and the number of varnish layers can be considered sources of variation for the analyzed properties.

3.5. FTIR Spectroscopy

In Figure 13, the FTIR spectra are presented for the spruce wood samples before varnishing (Figure 13a) and after varnishing with the three types of varnishes, each with the three categories of film thickness, resulting from 5, 10 and 15 layers of varnish (Figure 13b–d). Each type of varnish was also analyzed as a cured film on a glass slide for comparison. From the analysis of the presented spectra, for all types of varnishes (LU, LS, NC) and all types of wooden supports (SA, SD), it was found that they are like the spectra of the corresponding varnish films. This result denotes the fact that the wood structure was completely covered and was no longer visible in the FTIR spectra, not even in the case of the thinnest five-layer varnish finishing. For instance, specific absorption bands related to the main wood components, such as skeletal vibration of lignin (1507 cm^{-1}), other lignin-related bands (region $1600\text{--}1640\text{ cm}^{-1}$, 1261 cm^{-1}), C–H deformation vibration in cellulose and hemicelluloses (1368 cm^{-1}) and C–O stretch vibrations in carbohydrates (1025 cm^{-1}) were not visible at all in the spectra of varnished samples. At the same time, the absorption of hydroxyl groups ($3300\text{--}3400\text{ cm}^{-1}$), present in large amounts in all the wood's main components, was much receded, while the entire spectrum in the fingerprint region ($1750\text{--}600\text{ cm}^{-1}$) was totally changed for the varnished samples compared to bare wood.

Higher film thicknesses (10 or 15 layers of varnish) or different classes of substrate (A, D) did not bring any change in terms of surface chemistry, the spectra being practically identical for a certain type of varnish for both class A and class D spruce wood and all film thicknesses. On the other hand, the spectra of the three types of varnishes were significantly different due to their different chemical compositions and structural features. It is important to say that even if a certain chemical feature (functional group, type of substructure or bond) is common to more compounds, the FTIR spectra will be different, with shifts of the respective absorption, depending on the whole chemical structural context of each compound. This is particularly visible in the fingerprint region of the FTIR spectra. Compared to unvarnished wood, for varnished wood, the most pronounced absorptions were the double band $2926\text{--}2858\text{ cm}^{-1}$, corresponding to aliphatic methylene and methyl groups (asymmetric and symmetrical C–H stretch), and the bands at 1724 cm^{-1} (LU), 1722 cm^{-1} (NC) and 1708 cm^{-1} (LS), all assigned to non-conjugated carbonyl groups in either carboxylic acids, esters aldehydes or ketones. These two features may indicate the

presence of compounds with long aliphatic carbon chains and carbonyl groups, a good indication for coating materials with polymeric structures having unconjugated carbonyl groups in their chemical structure. For the samples varnished with nitrocellulose, a high absorption band at 1644 cm^{-1} , specific to the $-\text{NO}_2$ group associated with a methylene— CH_2 —group (bending) in nitrocellulose, was highlighted. This is different from the moderate, not well-defined absorption at 1643 cm^{-1} , visible in the spectra of unvarnished wood, associated with conjugated and aromatic carbonyl groups, which might be present in the structure of lignin [41–44]. In the next range of the spectra, there were noted close peaks at 1271 cm^{-1} (NC), 1258 cm^{-1} (LU), and 1242 cm^{-1} (LS) for the three types of varnishes, which can be associated with specific structural features of these materials as follows: symmetrical stretch of $-\text{NO}_2$ (valence vibration) for samples varnished with nitrocellulose varnish; C–O–C (stretching) of oxirane groups for oil-based varnish; and O–H (bending) and C–O (stretching) in hydroxyl $-\text{OH}$, carboxyl $-\text{COOH}$, and ester groups for alcoholic varnish LS. In unvarnished wood, the peak at 1025 cm^{-1} , assigned to C–O vibration in ethers and alcohols, is associated with cellulose and hemicelluloses; for the varnished samples, similar vibrations were observed at slightly different wavenumbers: 1004 cm^{-1} (LS), highlighting C–O (stretching) in alcohols, ether bonds, and acetals; 1065 cm^{-1} (NC), highlighting C–O (stretching) in the pyranose ring in nitrocellulose; and 1067 cm^{-1} (LU) C–O (stretching) of primary alcohols, highlighting the chemical structure particularities of each film-forming resin.

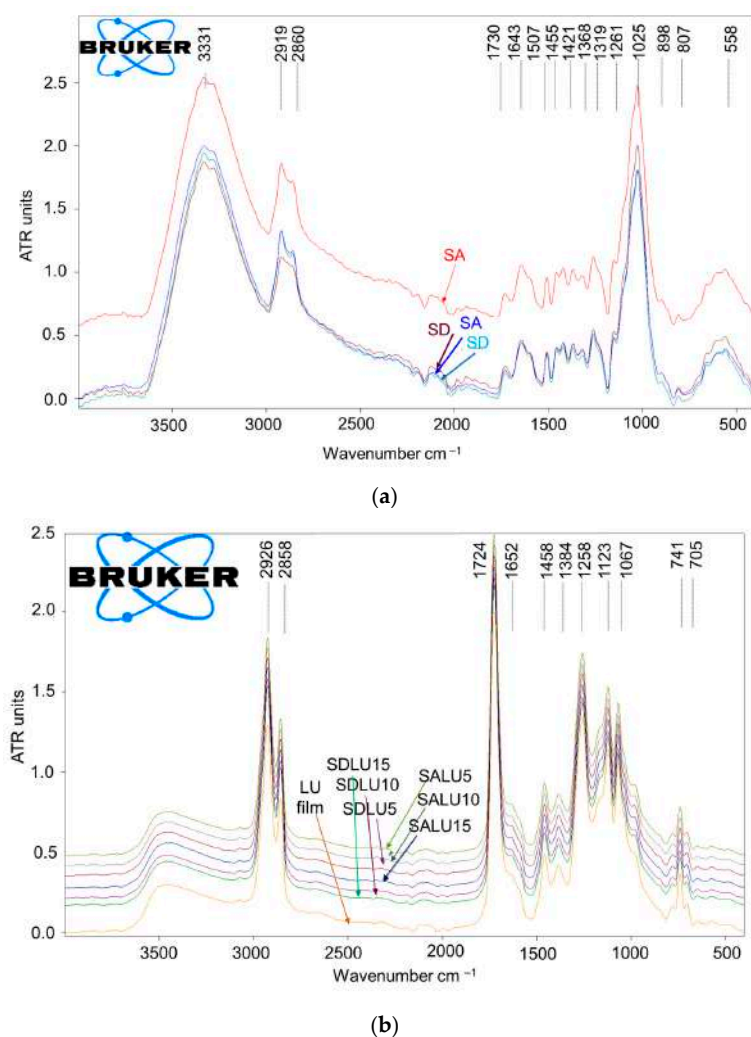


Figure 13. Cont.

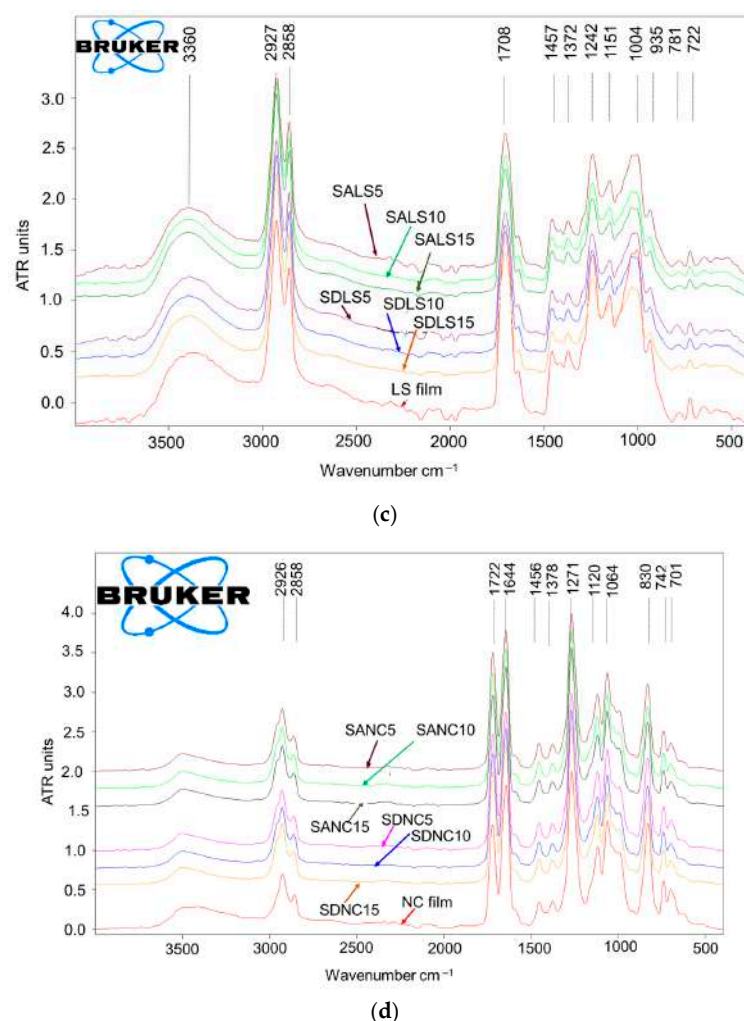


Figure 13. FTIR spectrum: (a) unvarnished samples—spruce wood (SA—spruce grade A, SD—spruce grade D); (b) wood samples with oil-based varnish; (c) samples with spirit varnish; (d) samples with nitrocellulose varnish.

4. Conclusions

This study presents the surface changes in terms of color, morphology and chemical fingerprint of spruce wood varnished with three types of varnishes (polymeric and alcohol solvent). The research highlighted the following aspects:

- The color parameters depend on the type of varnish and the thickness of the varnish film; the largest changes in redness and yellowness are recorded when applying the five layers containing the coloring pigments.
- The fastest stabilization of color parameters was observed with nitrocellulose varnish.
- Spruce wood with wide annual rings and a higher proportion of early wood (quality class D) has 25% higher surface energy compared to spruce wood with narrow annual rings (class A).
- The varnish film modifies the surface energy of the wood, reducing it by approximately 50% compared to unvarnished wood, the lowest values being recorded for oil-based varnish.
- Polar and dispersive energy depend on the varnish solvent and the number of layers applied.
- The varnish film modifies the FTIR absorption bands, completely covering the wood, leading to the formation of a new layered material consisting of the wood–varnish interface and the varnish film.

Future studies are needed to determine which varnish recipe offers the best viscoelastic properties of soundboard for dynamics in musical instrument construction.

Author Contributions: Conceptualization, M.D.S., M.C. and M.M.; methodology, F.D., M.D.S., M.C., M.C.T. and M.M.; software, M.M., M.C.T. and F.D.; validation, M.D.S. and F.D.; formal analysis, M.D.S., M.C. and M.C.T.; investigation, M.D.S., M.C. and M.C.T.; resources, M.D.S.; data curation, M.M.; writing—original draft preparation, M.M. and M.D.S.; writing—review and editing, M.C.T., M.C. and F.D.; visualization, F.D.; supervision, M.C.T.; project administration, M.D.S.; funding acquisition, M.D.S. All authors have read and agreed to the published version of the manuscript.

Funding: This research was supported by a grant from UEFISCDI Romania, project number 61PCE/2022, PN-III-P4-PCE2021-0885, ACADIA—Qualitative, dynamic and acoustic analysis of anisotropic systems with modified interfaces.

Institutional Review Board Statement: Not applicable.

Data Availability Statement: The original contributions presented in this study are included in the article. Further inquiries can be directed to the corresponding author.

Acknowledgments: This research was supported by a grant from UEFISCDI, project number 61PCE/2022, PN-III-P4-PCE2021-0885, ACADIA—Qualitative, dynamic and acoustic analysis of anisotropic systems with modified interfaces. We are also grateful to the technical staff of Glia Musical Instruments, Reghin, a Romanian manufacturer of musical string instruments, for supplying the specimens.

Conflicts of Interest: The authors declare no conflicts of interest.

References

- Španić, N.; Jambrečević, V.; Klarić, M. Basic chemical composition of wood as a parameter in raw material selection for biocomposite production. *Cellul. Chem. Technol.* **2018**, *52*, 163–169.
- Srndovic, A.S. Interactions between Wood Polymers in Wood Cell Walls and Cellulose/Hemicellulose Biocomposites. Ph.D. Thesis, Chalmers University of Technology, Gothenburg, Sweden, 2011.
- Gh, P.; Popa, V.I. *Chimia și Prelucrarea Chimică a Lemnului*; Publisher Lux Libris: Brasov, Romania, 1997; Volume II. (In Romanian)
- Stanciu, M.D.; Teodorescu, H.D.; Vlase, S.; Mihalcica, M.; Cosnită, M.; Savin, A. Multiscale assessment of artificial aging treatment of polysaccharides from tonewood species. *Int. J. Biol. Macromol.* **2024**, *274*, 133310. [[CrossRef](#)] [[PubMed](#)]
- Sahin, H.T. Wood-Water Interactions as Affected by Chemical Constituents of Woods. *Asian J. Chem.* **2008**, *20*, 3267–3276.
- Zhou, J.; Wang, X.; He, L.; Wan, K.; Guo, Y.; Zhang, J.; Miao, Y.; Liu, Z. The Changes of Acoustic Vibration Properties of Spruce Wood During the Multi-Layered Alcohol Varnish Coating Process. *Forests* **2024**, *15*, 2212. [[CrossRef](#)]
- Echard, J.-P.; Lavédrine, B. Review on the characterisation of ancient stringed musical instruments varnishes and implementation of an analytical strategy. *J. Cult. Herit.* **2008**, *9*, 420–429. [[CrossRef](#)]
- Caruso, F.; Chillura Martino, D.F.; Saverwyns, S.; Van Bos, M.; Burgio, L.; Di Stefano, C.; Peschke, G.; Caponetti, E. Micro-analytical identification of the components of varnishes from South Italian historical musical instruments by PLM, ESEM-EDX microFTIR, GC-MS, and Py-GC-MS. *Microchem. J.* **2014**, *116*, 31–40. [[CrossRef](#)]
- Weththimuni, M.L.; Canevari, C.; Legnani, A.; Licchelli, M.; Malagodi, M.; Ricca, M.; Zeffiro, A. Experimental characterization of oil-colophony varnishes: A preliminary study. *Int. J. Conserv. Sci.* **2016**, *7*, 813–826.
- Odlyha, M.; Lucejko, J.J.; Lluveras-Tenorio, A.; di Girolamo, F.; Hudziak, S.; Strange, A.; Bridarolli, A.; Bozec, L.; Colombini, M.P. Violin Varnishes: Microstructure and Nanomechanical Analysis. *Molecules* **2022**, *27*, 6378. [[CrossRef](#)]
- Sedighi Gilani, M.; Pflaum, J.; Hartmann, S.; Kaufmann, R.; Baumgartner, M.; Schwarze, F.W.M.R. Relationship of vibro-mechanical properties and microstructure of wood and varnish interface in string instruments. *Appl. Phys. A* **2016**, *122*, 260. [[CrossRef](#)]
- Lämmlein, S.L.; Mannes, D.; Van Damme, B.; Schwarze, F.W.M.R.; Burgert, I. The influence of multi-layered varnishes on moisture protection and vibrational properties of violin wood. *Sci. Rep.* **2019**, *9*, 18611. [[CrossRef](#)] [[PubMed](#)]
- Albano, M.; Comelli, D.; Fiocco, G.; Mattonai, M.; Lucejko, J.J.; Zoia, L.; Colombini, M.P.; Malagodi, M. Chemical modification of wood induced by the traditional making procedures of bowed string musical instruments: The effect of alkaline treatments. *Herit. Sci.* **2022**, *10*, 76. [[CrossRef](#)]

14. Stanciu, M.D.; Cosnita, M.; Gliga, G.V.; Gurau, L.; Timar, C.M.; Guiman, M.V.; Năstac, S.M.; Roșca, I.C.; Bucur, V.; Dinulică, F. Tunable Acoustic Properties Using Different Coating Systems on Resonance Spruce Wood. *Adv. Mater. Interfaces* **2024**, *1*, 2300781. [\[CrossRef\]](#)
15. Minato, K.; Akiyama, T.; Yasuda, R.; Yano, H. Dependence of Vibrational Properties of Wood on Varnishing during Its Drying Process in Violin Manufacturing. *Holzforschung* **1995**, *49*, 222–226. [\[CrossRef\]](#)
16. Ono, T. Effects of Varnishing on Acoustical Characteristics of Wood Used for Musical Instrument Soundboards. *J. Acoust. Soc. Jpn. E* **1993**, *14*, 397–407. [\[CrossRef\]](#)
17. Schelleng, J.C. Acoustical Effects of Violin Varnish. *J. Acoust. Soc. Am.* **1968**, *44*, 1175–1183. [\[CrossRef\]](#)
18. Korifi, R.; Le Dréau, Y.; Antinelli, J.-F.; Valls, R.; Dupuy, N. CIEL*a*b* color space predictive models for colorimetry devices—Analysis of perfume quality. *Talanta* **2013**, *104*, 58–66. [\[CrossRef\]](#) [\[PubMed\]](#)
19. Pelit, H. The effect of different wood varnishes on surface color properties of heat-treated wood materials. *J. Fac. For. Istanbul Univ.* **2017**, *67*, 262–274. [\[CrossRef\]](#)
20. Skrodzka, E.B.; Linde, B.B.J.; Krupa, A. Modal parameters of two violins with different varnish layers and subjective evaluation of their sound quality. *Arch. Acoust.* **2013**, *38*, 75–81. [\[CrossRef\]](#)
21. Chung, W.Y. SHP Studies on the vibrational modal analysis of solid woods for making the violin—Part 2. The effects of coating materials on the resonant frequency of European spruce and maple. *Korea Furnit. Soc.* **2000**, *11*, 45–52.
22. Schleske, M. Empirical Tools in Contemporary Violin Making: Part, I. Analysis of Design, Materials, Varnish, and Normal Modes. *Catgut Acoust. Soc. J.* **2002**, *4*, 50–64.
23. Obataya, E.; Ohno, Y.; Norimoto, M.; Tomita, B. Effects of oriental lacquer (urushi) coating on the vibrational properties of wood used for the soundboards of musical instruments. *Acoust. Sci. Technol.* **2001**, *22*, 27–34. [\[CrossRef\]](#)
24. Simonnet, C.; Gibiat, V.; Halar, J. Physical and Chemical Properties of Varnishes and Their Vibrational Consequences. *PACS Ref.* **2002**, *43*, 75.
25. Gliga, G.V.; Campean, M.; Georgescu, S.V. Violin Manufacturing Technology. In *Interdisciplinary Approach to the Violin*; Stanciu, M.D., Bucur, V., Eds.; Springer: Cham, Switzerland, 2025. [\[CrossRef\]](#)
26. STAS 10824-76; Half-Staffs for Musical Instruments with Strings and Bow. Romanian Institute for Standardization: Bucharest, Romania, 1976. Romanian standard. (In Romanian)
27. Dinulică, F.; Stanciu, M.D.; Savin, A. Correlation between Anatomical Grading and Acoustic–Elastic Properties of Resonant Spruce Wood Used for Musical Instruments. *Forests* **2021**, *12*, 1122. [\[CrossRef\]](#)
28. Stanciu, M.D.; Guiman, M.V.; Năstac, S.M. New Challenges in Assessment of the Acoustic Properties of Coating Polymers. *Polymers* **2025**, *17*, 1418. [\[CrossRef\]](#) [\[PubMed\]](#)
29. Lämmlein, S.L. Violin Varnishes and Tonewood: Relationships of Vibromechanical and Moisture Sorption Properties. Ph.D. Thesis, ETH Zurich, Zurich, Switzerland, 2020.
30. Lämmlein, S.; Künniger, T.; Rüggeberg, M.; Schwarze, F.W.M.R.; Mannes, D.; Burgert, I. Frequency dependent mechanical properties of violin varnishes and their im-pact on vibro-mechanical tonewood properties. *Results Mater.* **2020**, *9*, 100137. [\[CrossRef\]](#)
31. Olteanu, L.; Teischinger, A.; Hansmann, C. Wood surface discoloration due to simulated indoor sunlight exposure. *Holz Roh Werkst.* **2008**, *66*, 51–56. [\[CrossRef\]](#)
32. Liu, X.Y.; Timar, M.C.; Varodi, A.M.; Sawyer, G. An investigation of accelerated temperature-induced ageing of four wood species: Colour and FTIR. *Wood Sci. Technol.* **2017**, *51*, 357–378. [\[CrossRef\]](#)
33. Liu, X.Y.; Timar, M.C.; Varodi, A.M.; Nedelcu, R.; Torcătoru, M.J. Colour and Surface Chemistry Changes of Wood Surfaces Coated with Two Types of Waxes after Seven Years Exposure to Natural Light in Indoor Conditions. *Coatings* **2022**, *12*, 1689. [\[CrossRef\]](#)
34. Gurău, L.; Timar, M.C.; Coșereanu, C.; Cosnita, M.; Stanciu, M.D. Aging of Wood for Musical Instruments: Analysis of Changes in Color, Surface Morphology, Chemical, and Physical-Acoustical Properties during UV and Thermal Exposure. *Polymers* **2023**, *15*, 1794. [\[CrossRef\]](#)
35. Manzo, G.; Tippner, J.; Zatloukal, P. Relationships between the Macrostructure Features and Acoustic Parameters of Resonance Spruce for Piano Soundboards. *Appl. Sci.* **2021**, *11*, 1749. [\[CrossRef\]](#)
36. STATISTICA, Version 8.0; Data Analysis Software System; StatSoft: Tulsa, OK, USA, 2007; Available online: <http://www.statsoft.com> (accessed on 28 July 2025).
37. Yin, H.; Moghaddam, M.S.; Tuominen, M.; Dédinaït, A.; Wålinder, M.; Swerin, A. Wettability performance and physicochemical properties of UV exposed superhydrophobized birch wood. *Appl. Surf. Sci.* **2022**, *584*, 152528. [\[CrossRef\]](#)
38. Patera, A.; Derome, D.; Griffa, M.; Carmeliet, J. Hysteresis in swelling and in sorption of wood tissue. *J. Struct. Biol.* **2013**, *182*, 226–234. [\[CrossRef\]](#)

39. Ding, Y.; Shakoorioskooie, M.; Mannes, D.; Zhang, Z.; Chernyshov, D.; Burgert, I. Laser-drilled functional wood materials show improved dimensional stability upon humidity changes—a neutron imaging analysis. *J. Mater. Chem. A* **2025**, *13*, 6364–6375. [[CrossRef](#)]
40. He, L.; Zhang, T.; Zhao, X.; Zhao, Y.; Xu, K.; He, Z.; Yi, S. Synergistic effect of tung oil and heat treatment on surface characteristics and dimensional stability of wood. *Colloids Surf. A Physicochem. Eng. Asp.* **2023**, *665*, 131233. [[CrossRef](#)]
41. Han, X.; Wang, Z.; Zhang, Q.; Pu, J. An effective technique for constructing wood composite with superior dimensional stability. *Holzforschung* **2020**, *74*, 435–443. [[CrossRef](#)]
42. Meiorin, C.; Aranguren, M.I.; Mosiewicki, M.A. Polymeric networks based on tung oil: Reaction and modification with green oil monomers. *Eur. Polym. J.* **2015**, *67*, 551–560. [[CrossRef](#)]
43. Peng, Y.; Wang, Y.; Zhang, R.; Wang, W.; Cao, J. Improvement of wood against UV weathering and decay by using plant origin substances: Tannin acid and tung oil. *Ind. Crops Prod.* **2021**, *168*, 113606. [[CrossRef](#)]
44. Hang, J.; Yan, X.; Li, J. A Review on the Effect of Wood Surface Modification on Paint Film Adhesion Properties. *Coatings* **2024**, *14*, 1313. [[CrossRef](#)]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.

Article

New Challenges in Assessment of the Acoustic Properties of Coating Polymers

Mariana Domnica Stanciu ^{1,*} , Maria Violeta Guiman ¹ and Silviu Marian Năstac ^{1,2} 
¹ Department of Mechanical Engineering, Transilvania University of Braşov, B-dul Eroilor 29, 500036 Braşov, Romania; violeta.guiman@unitbv.ro (M.V.G.); silviu.nastac@ugal.ro (S.M.N.)

² Faculty of Engineering and Agronomy, Braila, “Dunarea de Jos” University of Galati, 999074 Braila, Romania

* Correspondence: mariana.stanciu@unitbv.ro

Abstract: The study presented in this paper investigates the influence of coating polymers on the acoustic properties of resonant spruce wood. It evaluates absorption, acoustic reflection, and resonance frequency spectrum characteristics in both unvarnished and varnished samples, with the interface between the coating polymer and the wood modifying the acoustic response. The novelty of the research consists in evaluating the acoustic and dynamic parameters of resonant spruce wood boards, varnished with varnishes with different chemical properties (oil-based varnish, spirit varnish, nitrocellulose varnish). The study focuses on the influence of the type of varnish and the thickness of the varnish film on the frequency spectrum, damping coefficient, quality factor, acoustic absorption coefficient, and sound reflection. The sound absorption coefficient increases with the number of varnish layers and is influenced by the sound's frequency range, the type of varnish, and the quality of the wood—factors that collectively enhance acoustic performance. For instance, oil-based varnish applied in 5 or 10 layers contributes to a fuller sound at a frequency of 1.5 kHz. In contrast, spirit varnish, which has a lower acoustic absorption coefficient at this frequency, and a reduced damping coefficient, can lead to a nasal tone, although the frequency spectrum turns out to have the richest. Applying more than 10 layers of varnish softens the sound when using oil-based varnish but sharpens it with spirit varnish on resonant wood. Thus, the acoustic performance of a soundboard can be tailored by selecting the appropriate varnishing system and number of layers applied. However, a detailed analysis of the timbre of musical instruments finished with these varnishes is necessary to confirm their influence on the acoustic quality of the instruments.

Keywords: coating polymers; acoustic properties; resonance spruce; modal analysis; impedance tube



Academic Editor: Antonio Pizzi

Received: 23 April 2025

Revised: 16 May 2025

Accepted: 19 May 2025

Published: 21 May 2025

Citation: Stanciu, M.D.; Guiman, M.V.; Năstac, S.M. New Challenges in Assessment of the Acoustic Properties of Coating Polymers. *Polymers* **2025**, *17*, 1418. <https://doi.org/10.3390/polym17101418>

Copyright: © 2025 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 (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Most studies on resonant spruce have focused on analyzing its acoustic properties from the perspective of sound propagation speeds in the three principal directions, the quality factor, damping coefficient, resonance frequencies, and acoustic radiation [1,2]. Softwoods used in violin top plates exhibit a high level of acoustic performance, characterized by high sound propagation speeds in the longitudinal direction (around 5500 m/s), high elastic moduli (approx. 14–15 GPa), strong acoustic radiation, and efficient acoustic energy conversion [1,2]. Resonance spruce wood also displays moderate acoustic impedance, moderate to low density, low damping, and high anisotropy—meaning a significant variation in properties depending on the direction [3–6]. However, the acoustic and vibrational phenomena in violin wood are complex, as sound energy is transformed into absorbed,

reflected, and transmitted energy [7–10]. Consequently, the anatomical structure of the wood has a crucial role in the acoustics of the musical instrument, as demonstrated in numerous studies [11–14]. In addition, the wood–varnish system significantly influences the transmission of acoustic energy. This system forms two distinct environments through which sound travels, with the type of varnish being a defining factor. From a material structure perspective, the timbre of a violin results from a layered system composed of the wood (substrate), the wood–varnish interface, and the varnish film (coating) [15–18]. While the interior of the violin body remains unvarnished, the exterior is fully coated with varnish, leading to different absorption and reflection phenomena at the interfaces between varnished wood and external air, and between unvarnished wood and the air inside the resonator. Studies [19–24] have shown that sound energy absorption in wood is accompanied by mechanical, acoustic, and thermal phenomena. Structurally, the number of pores (cavities, channels, and interstices), their dimensions, interconnections, and the interface between external surfaces and internal pores are key characteristics that affect the absorption, reflection, and transmission of acoustic energy. These aspects have been the focus of numerous studies [25–28]. Yin and Guan (2024) [29] emphasized the influence of structural parameters on sound absorption performance, depending on the positioning of layers with varying elastic and porous properties relative to the incident acoustic energy. Figure 1 illustrates how incident acoustic energy (E_i) is reflected (E_r), absorbed (E_{a1} , E_{a2}), and transmitted (E_{t1} , E_{t2} , E_{t3}) through the media it encounters—namely the lacquer film (1) and the wood (2), which together form a layered system with distinct material properties.

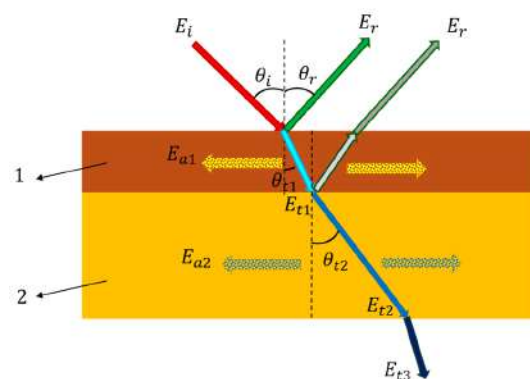


Figure 1. Sound wave incident into a material with layers having different elastic and absorbing properties.

The relationship between the acoustic properties of resonant wood and the different types of varnishes applied has been analyzed from physical, elastic, morphological, and chemical perspectives, as highlighted in studies [28–30]. However, it has been found that the existing literature is limited in terms of research on the effects of coatings—particularly the type and thickness—on the sound absorption coefficients of solid wood materials such as violin soundboards.

Previous studies [30,31] focused on characterizing the morphology of both unvarnished and varnished surfaces of resonant wood, as well as determining the acoustic absorption and reflection coefficients for materials coated with oil-based and alcohol-based varnishes. The acoustic absorption coefficient indicates the material's ability to absorb sound waves across various frequencies. In contrast, the reflection of sound waves refers to the phenomenon in which waves return to the medium from which they originated upon encountering a boundary with another medium of different density. To characterize this reflection phenomenon, a quantity known as the reflection coefficient—or acoustic reflection factor—is introduced and determined empirically. The reflection coefficient is

defined as the ratio between the amplitude of the reflected wave and the amplitude of the incident wave.

The novelty of the research presented in this article lies in the comparative analysis of acoustic parameters—specifically sound absorption and reflection coefficients—as influenced by varnish film thickness, varnish type (oil-based varnish, spirit varnish, nitrocellulose varnish), and the anatomical quality of spruce wood. The acoustic absorption and reflection coefficients were determined using the transfer-function method.

2. Materials and Methods

2.1. Samples Preparation

In the first stage, 18 spruce wood boards with anatomical and physical characteristics typical of resonant wood—classified as quality grades A and D—were prepared, as shown in Table 1 [31]. The unvarnished spruce plates from grades A and D (denoted SA and SD), with a moisture content of 6–8% and dimensions of $240 \times 80 \times 4 \text{ mm}^3$, were varnished using three types of varnish: oil-based varnish (coded LU), spirit varnish (LS), and nitrocellulose varnish (NC). Each varnish type was applied in three different layer thicknesses related to the number of layers: $40 \pm 10 \mu\text{m}$ (coded 5), $80 \pm 10 \mu\text{m}$ (coded 10), and $130 \pm 10 \mu\text{m}$ (coded 15). The base coat was sanded using 280-grit sandpaper, and each subsequent varnish layer was sanded with 320-grit sandpaper. The varnish application was carried out at a musical instrument factory, following standard lacquering procedures used for violins. From each type of board, four circular samples with a diameter of 29 mm were extracted for testing using the impedance tube method, as illustrated in Figure 2. Table 2 presents the types of samples prepared for the acoustic impedance tube and their physical characteristics.

Table 1. The anatomical features of the spruce wood sample from two different quality grades [31].

Physical Features	Grade/Average Value/STDV			
	A	STDV	D	STDV
Annual rings width (mm)	0.71	0.005	2.28	0.005
Early wood width (mm)	0.54	0.011	1.74	0.029
Late wood width (mm)	0.18	0.013	0.54	0.026
Early wood proportion (%)	74.97	1.519	76.36	1.138
Late wood proportion (%)	25.03	1.519	23.64	1.136
Density ρ (kg/m^3)	409.5	28.50	420.00	26.00

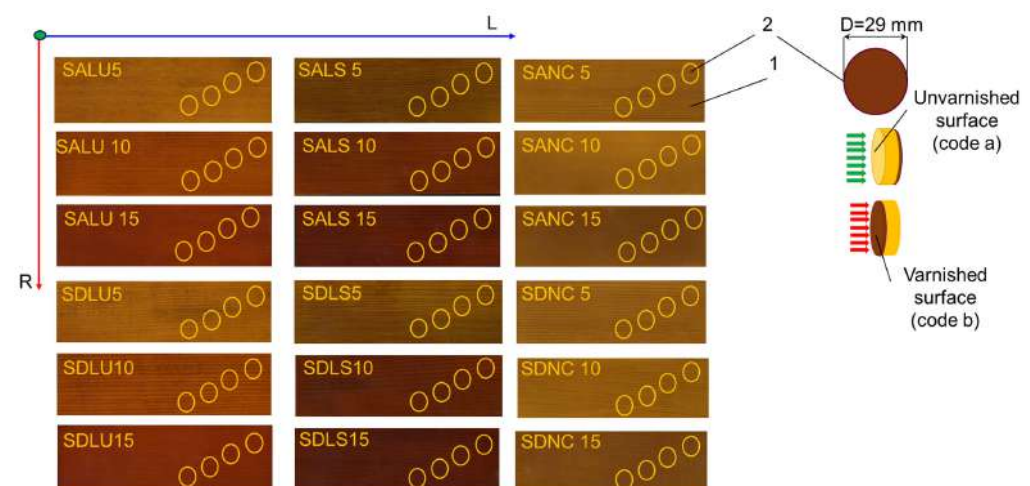


Figure 2. The specimens prepared for study: (Legend: 1—sample for modal analysis test; 2—sample for impedance tube test; D—sample diameter; L—longitudinal direction of wood; R—radial direction of wood).

Table 2. The physical features of the cylindrical varnished samples (Legend: SALU5—spruce wood grade A, varnished with oil-based varnish, 5 layers; SALS5—spruce wood grade A, varnished with spirit varnish, 5 layers; SANC5—spruce wood grade A, varnished with nitrocellulose varnish, 5 layers; SALU10—spruce wood grade A, varnished with oil-based varnish, 10 layers; SALS10—spruce wood grade A, varnished with spirit varnish, 10 layers; SANC10—spruce wood grade A, varnished with nitrocellulose varnish, 10 layers; SALU15—spruce wood grade A, varnished with oil-based varnish, 15 layers; SALS15—spruce wood grade A, varnished with spirit varnish, 15 layers; SANC15—spruce wood grade A, varnished with nitrocellulose varnish, 15 layers).

Type of Varnished Samples	No. of Samples	Thickness of Varnish Layer (μm)	Mass (g)
SALU5 SALS5 SANC5	4	40 ± 10	1.146 1.167 1.348
SALU10 SALS10 SANC10	4	80 ± 10	1.322 1.188 1.449
SALU15 SALS15 SANC15	4	130 ± 10	1.376 1.327 1.517
SDLU5 SDLS5 SDNC5	4	35 ± 10	1.186 1.125 1.144
SDLU10 SDLS10 SDNC10	4	70 ± 10	1.258 1.168 1.215
SDLU15 SDLS15 SDNC15	4	120 ± 10	1.337 1.189 1.443

2.2. Experimental Set-Up

2.2.1. The Modal Analysis of Varnished Plates

Experimental modal analysis of spruce wooden plates (1) before varnish (coded SA and SD) and after finishing (coded SALU, SDLU, SALS, SDLS, SANC, SDNC) consisted of exciting them with an impact hammer type B&K 8204 (4) [26,27,31–33]. Each plate was supported by elastic elements (2), thus simulating a system with a free structure (Figure 3). For the elastic supports (2) of the plates, a rigid frame was used, with a cantilever beam (3).

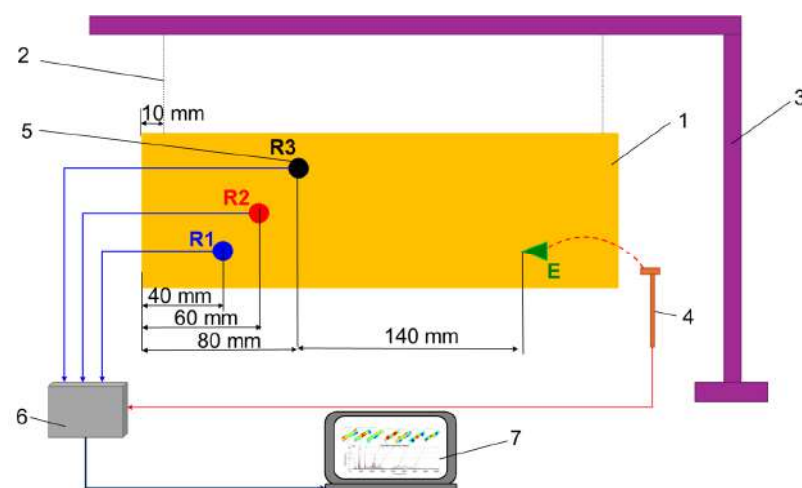


Figure 3. Experimental set-up for modal analysis (Legend: 1—sample; 2—elastic supports; 3—rigid frame of experimental bench; 4—impact hammer (applied in point, denoted E); 5—accelerometers (denoted with signal R1, signal R2, signal R3); 6—dynamic data acquisition board; 7—laptop).

The resulting signal was received by means of three accelerometers of the type B&K 4517–002 (5), placed according to the scheme shown in Figure 3. The generated signals from R1, R2, and R3 accelerometers were passed through a signal conditioner to a NI USB-9233 dynamic data acquisition board (6) manufactured by National Instruments (Austin, TX, USA), and connected to a laptop (7). The signal was processed using an application developed in MatLab© software, R2024a version (Figure 3). To obtain the values of the fundamental frequencies and the damping factor, all the signals from R1, R2, and R3 accelerometers were graphically processed, resulting in an analysis in time and frequency. The tests were carried out in the laboratory, under controlled conditions of temperature (22 ± 2 °C) and relative air humidity ($55 \pm 5\%$). From frequency analysis, the logarithmic decrement $\tan \delta$ (dimensionless) was determined, which represents the internal friction manifested by the loss of mechanical energy in the process of vibration propagation, knowing the resonance frequency f_r and its amplitude as can be seen in Figure 4. Thus, for each resonance frequency in the frequency spectrum, the two frequencies f_{r1} f_{r2} were determined, extracted at 0.707 from the magnitude of each resonance frequency, as seen in Figure 4, after which the values were introduced into the logarithmic decrement relation (1) [33,34]. The quality factor Q was calculated with the relation (2) [33,34].

$$\tan \delta = \frac{(f_{r2} - f_{r1})}{f_r}, \quad (1)$$

$$Q = \frac{1}{\tan \delta} \quad (2)$$

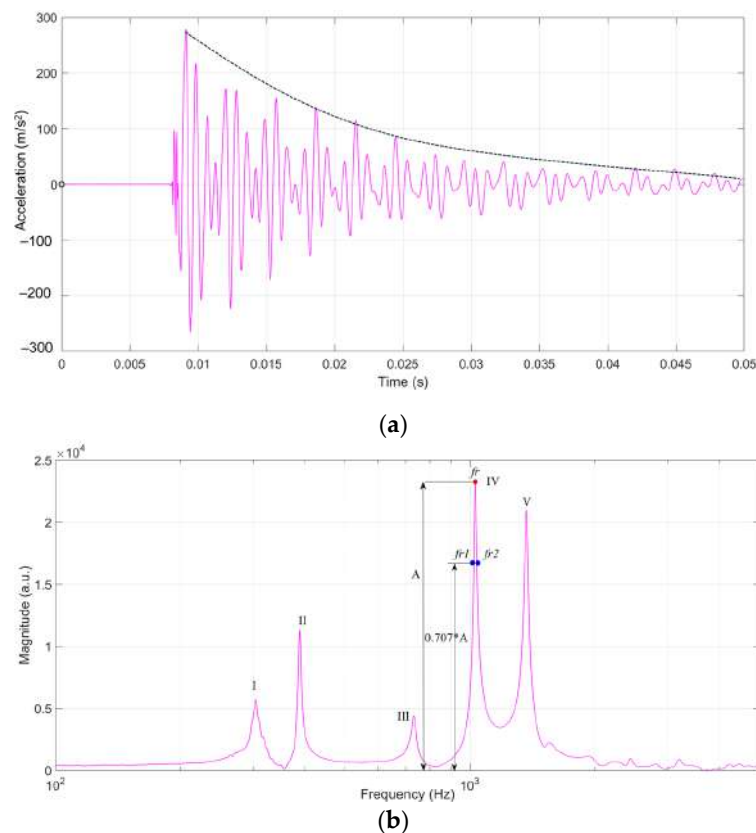


Figure 4. Schematic of the method of extracting quantities for calculating the logarithmic decrement and the quality factor: (a) time domain analysis; (b) frequency spectrum (I, II, III, IV, V—resonance frequency (f_r), frequencies f_{r1} f_{r2} extracted at 0.707 from the magnitude).

2.2.2. The Impedance Tube Method

The sound absorption coefficient (denoted SAC) of the samples was measured using an impedance tube, following the standard procedures outlined in standards ISO 11654:1997, ISO 10534-2/1998 and ASTM E1050-12/1998. These methods are based on the transfer function method with two microphones (TFM) [34–37]. The impedance tube enables measurements under normal incidence conditions (zero-degree angle) with a controlled frequency band for the incident acoustic waves. The sound reflection coefficient (SRC) was also evaluated. This parameter depends on the material's surface profile, the frequency of the traveling wave, and the angle of incidence—that is, the angle between the wavefront and the normal surface [35–39]. The general setup used to evaluate the sound absorption and reflection coefficients is illustrated schematically in Figure 5. Each circular sample, with a diameter of 29 mm (1), was placed into the sample holder of an impedance tube (2), model 4206 from Brüel & Kjær (Nærum, Denmark). Acoustic signals in the frequency range of 100 Hz to 6.4 kHz were generated inside the tube using a speaker (3). The signals captured by the microphones (4) were processed via a signal conditioner and DAQ data acquisition board (5), and subsequently analyzed using a computer system (6). Each sample was tested on both its unvarnished and varnished surfaces to identify differences in sound absorption coefficients attributable to the varnish layers [34]. Accordingly, when coding the samples, the notation “a” was used for the unvarnished surface exposed to sound pressure from the impedance tube, and “b” for the varnished surface. The evaluation was based on the measured minimum and maximum sound pressure levels. In total, 144 measurements were performed. All tests were conducted in a laboratory environment with controlled conditions: temperature (22 ± 2 °C) and relative humidity ($55 \pm 5\%$).

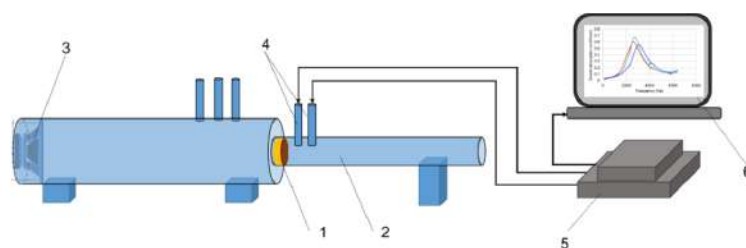


Figure 5. Experimental set-up for acoustic impedance tube method (1—sample; 2—impedance tube; 3—speaker; 4—microphone; 5—data acquisition board; 6—computer).

2.2.3. The Processing Data

Based on experimental data, the resonance frequencies, damping, quality factor, reflection coefficient, and impedance ratio were analyzed in relation to the thickness and type of varnish. The data processing involved calculating quantitative variables, including average, minimum, and maximum values, as well as the coefficient of variation.

3. Results and Discussion

3.1. Resonance Frequencies Spectrum

The natural frequencies of the tested plates depend on the anatomical structure associated with their quality grade, as well as the type and thickness of the varnish. Figure 6 selectively presents the frequency spectra of both unvarnished plates and plates varnished with five layers from each varnish category and anatomical class. The fundamental frequency is defined as the first frequency in the spectrum. For the unvarnished plates (Figure 6a,b), the fundamental frequency also corresponds to the dominant frequency. In contrast, for the varnished plates, the dominant frequency often corresponds to a higher-order harmonic within the frequency spectrum. All peaks representing resonance frequencies—associated

with different vibration modes—were extracted for each tested plate. The values of these frequencies, categorized by interval, are displayed in the graphs shown in Figure 7.

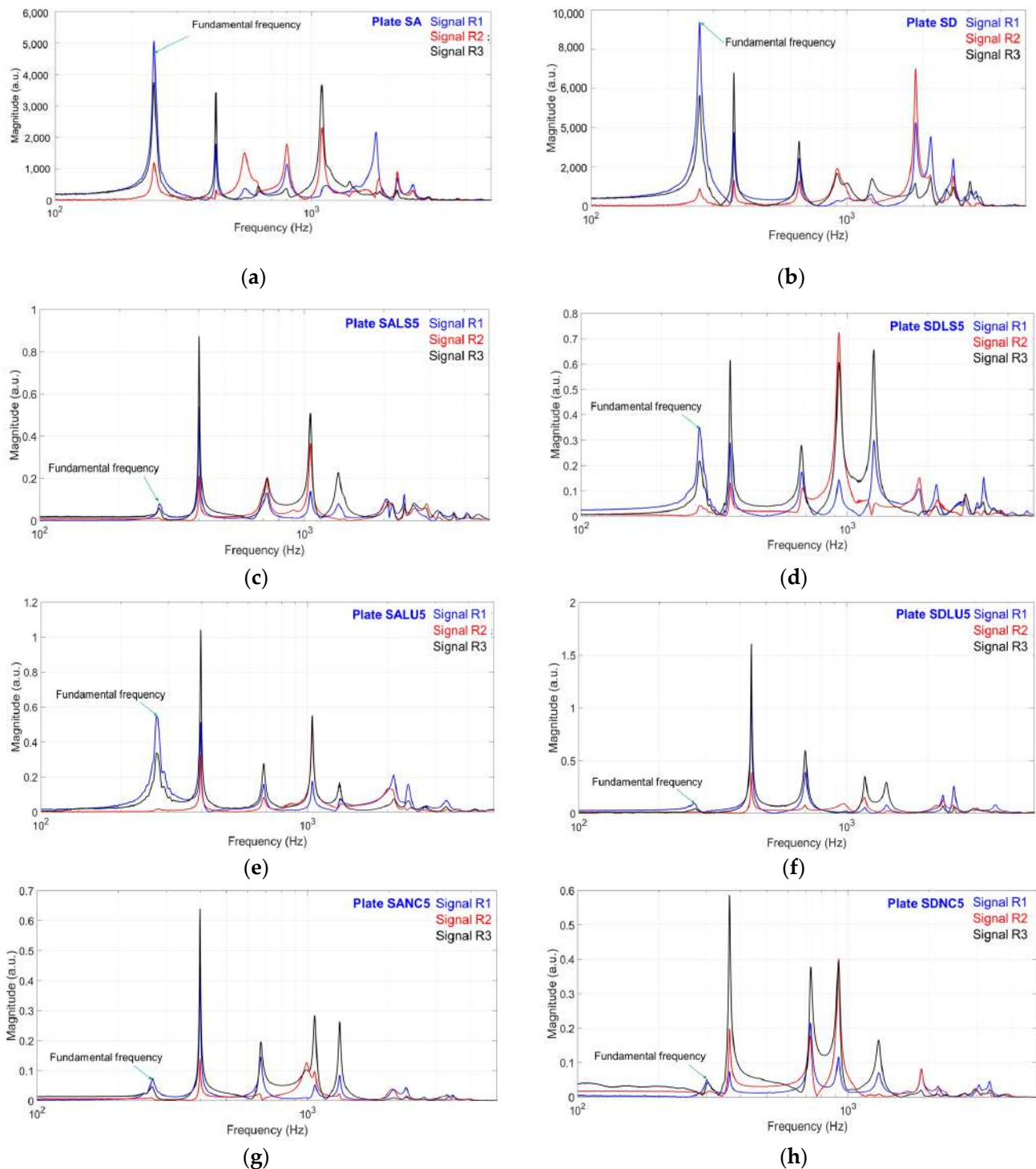


Figure 6. Frequency spectrum of tested plates: (a) unvarnished plate, grade A; (b) unvarnished plate grade D; (c) spirit varnish plate, grade A; (d) spirit varnish plate, grade D; (e) oil-based varnish plate, grade A; (f) oil-based varnish plate, grade D; (g) nitrocellulose varnish plate, grade A; (h) nitrocellulose varnish plate, grade D.

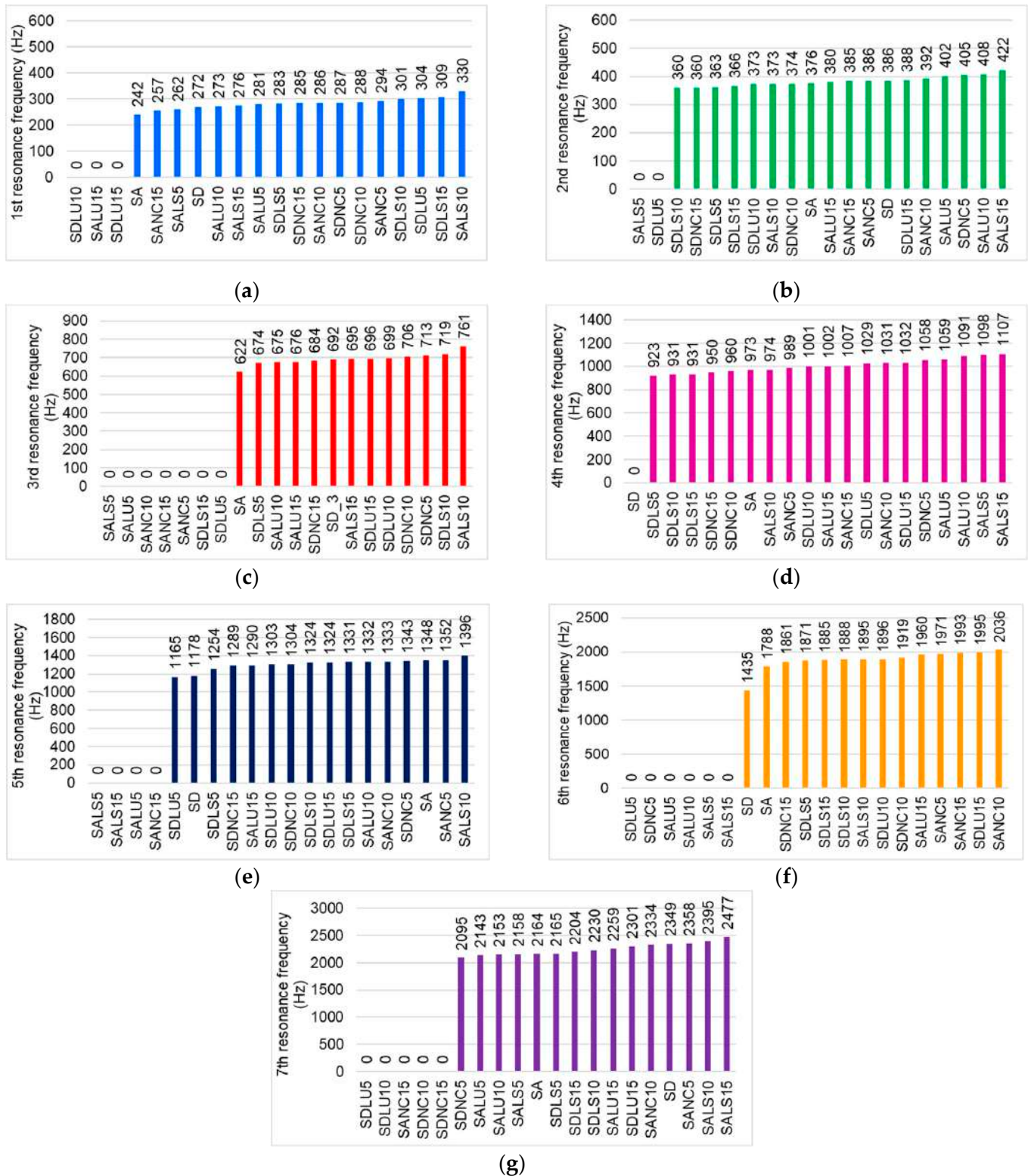
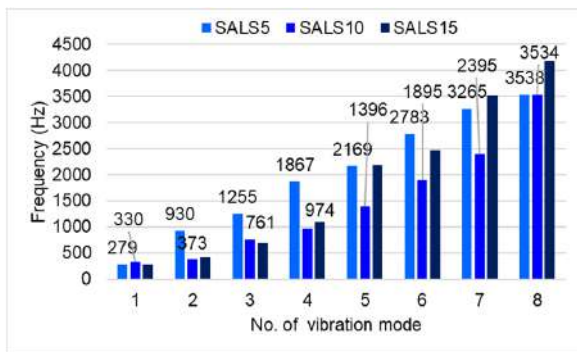


Figure 7. Values of resonance frequencies of studied plates: (a) first resonance frequency from 240 to 350 Hz; (b) second resonance frequency from 350 to 450 Hz; (c) third resonance frequency from 610 to 760 Hz; (d) fourth resonance frequency from 920 to 1120 Hz; (e) fifth resonance frequency from 1150 to 1400 Hz; (f) sixth resonance frequency from 1400 to 2058 Hz; (g) seventh resonance frequency from 2090 to 2600 Hz.

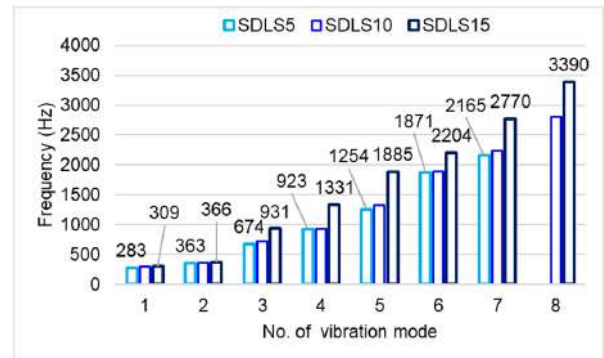
Figure 7 illustrates the main resonance frequency ranges in relation to the characteristic vibrational modes of violins (modes A_0 , CBR, C4, B^+ , B^-) [15,16,19,20]. The analyzed plates are arranged in ascending order according to the resonance frequency value for each corresponding mode. In Figure 7a, the first resonance frequencies of the tested boards are shown. The highest values for the first frequency are observed in samples coated with spirit and nitrocellulose varnishes. These frequencies correspond to the A_0 mode of violin bodies [14,15,17–19]. Notably, the boards varnished with 10 and 15 layers of oil-based varnish do not exhibit resonance within the 240–330 Hz range. In the subsequent range, 360–422 Hz—corresponding to the CBR (Center Bout Rotation) mode—it is observed that some boards, despite differences in varnish type, layer thickness, or wood quality, share identical resonance frequencies. For example, boards varnished with 15 layers of nitrocellulose varnish and 10 layers of spirit varnish, both made from class D spruce, exhibit a frequency of 360 Hz. Similarly, boards coated with 10 layers of oil-based varnish (class D) and 10 layers of spirit varnish (class A) show the same resonance frequency of 376 Hz. Additionally, both the SANC5 and SD boards show a frequency of 386 Hz. This suggests that a specific combination of anatomical wood structure, varnish type, and coating thickness can produce identical resonance behavior.

The highest frequency in this second vibration mode is observed in sample SALS15 at 422 Hz (Figure 7b). The next resonance frequency range, 622–761 Hz, corresponds to the C4 mode (Figure 7c). Not all boards exhibit resonances within this range—for instance, class A boards varnished with 5 layers (regardless of varnish type), boards coated with 10 and 15 layers of nitrocellulose varnish, and class D boards with 10 layers of spirit varnish show no resonance here. The highest frequencies in this range are found in class D boards varnished with 10 layers of alcohol-based or nitrocellulose varnish. The fourth vibration mode, with resonance frequencies between 923 and 1107 Hz (Figure 7d), is present across all boards and is dominated by the varnished plates. A clear pattern emerges: for this mode, resonance frequencies tend to polarize based on the wood quality class and varnish type. Class D boards varnished with nitrocellulose exhibit the lowest frequencies, followed by those coated with spirit varnish. In contrast, boards varnished with oil-based varnish tend to show dominant frequencies above 1029 Hz. These findings align with conclusions from [30], which observed that alcohol-based varnish contributes more to damping than to stiffness, and that coating both surfaces of spruce significantly reduces its acoustic (radiation) properties. For the higher-order modes, it is observed that the ability to dampen high frequencies depends strongly on the type of finish applied to the plates (Figure 7e–g).

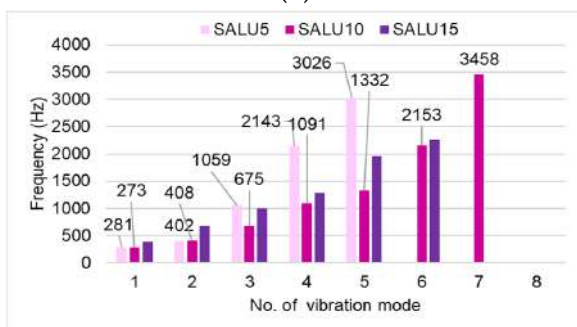
The influence of lacquer film thickness on the vibration modes and resonance frequency spectrum of the tested plates is illustrated in Figure 8. In terms of the number of harmonics, boards varnished with spirit varnish exhibit the richest frequency spectra, regardless of the varnish thickness or the quality class of the spruce wood (Figure 8a,b). For oil-based varnish, the most favorable combinations are class A wood with a film thickness of 10 layers, and class D wood with a film of 5 layers (Figure 8c,d). In contrast, a thick nitrocellulose varnish layer results in a reduction in the frequency spectrum in class A spruce boards. For class D wood, a general decrease in resonance frequencies is observed as the varnish film thickness increases (Figure 8e,f). Compared to unvarnished wood (Figure 8g), which exhibits the richest frequency spectrum overall, the application of varnish consistently leads to an increase in the fundamental frequency value.



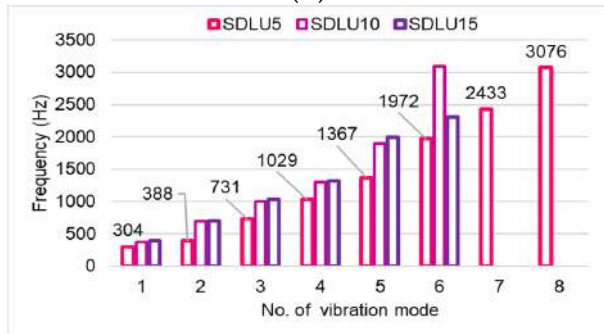
(a)



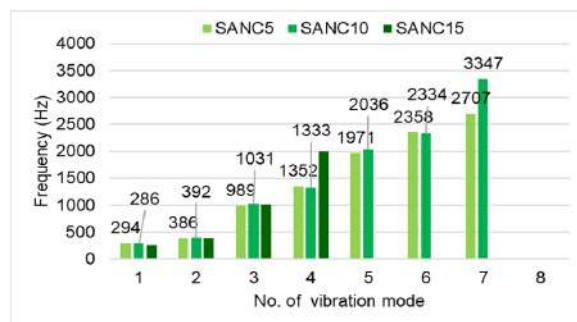
(b)



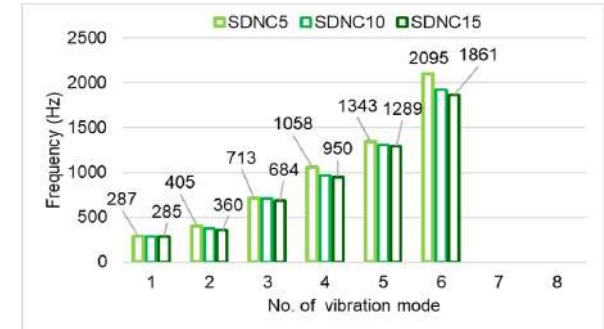
(c)



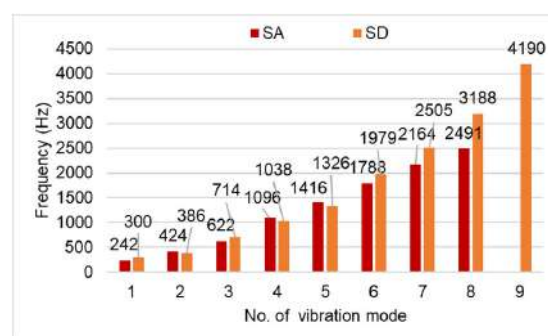
(d)



(e)



(f)



(g)

Figure 8. Distribution in frequency of the first eight peaks in ascending order of studied plates: (a) spruce plates grade A, spirit varnish; (b) spruce plates grade D, spirit varnish; (c) spruce plates grade A, oil-based varnish; (d) spruce plates grade D, oil-based varnish; (e) spruce plates grade A, nitrocellulose varnish; (f) spruce plates grade D, nitrocellulose varnish; (g) unvarnished spruce plates grade A and D.

3.2. Damping of Varnished Plates

Analysis of the frequency spectrum reveals that the evaluated parameters influence the acoustic spectrum in different ways, highlighting the need to examine the vibration damping coefficient. Since previous studies have shown that surface finishing increases the mass of the sample, the radial stiffness, and internal friction, this study analyzed spruce wood boards with various finishes and thicknesses. Figure 9a,b illustrates the variability of the damping coefficient, expressed as $\tan \delta$. It is evident that varnished boards exhibit higher damping values compared to unvarnished boards. The greatest variability in damping values is observed in class A boards varnished with oil-based varnish (10 and 15 layers), as well as in class D boards finished with 5 and 10 layers of oil-based varnish and those coated with nitrocellulose varnish.

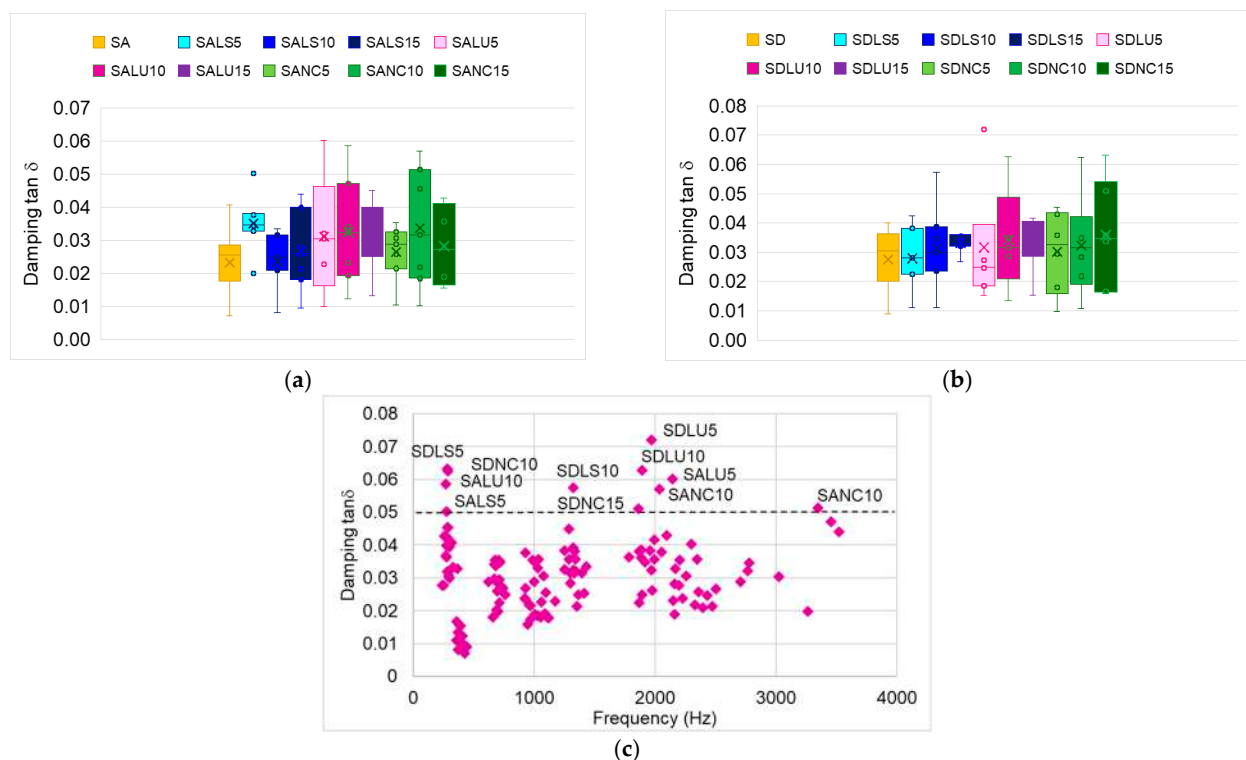


Figure 9. Variability of damping: (a) for plates made from spruce wood grade A; (b) for plates made from spruce wood grade D; (c) with frequency.

Regarding vibration damping across frequency ranges, Figure 9c shows that for frequencies below 1000 Hz, damping exceeds 0.05 for the SDLS5, SALS5, SALU10, and SDNC10 boards. In the 1–2 kHz range, damping is greater than 0.05 for the SDLS10, SDNC15, SDLU10, and SDLU5 boards. For high frequencies above 2 kHz, elevated damping values are observed in the SALU5 and SANC10 boards. In contrast, the remaining board types show damping values below 0.05 across the entire frequency range analyzed.

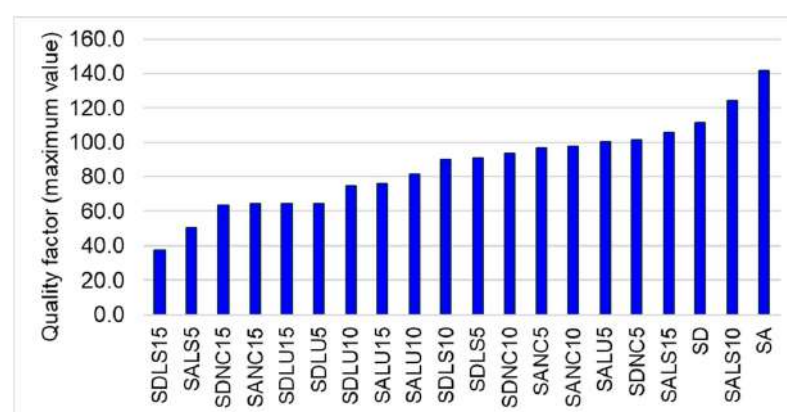
A low $\tan \delta$ is one of the key conditions for ensuring the acoustic quality of resonance plates. The minimum and maximum values of the damping coefficient, along with the frequencies at which these values were recorded, are summarized in Table 3. The lowest damping values are found in uncoated plates, while the highest maximum damping values occur in plates varnished with oil-based varnish (SDLU5, SDLU10) and nitrocellulose varnish (SDNC10, SDNC15).

Table 3. Summary of mean, standard deviations minimum and maximum values of damping coefficient.

Samples	Average Value of Damping & STDV	Minimum Value of Damping $\tan \delta$	Frequency (Hz) for Minim $\tan \delta$	Maximum Value of Damping $\tan \delta$	Frequency (Hz) for Maxim $\tan \delta$
SA	0.023 (0.0099)	0.007	425	0.041	319
SALS5	0.035 (0.0090)	0.020	3265	0.050	279
SALS10	0.024 (0.0083)	0.008	373	0.033	330
SALS15	0.027 (0.0120)	0.009	422	0.040	276
SALU5	0.031 (0.0180)	0.010	402	0.060	2143
SALU10	0.032 (0.0160)	0.012	408	0.059	273
SALU15	0.032 (0.0110)	0.013	380	0.045	1290
SANC5	0.026 (0.0080)	0.010	386	0.035	989
SANC10	0.034 (0.0180)	0.010	392	0.057	2036
SANC15	0.028 (0.0130)	0.016	385	0.043	257
SD	0.028 (0.0100)	0.009	446	0.040	300
SDLS5	0.028 (0.0100)	0.011	363	0.042	283
SDLS10	0.031 (0.0150)	0.011	360	0.057	1324
SDLS15	0.033 (0.0033)	0.027	931	0.036	1331
SDLU5	0.032 (0.0190)	0.015	388	0.072	1972
SDLU10	0.034 (0.0180)	0.013	373	0.063	1896
SDLU15	0.034 (0.0097)	0.015	388	0.042	1995
SDNC5	0.030 (0.0140)	0.010	405	0.045	287
SDNC10	0.032 (0.0170)	0.011	374	0.063	288
SDNC15	0.036 (0.0190)	0.016	950	0.063	285

3.3. Quality Factor

The quality factor (Q) was calculated for the dominant frequency of each board, and the results are presented in ascending order in Figure 10. The highest Q values—exceeding 100—were recorded for the unvarnished SA and SD boards, as well as for SALS10, SALS15, and SDNC5. High-quality factor values, ranging between 80 and 100, were also observed in boards such as SALU10, SDLS10, SDLS5, SDNC10, SANC5, and SANC10. The remaining boards showed Q values below 80, with the lowest values corresponding to those varnished with spirit or nitrocellulose varnish in 10 and 15 layers.

**Figure 10.** Variation in quality factors of tested plates.

Quantitatively, the quality factor of class A resonance spruce was found to be approximately 10% higher than that of class D wood (Figure 11). The application of varnish generally reduces the quality factor, with the extent of reduction depending on the type of solvent used. The greatest decrease in Q was observed with oil-based varnish—approximately 33% for class D and 25% for class A. This was followed by nitrocellulose varnish (24% for class A and 16% for class D), and alcohol-based varnish (18% for class A and 29% for class

D). These results offer practical guidance for violin makers, who can select the optimal combination of varnish type and wood quality to minimize adverse effects on the quality factor. Based on the findings, the best combinations are class A wood with oil-based or spirit varnish, and class D wood with nitrocellulose varnish.

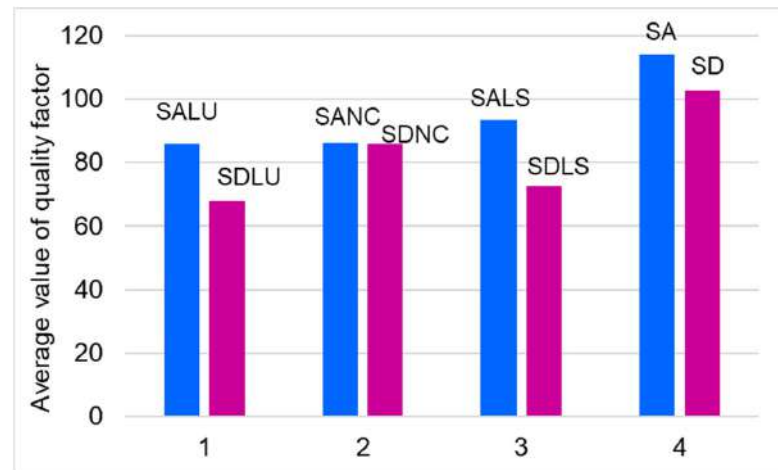


Figure 11. The influence of varnish on quality factor of spruce wooden plates.

According to studies [14,15,18,19] on violins in the white (unvarnished) state and those varnished with spirit- and oil-based varnishes, varnishing does not alter the mode shapes but does influence the modal frequencies—particularly the $B(1^-)$ and $B(1^+)$ modes. Violin plates varnished with spirit varnish exhibit higher modal frequencies compared to those coated with oil-based varnish.

3.4. Sound Absorption Coefficient

Based on the experimental data, the sound absorption coefficient (SAC) was determined, as shown in Figure 12. Regardless of which side was tested, the SAC values remained below 0.6. However, compared to unvarnished wood, the varnished samples exhibited SAC values approximately 25–30% lower than those of the unvarnished side. When comparing the different sample types, the lowest SAC values were observed in samples varnished with nitrocellulose varnish, regardless of which side was exposed to the incident acoustic energy. For samples varnished with oil-based and spirit varnishes, the unvarnished side consistently showed higher SAC values than the varnished side. Additionally, the maximum acoustic absorption for the varnished surfaces occurred at higher frequencies, around 4 kHz. The acoustic behavior also varies depending on the anatomical structure of the wood. Although the proportion of latewood and earlywood is approximately the same in both quality classes, class D wood—characterized by annual ring widths approximately three times larger—exhibits different acoustic absorption capacities. These differences, however, are reduced by the application of the varnish film (Figure 13). The variations in absorption and reflection observed between the two surfaces—due to differences in structure, roughness, and porosity—are intentionally utilized in the construction of musical instruments with a resonant body. These surface-specific acoustic properties contribute to the instrument’s overall tonal quality.

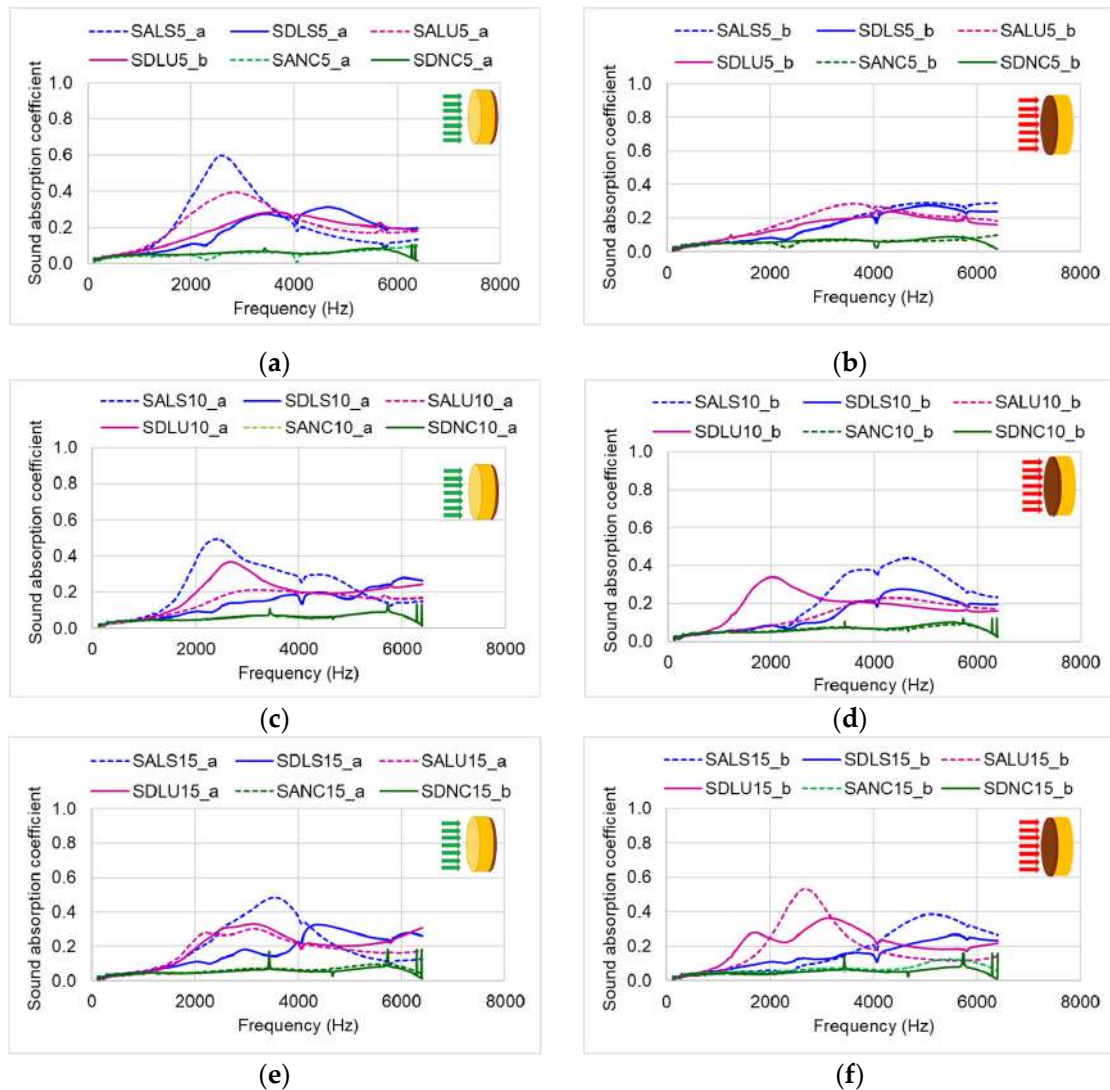


Figure 12. Average values of the acoustic absorption coefficient depending on the type of varnish applied to the wood samples: (a) 5-layer thickness, with the unvarnished side exposed; (b) 5-layer thickness, with the varnished side exposed; (c) 10-layer thickness, with the unvarnished side exposed; (d) 10-layer thickness, with the varnished side exposed; (e) 15-layer thickness, with the unvarnished side exposed; (f) 15-layer thickness, with the varnished side exposed.

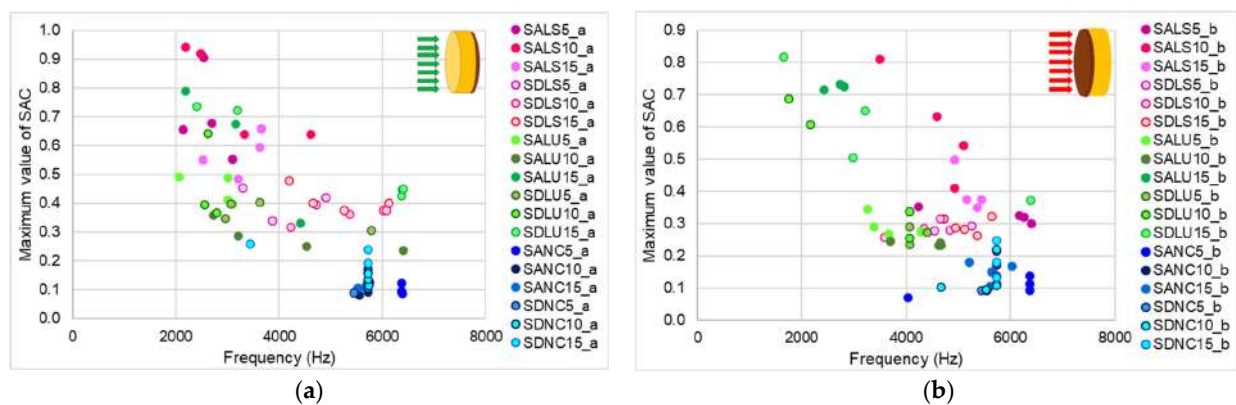


Figure 13. Maximum values of the sound absorption coefficient in relation to frequency: (a) unvarnished side in case of studied samples; (b) varnished side in case of studied samples.

3.5. Sound Reflection Coefficient

Since the impedance tube is considered an acoustically closed system, any portion of the incident wave that is not reflected by the material must be absorbed. For materials used in violin construction, it is therefore essential to understand both the acoustic absorption coefficient and the reflection coefficient. As shown in Figure 14, the reflection coefficients of samples varnished with different types of varnish range from 0.6 to 1. An increase in varnish film thickness corresponds to an increase in sound reflection, indicating that thicker coatings enhance the material's reflective properties.

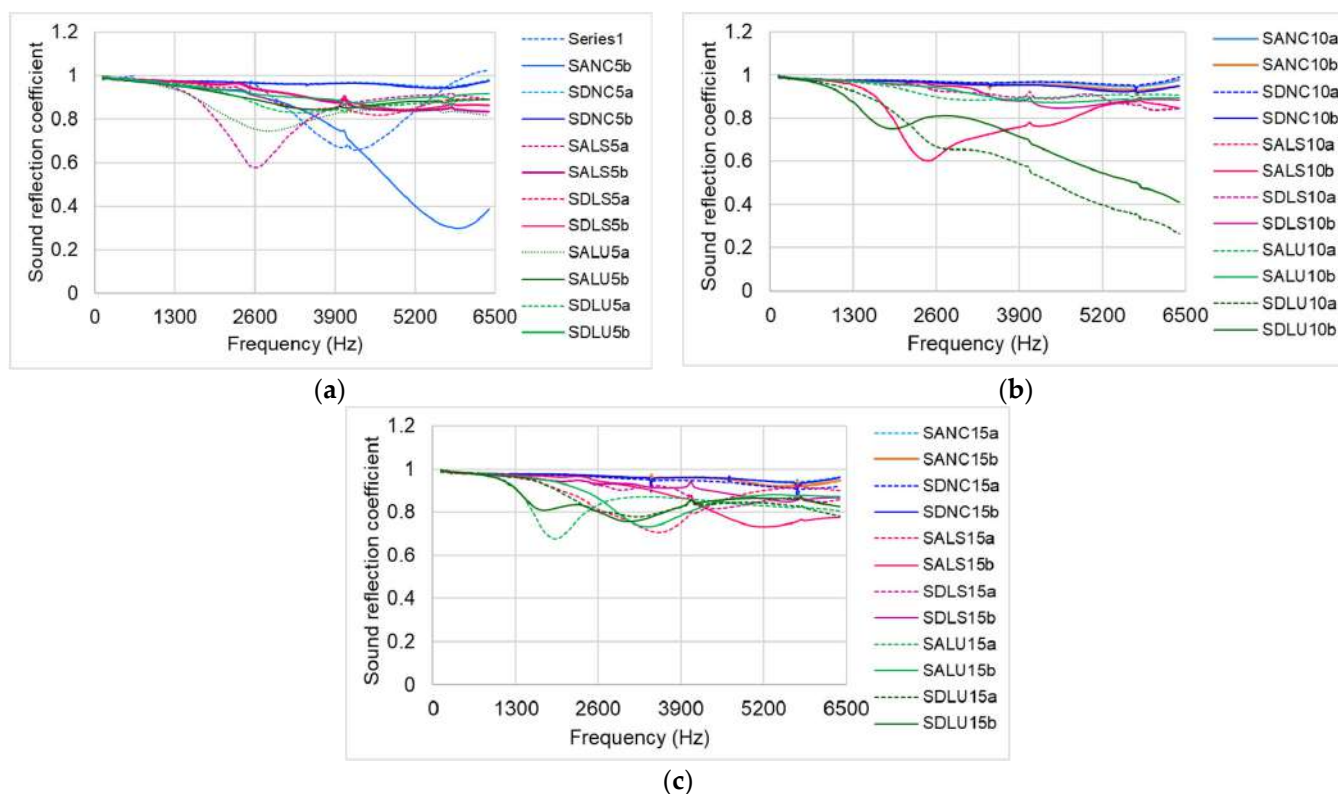


Figure 14. Sound reflection coefficient: (a) 5-layer thickness; (b) 10-layer thickness; (c) 15-layer thickness.

Thus, sound reflection depends on the thickness and density of the bi-material system formed by the wood and the finish. The high sound reflection observed in samples varnished with nitrocellulose and alcohol-based varnishes can be attributed to the properties of the solvents used. In contrast, the lowest reflection coefficient values are recorded for samples varnished with oil-based varnish. Because the drying process at the wood–finish interface takes longer for oil-based varnishes, the acoustic properties may continue to change over time, warranting further analysis of these parameters in the long term.

Figure 15 illustrates the relationship between varnish type, coating thickness, and spruce wood grade for three key acoustic parameters: the absorption coefficient of the unvarnished surface (Figure 15a), the absorption coefficient of the varnished surface (Figure 15b), and the damping of the dominant frequency (Figure 15c). Across all parameters, nitrocellulose varnish consistently yields the lowest values, while spirit varnish shows the opposite trend, producing the highest values.

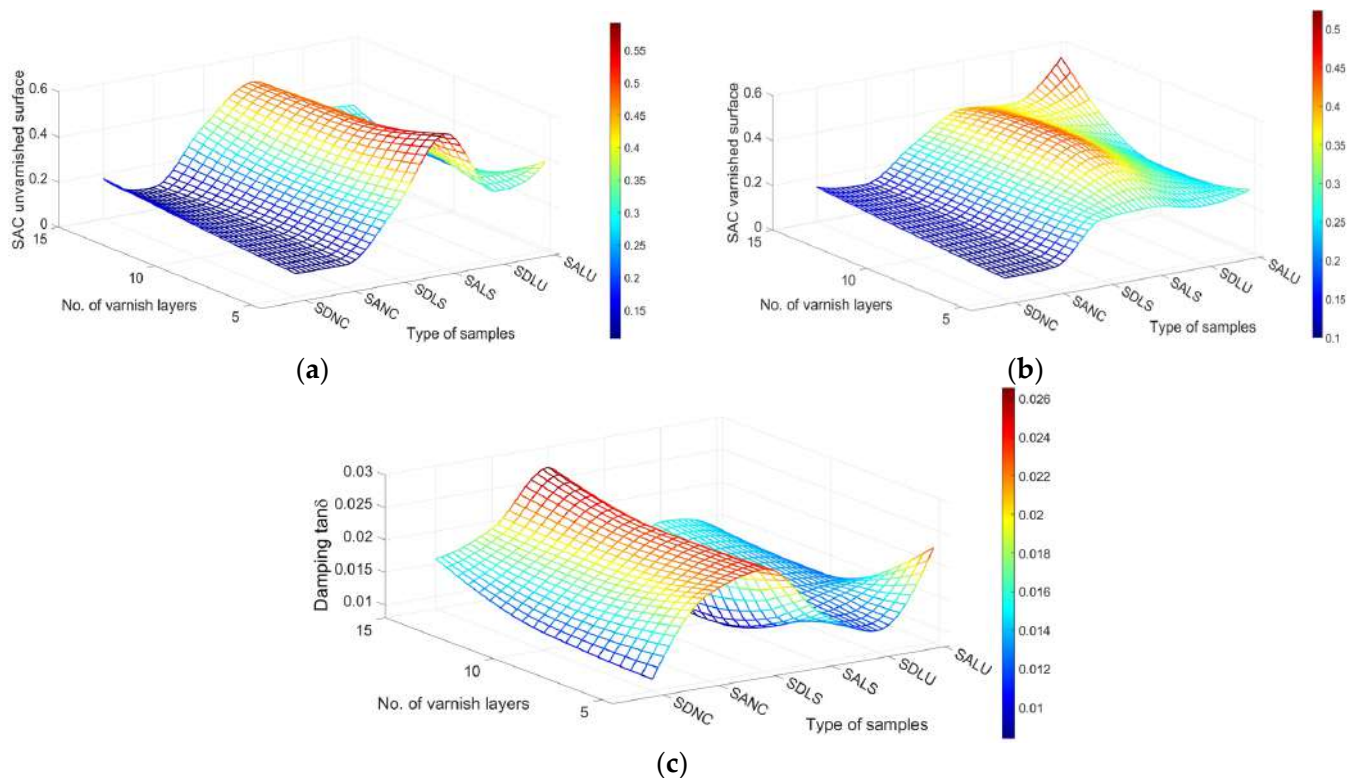


Figure 15. Variation in acoustic parameters: (a) sound absorption coefficient for unvarnished surface of samples; (b) sound absorption coefficient for varnished surface of samples; (c) damping of varnished samples.

4. Conclusions

In this study, the acoustic properties of unvarnished and varnished spruce resonance wood—coated with three different types of varnishes commonly used in musical instrument manufacturing—were investigated from a new perspective. Modal analysis was employed to determine resonance frequencies, quality factors, and damping, while the impedance tube method was used to measure sound absorption and reflection coefficients. The key findings are as follows:

- The varnish film alters the frequency spectrum, both in terms of the number and values of resonant frequencies, due to increased stiffness of the plates. The fundamental frequency is higher than that of unvarnished wood.
- Unvarnished spruce wood exhibits the highest quality factor (Q). The quality factor is influenced by the anatomical quality of the spruce wood in correlation with the type of varnish applied.
- The highest damping coefficient values were observed in class D spruce boards varnished with oil-based and nitrocellulose varnishes. The highest acoustic absorption coefficients were found in samples varnished with 15 layers of oil-based varnish at 2672 Hz, and in those coated with 10 layers of spirit varnish at 4650 Hz.
- The richest frequency spectrum was recorded in boards coated with spirit varnish, though all samples exhibited frequencies within the 270–3500 Hz range.
- The sound absorption of unvarnished surfaces is significantly affected by the presence of varnish on the opposite surface.
- The highest reflection coefficient values were recorded in samples varnished with nitrocellulose varnish.

However, due to the slow and varying drying processes of varnish within the wood, these acoustic parameters may change over time. As such, it is recommended that measures be repeated after a minimum of 6 months, as suggested by previous research in the field. Future research will focus on two main directions: rheological analysis of acoustic parameters over time, and the acoustic evaluation of violins varnished with these different varnish types.

Author Contributions: Conceptualization, M.D.S. and M.V.G.; methodology, M.V.G. and S.M.N.; software, M.D.S.; validation, M.V.G. and S.M.N.; formal analysis, M.D.S. and S.M.N.; investigation, M.V.G. and S.M.N.; resources, M.D.S.; data curation, M.D.S. and M.V.G.; writing—original draft preparation, M.D.S.; writing—review and editing, S.M.N.; visualization, M.V.G.; supervision, S.M.N.; project administration, M.D.S.; funding acquisition, M.D.S. All authors have read and agreed to the published version of the manuscript.

Funding: This research was supported by a grant from UEFISCDI Romania, project number 61PCE/2022, PN-III-P4-PCE2021-0885, ACADIA—Qualitative, dynamic, and acoustic analysis of anisotropic systems with modified interfaces.

Institutional Review Board Statement: Not applicable.

Data Availability Statement: The original contributions presented in this study are included in the article. Further inquiries can be directed to the corresponding author.

Acknowledgments: We are grateful to the technical staff of Gliga Musical Instruments, Reghin, a Romanian manufacturer of musical string instruments, for supplying the specimens.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Bucur, V.; Archer, R.R. Elastic constants for wood by an ultrasonic method. *Wood Sci. Technol.* **1984**, *18*, 255–265. [\[CrossRef\]](#)
2. Bucur, V. *Acoustics of Wood*, 2nd ed.; Springer: Berlin/Heidelberg, Germany, 2006; pp. 173–196.
3. Cao, L.; Fu, Q.; Si, Y.; Ding, B.; Yu, J. Porous materials for sound absorption. *Compos. Commun.* **2018**, *10*, 25–35. [\[CrossRef\]](#)
4. Woodhouse, J. On the Playability of violins. Part I: Reflection Functions. *Acta Acust. United Acust.* **1993**, *78*, 125–136.
5. Eun-Suk, J.; Chun-Won, K. Sound absorption characteristics of three species (binuang, balsa and paulownia) of low density hardwood. *Holzforschung* **2021**, *75*, 1115–1124. [\[CrossRef\]](#)
6. Sedighi Gilani, M.; Pflaum, J.; Hartmann, S.; Kaufmann, R.; Baumgartner, M.; Schwarze, F.W.M.R. Relationship of vibro-mechanical properties and microstructure of wood and varnish interface in string instruments. *Appl. Phys. A* **2016**, *122*, 260. [\[CrossRef\]](#)
7. Viala, R.; Placet, V.; Cogan, S. Simultaneous non-destructive identification of multiple elastic and damping properties of spruce tonewood to improve grading. *J. Cult. Herit.* **2020**, *42*, 108–116. [\[CrossRef\]](#)
8. Spycher, M.; Schwarze, F.W.M.R.; Steiger, R. Assessment of resonance wood quality by comparing its physical and histological properties. *Wood Sci. Technol.* **2008**, *42*, 325–342. [\[CrossRef\]](#)
9. Schelleng, J.C. Acoustical Effects of Violin Varnish. *J. Acoust. Soc. Am.* **1968**, *44*, 1175–1183. [\[CrossRef\]](#)
10. Schleske, M. Contemporary violin making. Analysis of design, materials, varnish and normal modes. *Catgut Acoust. Soc. J.* **2002**, *4*, 50–65.
11. Obataya, E.; Ohno, Y.; Norimoto, M.; Tomita, B. Effects of oriental lacquer (urushi) coating on the vibrational properties of wood used for the soundboards of musical instruments. *Acoust. Sci. Technol.* **2001**, *22*, 27–34. [\[CrossRef\]](#)
12. Lämmlein, S.L.; Mannes, D.; Schwarze, F.W.M.; Burgert, I.; Sedighi Gilani, M. Combined Experimental and Numerical Investigation of Vibro-Mechanical Properties of Varnished Wood for Stringed Instruments. In *Model Validation and Uncertainty Quantification*; Conference Proceedings of the Society for Experimental Mechanics Series; Barthorpe, R., Platz, R., Lopez, I., Moaveni, B., Papadimitriou, C., Eds.; Springer: Cham, Switzerland, 2017; Volume 3. [\[CrossRef\]](#)
13. Lämmlein, S.L.; Van Damme, B.; Mannes, D.; Schwarze, F.W.M.; Burgert, I. Violin varnish induced changes in the vibro-mechanical properties of spruce and maple wood. *Holzforschung* **2020**, *74*, 765–776. [\[CrossRef\]](#)

14. Lämmlein, S.; Künniger, T.; Rüggeberg, M.; Schwarze, F.W.M.R.; Mannes, D.; Burgert, I. Frequency dependent mechanical properties of violin varnishes and their im-pact on vibro-mechanical tonewood properties. *Results Mater.* **2020**, *9*, 100137. [\[CrossRef\]](#)
15. Echard, J.P.; Lavédrine, B. Review on the characterization of ancient stringed musical instruments varnishes and implementation of an analytical strategy. *J. Cult. Herit.* **2008**, *9*, 420–429. [\[CrossRef\]](#)
16. Chung, W.Y. SHP Studies on the vibrational modal analysis of solid woods for making the violin—Part 2. The effects of coating materials on the resonant frequency of European spruce and maple. *Korea Furnit. Soc.* **2000**, *11*, 45–52.
17. Woodhouse, J. The acoustics of “A0-B0 mode matching” in the violin. *Acust. Acta Acust.* **1998**, *84*, 947–956.
18. Gough, C. The violin. Chladni patterns, plates, shells and sounds. *Eur. Phys. J. Spec. Top.* **2007**, *14*, 77–101. [\[CrossRef\]](#)
19. Bissinger, G. Structural acoustics of good and bad violins. *J. Acoust. Soc. Am.* **2008**, *124*, 1764. [\[CrossRef\]](#)
20. Ali Ahmed, S.; Adamopoulos, S. Acoustic properties of modified wood under different humid conditions and their relevance for musical instruments. *Appl. Acoust.* **2018**, *140*, 92–99. [\[CrossRef\]](#)
21. Ono, T. Effects of varnishing on acoustic characteristics of wood used for musical instrument soundboards. *J. Acoust. Soc. Jpn.* **1993**, *14*, 397–407. [\[CrossRef\]](#)
22. Skrodzka, E.B.; Linde, B.B.J.; Krupa, A. Modal parameters of two violins with different varnish layers and subjective evaluation of their sound quality. *Arch. Acoust.* **2013**, *38*, 75–81. [\[CrossRef\]](#)
23. Bucur, V. Chapter 3—Mechanical Characterization of Materials for String Instruments. In *Handbook of Materials for String Musical Instruments*; Springer: Berlin/Heidelberg, Germany, 2016; pp. 93–132.
24. Bucur, V. Chapter 8—Ageing of musical instruments—About the old and new instruments. In *Handbook of Materials for String Musical Instruments*; Springer: Berlin/Heidelberg, Germany, 2016; pp. 325–372.
25. Stanciu, M.D.; Nastac, S.M.; Savin, A. Comparison Between Acoustic Spectral Evolutions of Violins Before and After Varnishing. In Proceedings of the 16th International Conference Interdisciplinarity in Engineering, Târgu Mureş, Romania, 6–7 October 2022; Inter-Eng 2022, Lecture Notes in Networks and Systems. Moldovan, L., Gligor, A., Eds.; Springer: Cham, Switzerland, 2023; Volume 605. [\[CrossRef\]](#)
26. Guan, C.; Zhang, H.; Wang, X.; Miao, H.; Zhou, L.; Liu, F. Experimental and Theoretical Modal Analysis of Full-Sized Wood Composite Panels Supported on Four Nodes. *Materials* **2017**, *10*, 683. [\[CrossRef\]](#) [\[PubMed\]](#)
27. Guiman, M.V.; Stanciu, M.D.; Nastac, S.M.; Gliga, V.G.; Savin, A. Free Vibration Analysis of Orthotropic Thin Rectangular Plates. In Proceedings of the 17th International Conference Interdisciplinarity in Engineering, Târgu Mureş, Romania, 5–6 October 2023; Inter-ENG 2023, Lecture Notes in Networks and Systems. Moldovan, L., Gligor, A., Eds.; Springer: Cham, Switzerland, 2024; Volume 926. [\[CrossRef\]](#)
28. Harris, N.; Sheldon, R.; Johnston, J.A. Recreation of the Particulate Ground Varnish Layer Used on Many Violins Made before 1750. *J. Violin. Soc. Am. VSA Pap.* **2007**, *XXI*, 1–15.
29. Yin, Y.; Guan, W. Sound Absorption Characteristics of Unsaturated Porous Material Calculated by Modified Transfer Matrix Method. *Buildings* **2024**, *14*, 466. [\[CrossRef\]](#)
30. Xu, W.; Fang, X.; Han, J.; Wu, Z.; Zhang, J. Effect of Coating Thickness on Sound Absorption Property of Four Wood Species Commonly Used for Piano Soundboards. *Wood Fiber Sci.* **2020**, *52*, 28–43. [\[CrossRef\]](#)
31. Dinulică, F.; Stanciu, M.D.; Savin, A. Correlation between Anatomical Grading and Acoustic–Elastic Properties of Resonant Spruce Wood Used for Musical Instruments. *Forests* **2021**, *12*, 1122. [\[CrossRef\]](#)
32. Stanciu, M.D.; Cosnita, M.; Gliga, G.V.; Gurau, L.; Timar, C.M.; Guiman, M.V.; Năstac, S.M.; Roşca, I.C.; Bucur, V.; Dinulică, F. Tunable Acoustic Properties Using Different Coating Systems on Resonance Spruce Wood. *Adv. Mater. Interfaces* **2024**, *1*, 2300781. [\[CrossRef\]](#)
33. Stanciu, M.D.; Dinulica, F.; Bucur, V.; Gliga, G.V.; Nastac, S.M.; Campean, M. Changing the vibrational behavior of the wooden thin arched plates—The maestro violins experimental study case. *Thin-Walled Struct.* **2022**, *174*, 109042. [\[CrossRef\]](#)
34. Zhou, J.; Wang, X.; He, L.; Wan, K.; Guo, Y.; Zhang, J.; Miao, Y.; Liu, Z. The Changes of Acoustic Vibration Properties of Spruce Wood During the Multi-Layered Alcohol Varnish Coating Process. *Forests* **2024**, *15*, 2212.
35. ISO 11654:1997; Acoustics: Sound Absorbers for Use in Buildings. Rating of Sound Absorption. International Organization for Standardization (ISO): Geneva, Switzerland, 1997.
36. ISO 10534:1998; Acoustics—Determination of Sound Absorption Coefficient and Impedance in Impedance Tubes: Part 1: Method Using Standing Wave Ratio, Part 2: Transfer-Function Method. International Organization for Standardization (ISO): Geneva, Switzerland, 1998.
37. ASTM E1050:1998; Standard Test Method for Impedance and Absorption of Acoustical Materials Using a Tube, Two Microphones and a Digital Frequency Analysis System. ASTM International: West Conshohocken, PA, USA, 1998.

38. Akar, Ö.; Willner, K. Investigating the modal behavior of a violin top and a back plate. In Proceedings of the 40th IMAC, A Conference and Exposition on Structural Dynamics, Orlando, FL, USA, 7–10 February 2022; Topics in Modal Analysis & Parameter Identification. Volume 8, pp. 37–44.
39. Zhao, X.; Liu, Y.; Zhao, L.; Yazdkhasti, A.; Mao, Y.; Siciliano, A.P.; Dai, J.; Jing, S.; Xie, H.; Li, Z. A scalable High-Porosity Wood for Sound Absorption and Thermal Insulation. *Nat. Sustain.* **2023**, *6*, 306–315. [[CrossRef](#)]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.

Article

Analysis of the Anisotropy of Sound Propagation Velocity in Thin Wooden Plates Using Lamb Waves

Dagmar Faktorová ¹, Mariana Domnica Stanciu ^{2,*} , Michal Krbata ¹ , Adriana Savin ^{2,3,*} , Marcel Kohutiar ¹ , Milan Chlada ⁴ and Silviu Marian Năstac ^{2,5} 

¹ Faculty of Special Technology, Alexander Dubcek University of Trenčín, 911 06 Trenčín, Slovakia; dagmar.faktorova@tnuni.sk (D.F.); michal.krbata@tnuni.sk (M.K.); marcel.kohutiar@tnuni.sk (M.K.)

² Faculty of Mechanical Engineering, Transilvania University of Braşov, 29 Eroilor Blvd., 500036 Braşov, Romania; silviu.nastac@ugal.ro

³ National Institute of Research and Development for Technical Physics, 47 D. Mangeron Blvd., 700050 Iasi, Romania

⁴ Institute of Thermomechanics of the CAS, v. v. i. Dolejškova 1402/5, 18200 Prague, Czech Republic; chlada@it.cas.cz

⁵ Faculty of Engineering and Agronomy, Braila, 810017, “Dunarea de Jos” University of Galati, 810017 Galati, Romania

* Correspondence: mariana.stanciu@unitbv.ro (M.D.S.); asavin@phys-iasi.ro (A.S.)

Abstract: The objective of the study was to analyze the influence of coating treatments on sound propagation speeds in thin boards, along the longitudinal and radial directions of resonance wood. The samples studied were thin boards made of spruce and maple wood with dimensions of 240 mm × 80 mm × 4 mm (length × width × thickness) subjected to different coating treatments (oil-based varnish and alcohol varnish) as well as unvarnished samples, exposed to radiation UV, and specimens treated in the saline fog. The test method consisted of evaluating the propagation speeds of Lamb waves applied to thin plates, according to a semicircular test model, so that the results highlighted both the acoustic response in the longitudinal and radial directions as well as the variation in the anisotropy of the samples with the change in the sound propagation direction relative to wood fibers. Based on the statistical analysis, sound propagation speed profiles were obtained in each of the 38 directions analyzed for all wood samples. The results highlighted that the oil-based varnish led to a decrease in the speed of propagation in the radial direction, compared to the alcoholic varnish, whose major effect was in the longitudinal direction, on the spruce wood. On maple wood, increasing the number of varnish layers, regardless of the type of varnish, led to a decrease in the anisotropy ratio between the longitudinal and radial directions.

Keywords: varnish; anisotropy; Lamb waves; coating treatments; spruce; maple



Citation: Faktorová, D.; Stanciu, M.D.; Krbata, M.; Savin, A.; Kohutiar, M.; Chlada, M.; Năstac, S.M. Analysis of the Anisotropy of Sound Propagation Velocity in Thin Wooden Plates Using Lamb Waves. *Polymers* **2024**, *16*, 753. <https://doi.org/10.3390/polym16060753>

Academic Editors: Ľuboš Krišťák, Roman Reh, Eugenia Mariana Tudor and Marius Cătălin Barbu

Received: 17 January 2024

Revised: 6 March 2024

Accepted: 7 March 2024

Published: 9 March 2024



Copyright: © 2024 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 (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Wooden material, due to its remarkable properties, traditionally presents wide applicability. Wood, through its cellular structure, shape and way of organizing the wood cells in the three main directions, and content of lignin, cellulose, and hemicelluloses, confers optimal physical, mechanical, and acoustic properties for musical instruments with strings and a resonator body. The physical properties (density) and mechanical properties of wood (elastic constants and damping) influence the acoustic properties of wood (speed of sound, characteristic impedance, and sound radiation) because sound is produced by the vibrations of the material [1–3]. According to [2], the parameters that reflect the vibrational and acoustic quality of wood are the relative acoustic conversion efficiency as the ratio of acoustic energy radiated to the vibration energy, the anisotropy of wood calculated as the ratio between dynamic Young’s modulus and dynamic shear modulus. Thus, a high specific dynamic modulus in the longitudinal direction, a high anisotropy factor, and a low

damping are indicators of the tone quality of the soundboard. From the point of view of the fiber orientation compared to the cutting directions of the wooden boards, [3] considers that the grain angle influences the anisotropy of viscoelastic vibrational properties, just as [2,4] correlates the acoustic qualities of wood with the effect of the angle of the microfibril on the damping and specific dynamic Young's modulus.

On the other hand, the accessibility of this resource since ancient times and its easy workability have consecrated wood as a lignocellulose composite material for numerous musical instruments [1].

The reaction of wood in the interaction with sound waves depends on the transmitted sound energy, as well as the nature and condition of the wood: the macro- and microscopic structure of the wood—cell, membrane construction, fiber size, cohesion, humidity, elastic properties, etc. Spruce and maple wood (resonance wood) are wood with a very fine structure and physical properties suitable for the construction of stringed musical instruments [5,6].

According to [7,8], who identified the origin of the resonance wood of the musical instruments belonging to the Cherubini Conservatory Collection in Florence, the most important areas for the production of soundboards were the Eastern Alps (with regions from Italy and Slovenia), Bavarian forests, and the Carpathian Mountains (Poland, Romania, and southern Russia). The resonance wood from the central–northern area of the Eastern Carpathians presents special physical and acoustic properties that have been studied, with them being correlated with the anatomical quality classes used by luthiers [8–11]. The choice of raw material by luthiers is based on rigorous physical and acoustic criteria, with the resonance wood thus being classified in correlation with the quality and price of the musical instrument. The properties of the materials used in the construction of stringed musical instruments show great variability, and that is why the first stage in the manufacture of musical instruments is the choice of wood [12–14]. The basic characteristic that distinguishes resonance wood from the ordinary type is the very homogeneous anatomical structure, obtained from the small and uniform width of the annual rings as well as the small proportion of late wood. The microscopic structure of spruce wood consists of vessels, resin canals, and cellular composition. The length of the tracheids shows a significant increase when moving away from the pith and parcel. The vessels in the ring assembly are 1.1–6.0 mm long. Tracheid length decreases with latitude. The resin canals are visible only with a magnifying glass and are rare (25–35 pcs/cm²). The cellular composition consists of 95% tracheids, 3.6% resiniferous formations, 1.4% radial parenchyma, and a proportion of wood voids of 71% [15–17].

From an anatomical point of view, maple wood is made up of vessels (trachea), wood parenchyma, radial parenchyma, and fibers. The vessels are small and rare, and the fibers occupy about 75% of the volume of the wood substance. The porosity (proportion of voids) is 60% of the apparent volume. Maple wood is part of the category of hardwoods with scattered pores, with these being small, visible with a magnifying glass, and quite rare. They are, therefore, unevenly scattered among the early and late wood and their size and thickness decrease towards the outer limit of the annual ring.

Producers choose wood according to its cost and mechanical, artistic, and mechanical processing criteria without, however, having the guarantee of the performance of the final product, even in the conditions of the best acoustic performance of the wood [3,8]. The wood used in the construction of musical instruments is covered with lacquer films that have the role of protecting the musical instrument from wear and fluctuations in ambient humidity. Depending on the type of varnish (the solvent), the thickness of the film, the degree of penetration into the wood, the physical and mechanical properties of the newly formed system (wood–wood/varnish interface and the varnish film) show elastic, acoustic, and dynamic properties different from those of untreated wood [2–4].

Lately, there has been increased interest in scientific research on these materials by applying direct and indirect methods and the appropriate use of measuring instruments [16]. Non-destructive techniques (NDT/E) involve the identification of properties without

measuring them and preserving the structural integrity of the wood [11–13]. Simulation methods using the finite element method (FEM) can be used for the evaluation techniques of material properties even when they have complex behavior [11–13]. Ultrasonic (US) and ultrasonic resonance (RUS) methods as part of NDT/E methods successfully achieve the results obtained by standard static methods [14–17].

The results obtained in determining the propagation speeds of US in wood depend on the orientation of the structure in relation to the sound source (longitudinal—L, radial—R, and tangential—T) [18–21], according to the axes that identify its spatial directions. The propagation speed of US through wood is a fundamental parameter in the characterization of resonant wood, with it being dependent on the density of the wood as well as the modulus of elasticity [22,23]. From a mechanical point of view, to understand the elastic behavior of resonant wood, it is necessary to determine the propagation speeds in the three directions. The method based on US propagation as a non-destructive method involves nine propagation speeds in accordance with the directions of mechanical oscillation [22–24]. According to [20,21], the structural anisotropy of wood can be determined using different methods: either by calculating the ratios between the longitudinal and transverse wave velocities in the three main directions of symmetry or based on the ratios between shear velocities, or through the estimation of wood anisotropy deals with velocity invariants. The analysis of the anisotropy of wooden plates based on the propagation of Lamb waves provides useful information not only about the propagation velocity of horizontal shear waves but also the dispersion phenomena that depend on the geometry of the structure, the dependence between the wave number, and the frequency of the particular mode that can be obtained by a numerical solution of the Rayleigh–Lamb frequency equation [25–27]. According to [18,28,29], for bulk waves, it is already well known that the anisotropy implies a difference between the group velocity and the phase velocity. It is shown here that this phenomenon also occurs for Lamb waves, with it affecting both the speed and direction of propagation.

This paper aims to emphasize the effect of the acoustic anisotropy of wood as a result of the preferential orientation of the anatomical elements and the different surface treatments applied to spruce and maple wood. The novelty of the study consists of the analysis of the acoustic anisotropy of wood subjected to different surface treatments (artificial aging, salt spray, and different types of finishes).

2. Materials and Methods

2.1. Materials

Spruce (*Picea abies* Karst L.) and maple (*Acer pseudoplatanus* L.) wood specimens were included in the tests, with dimensions $80 \times 4 \times 240$ mm³ corresponding to the radial $\times$ tangential $\times$ longitudinal directions, which were tested (according to ISO13061-1:2014/Amd1:2017 [30]) under laboratory conditions (20 °C and relative humidity (RH) of 65%). In Figure 1, the geometry and physical aspects of the samples are presented. From the point of view of the anatomical structure of the wood, two quality classes were analyzed: class A representing wood with a fine anatomical structure, with narrow and regular annual rings (for spruce wood) and wavy fibers (for maple wood), and class D representing wood with a coarser anatomical structure, with annual rings wider and irregular in width (for spruce wood) without wavy fibers (for maple wood) [10,23].

The samples were subjected to different surface treatments to check to what extent these treatments influence the degree of anisotropy of the wood. Table 1 shows the characteristics of the investigated samples. The moisture content was monitored using a Merlin HM8-WS1 (Tumeltsham, Austria) moisture meter and the mass was measured with a Kern & Sohn Weighing Balance, EWJ 600-2SM, Balingen, Germany.

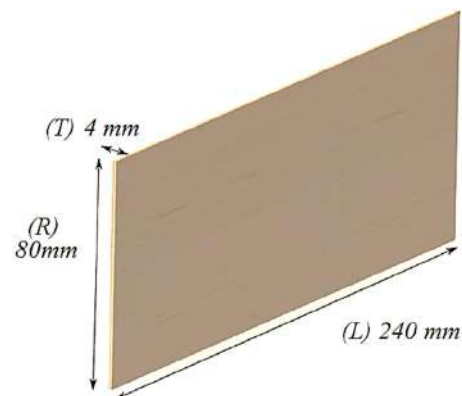


Figure 1. The geometry of the samples.

Table 1. Physical properties: wood species (WS), density (ρ), equilibrium moisture content (EMC), and type of treatment (T).

Samples Code	WS	ρ (kgm ⁻³)	EMC (%)	AML (g/m ²)	T
MDHD15.1	spruce	391.01 (33.42)	6.4 (0.4)	0.000	Untreated
MAHD10.3	spruce	470.83 (18.68)	7.9 (0.5)	0.000	
PDNC15.1	maple	605.72 (17.54)	6.1 (0.3)	0.000	
PANC10.1	maple	656.90 (15.82)	7.3 (0.5)	0.000	
MDUV2	spruce	421.50 (27.92)	6.8 (0.5)	−10.318	UV exposure 300 h
MAUV2	spruce	473.45 (18.32)	6.2 (0.4)	−13.979	
PDUV3	maple	565.40 (17.62)	6.2 (0.2)	−12.432	
PAUV3	maple	640.36 (11.75)	6.4 (0.7)	−17.813	
MDSAL2	spruce	429.33 (10.19)	8.3 (1.3)	16.047	Salt fog exposure NaCl 3.5% 72 h
MASAL2	spruce	491.16 (13.81)	8.8 (1.4)	21.563	
PDSAL1	maple	679.17 (35.24)	9.1 (1.2)	27.135	
PASAL1	maple	669.77 (24.71)	8.5 (1.8)	30.146	
MALU5.3	spruce	399.31 (45.60)	7.4 (0.9)	11.755	5 layers of oil-based varnish
MDLU5.2	spruce	407.85 (37.50)	7.8 (0.7)	9.807	
PALU5.1	maple	662.57 (33.14)	8.4 (0.6)	8.375	
PDLU5.3	maple	652.23 (19.20)	7.4 (0.5)	6.938	
MALU10.2	spruce	556.98 (29.40)	7.8 (0.3)	15.969	10 layers of oil-based varnish
MDLU10.2	spruce	496.42 (32.12)	7.3 (0.7)	17.526	
PALU10.1	maple	705.36 (41.24)	8.7 (0.3)	14.708	
PDLU10.1	maple	611.77 (32.15)	8.2 (0.4)	14.380	
MALU15.2	spruce	522.55 (21.35)	8.0 (0.5)	22.979	15 layers of oil-based varnish
MDLU15.2	spruce	511.99 (22.31)	7.9 (0.4)	23.599	
PALU15.1	maple	744.69 (34.32)	8.3 (0.3)	23.443	
PDLU15.1	maple	694.91 (21.12)	7.8 (0.6)	24.229	
MALS5.2	spruce	430.08 (36.23)	7.2 (0.4)	2.865	5 layers of spirit varnish
PALS5.2	maple	657.79 (15.43)	7.3 (0.2)	11.453	
MALS10.2	spruce	417.60 (18.45)	7.5 (0.2)	7.042	10 layers of spirit varnish
PALS10.2	maple	672.47 (21.34)	7.1 (0.3)	12.896	
MALS15.2	spruce	491.42 (35.82)	7.6 (0.5)	13.234	15 layers of spirit varnish
PALS15.2	maple	621.58 (28.12)	7.7 (0.2)	16.651	

The samples were obtained by cutting radially longitudinally from the boards, which, after natural drying, were conditioned in a drying chamber up to a moisture content of 6–8%. Both nowadays and in the past, stringed musical instruments were covered with varnish to protect them from variations in atmospheric humidity and dirt [31–33]. Current studies with modern methods of determining the chemical fingerprint of the varnish layers

on old violins have highlighted the fact that luthiers used recipes based on alcohol-solvent resins, with oils, or the wood was treated with salts like borax and the sulfates of Zn, Cu, Cr, Na, and Fe [32,34]. Based on these considerations, currently, the most well-known types of varnishes used for maestro- and professional-level musical instruments are those with an oil-based solvent and those with an alcoholic solvent (spirit) [32–35]. Not only is the chemical composition of the surface treatment important but also the thickness of the varnish film and the varnish–wood interface, aspects highlighted in studies [36–38]. The type of varnish and its thickness correlated with the number of layers applied in the finishing process influence the tonality of the musical instrument as a result of not only the difference in stiffness between the wood and the varnish film but also as an effect of the increase in the mass of the layered material (wood–varnish) [31,32,38]. Thus, in the presented study, spruce and maple wood samples covered with a number of layers of lacquer were analyzed according to the procedures applied at a violin factory (5, 10, and 15 layers). Therefore, some of the samples were kept as control samples, others were exposed to artificial aging with UV radiation, another set of samples were varnished with oil-based varnish and spirit varnish with a different number of layers (5, 10, 15), and another set of samples were exposed to the salt fog, as can be seen in Table 1.

According to [36,38], to compare the mass changes of the spruce and maple boards before and after surface treatments (VS varnish system, UV exposure, and salt fog exposure), the changes were evaluated as area mass loading (AML) calculated based on mathematical relation (1):

$$AML = \frac{m_t - m_w}{b * l}, \quad (1)$$

where AML is area mass loading induced by treatment ($\text{g} \cdot \text{m}^{-2}$); m_t —the final mass of the treated wood; m_w —the initial mass of the wooden sample; b —the width of the plate; and l —length of the plate [36,38].

2.2. Methods

2.2.1. Experimental Set-Up

Basically, ultrasound (US) non-destructive evaluation consists of applying physical elastic waves to the sample tested and analyzing the interaction between the material samples and the field [19,39–41].

A problem associated with the propagation of Lamb waves is the coexistence of several modes of oscillation in the plate, which leads to difficulties in interpreting the results. The higher-order modes of oscillation start to propagate when the thickness of the plate becomes comparable to the wavelength of the longitudinal and transverse waves. Lamb waves are guided elastic plate waves that can be described as a combination of compression waves (P-waves) and shear waves (S-waves) [22,42]. For the excitation of Lamb waves in the lowest mode, transducers with Hertzian contact are used. A diagram of the system that generates and detects the Lamb waves for measurement is presented in Figure 2.

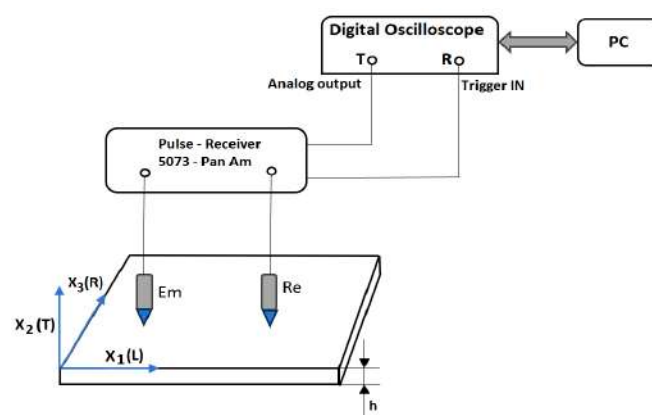


Figure 2. Experimental set-up.

A piezo-electric transducer, of very low eigenfrequency (tens of kilohertz), is coupled to a buffer rod made of a material of elasticity module E_1 and Poisson coefficient ν_1 which has a spherical bumped head of radius R at one end. The buffer rod is compressed onto a plate (with elasticity module E_2 and the Poisson coefficient ν_2). To increase the reliability and assurance of the quality of measurement, the ultrafine force presses the US sensors at constant value. The speed of the Lamb waves generated by Hertzian contact was determined, placing the emission and the reception transducer on the sample taken into study, measuring with $\pm 10 \mu\text{m}$ precision the distance between the centers of the transducer and measuring with $0.1 \mu\text{s}$ precision the time between the generation of the Lamb wave and its reception. The two buffer rods of the US sensors used at the emission and reception are both identical, with them being made of the 7075-T6 aluminum–magnesium alloy, with a density of $2.7 \times 10^3 \text{ kg/m}^3$, Young's modulus of $7 \times 10^{10} \text{ N/m}^2$, Poisson coefficient of 0.34, and point curvature radius of 2 mm. The US sensors are connected to a 5073PR Pulse Receiver—equipment from Panametrics NDT USA (Olympus Corporation, Waltham, MA, USA). The visualization of the signal and the measurement of the time of propagation were made using a Le Croy Wave Runner 64Xi digital oscilloscope (LeCroy Corporation, Chestnut Ridge, NY, USA), with it having a sampling frequency of 10 GS/s [23,24].

The signals emitted by the transmitter positioned at point E (Figure 3) were successively measured at points B1–B19 and A1–A19 as points on a semicircle, located at an interval of 10 degrees and a radius of 70 mm. The triangle symbol in points denoted E represents the position of the transmitter, and the circle symbol arranged in the form of a semicircle or quarter circle represents the successive position of the receiver. In order to avoid the dissipative behavior of the Lamb waves in the wood specimens, an equidistant distribution of the position of the transducers was chosen so that the effect of the anisotropy of the wood structure could be highlighted [18,27–29].

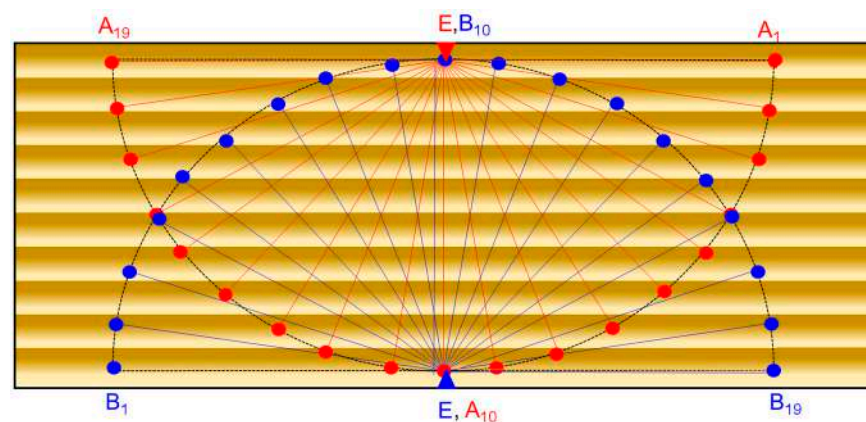


Figure 3. The measured points on the samples.

2.2.2. Statistical Analysis

The data were analyzed to evaluate the anisotropy of the material samples in terms of the change in the speed of sound with respect to the direction of propagation. The distribution of resonance points on a board made of a given type of material seems to be largely influenced by the changes in the speed of sound propagation in different directions and can affect the acoustic impression of the musical instrument produced. The question remains as to the overall subjective assessment of the quality of the instrument, which is influenced by other factors but cannot be captured by the distribution of sound velocities alone. In this limited sense, the data were analyzed with a focus on selecting the most significant wood samples. Factor analysis (FA) was used as a basic tool to identify possible dependencies in the data. Based on the Q-factor analysis (QFA), several clusters of samples with similar anisotropy were extracted.

3. Results and Discussion

3.1. Grain Angle Dependence of Lamb Wave Velocity in Wooden Plates

Since wood is an anisotropic material both in terms of morphology and properties, the changes regarding the wave propagation capacity vary gradually with the direction of the fibers. In Figure 4, it can be seen that for all samples, the speed of Lamb waves in the radial direction ranges between 1.4 to 3 times lower than in the longitudinal direction, depending on the species, the structure of the wood, and the type of treatment applied.

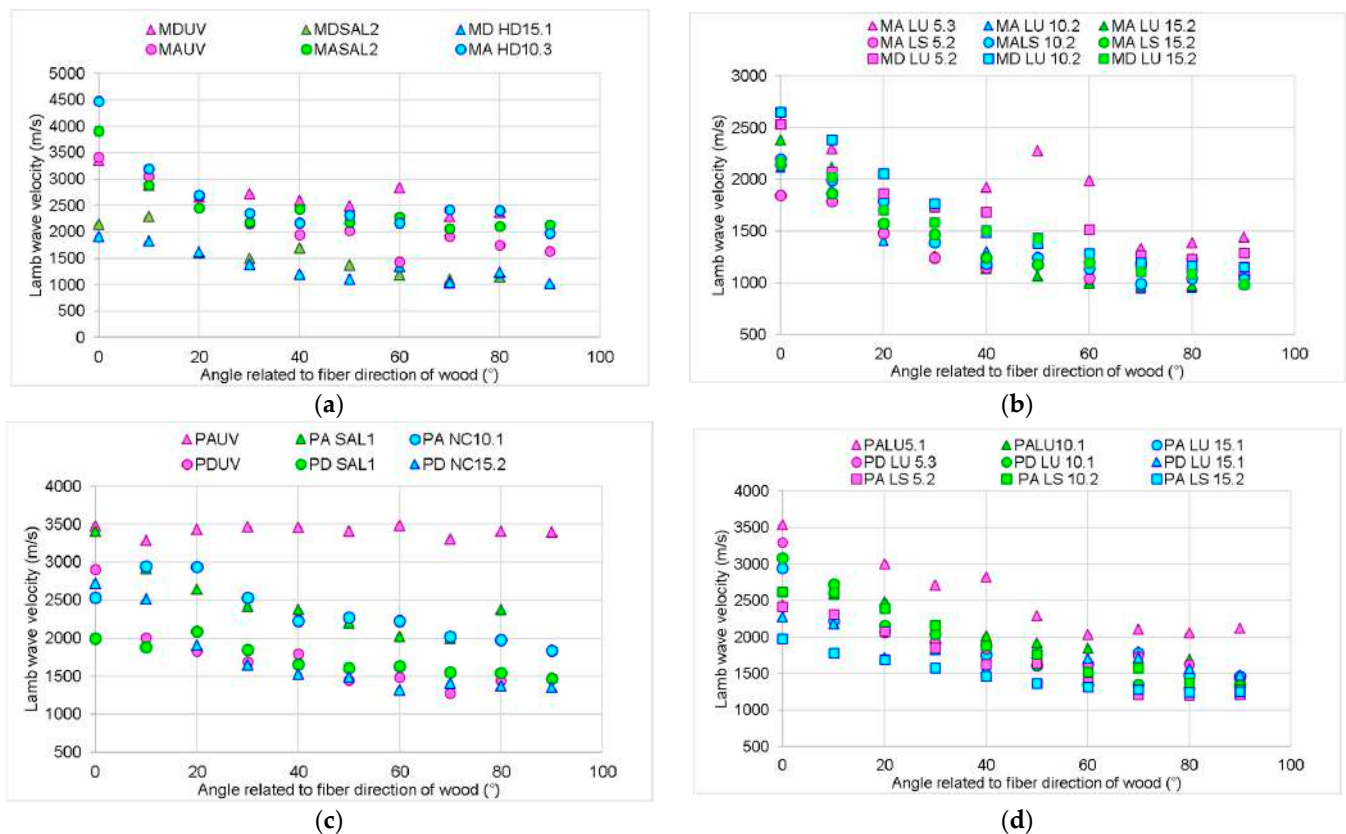


Figure 4. The variation in Lamb wave velocity in wooden plates with fiber angle variations: (a) spruce wood sample untreated, UV aged, and salt fog exposed; (b) spruce wood sample finished with oil-based varnish and spirit varnish; (c) maple wood sample untreated, UV aged, and salt fog exposed; (d) maple wood sample finished with oil-based varnish and spirit varnish.

The treatments applied to the boards influence their response to the propagation of waves in the board. Thus, artificial aging via exposure to UV radiation and slight thermal degradation for 300 h led to a decrease in both longitudinal (24%) and radial (1.7%) propagation speeds compared to the untreated wood. On the other hand, the coating with varnish films produced a wave dispersion phenomenon, with their speed decreasing in the longitudinal direction by 42–58% and the alcoholic varnish affecting the propagation of sounds the most in both spruce and maple wood (Figure 5). In the radial direction, the oil-based varnish applied on spruce wood is the one that presents the lowest values of the wave propagation speed, with it being 60% lower than the speed of the control samples. In the case of maple wood, the film of alcoholic varnish reduces the sound propagation speed the most, by 32% compared to the control sample (untreated).

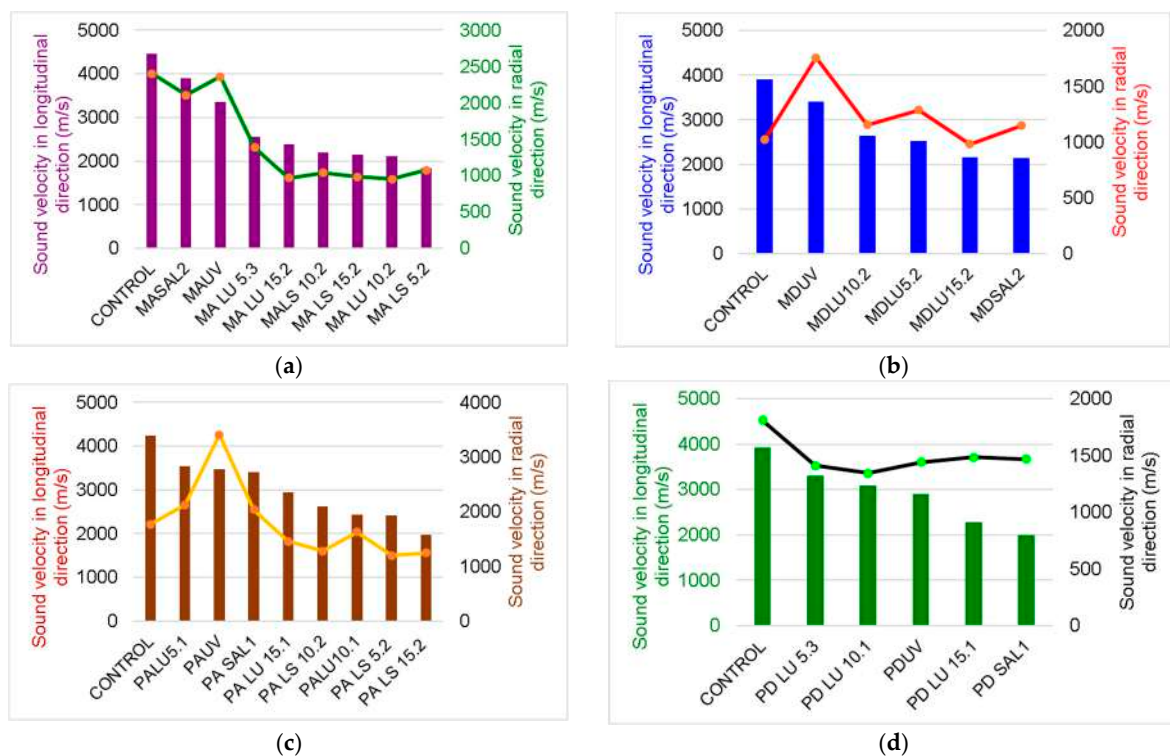


Figure 5. The influence of surface treatment on longitudinal and radial wave velocity in wooden plates: (a) spruce wood sample for maestro musical instruments; (b) spruce wood sample for school musical instruments; (c) maple wood sample for maestro musical instruments; (d) maple wood sample for school musical instruments.

Sound propagation in spruce and maple wood depends on the type, organization, and three-dimensional shape of the anatomical elements of each species. In spruce wood (*Picea abies* Karst L.) in the longitudinal direction, tracheids constitute 90% of the wood volume and are approximately 100 times longer than they are wide, with them overlapping with adjacent cells both in the upper and lower parts by 20–30% of their length. This construction ensures the rapid propagation of waves in softwood [42–45]. In Figure 6a,c, the microscopic view in the tangential direction of spruce wood in relation to the measurement principle can be noted. In the radial direction, the transmitted waves meet the tracheids whose walls show thicknesses that increase from earlywood to latewood, so it can be considered a layered material (with each annual ring being a layer) (Figure 6b).

In the radial direction, spruce wood contains radial parenchyma cells that have a geometry like rectangular prisms with dimensions of 15 μm high by 10 μm wide and 150–250 μm long in the radial or horizontal direction [8,21]. In the case of maple wood (*Acer pseudoplatanus* L.), the anatomical architecture is more complex than that of spruce wood, with it being made up of fibers, vessels, and axial parenchyma cells, with different shapes, organization, and quantity [42,43]. The vessels are small and rare, and the fibers occupy about 75% of the volume of the woody substance, the proportion of voids is 60% of the apparent volume, and from the point of view of organization, maple wood is part of the hardwoods with diffused, small pores, visible with a magnifying glass and quite rare, with their size and thickness decreasing towards the outer limit of the annual ring (Figure 6d–f) [44,45]. The vessels have average lengths between 350–800 μm , with small diameters, <50 μm . As a result, the propagation of sounds in maple wood differs from that of spruce wood; the waves propagate through a structure with a different organization and construction.

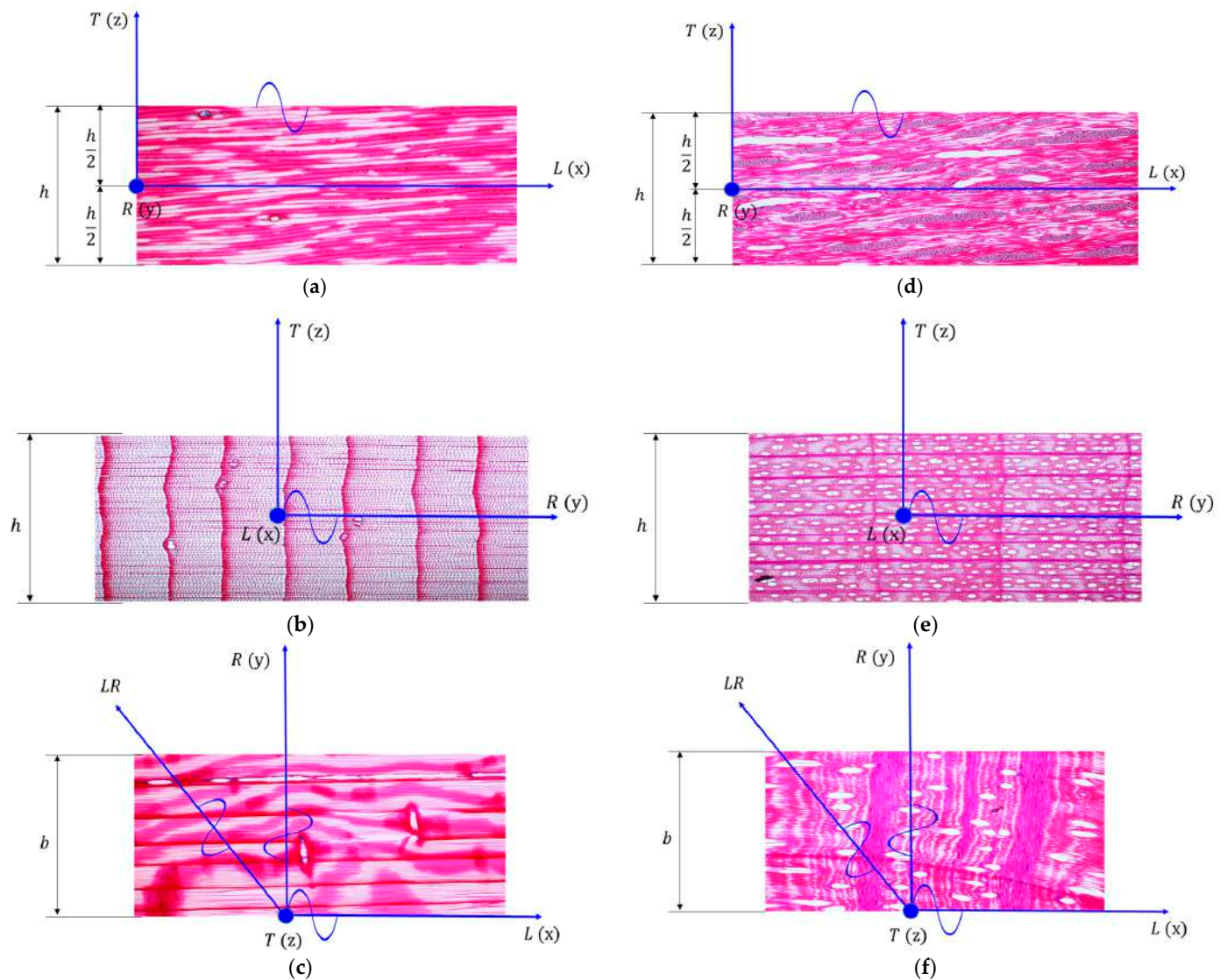


Figure 6. The microscopic views of the main section of wood related to the Lamb wave direction in the studied plates: (a) tangential section of spruce wood; (b) cross-section of spruce wood; (c) radial section of spruce wood; (d) tangential section of maple wood; (e) cross-section of maple wood; (f) radial section of maple wood.

Figure 7 highlights the variation in Lamb wave speeds measured on a circular trajectory applied to the wooden board. The angles of 0 and 180 degrees correspond to the longitudinal axis of the wood, and the angle of 90 degrees corresponds to the radial axis. Thus, it can be observed that between the two directions, L and R, the structural anisotropy of the wood is at its maximum, results highlighted in other studies [18–21].

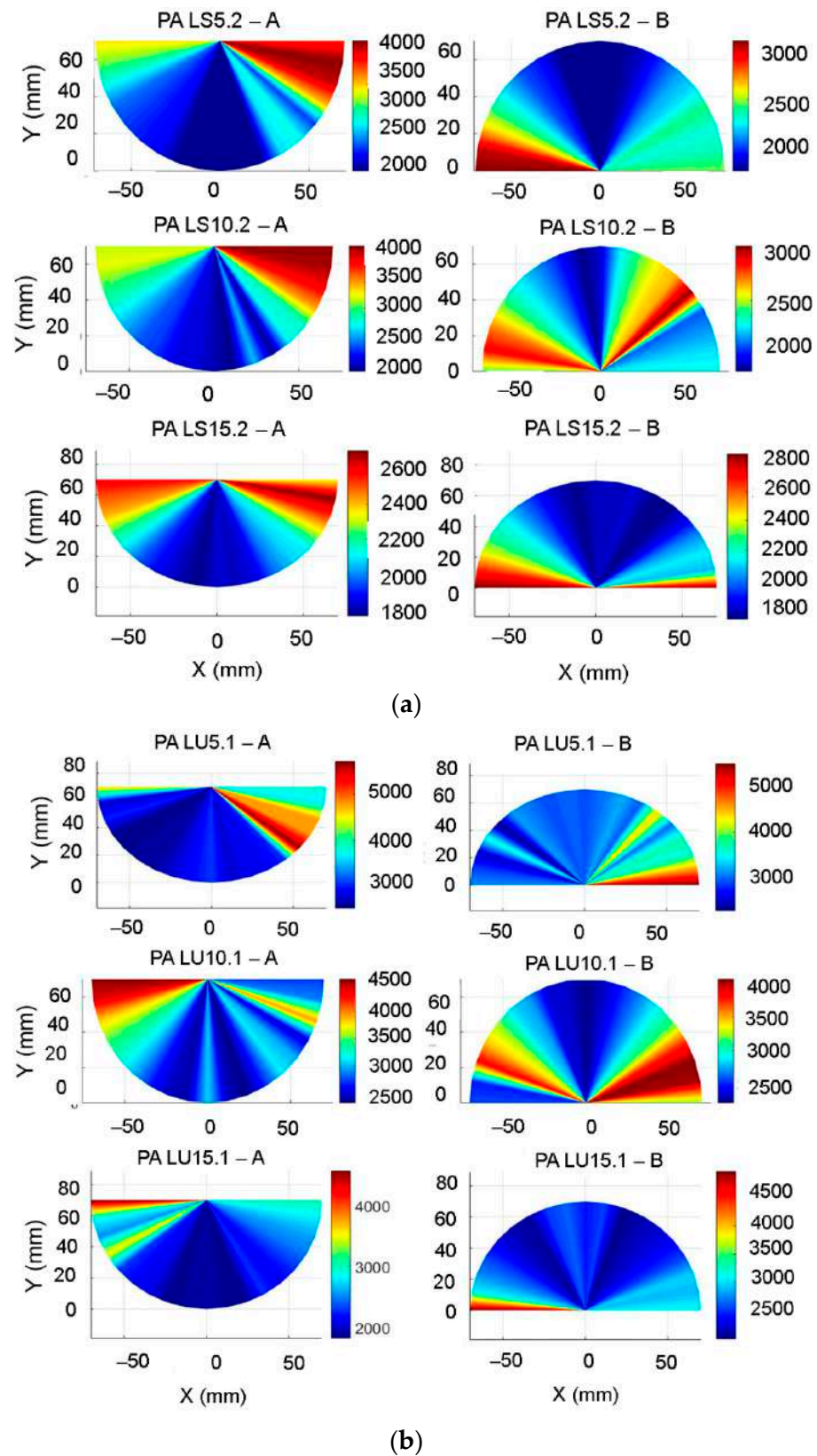


Figure 7. Cont.

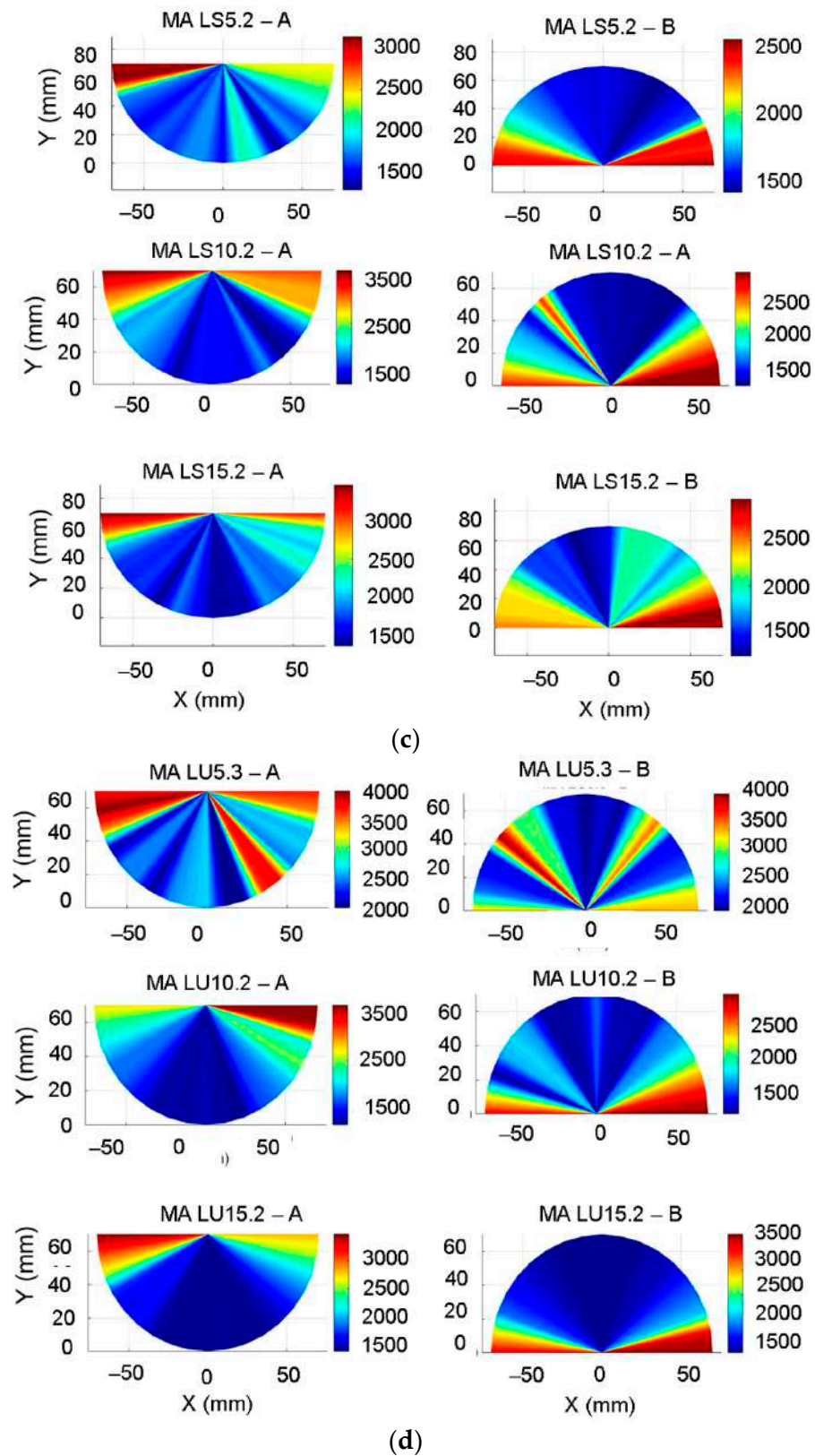


Figure 7. The variation in Lamb wave speeds with the rotation of the receiver position: (a) maple samples covered with spirit varnish; (b) maple samples covered with oil-based varnish and spirit varnish; (c) spruce samples covered with spirit varnish; (d) spruce wood sample finished with oil-based varnish.

Similar results were reported by [46], who analyzed spruce and sycamore wood samples from three types of quality classes: the highest, the moderate quality class, and the control samples, obtaining the following values for the investigated elastic and acoustic parameters: for high-quality spruce wood samples versus a control wood sample, the sound velocity in the longitudinal c_L and radial c_R directions of $c_L = 5103 \pm 280$ m/s and $c_R = 1365 \pm 201$ m/s versus the control wood sample $c_L = 5388 \pm 134$ m/s and $c_R = 1124 \pm 93$ m/s. For sycamore, ref. [46] obtained, $c_L = 3894 \pm 310$ m/s and $c_R = 1662 \pm 97$ m/s. Estimations of the elastic and acoustic properties were made using methods based on ultrasound [21], reported for resonance spruce with the following longitudinal velocities $c_L = 5600$ m/s; tangential velocity $c_T = 1600$ m/s; and radial velocity $c_R = 2000$ m/s, and for shear velocity, $c_{LT} = 1425$ m/s; $c_{RT} = 298$ m/s; and $c_{LR} = 1374$ m/s and for common spruce, $c_L = 5353$ m/s; $c_T = 1146$ m/s; and $c_R = 1580$ m/s; and for shear velocity, $c_{LT} = 1230$ m/s; $c_{RT} = 477$ m/s; and $c_{LR} = 1322$ m/s. For curly maple, the values determined using ultrasonic method are: $c_L = 4350$ m/s; $c_T = 1914$ m/s; and $c_R = 2590$ m/s, and for shear velocity $c_{LT} = 1468$ m/s; $c_{RT} = 812$ m/s; and $c_{LR} = 1744$ m/s, since for common Sycamore, the values are $c_L = 4695$ m/s; $c_T = 1878$ m/s; and $c_R = 2148$ m/s, and for shear velocity, $c_{LT} = 1148$ m/s; $c_{RT} = 630$ m/s; and $c_{LR} = 1354$ m/s. Ref. [47] noticed that for the ratio of the sounds velocities in wood in the two longitudinal and radial directions, within the same wood species, for the spruce samples, the ratio CL:CR was 3.257, and for the samples of maple wood, the ratio was 2.17.

3.2. Statistical Results

In order to verify the continuity of the measurement points, a correlation analysis of the values collected for all material samples was performed, considering the values measured on the two semicircles A and B as forming a fictitious circle. In the correlation matrix in Figure 8, a “butterfly” distribution of correlation values can be observed, with a diagonal symmetry that corresponds to the orientation symmetry of the wood fibers.

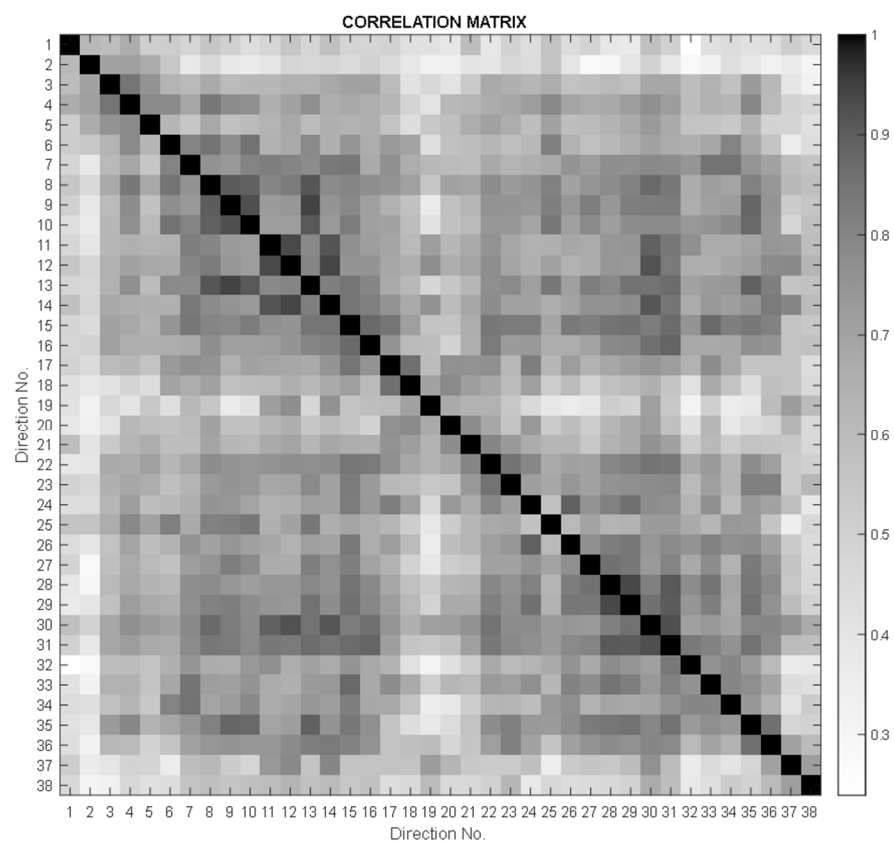


Figure 8. “Butterfly” distribution of correlation values.

The anisotropy of the sound propagation speeds in the wood samples is highlighted in the polar graph of the speeds in each of the 38 directions for all of the wood samples (Figure 9).

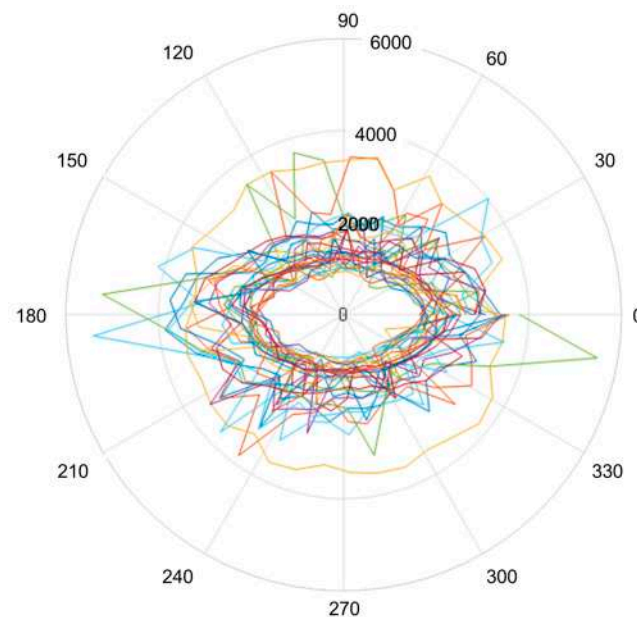


Figure 9. Polar graphs of sound velocities for each sample.

This summary shows the variability of the measured values with respect to the different directional dependencies, as well as the relatively large variation in the maximum speed measured in individual samples. Using the Q-variant of FA (based on a transposed data matrix and resulting in a clustering scheme, see the left part of Figure 8), it was possible to point to certain samples that had a particular pattern of anisotropy. Based on the Q-factor analysis (QFA), several groups of samples with similar anisotropy were extracted, depending on the wood species, the applied treatment, or the anatomical characteristics. In some of these groups, only a specific sample belongs to a cluster and therefore can be declared exceptional in its own way. These selected samples are due to the type of wood and different treatment methods. Using QFA, the measured parameters are ordered into a so-called individual profile, which helps to identify similar characteristics. By applying the RMS (the square root of the mean square) and STD (the standard deviation) complementary diagrams, it was found that the PA UV3 sample appears as a very unique sample with only one large affiliation (the dark highlighted value in Figure 10a) in the third group. This is a sample with a very high mean velocity (Figure 10b) and, in contrast, a small anisotropy (low STD value—Figure 10c). PD sample SAL1 has a similar small anisotropy. However, it does not have such high speeds and therefore represents a specific type in itself, defining another cluster, number 10. The sample MA HD10.3, which has an exceptional anisotropy (see the maximum measured standard deviation), defines cluster 1, to which samples such as PD LU5.3, PA SAL1, and several others with less similarity are assigned. Based on the above, several samples can be identified that are representative of “their” characteristic group. These are as follows: MA HD 10.3, PA LS 10.2, PA UV 3, MA UV 2, PA LU 5.1, PA LU 10.1, MA SAL 2, and MA LU 5.3. Cluster No. 7 is interesting in this respect, where two very similar velocity profiles are obtained from different wood species (Maple PA NC 10.1 and Spruce MD LU 15.2).

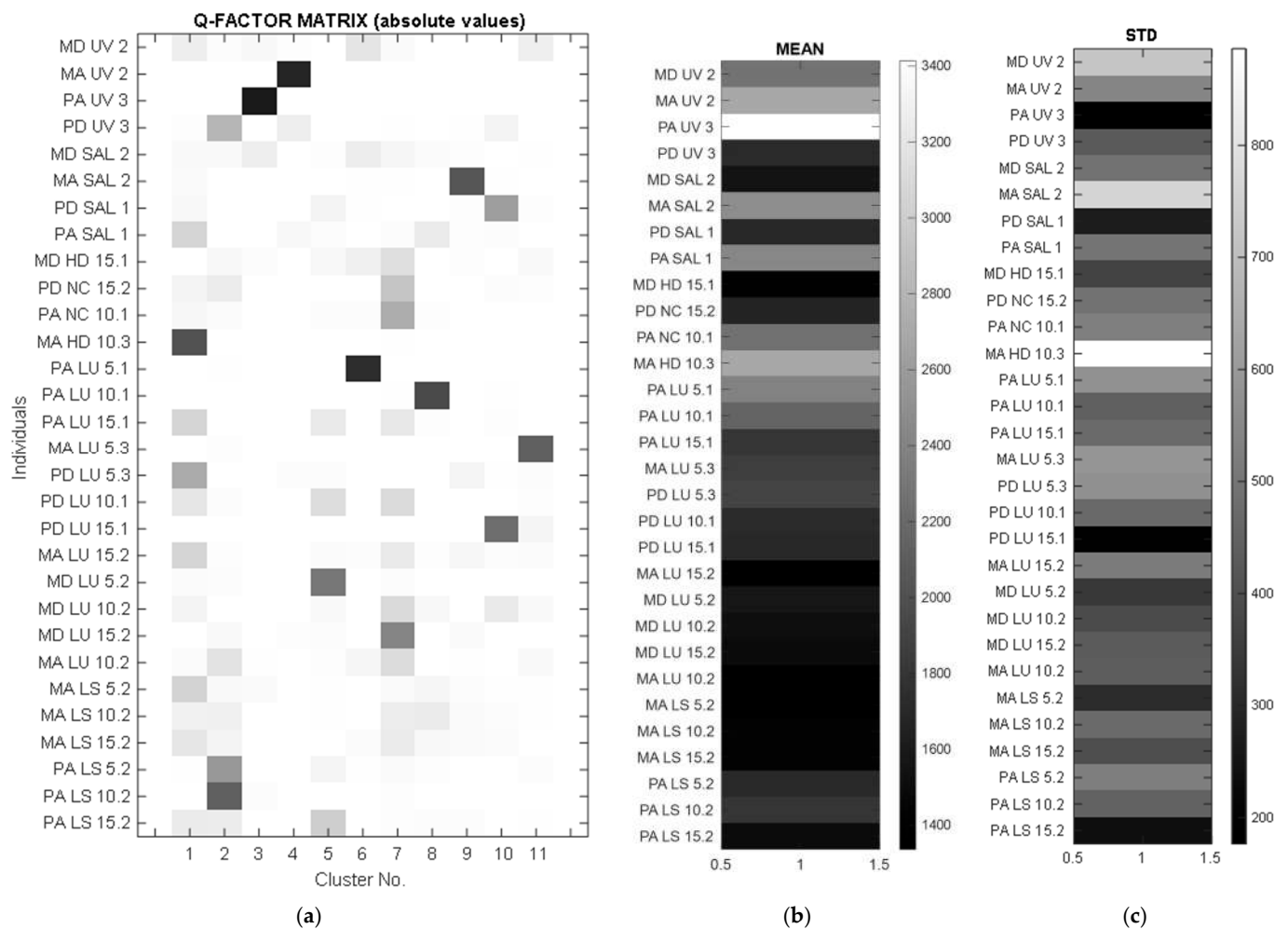


Figure 10. Comparative analysis of statistical data: (a) Q-FA clustering scheme; (b) the square root of the mean square values; (c) STD values for each sample.

4. Conclusions

The use of non-destructive control to determine the sound propagation speeds in different stages of the finishing of musical instruments can be a modern and precise method of optimizing the finishing technology to obtain the desired acoustic features, depending on the quality of the wood, the type of varnish and the treatments applied. The results of this study help instrument manufacturers to integrate new technologies with the art of luthiers and also apply innovative solutions for treating resonance wood, which they can later verify using the ultrasound method. Based on the obtained experimental data, the following conclusions were drawn:

1. The treatment applied to the surface of the wooden resonance plates influences the sound propagation speed both in the longitudinal and radial directions. The acoustic behavior of the wood depends both on the type of treatment and the anatomical characteristics of the wood, with differences in propagation speeds being recorded between samples of the same woody species but with different anatomical structures.
2. In spruce wood samples, the film of alcohol varnish reduces the speed of propagation of sounds by approximately 42–58% in the longitudinal direction, and in the radial direction, the oil-based varnish reduces the speed of propagation by 60%.
3. In the maple wood samples, the anisotropy ratio between the longitudinal and radial directions decreases with the increase in the thickness of the varnish film.

Author Contributions: Conceptualization, D.F., A.S., M.D.S. and M.C.; methodology, A.S., M.K. (Michal Krbata), M.K. (Marcel Kohutiar) and M.C.; software, D.F., M.D.S., S.M.N. and M.C.; validation, M.K. (Michal Krbata) and M.K. (Marcel Kohutiar); formal analysis, A.S., M.C., S.M.N. and M.D.S.; investigation, D.F., A.S. and M.C.; resources, M.D.S., M.K. (Michal Krbata) and M.K. (Marcel Kohutiar); data curation, D.F., A.S. and M.C.; writing—original draft preparation, A.S., M.D.S. and M.C.; writing—review and editing, D.F., M.K. (Michal Krbata) and M.K. (Marcel Kohutiar); visualization, M.C. and S.M.N.; supervision, M.D.S. and A.S.; project administration, M.D.S., D.F. and M.C.; funding acquisition, M.K. (Michal Krbata), M.K. (Marcel Kohutiar) and M.D.S. All authors have read and agreed to the published version of the manuscript.

Funding: This research was supported by a grant from the UEFISCDI (Unitatea Executiva pentru Finantarea Cercetării, Dezvoltării și Învățământului Superior din România), project number 61PCE/2022, PN-III-P4-PCE2021-0885, ACADIA—Qualitative, dynamic and acoustic analysis of anisotropic systems with modified interfaces.

Institutional Review Board Statement: Not applicable.

Data Availability Statement: Data are contained within the article.

Acknowledgments: We are also grateful to the technical staff of Gliga Musical Instruments, Reghin, Romania, for supplying the specimens. We are grateful to Cătălin Roibu and his colleagues for the microscopic specimens prepared and analyzed in the Forest Biometrics Laboratory, “Stefan cel Mare” University of Suceava, Romania. Milan Chlada would like to acknowledge the support of the Institute of Thermomechanics of the Czech Academy of Sciences, grant No. RVO:61388998. Adriana Savin would like to acknowledge the support of the Ministry of Research, Innovation and Digitalization, Romania, through Project PN 23-11-01-02.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Wegst, U.G.K. Wood for sound. *Am. J. Bot.* **2006**, *93*, 1439–1448. [[CrossRef](#)] [[PubMed](#)]
2. Obataya, E.; Ono, T.; Norimoto, M. Vibrational properties of wood along the grain. *J. Mater. Sci.* **2000**, *35*, 2993–3001. [[CrossRef](#)]
3. Brémaud, I.; Gril, J.; Thibaut, B. Anisotropy of wood vibrational properties: Dependence on grain angle and review of literature data. *Wood Sci. Technol.* **2011**, *45*, 735–754. [[CrossRef](#)]
4. Ono, T. Effect of grain angle on dynamic mechanical properties of wood. *J. Soc. Mater. Sci. Jpn.* **1983**, *32*, 108–113. [[CrossRef](#)]
5. Sedighi Gilani, M.; Pflaum, J.; Hartmann, S.; Kaufmann, R.; Baumgartner, M.; Schwarze, F.W.M.R. Relationship of vibro-mechanical properties and microstructure of wood and varnish interface in string instruments. *Appl. Phys. A* **2016**, *122*, 260. [[CrossRef](#)]
6. Bucur, V. *Handbook of Materials for String Musical Instruments*; Springer: Berlin/Heidelberg, Germany, 2016. [[CrossRef](#)]
7. Bernabei, M.; Bontadi, J. Determining the resonance wood provenance of stringed instruments from the Cherubini Conservatory Collection in Florence, Italy. *J. Cult. Herit.* **2011**, *12*, 196–204. [[CrossRef](#)]
8. Schmidt-Vogt, H. *Die Fichte Band I. Taxonomie-Verbreitung-Morphologie-Ökologie-Waldgesellschaften*; Paul Parey: Hamburg/Berlin, Germany, 1977.
9. Dinulică, F.; Albu, C.T.; Borz, S.A.; Vasilescu, M.M.; Petritan, I.C. Specific structural indexes for resonance Norway spruce wood used for violin manufacturing. *Bioresources* **2015**, *10*, 7525–7543. [[CrossRef](#)]
10. Dinulică, F.; Stanciu, M.D.; Savin, A. Correlation between Anatomical Grading and Acoustic–Elastic Properties of Resonant Spruce Wood Used for Musical Instruments. *Forests* **2021**, *12*, 1122. [[CrossRef](#)]
11. Viala, R.; Placet, V.; Cogan, S. Simultaneous non-destructive identification of multiple elastic and damping properties of spruce tonewood to improve grading. *J. Cult. Herit.* **2020**, *42*, 108–116. [[CrossRef](#)]
12. Carlier, C.; Alkadri, A.; Gril, J.; Bremaud, I. Revisiting the notion of “resonance wood” choice: A departementalized approach from violin makers’ opinion and perception to characterization of material properties variability. wooden musical instruments. Wooden musical instruments—Different forms of knowledge: Book of end of WoodMusICK COST Action FP1302. 2018, pp. 119–142. Available online: <https://hal.science/hal-02051004/document> (accessed on 16 January 2024).
13. Caldersmith, G. Vibrations of orthotropic rectangular plates. *Acta Acust. United Acust.* **1984**, *56*, 144–152.
14. McIntyre, M.; Woodhouse, J. On measuring wood properties, part 1–3. *J. Catgut Acoust. Soc.* **1984**, *42*, 1984–1986.
15. Warguła, Ł.; Wojtkowiak, D.; Kukla, M.; Talaśka, K. Symmetric nature of stress distribution in the elastic-plastic range of Pinus L. pine wood samples determined experimentally and using the finite element method (FEM). *Symmetry* **2021**, *13*, 39. [[CrossRef](#)]
16. Wang, R.; Liang, F.; Wang, B.; Mou, X. ODCA-YOLO: An Omni-Dynamic Convolution Coordinate Attention-Based YOLO for Wood Defect Detection. *Forests* **2023**, *14*, 1885. [[CrossRef](#)]

17. Gonçalves, R.; Trinca, A.J.; Cerri, D.G.P. Comparison of elastic constants of wood determined by ultrasonic wave propagation and static compression testing. *Wood Fiber Sci.* **2011**, *43*, 64–75.
18. Duquenme, L.; Moulin, E.; Assood, J.; Grandel, S. Transient modeling of Lamb wave generated in viscoelastic materials by surface bonded piezoelectric transducers. *J. Acoust. Soc. Am.* **2004**, *116*, 133–141. [\[CrossRef\]](#)
19. Fang, Y.; Lin, L.; Feng, H.; Lu, Z.; Emms, G.W. Review of the use of air-coupled ultrasonic technologies for nondestructive testing of wood and wood products. *Comput. Electron. Agric.* **2017**, *137*, 79–87. [\[CrossRef\]](#)
20. Bucur, V.; Archer, R.R. Elastic constants for wood by an ultrasonic method. *Wood Sci. Technol.* **1984**, *18*, 255–265. [\[CrossRef\]](#)
21. Bucur, V. Varieties of resonance wood and their elastic constants. *J. Catgut Acoust. Soc.* **1987**, *47*, 42–48.
22. Bucur, V. Wood structural anisotropy estimated by acoustic invariants. *IAWA Bull.* **1988**, *9*, 67–74. [\[CrossRef\]](#)
23. Dinulică, F.; Savin, A.; Stanciu, M.D. Physical and Acoustical Properties of Wavy Grain Sycamore Maple (*Acer pseudoplatanus* L.) Used for Musical Instruments. *Forests* **2023**, *14*, 197. [\[CrossRef\]](#)
24. Schmerr, L.W., Jr. *Fundamentals of Ultrasonic Nondestructive Evaluation—A Modeling Approach*; Plenum Press: New York, NY, USA, 1998.
25. Grimberg, R.; Savin, A.; Steigmann, R.; Stanciu, M.D.; Grum, J. Determination of Elastic Properties of CFRP Using Lamb Waves Resonant Spectroscopy. In Proceedings of the 2nd International Symposium on NDT in Aerospace, Hamburg, Germany, 22–24 November 2010.
26. Alleyne, D.N.; Cawley, P. A two dimensional Fourier transform method for the measurement of propagating multimode signals. *J. Acoust. Soc. Am.* **1991**, *89*, 1159–1168. [\[CrossRef\]](#)
27. Neau, G.; Deschamps, M.; Lowe, M.J.S. Group velocity of Lamb waves in anisotropic plates: Comparison between theory and experiments. *AIP Conf. Proc.* **2001**, *557*, 81–88. [\[CrossRef\]](#)
28. Kuznetsov, S.V. Resonance phenomena in layered media: Merging proper and quasi-resonances. *Z. Angew. Math. Phys.* **2023**, *74*, 245. [\[CrossRef\]](#)
29. Nowak, T.; Hamrol-Bielecka, K.; Jasienko, J. Non-destructive testing of wood—correlation of ultrasonic and stress wave test results in glued laminated timber members. *Annals of Warsaw University of Life Sciences-SGGW. For. Wood Technol.* **2015**, *92*, 317–324.
30. *ISO 13061-1:2014/Amd 1:2017*; Physical and Mechanical Properties of Wood. Test Methods for Small Clear Wood Specimens. Part 1: Determination of Moisture Content for Physical and Mechanical Tests. ISO: Geneva, Switzerland, 2017.
31. Schelleng, J.C. Acoustical Effects of Violin Varnish. *J. Acoust. Soc. Am.* **1968**, *4*, 1175–1183. [\[CrossRef\]](#)
32. Schleske, M. Contemporary violin making. Analysis of design, materials, varnish and normal modes. *Catgut Acoust. Soc. J.* **2002**, *4*, 50–65.
33. Nagyvary, J.; Guillemette, R.N.; Spiegelman, C.H. Mineral Preservatives in the Wood of Stradivari and Guarneri. *PLoS ONE* **2009**, *4*, e4245. [\[CrossRef\]](#) [\[PubMed\]](#)
34. Cai, W.; Tai, H.-C. String Theories: Chemical Secrets of Italian Violins and Chinese Guqins. *AsiaChem* **2020**, *11*, 10–17. [\[CrossRef\]](#)
35. Skrodzka, E.B.; Linde, B.J.B.; Krupa, A. Modal Parameters of Two Violins with Different Varnish Layers and Subjective Evaluation of Their Sound Quality. *Arch. Acoust.* **2013**, *38*, 75–81. [\[CrossRef\]](#)
36. Lämmlein, S.L.; Van Damme, B.; Mannes, D.; Schwarze, F.W.M.; Burgert, I. Violin varnish induced changes in the vibro-mechanical properties of spruce and maple wood. *Holzforschung* **2020**, *4*, 765–776. [\[CrossRef\]](#)
37. Odlyha, M.; Lucejko, J.J.; Lluveras-Tenorio, A.; di Girolamo, F.; Hudziak, S.; Strange, A.; Bridarolli, A.; Bozec, L.; Colombini, M.P. Violin Varnishes: Microstructure and Nanomechanical Analysis. *Molecules* **2022**, *27*, 6378. [\[CrossRef\]](#)
38. Stanciu, M.D.; Cosnita, M.; Gliga, G.V.; Gurau, L.; Timar, C.M.; Guiman, M.V.; Năstac, S.M.; Roșca, I.C.; Bucur, V.; Dinulică, F. Tunable Acoustic Properties Using Different Coating Systems on Resonance Spruce Wood. *Adv. Mat. Interfaces* **2024**, *1*, 2300781. [\[CrossRef\]](#)
39. Stobbe, D.M.; Grünsteidl, C.M.; Murray, T.W. Propagation and Scattering of Lamb Waves at Conical Points in Plates. *Sci. Rep.* **2019**, *9*, 15216. [\[CrossRef\]](#)
40. Bucur, V. A Review on Acoustics of Wood as a Tool for Quality Assessment. *Forests* **2023**, *14*, 1545. [\[CrossRef\]](#)
41. Fathi, H.; Kazemirad, S.; Nasir, V. A nondestructive guided wave propagation method for the characterization of moisture-dependent viscoelastic properties of wood materials. *Mater. Struct.* **2020**, *53*, 147. [\[CrossRef\]](#)
42. Wiedenhoeft, A.C.; Miller, R.B. Structure and Function of Wood. In *Handbook of Wood Chemistry and Wood Composites*; Rowell, R.M., Ed.; CRC Press: Boca Raton, FL, USA, 2005.
43. Dinulică, F. *Forest Products: Structure and Properties of Wood (in Romanian Language)*; Publishing House Transilvania University of Brasov: Brasov, Romania, 2021.
44. Gurău, L.; Timar, M.C.; Coșereanu, C.; Cosnita, M.; Stanciu, M.D. Aging of Wood for Musical Instruments: Analysis of Changes in Color, Surface Morphology, Chemical, and Physical-Acoustical Properties during UV and Thermal Exposure. *Polymers* **2023**, *15*, 1794. [\[CrossRef\]](#) [\[PubMed\]](#)
45. Guiman, M.V.; Stanciu, M.D.; Roșca, I.C.; Georgescu, S.V.; Năstac, S.M.; Câmpăan, M. Influence of the Grain Orientation of Wood upon Its Sound Absorption Properties. *Materials* **2023**, *16*, 5998. [\[CrossRef\]](#)

46. Spycher, M.; Schwarze, F.W.M.R.; Steiger, R. Assessment of resonance wood quality by comparing its physical and histological properties. *Wood Sci. Technol.* **2008**, *42*, 325–342. [[CrossRef](#)]
47. Crețu, N.; Roșca, I.C.; Stanciu, M.D.; Gliga, V.G.; Cerbu, C. Evaluation of Wave Velocity in Orthotropic Media Based on Intrinsic Transfer Matrix. *Exp. Mech.* **2022**, *62*, 1595–1602. [[CrossRef](#)]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.

Article

Degradation of Mechanical Properties of Pine Wood Under Symmetric Axial Cyclic Loading Parallel to Grain

Mariana D. Stanciu , Horațiu D. Teodorescu and Sorin Vlase

Department of Mechanical Engineering, Transilvania University of Braşov, B-dul Eroilor 29, 500036 Braşov, Romania; draghicescu.teodorescu@unitbv.ro (H.D.T.); svlase@unitbv.ro (S.V.)

* Correspondence: mariana.stanciu@unitbv.ro; Tel.: +40-740-555-566

Received: 24 August 2020; Accepted: 21 September 2020; Published: 23 September 2020



Abstract: The mechanical properties of wood, respectively the elastic, plastic, and strength properties, depend on a large number of factors, due both to its structural and physical characteristics, as well as to the size, direction, nature, and speed of application of forces. Wood, generally considered to be a viscous-elastic material, has creep deformations over time under the effect of a constant load. In this study the behavior of pine wood samples was investigated due to its large utilization in different finished products, such as roof construction, furniture, outdoor applications, garden furniture, and toys. The paper aims to analyze the viscoelastic behavior of pine wood subjected to cyclically loading to traction-compression with different loads (1 kN; 1.5 kN; 2 kN), applied at different speeds (1 mm/min; 10 mm/min). It was observed that, at low speeds (1 mm/min) and low intensities of the applied force, it was possible to distinguish the three creep regions specific to wood: the primary area (primary flow), the secondary area, and finally the tertiary creep. As the force increases, the law of variation of the wood flow changes. The degradation of longitudinal elasticity modulus occurs with the increase of the number of cycles, so after 20 alternating symmetrical cycles of traction-compression of the pine wood samples, there is a decrease of its values by 35%.

Keywords: pine wood; symmetric axial cyclic loading; viscous-elastic behavior; degradation of mechanical properties; creep

1. Introduction

Wood, due to its polymeric and layered structure, is considered a natural composite material. Thus, the late wood and early wood can be considered composite layers [1,2]. Their widths, proportion and density vary, depending on the specific environment and soil conditions from year to year [3]. Wood consists of a very complex system of fibers, cells, cementing substances, etc., whose physical and chemical cohesion poses particular problems in the calculations of strength and rigidity, compared to homogeneous and isotropic materials such as, for example, metals [4–6]. Nowadays, wood and wood-based materials have re-entered the attention of architects and builders, being a material with numerous physical, mechanical, acoustic, and workability qualities. Numerous studies on the mechanical properties of softwood used in construction have been conducted to highlight the correlations between wood structure, quality class, type of mechanical stress, and failure modes [2,7,8].

Taking into account the structural changes produced by cyclic stresses as well as the modification of the tensile breaking section of wooden samples, Christoforo et al. [4] present a mathematical model for determining the shape coefficient that expresses the relationship between the actual breaking area and the theoretical area. The tension is distributed at the request of parallel traction with fiber of the different wood species from Brazil.

However, the cyclic stresses of wooden structures lead to a constant reduction of wood strength by accumulating deformation energy and producing plastic deformations at the cell walls. Studies have shown that, to predict the behavior of wood over time, the design and construction of structural elements must take into account not only the values of allowable stresses, but also the ability to load wood under cyclic load, respectively the creep and relaxation function of wood [9–11]. Gong et al. [1] analyzed the failure mechanism of softwood subject to compression cyclic stresses parallel to the fibres, noting that the process of mechanical degradation is accompanied by a structural degradation characterized by three stages: kink initiation, kink growth, and finally macroscopic failure. Similar to the composite materials and kinking fibres of them studied by Pinho et al. [12], the wood fibres kinking failure occurs because of local microstructural defects, such as fibres misalignments and longitudinal cracking. the wood fibres misalignments lead to shearing stresses between the fibres and longitudinal cracks or parenchyma rays' disposals act as stress concentrators.

Konstantinov et al. [9] analyzed the influence of the texture orientation of the wood on the strength and deformation properties of wood and also the degradation of mechanical and dynamical properties of wood subjected to cyclic loads in the conditions of lateral confinement, being studied three species: pine, birch and sequoia. They noticed that at a low strain rate, the damage to the specimen was seen to be insignificant, while at a high strain rate the integrity of the specimen was exceeded leading to sample failure. Yildirim et al. [13] examined the fatigue and static strength of Scots pine and beech wood subjected to bending test. They noticed that the fatigue failures began to occur as the stress level was or above 40% of Scots pine specimen's average of modulus of rupture (MOR) and for beech specimens, fatigue failures began to occur when the stress level was above 50% of beech specimen's average MOR. Some studies analyze the fatigue behavior of chemically or thermally modified wood compared to control samples, finding that both the modulus of bending elasticity (MOE) increased by about 21% in the case of pine wood modified by impregnation with phenol formaldehyde resin [10]. Regarding the behaviour of Scots pine (*Pinus sylvestris*) as control samples and thermally modified subjected to cyclic bending, Sharapov et al. [11] performed studies applying asymmetric sinusoidal cyclic oscillations at 20 Hz frequency and load ratio $p = 0.3$. Three types of variables they analyzed in experiments: the thermal treatment temperature (160, 190, and 220 °C), the number of bending oscillations (103, 505 × 103 and 106), and the equilibrium moisture content at target climates of 20 °C and 35%, 65%, and 95% relative humidity (RH). Sharapov et al. [11] considered that the main influence on the residual MOR consist of the initial moisture content of the specimens before fatigue testing and the maximum thermal modification temperature. Based on experimental observations and mathematical models, Hassani et al. [14] and Andrianopoulos et al. [15] developed a three-dimensional orthotropic mechanical and mathematical model of wood, taking into account both the components of total deformation and rheological expressions, principles of moisture-stress analysis. In previous studies, Stanciu et al. [16,17] investigated the rheological characteristics of the black locust wood samples chemical treated with ammonia [16] and natural fibers composites [17] in terms of complex modulus, with its two components (the conservation modulus E' and the loss modulus E'') and the damping factor were determined dynamic mechanical analysis (DMA).

While numerous studies have presented failure analyses of wood subjected to axial stresses (or tensile or compression) or flexural stresses, little information is available about the structural and mechanical degradation of wood (softwood) subjected to symmetric axial cyclic tension, obtaining the Bauschinger effect. Wooden constructions, new or heritage, are subject to variable loading, such as precipitation (snow), wind, or dynamic loads from earthquakes, which requires a knowledge of the mechanical properties of wooden components, behavior over time, along with a description detailed defects or their degradation (resistance reduction factors). Pine wood, along with spruce wood, and fir wood, is very widely used in making construction/building elements that are subjected to loads in different directions and with different intensities and duration. So, the objective of the current study is to analyze the degradation of mechanical properties and structural failure produces by symmetric axial cyclic loading of Scots pine samples (*Pinus sylvestris*). The novelty of the paper consists of better

understanding of the mechanical behavior of softwood and determination of the hysteresis loops to tensile and compression. Also, the structural modifications of wood cells are presented by means of optical microscope.

2. Materials and Methods

2.1. Preliminary Tests

The wood species analyzed in this research was Scots pine samples (*Pinus sylvestris*) with 12% moisture contents (provided by the norm EN 384: 2004) [18]. In the first stage, a set of samples with different loading speeds were tested for tensile to rupture, in order to establish the maximum value of the load to alternating symmetrical cyclic stresses (Figure 1a). In Figure 1b, the characteristic curves of pine wood samples to different speed loading are presented. It can be noticed that the yield point for loading speed of 1 mm/min is around of 1 kN force and for loading speed of 10 mm/min, yield point corresponds to a load of 2 kN. From the preliminary results, the cyclic loading will range between 1 kN and 2 kN, with loading speeds of 1 mm/min and 10 mm/min.

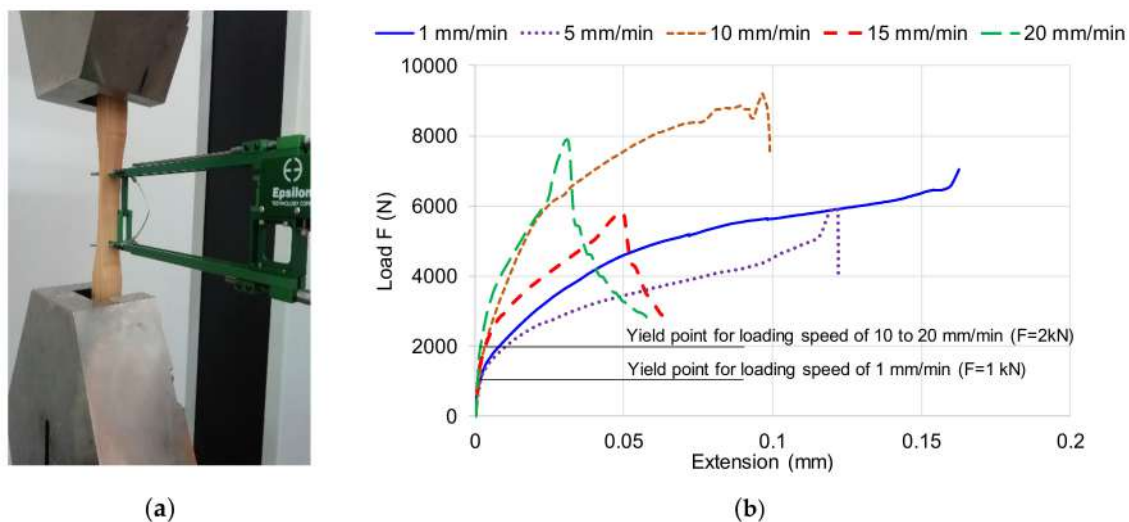


Figure 1. The preliminary test: (a) tensile test; (b) characteristic curves of pine wood subjected to tensile with different loading speeds.

2.2. Materials

Based on ASTM 04.10 Wood D143-09 [19] and EN 408 (2010) + A1 (2012) [20], the procedures and samples for axial cyclic tests were developed. The 18th cases as combination between loading intensity, number of cycles and speed of loading were analyzed on samples of solid wood of Scots pine cut radially, having the nominal dimensions of length $L = 150$ mm, width $b = 15$ mm, thickness $h = 5$ mm (Figure 2a). The Scots pine wood samples used in this study come from the Carpathian Mountains but they are provided by the trade market where ordinary customers buy it. The annual ring width of specimens ranges between 1.5 mm to 3 mm, so the Scots pine wood samples shows larger spreading of its annual values as Silvestru Grigore et al. [3] noticed.

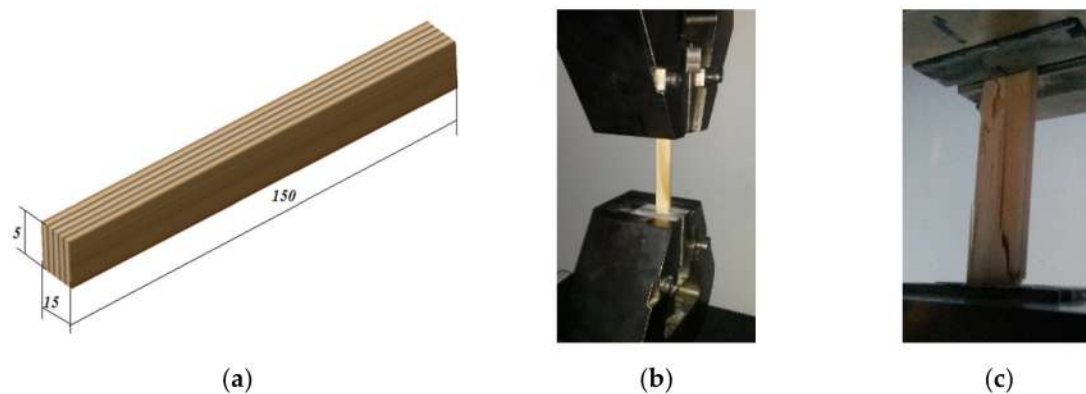


Figure 2. Experimental set-up: (a) the geometry of tested samples; (b) details of the sample in clamping jaws of the testing machine during the symmetric cyclic loading to tensile-compression; (c) Failure mode of sample tested to cyclic loading.

The first category of tests denoted A1 was the one in which the samples were subjected to loading with a speed of 1 mm/min with the force intensity of ± 1000 N, being formed by three sets of samples. The first set of samples P1, P2, P3 was subjected to the tensile-compression stresses parallel to wood grain in turn at 1 cycle (sample P1); at 10 cycles (sample P2) and at 20 cycles (sample P3). The next set of samples (B1) was subjected to symmetrical cyclic stresses with a speed of 1 mm/min with the force intensity of ± 1500 N in the same manner as previous samples: at 1 cycle (sample P4); at 10 cycles (sample P5) and at 20 cycles (sample P6). The C1 group of samples was subjected to cyclic stress at a load intensity of ± 2000 N, the loading speed of 1 mm/min, at 1 cycle (sample P7), at 10 cycles (sample P8), and at 20 cycles, (sample P9). The second category of pine specimens denoted with A10; B10; C10 was subjected at a speed of 10 mm/min, having similarly to the first category, three sets of samples tested at different intensities of the applied load. The input data of tested samples are presented in Table 1.

Table 1. Input data for experimental tests.

Set of Tests	Sample	No of Cycles	Gauge Length (mm)	Speed (mm/min)	Width (mm)	Thickness (mm)	Area (mm ²)	Limit of Tensile/Compression Loading (kN)
A1	P1	1	60	1	15	5	75	± 1
	P2	10	60	1	15	5	75	± 1
	P3	20	60	1	15	5	75	± 1
B1	P4	1	60	1	5	5	75	± 1.5
	P5	10	60	1	15	5	75	± 1.5
	P6	20	60	1	15	5	75	± 1.5
C1	P7	1	60	1	15	5	75	± 2
	P8	10	60	1	15	5	75	± 2
	P9	20	60	1	15	5	75	± 2
A10	P10	1	60	10	15	5	75	± 1
	P11	10	60	10	15	5	75	± 1
	P12	20	60	10	15	5	75	± 1
B10	P13	1	60	10	15	5	75	± 1.5
	P14	10	60	10	15	5	75	± 1.5
	P15	20	60	10	15	5	75	± 1.5
C10	P16	1	60	10	15	5	75	± 2
	P17	10	60	10	15	5	75	± 2
	P18	20	60	10	15	5	75	± 2

2.3. Methods

The samples were subjected to symmetric cyclic loading tensile-compression test using the universal testing machine type LS100 Lloyd's Instrument belonging to the Mechanical Engineering Department of Transilvania University of Brasov, in order to study the degradation of mechanical properties of a Scots pine wood. The specimens were loading with a constant speed of 1 mm/min and then 10 mm/min, being subjected successive to 1 cycle, 10 cycles and 20 cycles. The tensile

and compression displacements were measured simultaneously with applied loading (Figure 2b,c). For data acquisition, the Nexygen Plus software was used. After the tests, the characteristic curve, the specific deformation, the longitudinal elastic modulus, the rupture tension of each samples were determined, and on the basis of the load curves, the average deformation energy for each type of sample was calculated. The fracture of samples was analyzed with optical devices. Figure 2 shows the experimental equipment and some details from tests.

3. Results and Discussion

During the experimental investigations, numerous primary data were obtained that required processing so that the viscous-elastic behavior of pine wood can be characterized. Thus, in Figure 3 are presented the variations of the tensile-compression loading.

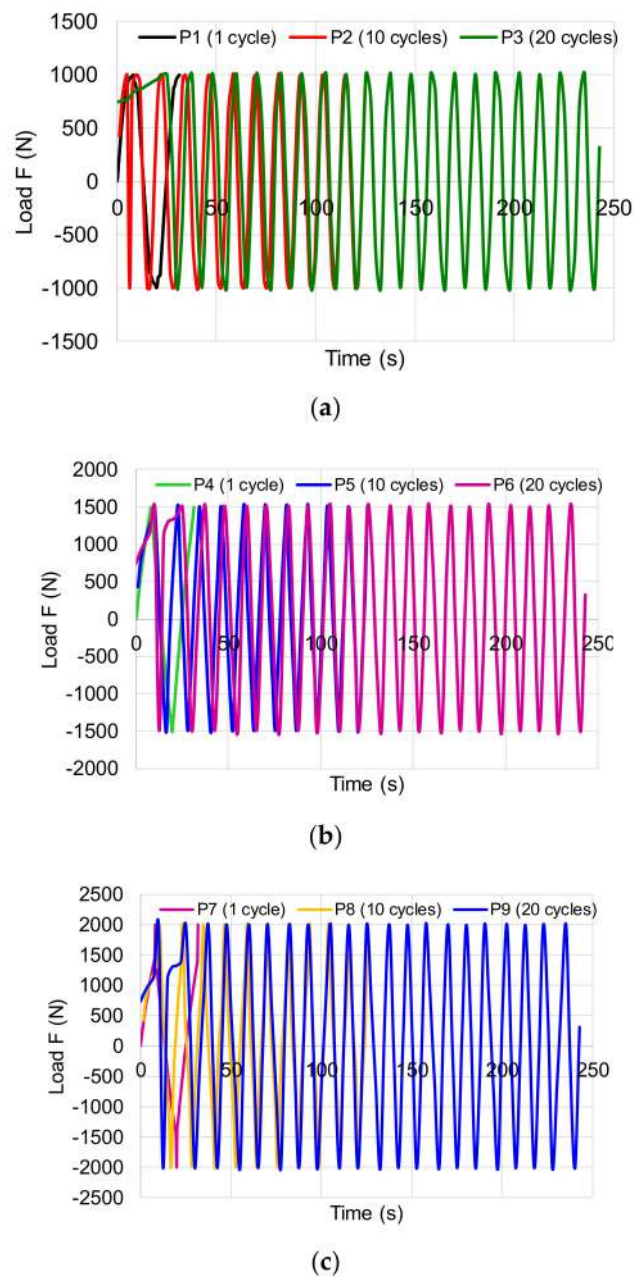


Figure 3. Variation of symmetric cyclic loading to tensile-compression: (a) ± 1000 N; (b) ± 1500 N; (c) ± 2000 N.

Figure 4 shows the hysteresis loop for the first stress cycle, being highlighted the values of lengthening and shortening the sample. The total strain range $\Delta\epsilon$ (the strains from A to C points) is calculated as total of tensile strain and compression strain containing both elastic and plastic strains. The true elastic strain range $\Delta\epsilon_e$ (the strains from A to D points) represents the recovery strain after a complete cycle and total true plastic strain range $\Delta\epsilon_p$ (the strains from D to 0 points) is the permanent strain after a complete loading cycle. The tensile recovered elastic strain from point B to point 0 can be observed in Figure 4a–f. In Table 2 are summarized the strains values for the first request cycle. Analyzing the six cases presented, it is observed that the lengthenings (traction strain) are greater than the shortenings (compression strain), pine wood being an anisotropic material, with a different behavior when subjected to traction, respectively compression. The difference between extensions and shortenings depends on the intensity of the force applied and the loading speed. As the applied load intensity increases, the percentage difference between traction and compression displacement increases, and as the load speed increases, they increase. Based on the Boltzmann superposition principle, which describes the response of a material to different loading histories and fitting the deformations peaks for each cycle [21,22], in Figure 5a–f are graphically represented the master curves covering the accumulated peak deformations in tensile (Figure 5a,c,e) and compression tests (Figure 5b,d,f). The behavior of the tested specimens differs in the two types of axial stresses. For the force of 1 kN and the stress rate of 1 mm/min, they can be distinguished in the graph in Figure 5a, the three wood-specific flow zones: the primary zone (primary flow) in which the displacements / deformations have a high growth rate from one cycle to another (the first four cycles), the secondary area in which there is a stagnation of displacements / deformations (the next 4–5 cycles), and finally, the tertiary creep in which there is again an increase in the speed of movement / deformation of the wood. This behavior is noticeable at low load speeds and low force intensities. As the force increases, the law of variation of the wood creep changes (Figure 5c,e). In the case of the variation of the compression strains, a rapid increase of them is observed with the increase of the stress cycles, regardless of the intensity of the force, as can be seen in Figure 5b,d,f. The main three zone in case of compression can be difficult distinguished, but the viscous-elastic behavior of wood is more pronounced in these cases (Figure 5c–f). These curves express the speed of accumulation of plastic deformations, which ultimately lead to damage of the structure.

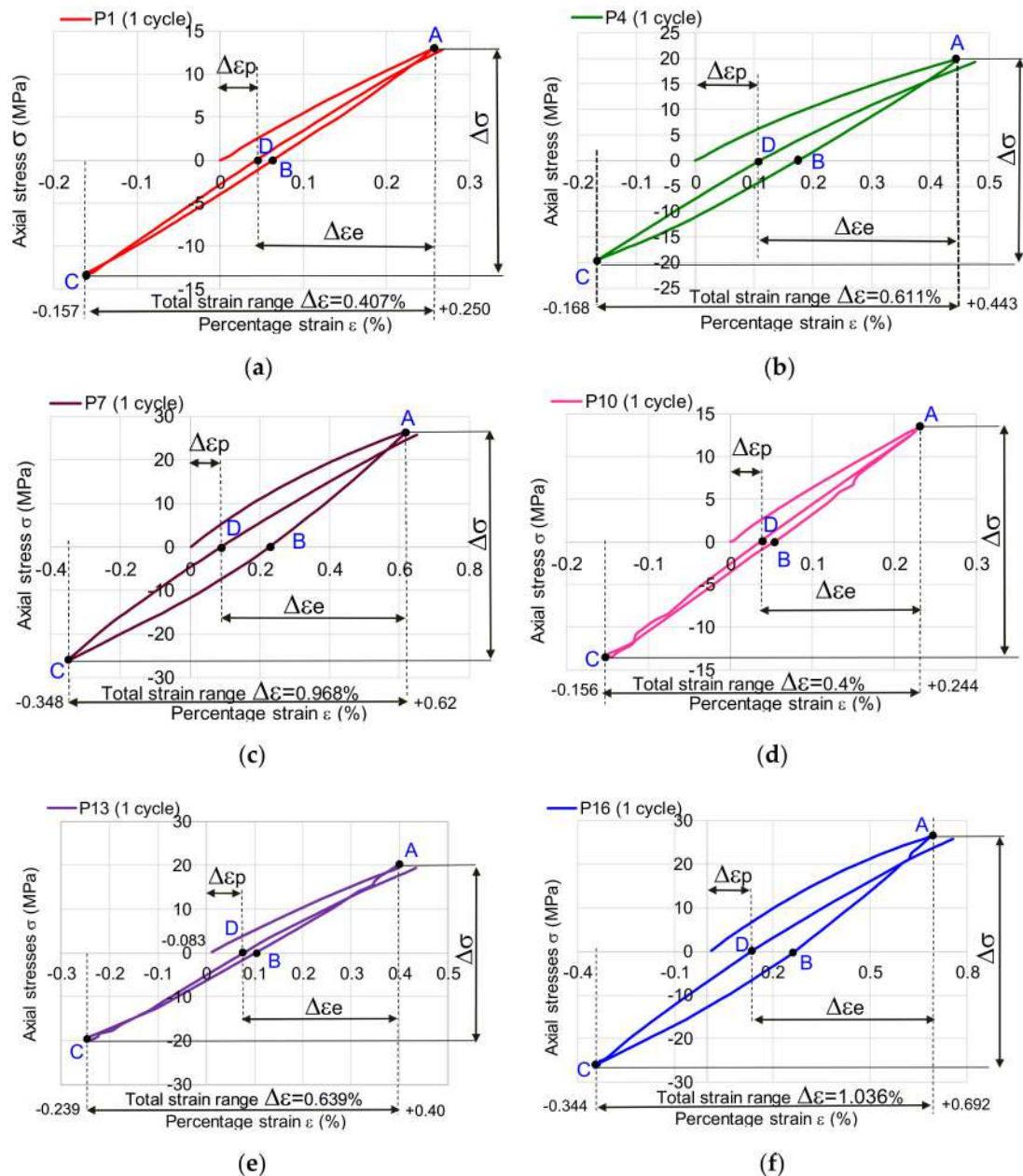


Figure 4. Hysteresis loops: (a) case of load speed of 1 mm/min and $F = \pm 1$ kN; (b) case of load speed of 10 mm/min and $F = \pm 1$ kN; (c) case of load speed of 1 mm/min and $F = \pm 1.5$ kN; (d) case of load speed of 10 mm/min and $F = \pm 1.5$ kN; (e) case of load speed of 1 mm/min and $F = \pm 2$ kN; (f) case of load speed of 10 mm/min and $F = \pm 2$ kN.

Table 2. The strains values collected for first cycle, where $\Delta\varepsilon$ is the total strain range; $\Delta\varepsilon_e$ —the true total elastic strain range; $\Delta\varepsilon_p$ —the true total plastic strain range; ε_t —elongation strain; ε_c —compression strain.

Set of Tests	$\Delta\varepsilon = \varepsilon_t + \varepsilon_c$ (%)	$\Delta\varepsilon_e$ (%)	$\Delta\varepsilon_p$ (%)	ε_t (%)	ε_c (%)
A1	0.407	0.2042	0.0458	0.250	0.157
B1	0.611	0.3422	0.1008	0.443	0.168
C1	0.969	0.5368	0.0832	0.620	0.349
A10	0.402	0.1982	0.0458	0.244	0.158
B10	0.639	0.3212	0.0788	0.400	0.239
C10	1.036	0.5566	0.1354	0.692	0.344

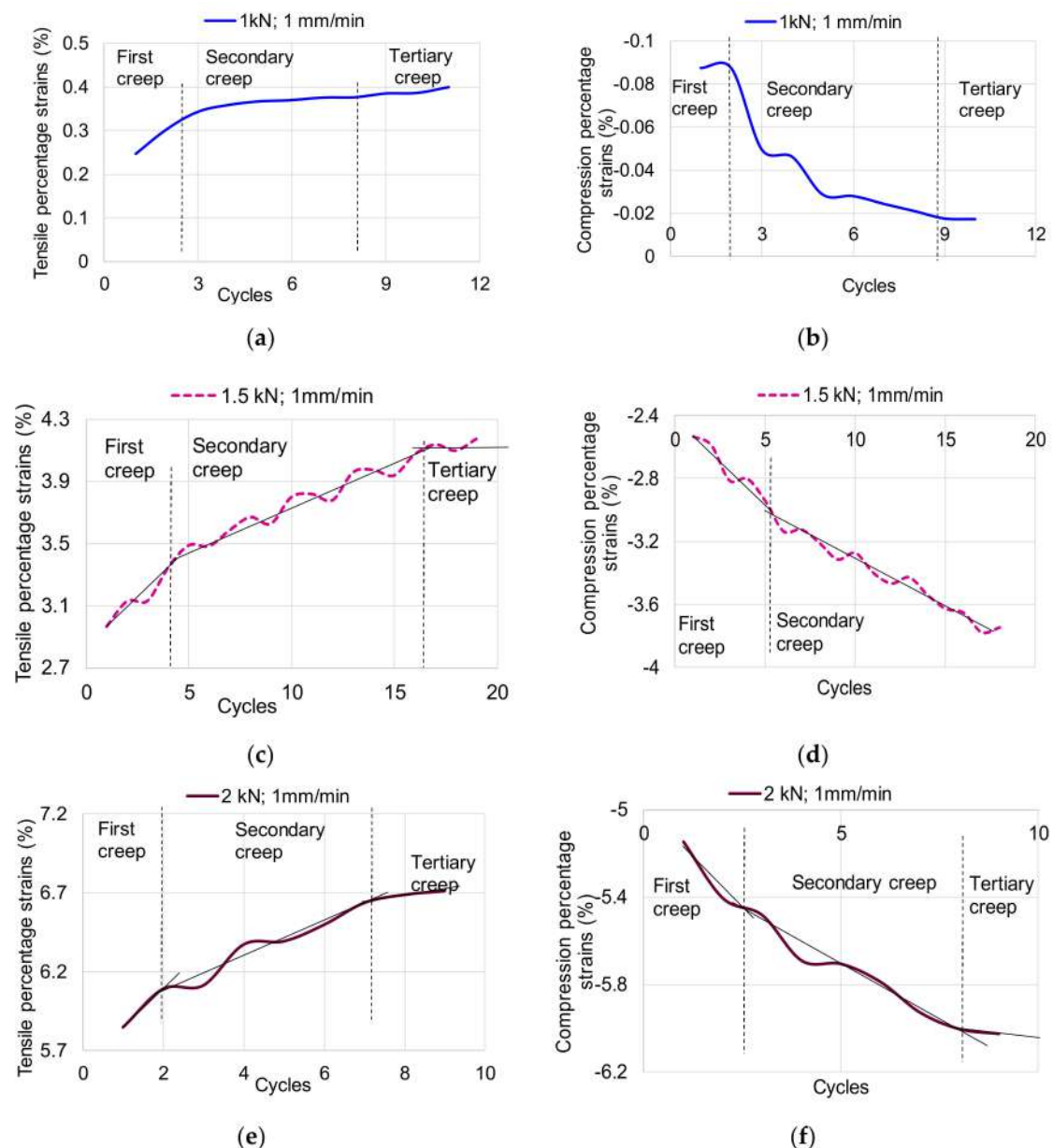


Figure 5. Master curves: (a) tensile strains of sample P3 subjected to 1 mm/min and $F = \pm 1$ kN; (b) compression strains of sample P3 subjected to 1 mm/min and $F = \pm 1$ kN; (c) tensile strains of sample P6 subjected to 1 mm/min and $F = \pm 1.5$ kN; (d) compression strains of sample P6 subjected to 1 mm/min and $F = \pm 1.5$ kN; (e) tensile strains of sample P9 subjected to 1 mm/min and $F = \pm 2$ kN; (f) compression strains of sample P9 subjected to 1 mm/min and $F = \pm 2$ kN.

The most important mechanical degradations occur in the first stress cycles as seen on the creep curve, specifically the first area (Figure 5). Thus, at a load of 1 kN, the longitudinal modulus of elasticity degrades by 12% of the initial value, compared to 20 cycles when the degradation is 15% of the initial value. (Figure 6). Increasing the loading intensity leads to increasing the degradation rate of 19% after 20 cycles in case of 1.5 kN and 28% in case of load of 2 kN. Increases the speed loading of 10 mm/min lead to a slight decreases of degradation rate (12%; 18% and 21% for each value of loading intensity). The obtained values are comparable with Ferreira et al. [23] which studied the pine wood samples subjected to tensile stresses. The mean value of elasticity modulus in the longitudinal direction parallel to the grain obtained by Ferreira et al. [23] is 4141 MPa, the sizes of samples being similar to those in the present study.

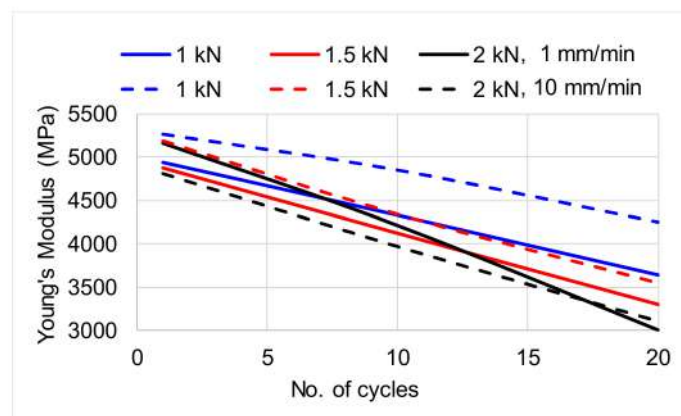


Figure 6. Degradation rate of Young's Modulus with cyclic loading.

The stress values are independent of the number of stress cycles and the stress rate. These have the same values both in traction and compression. The difference between the categories of values is given by the intensity of the applied loading. Thus, for the force of ± 1 kN, the average value of the maximum stress ranges between 13 and 14 MPa, for the force of ± 1.5 kN, the average value of the maximum stress is between 19 and 20 MPa, and for the force of ± 2 k, the average value of the maximum stress is between 26 and 27 MPa, as can be seen in Figure 7.

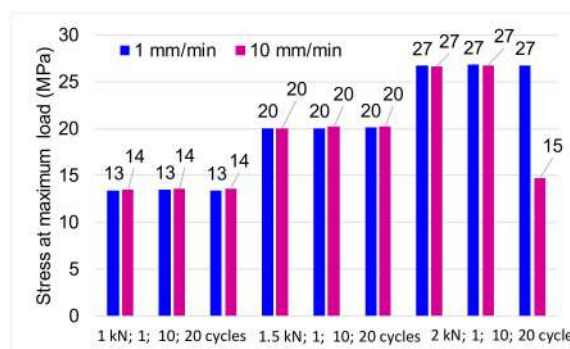
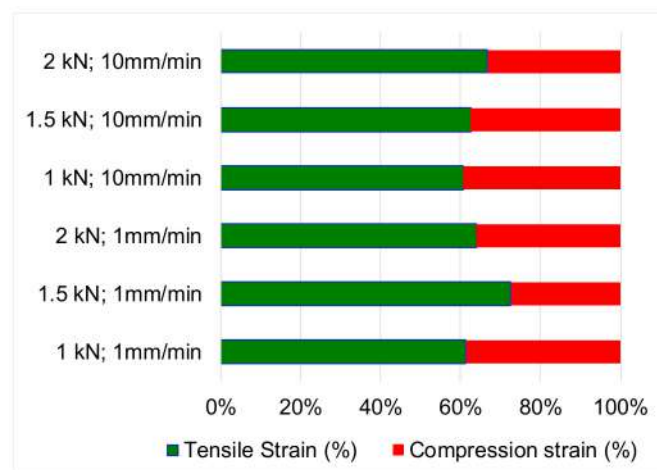


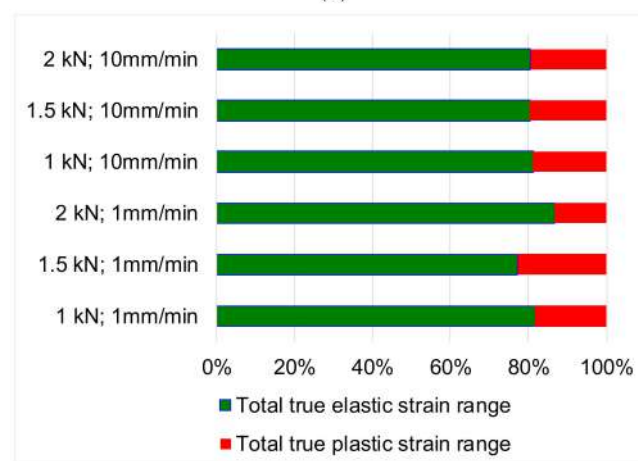
Figure 7. Variation of stresses at maximum load.

The values obtained give us an image of the quality class of the Scots pine samples studied, namely that they are part of quality class C45 according to wood standard. As the study was performed on small samples, it can be improved by additional studies on larger length samples to correlate the obtained results with the inhomogeneity and anisotropy of the material.

In Figure 8, the percentage variations of tensile and compression strains are presented for each studied case. The compression strains represent approximately 40% of the total deformation of the samples, the tensile strains being 60%. Due to the alternating symmetrical cycles, it is found that the total true plastic deformation represents approximately 20% of the total value of the deformations. This phenomenon occurs due to the fact that the wood fibers stretch beyond their flow limit, which leads to the appearance of viscous plastic deformations. During the compression stress, a part of the deformations produced at traction is recovered, adding to these the shortening of the wood, after which the resumption cycle. Thus, the structural degradation of pine wood occurs by the loss of wood resilience to tensile-compression stresses, changes that can be observed qualitatively in Figures 9 and 10, and quantitatively by changing mechanical properties. In practical applications, these phenomena can occur in the structural elements of the frames, at elements in the structure of stairs, furniture or buildings [24].



(a)



(b)

Figure 8. Comparison of strains in cases of different load speeds and intensity: (a) tensile and compression strains; (b) total true elastic and plastic strain range after a complete cycle.

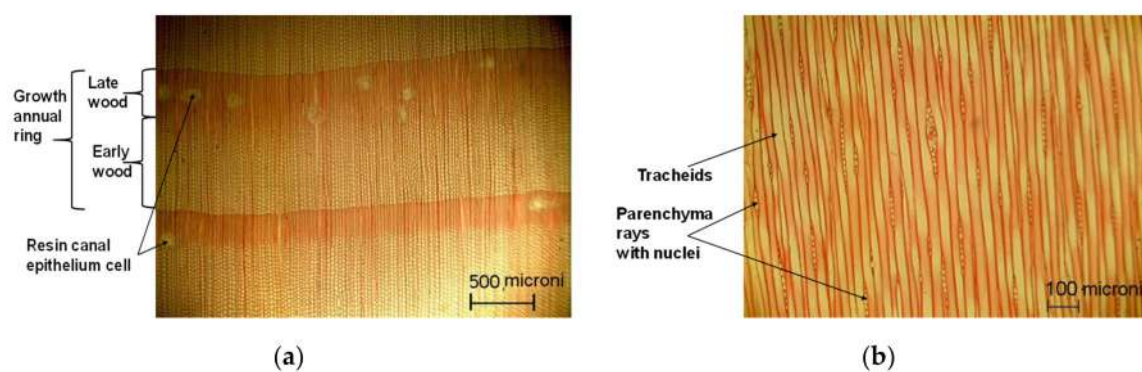


Figure 9. Cont.

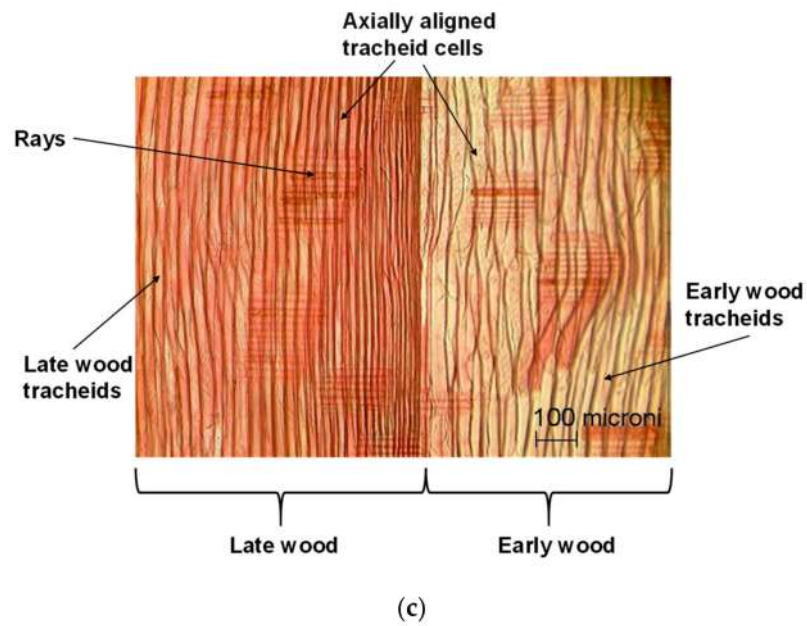


Figure 9. The microscopic view of Scots pine wood: (a) Cross section, magnification $\times 500$; (b) longitudinal—tangential section, magnification $\times 100$; (c) longitudinal—radial section, magnification $\times 100$.

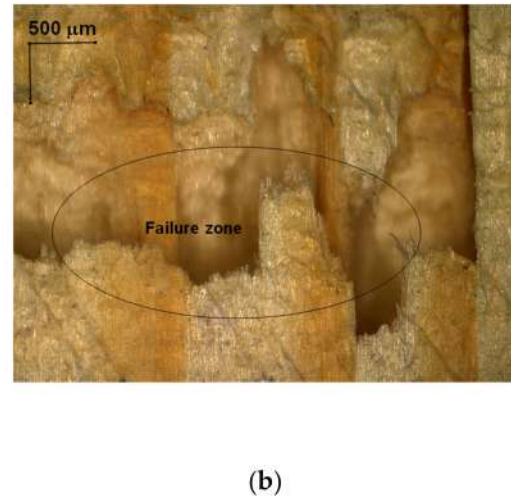
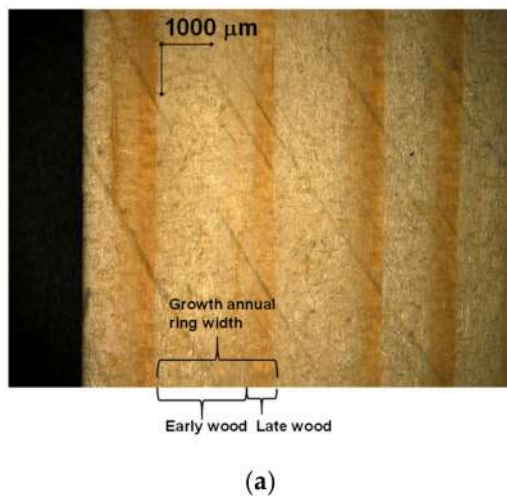


Figure 10. Cont.

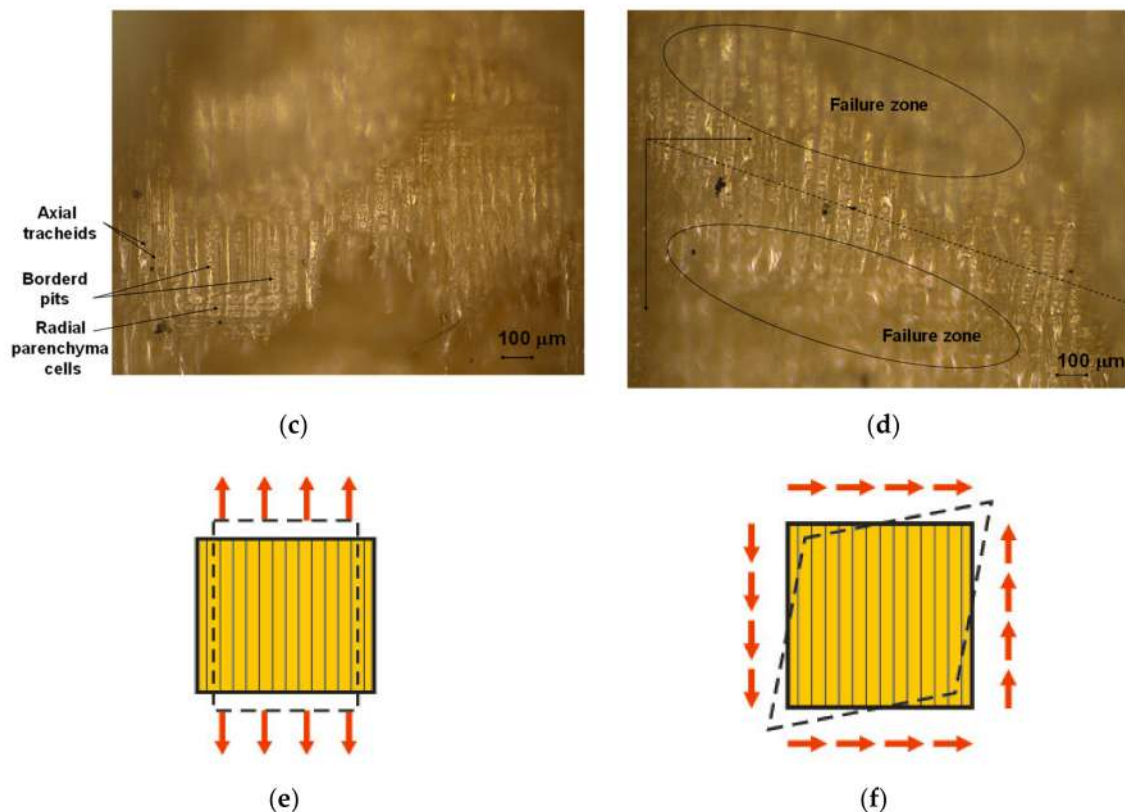


Figure 10. The structure of pine samples in different degradation stages: (a) initial macros-structure of wood samples, before test; (b) optical view of wood fracture after test; (c) microscopic view of tracheid cells failure, magnification $\times 100$; (d) failure trend line, magnification $\times 100$; (e) schematic representation of traction deformation; (f) schematic representation of wood failure due to anisotropy.

The microscopic structure of pine wood before loading can be seen in Figure 9, in the three main sections of wood. The annual rings are very distinctive and the differences between late wood and early wood are very visible (Figure 9a). Moreover, the resin canal can be observed in the transversal section. In the tangential-longitudinal section, the parenchyma rays with nuclei are very visible (Figure 9b). In the radial section, can be noticed the axially aligned tracheid cells with different sizes in late wood and early wood (Figure 9c).

However, due to the anisotropic characteristics of wood and the different strength of late wood and early wood layers, the fracturing mechanism does not occur in one direction [4]. Therefore, the rupture of the pine wood samples occurred at an angle of approximately 30 degrees to the direction of the fiber, as shown in Figure 10d. Because the failure plane is not perpendicular to the applied load direction, the tensile strength consists of the total or effective stress, which has normal and shear stresses as components, as claimed by Christoforo et al. [4] who studied the same phenomenon, but on tropical wood species. Analyzing the fracture of the pine wood samples subjected to tensile - compression uniaxial parallel to the fibers, it was found that the direction of normal stresses does not coincide with the main elastic directions, in addition to normal strains appear shearing strains, as shown by the generalized law of Hooke. At compression parallel to the fibers, the structural changes begin with the increase of the stress level, and the instability of the fibers is observed by the appearance of some macroscopic kinks [6,21,25]. The yielding of a material represents the transition from the initial state of a volume element from an elastic material to a different and irreversible state [12,26,27]. In the case of the specimen made of material with predominantly ductile behavior that is subjected to traction, the rupture occurs in successive stages (Figure 10): The peripheral areas yield under the action of tangential stresses, and the central area yields under the action of normal stresses.

Degradation of mechanical properties of wood samples subjected to symmetrical cyclic stresses accompanied by microstructure degradation of wood. If the structural damage in tension does not affect the stiffness degradation or the strength of the wood when a reversed load is applied in compression (stiffness recovery) as was shown in Figure 4, in contrary, the constitutive damage does reduce the tensile capacity of the material when a reverse loading from compression to tension is applied as Sirumbal-Zapata et al. [27] demonstrate in their study. In Figure 10b–d, all effects of mechanical phenomena as tensile softening brittle failure, stiffness cyclic degradation, and recovery after load-reversal, as well as compressive permanent plastic deformation due to ductile failure can be observed at microscopic levels. Gong and Smith [1], Pinho et al. [12], and Gutkin et al. [26] explain the phenomenon of kinks by the fact that tracheids in late wood have a higher rigidity than those in early wood. Thus, the first kinks develop between the late wood tracheids, at the boundary between two growth rings, the phenomenon spreading to the early wood tracheids. After cyclic traction-compression stresses, the buckling of the tracheids in the early wood results.

4. Conclusions

In this study, axially symmetrical cyclic loads (traction-compression) samples of pine wood in the direction parallel to the grain were tested. The degradation of the mechanical properties begins by the degradation of the wood structure as a result of the different resistance of the early wood and late wood layers, as well as the different viscous elastic responses to the traction and compression of the wood. Thus, after 20 alternately symmetrical cycles, the longitudinal modulus of elasticity decreases by approximately 28%, and with the increase of the loading speed, for some cases, there was even destruction of the samples. Also, the way of breaking the wood that occurs at an angle of approximately 30 degrees is noticed, which implies the appearance of shear stresses during the axially symmetrical cyclic stress. This study reveals that, in the strength calculations and in the design norms, it is necessary to introduce some coefficients that take into account the speed of wood degradation at cyclical stresses.

Author Contributions: Conceptualization, M.D.S. and V.S.; methodology, H.D.T. and M.D.S.; software, H.D.T.; validation, M.D.S. and V.S.; formal analysis, H.D.T. and M.D.S.; investigation, M.D.S. and H.D.T.; resources, H.D.T. and M.D.S.; data curation, M.D.S.; writing—original draft preparation, H.D.T. and M.D.S.; writing—review and editing, H.D.T. and V.S.; visualization, M.D.S.; supervision, V.S.; funding acquisition, M.D.S. and S.V. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Acknowledgments: We are grateful to Timar Cristina Maria for permission to use the microscopic views (Figure 9) from Catalog of micro-structural characteristics of materials for restoration and ecodesign (December 2009), CNCSIS Project IDEI 856/2008: Creation and implementation of a scientific research methodology on restoration—wood preservation and eco-design in the perspective of sustainable development. Project manager Chem. Maria Cristina TIMAR, Transilvania University of Brasov, Faculty of Wood Engineering). We are grateful to Transilvania University of Brasov, rector Ioan Vasile Abrudan for financial publication support.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Gong, M.; Smith, I. Short-term mechanical behaviour of softwood in high-stress-level compression parallel to grain. In Proceedings of the Fourth International Conference on the Development of Wood Science, Wood Technology and Forestry, Missenden Abbey, UK, 14–16 July 1999; pp. 25–34.
2. Ion, F.; Taranu, N.; Secu, A.; Entuc, I.S.; Scutaru, M.C.; Ungureanu, D. Evaluation of the wood strength class using the experimental approach. *Bull. Polytech. Inst. Iasi Constr. Archit. Sect.* **2017**, *63*, 121–132.
3. Silvestru Grigore, C.V.; Dinulică, F.; Spârchez, G.; Hălălișan, A.F.; Dincă, L.C.; Enescu, R.E.; Crișan, V.E. Radial Growth Behavior of Pines on Romanian Degraded Lands. *Forests* **2018**, *9*, 213. [[CrossRef](#)]
4. Christoforo, A.L.; Panzera, T.H.; Lahr, F.A.R. Estimation of tensile strength parallel to grain of wood species. *Eng. Agric.* **2019**, *39*, 533–536. [[CrossRef](#)]

5. Dai, D.; Fan, M. Wood fibres as reinforcements in natural fibre composites: Structure, properties, processing and applications. In *Natural Fibre Reinforcements. Materials, Processes and Applications*; Woodhead Publishing: Sawston, UK, 2014; pp. 3–65. [\[CrossRef\]](#)
6. Feio, A.; Machado, J.; Lourenco, P. Parallel to the grain behavior and NDT correlations for chestnut wood (*Castanea sativa* Mill). In Proceedings of the International Conference “Conservation of Historic Wooden Structures”, Florence, Italy, 22–27 February 2005.
7. Fakoor, M.; Sabour, M.H.; Khansari, N.M. A new approach for investigation of damage zone properties in orthotropic materials. *Eng. Solid Mech.* **2014**, *2*, 283–292. [\[CrossRef\]](#)
8. Gaff, M.; Gašparik, M. Effect of cyclic loading on modulus of elasticity of Aspen wood. *Bioresources* **2015**, *10*, 290–298. [\[CrossRef\]](#)
9. Konstantinov, A.Y.; Lomunov, A.K.; Iuzhina, T.N.; Gray, G.T., III. Investigation of wood anisotropy under dynamic loading. *Strength Ductility Probl.* **2018**, *80*, 555–565. [\[CrossRef\]](#)
10. Pečnik, J.G.; Kutnar, A.; Militz, H.; Schwarzkopf, M.; Schwager, H. Fatigue behavior of beech and pine wood modified with low molecular weight phenol-formaldehyde resin. *Holzforschung* **2020**. published online. [\[CrossRef\]](#)
11. Sharapov, E.; Mahnert, K.C.; Militz, H. Residual strength of thermally modified Scots pine after fatigue testing in flexure. *Eur. J. Wood Wood Prod.* **2016**, *74*, 875–884. [\[CrossRef\]](#)
12. Pinho, S.T.; Iannucci, L.; Robinson, P. Physically based failure models and criteria for laminated fibre-reinforced composites with emphasis on fibre kinking. Part II: FE implementation. *Compos. Part A* **2006**, *37*, 766–777. [\[CrossRef\]](#)
13. Yildirim, M.N.; Uysal, B.; Ozcifci, A.; Ertas, A.H. Determination of fatigue and static strength of scots pine and beech wood. *Wood Res.* **2015**, *60*, 679–686.
14. Hassani, M.M.; Wittel, F.K.; Hering, S.; Herrmann, H.J. Rheological Model for Wood. *Comp. Method Appl. M* **2014**, *283*, 1032–1060. [\[CrossRef\]](#)
15. Andrianopoulos, N.; Manolopoulos, V. Can Coulomb criterion be generalized in case of ductile materials? An application to Bridgman experiments. *Int. J. Mech. Sci.* **2012**, *54*, 241–248. [\[CrossRef\]](#)
16. Stanciu, M.D.; Şova, D.; Savin, A.; Iliáš, N.; Gorbacheva, G. Physical and Mechanical Properties of Ammonia-Treated Black Locust Wood. *Polymers* **2020**, *12*, 377. [\[CrossRef\]](#) [\[PubMed\]](#)
17. Stanciu, M.D.; Teodorescu, D.H.; Tămaş, F.; Terciu, O.M. Mechanical and Rheological Behaviour of Composites Reinforced with Natural Fibres. *Polymers* **2020**, *12*, 1402. [\[CrossRef\]](#) [\[PubMed\]](#)
18. EN 384. Structural Timber. In *Determination of Characteristic Values of Mechanical Properties and Density*; CEN European Committee for Standardization: Brussels, Belgium, 2004.
19. ASTM D143-14 Standard Test Method for Small Clear Specimen of Timber; American Society for Testing Material Standard: West Conshohocken, PA, USA, 2014.
20. EN 408. Timber Structures-Structural Timber and Glued Laminated Timber -Determination of Some Physical and Mechanical Properties; British Standards Institution: London, UK, 2003.
21. Varenik, K.A.; Varenik, A.S.; Sanzharovskij, R.C. Boltzmann principle of superposition in the theory of wood creep for deformations in time. In *IOP Conf. Series: Materials Science and Engineering*; IOP Publishing: Bristol, UK, 2018; Volume 441, p. 012057. [\[CrossRef\]](#)
22. Metri, V.; Briels, W.J. Brownian dynamics investigation of the Boltzmann superposition principle for orthogonal superposition rheology. *J. Chem. Phys.* **2019**, *150*, 014903. [\[CrossRef\]](#) [\[PubMed\]](#)
23. Ferreira, D.; Fonseca, E.; Pinto, C.; Borges, P. Tensile strength of pine and ash woods—experimental and numerical study. In Proceedings of the 6th International Conference on Mechanics and Materials in Design, Ponta Delgada, Azores, 26–30 July 2015.
24. Kloiber, M.; Drdácý, M.; Machado, J.S.; Piazza, M.; Yamaguchi, N. Prediction of mechanical properties by means of semi-destructive methods: A review. *Constr. Build. Mater.* **2015**, *101*, 1215–1234. [\[CrossRef\]](#)
25. Strömbro, J.; Gudmunson, P. Mechano-sorptive creep under compressive loading—A micromechanical model. *Int. J. Solids Struct.* **2008**, *45*, 2420–2450. [\[CrossRef\]](#)

26. Gutkin, R.; Pinho, S.T. Combining damage and friction to model compressive damage growth in fibre-reinforced composites. *J. Compos. Mater.* **2014**, *49*, 2483–2495. [[CrossRef](#)]
27. Sirumbal-Zapata, L.; Málaga-Chuquitaype, C.; Elghazouli, A. A three-dimensional plasticity-damage constitutive model for timber under cyclic loads. *Comput. Struct.* **2018**, *195*, 47–63. [[CrossRef](#)]



© 2020 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/>).



11th International Conference Interdisciplinarity in Engineering, INTER-ENG 2017, 5-6 October 2017, Tirgu-Mures, Romania

Reverse engineering in finite element analysis of the behaviour of lignocellulosic materials subjected to cyclic stresses

Mariana Domnica Stanciu^{*,a}, Amalia Florentina Ardeleanu^a, Horațiu Teodorescu Drăghicescu^a

^aTransilvania University of Brasov, Dep. of Mechanical Engineering, B-dul Eroilor nr. 29, Brasov, 500036, Romania

Abstract

In all engineering fields, continuous improvement of products and processes is being pursued. Reverse engineering is a fast and innovative method of converting a physical model into a virtual one based on its physical and mechanical characteristics. The paper aims to develop the geometric and numerical virtual model of the behavior of a lignocellulosic material subjected to cyclical stresses (tensile-compression) based on mechanical characteristics determined through experimental tests. The importance of this study consists of identifying the simulation method by comparing the experimental results with the numerical results (engineering objective) and developing the working methodology with effect in the education for sustainable development. Modeling with the finite element method (FEM) based on the physical model aimed to determine the results spectrum which are interpolating with the experimentally ones. Thus, the CAD model of the real sample was made by attributing its physical and elastic characteristics using the HyperMesh (preprocessing) and HyperWorks software (post-processing). The model was meshed into QUAD4 elements, after which it were simulated the cyclical stresses on tensile-compression in successive stages, keeping in memory of each stage the changes made at the structural level in the previous stage. Finally, the theoretical results were compared with the experimental ones. The obtained results provide information about distribution of stresses and strains on each layer of material according to the type of stress, traction or compression, for each loading cycle. The values obtained with FEA are close to the experimental ones. The minor differences are due to using an approximate decrease of the modulus of elasticity after each stress cycle. To obtained the real values of Young's Modulus after each cycle would have been necessary a big consumption of samples. The reverse engineering method has the advantage of material economy and the ability to carry out a large number of numerical models to replicate the material's behavior more accurately to cyclical loading and even improve its properties by designing a new material.

© 2018 The Authors. Published by Elsevier B.V.

Peer-review under responsibility of the scientific committee of the 11th International Conference Interdisciplinarity in Engineering.

* Corresponding author. Tel.: +40-740-555-566; fax: +40-268-410-525.

E-mail address: mariana.stanciu@unitbv.ro

Keywords: Reverse engineering (RE); cyclic loading; lignocellulosic materials; finite element analyses (FEA).

1. Introduction

The method called reverse engineering (denoted RE) is based on the partial or total reproduction of the geometric/physical properties of a real model. The process of capturing the digital image of some components is part of the reverse engineering method [1, 2]. Other researchers believe that this method is based on the production of components without the use of an engineering drawing [3, 4], and [5, 6] considered RE to be the development of a new geometry of a product by scanning an existing one and improving the CAD model after digital capture. In this paper, RE is used to analyze stress and strain states of wood samples subjected to cyclic loading – traction and compression, starting from the real test. The purpose of finite element analysis (denoted FEA) was to evaluate the possibility of using FEA for lignocellulosic materials, thus avoiding the consumption of samples and time for experimental tests. Thus, the analysis proceeded from the real behavior of cyclic pine wood samples, geometrically modeling samples and then simulating the cyclical loading. Finally, the spectrum of FEA results was evaluated, interpolated with experimental results.

Nomenclature

L	length of sample, in mm
b	width of sample, in mm
h	thickness of sample, in mm
E_L	Longitudinal Elasticity Modulus, in MPa
δ_{EL}	Decrement of E_L
G_{RT}	Transversal Elasticity Modulus, in MPa
δ_{GRT}	Decrement of G_{RT}
ν_{RT}	Poisson Coefficient
ρ	Density, in g/mm^3
F	axial loading, in N
$\Delta \ell$	Displacement, in mm
ε	strain, in [%]
σ	normal stress, in MPa

2. Finite element method applied on lignocellulosic samples

2.1. Preprocessing

In the real test, samples of radially-cut scots pine wood (*Pinus Sylvestris L.*), having the following dimensions: length $L = 150 \text{ mm}$, width $b = 15 \text{ mm}$, thickness $h = 5 \text{ mm}$ were analyzed. These were subjected to cyclic loading to tension and compression parallel with fibers (layers) with a force of 1000 N , using the LS100 Lloyd's Instruments test machine (Fig. 1, a and Fig. 2). The effective length of the specimen during the test was 100 mm . In the preprocessing stage performed in HyperMesh, the sample was modeled as a stratified material with one-dimensional layers of early wood (4 layers) and late wood (3 layers), having different mechanical characteristics (the wider layers represent the early wood, and the narrow - late wood). The material characteristics for each layer are shown in Table 1 and were taken from the literature [7]. Because of the relatively low of thickness and width of the layers, the material card – Mat 1 from HyperMesh library was used in the finite element analysis, which implies that each layer has homogeneous and isotropic properties, and in its entirety the sample will be a layered composite material. As far as boundary conditions are concerned, a grip in the test machine's rims was simulated. For this, the specimen was

fixed in the bottom on a distance of 22,5 mm. To simulate the load with a periodical variation, a RBE2 type element that distributes the force of 1000 N to the test area of the specimen was used in the finite element model (Figure 1). The discretization was made with QUAD4 type elements with the dimensions of 2,5 mm x 2,5 mm. In order to be able to simulate the cyclical load and damage to mechanical properties as accurately as possible, the hypothesis was adopted in which the value of the longitudinal elastic modulus of the material decreases by 500 MPa/cycle, and the transversal elasticity modulus by 100 MPa/cycle. The decrement values for each elasticity modulus were adopted based on results of successively simulation of cyclic loading with different values of decrement. The most appropriate value of strain and stresses compare to experimental ones were obtained using a decrements of 500 MPa/cycle in case of E_L and 100 MPa/cycle in case of G_{RT} .

Table 1. The mechanical properties of the main layers of wood samples (late wood and early wood).

Type of layer	Longitudinal Elasticity Modulus E_L (MPa) [1]	Decrement of E_L , δ_{EL}	Transversal Elasticity Modulus G_{RT} (MPa) [1]	Decrement of G_{RT}	Poisson Coefficient ν_{RT} [1]	Density ρ (g/mm^3)	Width b (mm)	Axial loading F (N)
Early wood	4340	500	770	100	0,3	3,1e-10	3,0	+/-1000
Late wood	9880	500	1590	100	0,3	6,3e-10	1,0	+/-1000

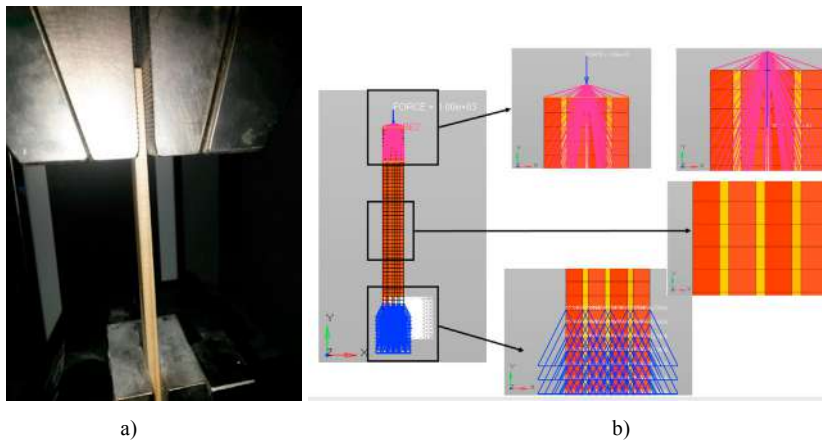


Fig. 1. (a) experimental gripping of specimen; (b) simulation of fixed and applied loading.

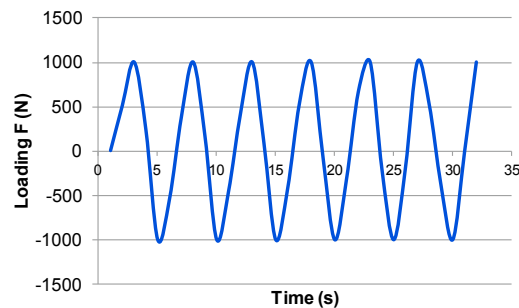


Fig. 2. The symmetric cyclic loading applied on samples.

2.2. Postprocessing

The postprocessing was performed in HyperWork, resulting in the variation of stresses and deformations with each stress cycle (Fig. 3 and 4). In Fig. 3, it can be seen that the length of the sample is extended at the tension stress compared to its shortening as a result of the compression stress of the first cycle.

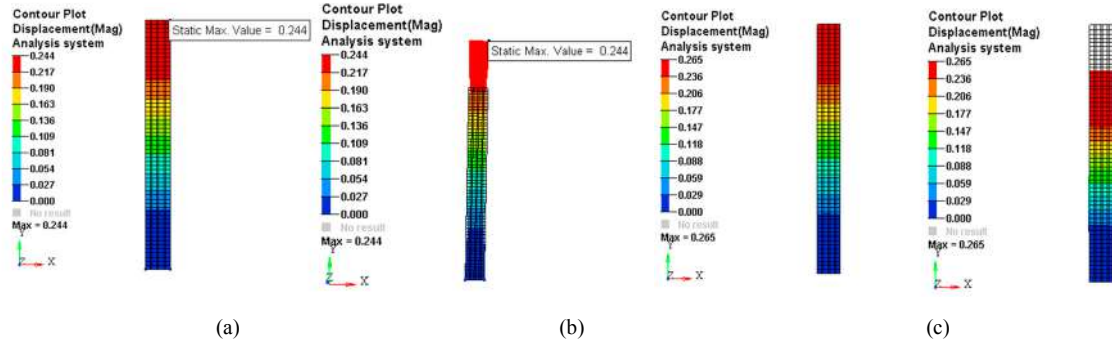


Fig. 3. (a) discretization model; (b) tensile strain; (c) compression strain.

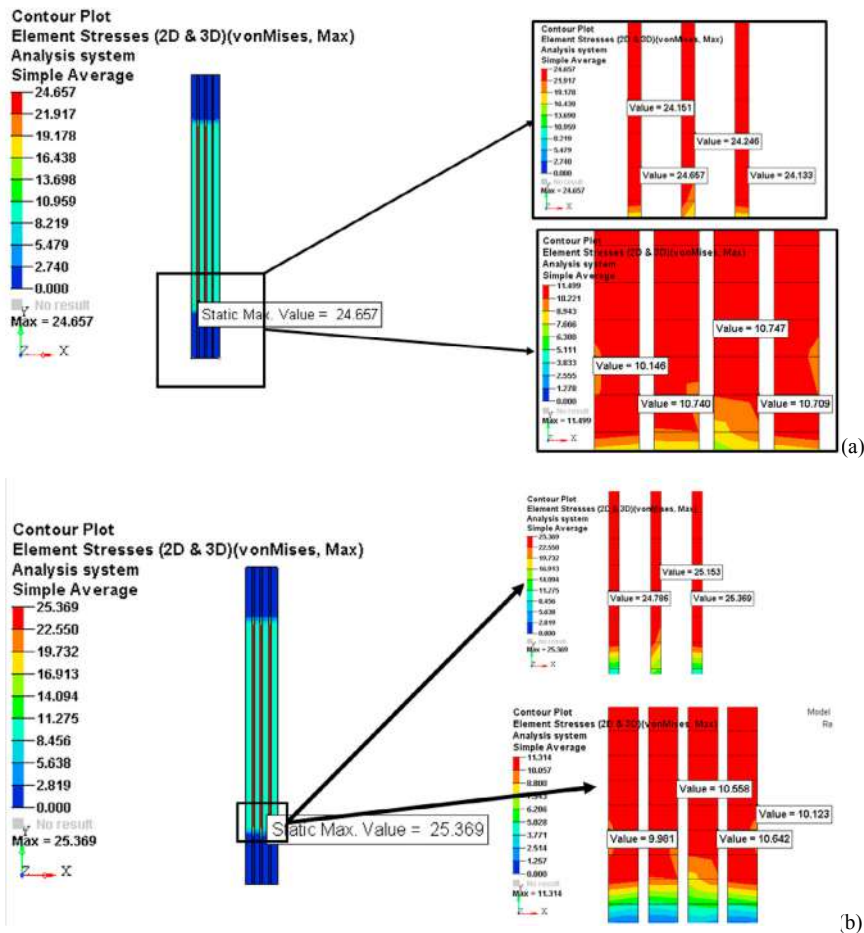


Fig. 4. (a) absolute values of tensile stresses; (b) absolute values of compression stresses both in early wood layer and late wood.

Thus, in order to simulate the structural behavior of the specimen with each stress cycle, each of the following cases keeps in mind the changes made at the structural level in the previous stress - strain and tension. Displacement values (lengths and shortenings) were extracted for each load cycle. Beside, the elastic properties were decreased to simulate the nonlinear behavior to fatigue. In Fig. 4 the traction / compression stress field is observed in both early and late. Both the shortening and the compression stress values are expressed as absolute values.

3. Results and discussion

3.1. Displacements

From the performed simulation, the values of the displacement were extracted for each type of loading and the strains were determined based on the calculation relations. In Table 2, besides the numerical values obtained are also the values determined experimentally. In Fig. 5 the displacements variation for each loading cycle is observed. With increasing number of cycles, displacements and, implicitly, strains increase by approximately 120% after 4 cycles and about 130% in the case of compressive stress. Comparing the FEA results with those obtained experimentally, we find that the trend of the deformation increase is similar to the modeling, but the curves describing this variation differ (Fig. 5).

Table 2. Values of displacements and strains obtained with FEM and experimental.

No. of cycle	Type of axial loading	Displacement Δl (mm) FEM	Total length L_i (mm)	Strain ε_{FEM} (%)	Displacement Δl (mm) EXP	Strain ε_{EXP} (%)
1	Tensile	0,24	100,24	0,240	0,224	0,374
	Compression	0,27	99,97	-0,269	0,044	-0,074
2	Tensile	0,29	100,26	0,290	0,077	0,129
	Compression	0,33	99,93	-0,329	0,115	-0,185
3	Tensile	0,38	100,31	0,380	0,361	0,601
	Compression	0,44	99,87	-0,438	0,374	-0,623
4	Tensile	0,53	100,40	0,530	0,440	0,734
	Compression	0,62	99,78	-0,617	0,290	-0,493

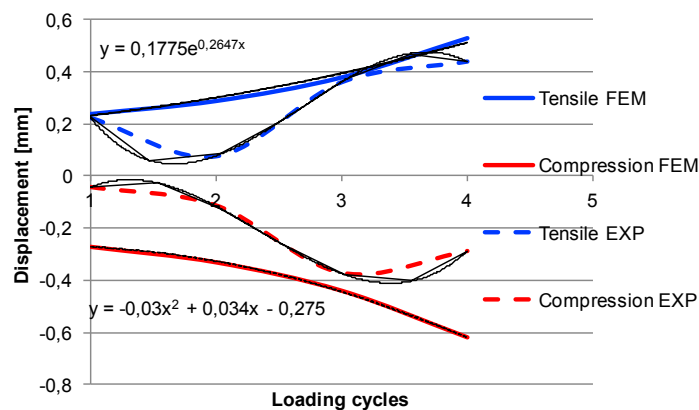


Fig. 5. Variation of displacement of sample with increasing of number of cyclic loading.

This is due both to the composite material theory on which the finite element software is based, as well as to the approaching method - the elastic characteristics of early woods and late wood with a constant value. In the FEA, the

each layer was modelled as orthotropic material and entire sample consist of alternate layers. The nonlinear behaviour of sample was obtained from combination of stresses and strain memory and from decreasing of elasticity modulus. Other used for wood modelling the theory of Hoffman Failure Criterion with modification to allow unequal maximum allowable stresses in tension and compression such as in timber [9].

3.2. Stress state

With respect to the von Mises stresses state determined by the finite element simulation, their maximum values were extracted for each layer at the adjacent points of the layers to analyze the variation of the normal stresses on the sample width (Table 3). It is noticeable that the early wood stresses are 56% lower than those in the late wood, due to both the longitudinal elastic modulus (lower wood stiffness of about 2 times the late wood) and its density. With the increase in the number of loading, the stresses in the early wood tend to decrease compared to the ones in the late wood, where there is a tendency to increase their value (Fig. 6, a).

This phenomenon explains the rupture of wood by delamination due to the occurrence of shear stresses at the interface between the two layers as the stress and strain differences and implicitly between the layers. According to [7, 8] the first phenomenon of wood failure occurs at the interface between early wood and late wood due to the different stiffness of the two layers.

Table 3. Values of stresses obtained with FEM and experimental (Legend: EW – early wood layer, LW- late wood layer).

Type of axial loading	The stresses on the vicinity points between layers of wood sample obtained with FEM σ (MPa)													
	EW1		LW2		EW3		LW4		EW5		LW6		EW7	
Tensile 1	10,15	10,74	24,42	24,66	10,75	10,00	22,77	23,21	10,28	10,71	24,22	24,13	10,65	10,18
Compression 1	-9,98	-10,4	-24,79	-25,18	-10,58	-10,43	-24,85	-24,94	-10,47	-10,64	-25,37	-24,81	-10,37	-9,94
Tensile 2	9,68	10,08	26,10	26,47	10,26	10,10	26,11	26,21	10,15	10,32	26,69	26,08	10,06	9,63
Compression 2	-9,30	-9,68	-27,63	-28,09	-9,86	-9,70	-27,68	-27,79	-9,75	-9,93	-28,33	-27,66	-9,66	-9,25
Tensile 3	9,80	9,34	30,13	29,55	8,82	8,94	29,29	24,25	7,31	8,70	29,60	30,45	9,46	10,01
Compression 3	-9,09	-8,67	-33,07	-32,42	-8,19	-8,32	-32,13	-29,67	-6,82	-8,06	-32,41	-33,36	-8,77	-9,30
Tensile 4	8,10	7,73	37,19	36,45	7,31	7,45	36,16	30,09	6,13	7,17	36,36	37,45	7,82	8,29

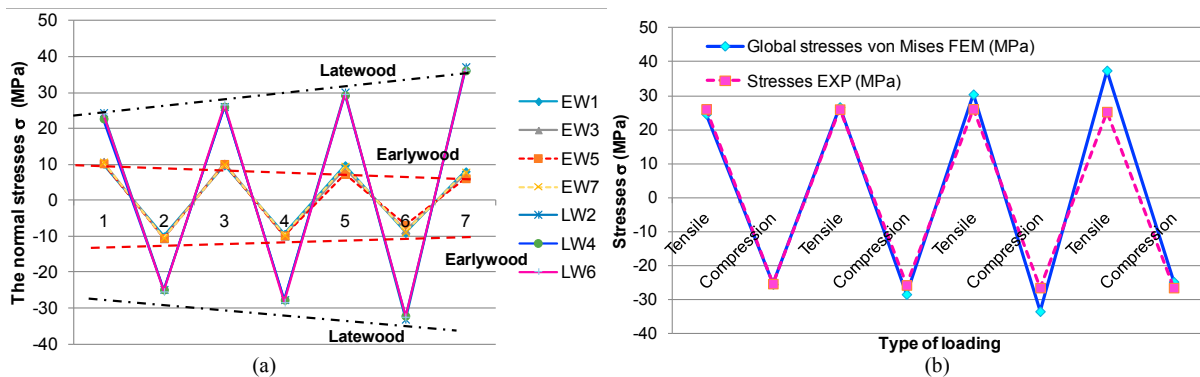


Fig. 6. a) variation of stresses with increasing of number of cyclic loading; b) variation of stresses with increasing of number of cyclic loading.

By analyzing comparatively the overall results of the experimentally determined and the simulated stresses, it is observed that the error increases by more than 5% starting with the third application cycle, which is explained by the

difference between the theory of computing the software in the linear domain and the nonlinear phenomena which take place in wood at the fatigue (Fig. 6, b).

Applying the reverse engineering in stress and strain analysis with finite element method is very useful to simulate the behavior of wood structure which in real test is difficult to measure such as the stresses state in each layer of wood structure.

Thus, in Fig. 7 it can be noticed the variation of stresses on each layer with increasing the loading cycles. The value of tensile stresses are higher than compression and compare to [10], the values are similarly. The compression stresses has lower values related to tensile stress both with FEM and experimental. In the case of a specimen made of predominantly ductile-containing material subjected to traction, rupture occurs in successive stages: the peripheral areas yield under tangential stresses (interfaces between layers), and the central area yields under the normal stresses [11].

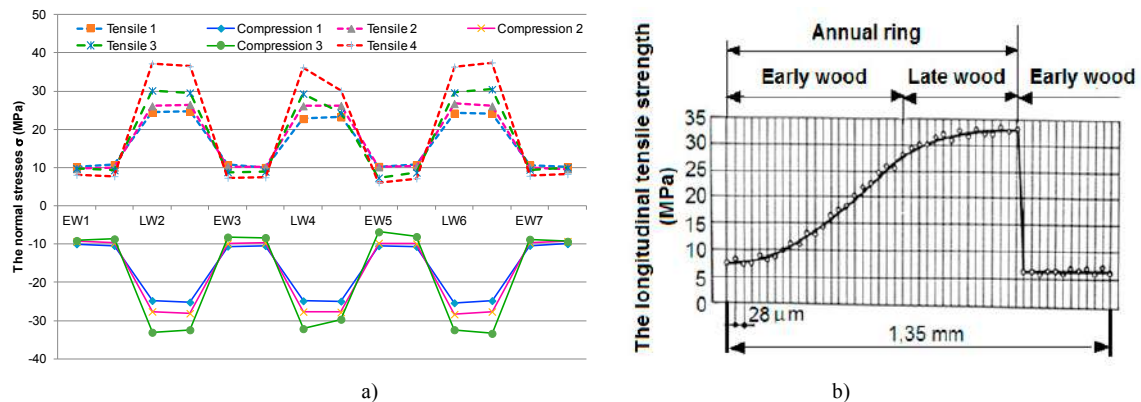


Fig. 7. a) The variation of normal stresses on layers for each loading cycle; b) the variation of longitudinal tensile strength obtained experimental by [10].

4. Conclusions

The paper aimed to apply the reverse engineering method to the finite element analysis of a layered composite material such as wood, starting from the experimental results obtained on pine wood specimens loading in longitudinal radial direction with alternating symmetrical traction-compression cycles. Following the study, it can be concluded that the FEA method reverses the global behavior of the tested samples, the results obtained with the 5th - Theory of Materials Resistance being suitable for cyclical stresses in the finite element simulations in the HyperMesh software. The finite element analysis was performed in the elastic field using as a factor for the approximation of the visco-elastic behavior of the wood, the decreasing of the elastic modulus for the late wood and the early wood. In order to obtain more accurate results (with an error below 5%), in terms of finite element calculation, it is recommended that there be better coordination between the force applied per cycle and the correlation of the mechanical characteristics with an exponential function in the case of traction and a polynomial in case of compression. To obtain a better correlation between FEA and experimental results, iteratively adjusting the parameters of the virtual model will be performed in order to achieve a behavior as close as possible to the real model.

Acknowledgements

This paper was supported by Program partnership in priority domains - PNIII under the aegis of MECS - UEFISCDI, project no. PN-III-P2-2.1-BG-2016-0017/85 SINOPTIC, project manager Stanciu M.D.

References

- [1] S. Cramer, D. Kretschmann, R. Lakes, T. Schmidt, Earlywood and latewood elastic properties in loblolly pine, *Holzforschung*, 59 (2005) 531–538.
- [2] S. Motavalli, R. Shamsaasef, Object-oriented modelling of a feature-based reverse engineering system, *Int. J. of Comp Integ. Man.* 9 (1996) 354–368.
- [3] R.J. Abella, J.M. Daschbach, R.J. McNichols, Reverse Engineering Industrial Applications, *Computers & Industrial Engineering* 26 (1994) 381–385.
- [4] Z. Xie, Z., Wang, J. & Zhang, Q., “Complete 3D measurement in Reverse Engineering using a multi-probe system”, *International Journal of Machine Tools & Manufacture*, 45(2005) 1474–1486.
- [5] N. Singh, Reverse Engineering – a General Review, *International Journal of Advanced Engineering Research and Studies*. 2 (2012) 24–28.
- [6] V. Raja, in: Raja V., Fernandes K.J. (Eds) *Reverse Engineering an Industrial Perspective*, cap. Introduction to Reverse Engineering, Springer, (2008) 1–9.
- [7] G. Meng, S. Ian, Short-term mechanical behaviour of softwood in high-stress-level compression parallel to grain. *The Fourth International Conference on the Development of Wood Science, Wood Technology and Forestry*. Forest Products Research Centre, Buckinghamshire Chilterns University College, High Wycombe, England. (1999) 25–34.
- [8] X. Yang, M. Gong, H. Chui, Short Term Creep Behaviour of CFRP-Reinforced Wood Composites Subjected to Cyclic Loading at Different Climate Conditions, *BioResources* 9 (2014) 1845–1857.
- [9] N. Tankut, A. N. Tankut, M. Zor, Finite Element Analysis of Wood Materials, *Drvna Industrija*. 65 (2014) 159–171.
- [10] I. Curtu, N. Ghelmeziu, *The mechanics of wood and wood based materials* (in Romanian language), Ed. Tehnica, Bucuresti, Romania. (1984) 156–157.
- [11] I. Curtu, M.N. Baba, M.D. Stanciu, Comparison of breaking theories studied for different wood species (beech, spruce, pine), in *Orasul Inteligent - Lucrarile editiei a XI a a Conferintei Anuale Zilele Academice ale ASTR*, 6–7 oct. 2016, Tg Mures, Ed AGIR. (2016) 169–174.

Oak particles size effects on viscous-elastic properties of wood polyester resin composite submitted to ultraviolet radiation

M. D. Stanciu¹ · V. Bucur² · C. S. Vâlcea¹ ·
A. Savin³ · R. Sturm⁴

Received: 14 April 2017
© Springer-Verlag GmbH Germany 2017

Abstract The aim of this paper is to use dynamic mechanical analysis to examine the modifications of the elasto-dynamical properties of a composite made of small waste oak particles of various sizes (0.04 and 1 mm) and a polyester resin (440-M888 POLYLITE), subjected to photo-degradation by UV radiation and thermal degradations induced by temperature variations between 30 and 120 °C. Oak (*Quercus robur*) waste particles used in this study were the unmerchantable by-product left after converting logs into lumber. The size of the waste oak particles significantly modifies the morphological and mechanical properties of lignocellulosic composites. On the other hand, UV radiation and thermal degradation are recognized as factors causing structural modification observed at the interface between the particles and the matrix. The rheological parameters (storage modulus E' , loss modulus E'' and damping $\tan \delta$) and the glass transition temperature were determined both before and after UV treatment with the DMA242 C Netzsch instrument. Structural morphological modifications related to the impact of photo-degradation on fibres and the matrix were observed with an atomic force microscope. A strong nonlinear effect of particle size on the mechanical and rheological properties of the composites was observed.

✉ M. D. Stanciu
mariana.stanciu@unitbv.ro

¹ Transilvania University of Brasov, 29 Eroilor Blvd, 500036 Brasov, Romania

² School of Science, RMIT University, Melbourne, VIC 3001, Australia

³ Nondestructive Testing Department, National Institute of Research and Development for Technical Physics, 47 D. Mangeron Blvd, 700050 Iasi, Romania

⁴ University of Ljubljana, Aškerčeva 6, 1000 Ljubljana, Slovenia

Introduction

Natural fibres like flax, hemp, jute, sisal, kenaf, coir, kapok, banana or wood particles are widely used in numerous types of bio-composite due to their ecological, biodegradable and remarkable physical and mechanical properties as well as their versatility. These composites are exposed to environmental and technological risks such as high relative humidity, temperature, UV radiation, reducing their resistance to various loadings. Sometimes, during wood-based composites manufacturing and especially during the mixture of two phases (reinforcing elements and matrix), congestion of natural fibres or particles leads to the formation of a stress concentrator and to low cohesion between the matrix and fibres (Ndiaye et al. 2012, 2013). Low thermal stability, dimensional variability of wood particles because of swelling and shrinkage phenomena, the presence of voids and other defects contribute to the low mechanical properties of wood-based composites (Ratanawilai et al. 2014; Kim et al. 2006).

Durability of wood-based composites is strongly affected by adverse environmental factors such as variations in relative air humidity, temperature, UV radiation, chemical and biological agents. Exposure to ultraviolet radiation triggers changes in the chemical structure on the composite surface, a phenomenon known as photolysis. At the same time, free radicals are formed by the dissociation of the C–H bonds in the polymer chains (Bismarck et al. 2006; Varganici et al. 2016). Simultaneous exposure to UV radiation and to temperature variations accelerates the degradation processes that occur in lignocellulosic composites, such as oxidation, chemical attack, degradation of the morphological characteristics of the surface, lowering the mechanical properties and reducing the occurrence of creep (Beg and Pickering 2008; Matuana and Kamdem 2002; Matuana et al. 2011).

Studies reported by Azwa et al. (2013) and Peng and Cao (2016) on wood-based composites (plastic wood composite) analysed the influence of several factors, such as particle volume fraction/resin, size of wood particles or fibre type used as reinforcing elements, on the mechanical properties of composites. The matrix used for the cohesion of the reinforcing elements was polypropylene (PP) or polyethylene (PE) (Ndiaye et al. 2012; Kim et al. 2006; Ratanawilai et al. 2014). Studies on lignocellulosic composites with polypropylene and polyethylene matrices have shown that the exposure to UV radiation modified the physical and mechanical properties of a thin superficial surface layer. The intensity of the degradation is different in the matrix and wood particles, the damaged layer having a rough appearance due to the deterioration of the polypropylene matrix (Peng and Cao 2016; Cerbu et al. 2010; Butylina et al. 2012). Photo-degradation is the main effect of UV environmental radiation on polymeric materials, which is shown by the following phenomena: breaking of chemical bonds between the polymer chain which leads to the formation of free radicals by dissociating C–H bonds from the polymer chains and to the oxidation of its surface as a result of peroxide radicals. These chemical reactions induced micro-cracking on the matrix and at the interfaces with fibres, weakening the composite (Darie et al. 2011; Maxwell et al. 2005). From a mechanical point of view, the exposure of lignocellulosic composites to UV

radiation can produce modifications of the elastic characteristics and can induce stress concentrations at the surface of the polymeric material (which can lead to its premature failure) (Teacă et al. 2013; Bodîrlău et al. 2009).

Moreover, an important role in the degradation of lignocellulosic composites is played by the size of the wood particles. During aggregation, the composites reinforced with small-sized particles have high surface energy, which diminished the adherence between particles and matrix and which implicitly leads to the increase in composite failure risk (Bagherpour 2012; Cipriano et al. 2013; Guo et al. 2014). However, it was observed that the composites reinforced with 0.2-mm particles have high moduli of elasticity and tensile strength. The same situation was observed for the composites made with polypropylene matrix (PP) (Stark and Berger 1997). Mechanical properties of wood plastic composites (WPC), determined by tensile and bending tests, show an increase in elasticity modulus E and yield modulus simultaneously with the increase in the particle size between 0.1 and 0.2 mm. These mechanical parameters are lower for composites with larger particles (1.00–4.00 mm) (Gozdecki and Wilczynski 2015). Rheological properties of wood-based composites are improved, if wood fibres are chemically treated. This effect is due to the extraction of low molecular weight compounds acting as plasticizers on the lignin-based matrix (Villani et al. 2017).

The literature is very scarce on the effects of various oak particles sizes on mechanical properties of lignocellulosic composites subjected to photo- and thermal degradation.

The aim of this paper is to examine the effects induced by UV radiation and thermal degradation on viscous-elastic properties of a composite having two main constituents: small waste oak particles of various sizes and a polyester resin (440-M888 POLYLITE). This polyester resin is used for outdoor applications due to its high resistance to environment factors. The effects of thermal degradation in terms of glass transition and heat deflection temperature were detected by thermal dynamical mechanical analysis. Atomic force microscope (AFM)-type NTEGRA Probe Nano-laboratory was used to monitor the morphological changes of the surface after photo- and thermal exposure in terms of mean square roughness (R_q).

Materials and methods

Sample preparation

Oak particles

Oak waste particles were collected from a sawmill of oak logs (*Quercus robur*), harvested from the Carpathian Mountains.

Granulometric analysis (equipment Fritsch) was used to grade oak waste particles into five classes, with sieves of the following sizes: 1, 0.4, 0.2, 0.1 and 0.04 mm. Oak particles were conditioned at 5–6% moisture content, and their specific gravity was determined with a pycnometer.

Oak particles were graded by size into five classes, namely: less than 0.04 mm; in the range 0.04 – 0.1 mm; in the range 0.1 – 0.2 mm; in the range 0.2 – 0.4 mm; and in the range 0.4 – 1 mm. Volume fibre fraction of 25% was kept constant for all composite specimens. The particles were mixed with 440-M888 POLYLITE—orthophthalic unsaturated polyester resin. The physical and mechanical properties of polyester resin are presented in Table 1.

For each type of materials reinforced with particles of a certain size, specimens were made by moulding. In this way, five types of composites were produced. The specimens were labelled as follows:

- L 0.04 Wood particles smaller than 0.04 mm;
- L 0.1 Wood particles between 0.04 and 0.1 mm;
- L 0.2 Wood particles between 0.1 and 0.2 mm;
- L 0.4 Wood particles between 0.2 and 0.4 mm;
- L 1.0 Wood particles between 0.4 and 1 mm.

In total, 10 specimens were produced. Table 2 summarizes the characteristics of these specimens.

Equipment

Viscous-elastic properties of specimens were determined with the dynamic mechanical analysis method, using the analyser DMA242 C Netzsch, Germany.

Before and after the UV radiation the surface morphology of the specimens was evaluated by the atomic force microscope (AFM)-type NTEGRA Probe Nanolaboratory, in semi-contact mode, by using a NSG 10 cantilever type, at a constant force. AFM measurements were processed by the NOVA 1.0.26 RC1 software which enables the measurement of roughness and the calculation of the average

Table 1 Characteristics of unsaturated polyester resin 440-M888 POLYLITE at 23 °C

Properties	Units	Value	Tested method
Brookfield viscosity LVF	mPa s(cP)	1100–1300	ASTM D 2196-86
Density	g/cm ³	1.10	ISO 2811-2001
PH (max.)	mgKOH/g	24	ISO 2114-1996
Styrene content	% of weight	43 ± 2	B070
Curing time: 1% Norpol peroxide 1	Minutes	35–45	G020
Tensile strength	MPa	50	ISO 527-1993
Longitudinal elasticity modulus	MPa	4600	ISO 5271993
Elongation	%	1.6	ISO 527-1993
Bending strength	MPa	90	ISO 178-2001
Elasticity modulus at bending	MPa	4000	ISO 178-2001
The shock resistance P4J	mJ/mm ²	5.0–6.0	ISO 179-2001
Volume contraction	%	5.5–6.5	ISO 3521-1976
Glass transition temperature	°C	62	ISO 75-1993

Table 2 Physical and geometric characteristics of tested specimens

Sample	Length L (mm)	Width l (mm)	Thickness h_i (mm)	Mass m_i (mm)	Density ρ (kg/m ³)
L 0.04–1	47.64	10.28	4.14	2.47	1218
L 0.04–2	49.89	10.23	4.27	2.67	1225
L 0.1–1	49.12	10.42	4.24	2.59	1193
L 0.1–2	47.41	10.51	4.09	2.45	1202
L 0.2–1	48.42	10.07	4.33	2.51	1188
L 0.2–2	50.00	10.15	4.73	2.87	1195
L 0.4–1	48.89	10.11	4.62	2.67	1169
L 0.4–2	49.95	10.00	4.35	2.56	1178
L 1.0–1	48.32	10.37	4.40	2.53	1147
L 1.0–2	49.99	10.03	4.41	2.55	1153

surface roughness (Coşniță 2014). 3D and 2D images were taken. The images of phase contrast of each sample were analysed for determining the surface roughness (R_q) which was determined for each specimen taking into account the root-mean-square average of the roughness profile ordinates for a surface of 0.025 mm².

Experimental set-up

Dynamic mechanical analysis (DMA) was used to determine the mechanical properties of specimens before and after treatment. The specimens were submitted to bending dynamic loading. The dynamic test with DMA consisted of two parts. Complex elastic modulus E^* , with its two components (the storage modulus E' and the loss modulus E''), and the damping factor $\tan \delta$ were determined firstly under isothermal conditions ($T = 30$ °C) and isochronous conditions ($t = 30$ min), by the variation of the loading frequency ($f = 1, 5, 10, 50$ Hz) with amplitude of 0.03 mm and secondly by the variation of temperature conditions in the range of 30–120 °C, with the rate of 2 °C/min. Accelerated photo-degradation process of the specimens was produced in a cylindrical chamber equipped with three fluorescent lamps, 18 W, Philips, situated at 120° with respect to each other. Specimens were clamped to a metal stand designed in such a way to expose evenly the entire surface to UV radiation. Specimens were exposed to UV-A radiation with a wavelength λ of 365 nm for 168 h (7 days), checking every 24 h the integrity and the clamping of the specimens. After exposure to UV radiation and temperature variation with DMA, the roughness surface of the specimens was re-evaluated by the atomic force microscope. Surface morphology of the specimens was measured with the atomic force microscope following the procedure specified in ISO 4287/1.

Results and discussion

In this section, the results will be commented concerning the UV effects on viscous-elastic properties of specimens under isothermal conditions and the effect of thermal degradation on specimen behaviour.

UV effects on viscous-elastic properties of wood-based composites— isothermal conditions ($T = 30\text{ }^{\circ}\text{C}$ (constant), $t = 30\text{ min}$)

Figure 1 shows the variation of E' modulus as a function of time of exposure, measured for two frequencies, 1 and 50 Hz, for the following specimens L 0.04, L 0.1, L 0.2, L 0.4 and L 1.0 submitted to UV radiation, compared with untreated reference specimens.

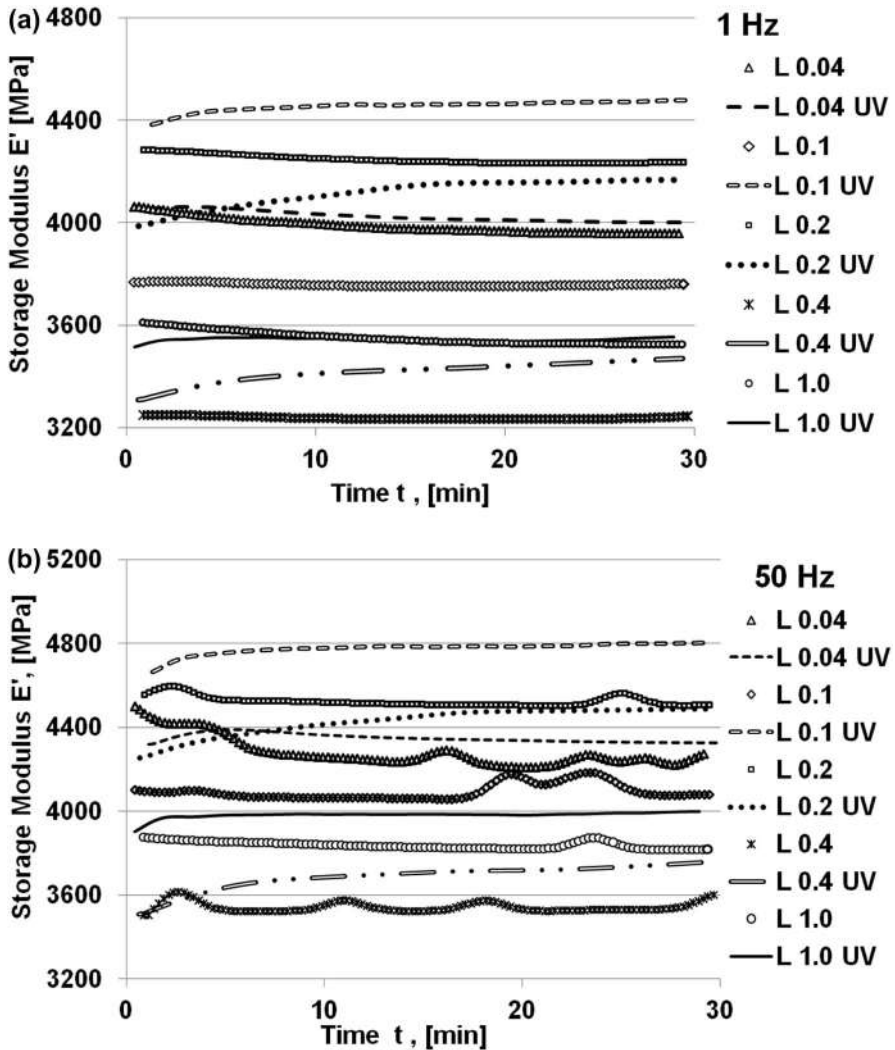


Fig. 1 Variation of storage modulus E' versus time in isothermal conditions for UV-exposed specimens and for reference, untreated specimens. Legend: **a** 1 Hz frequency loading; **b** 50 Hz frequency loading. UV—ultraviolet treatment; the code of the specimens is L 0.04, L 0.1, etc.

As a general trend, it was observed that UV radiation exposure caused increasing specimens' stiffness, induced by the specific behaviour of the resin. This trend is regardless of frequency. This observation is in agreement with Benini et al. (2011). However, a particular behaviour was observed in the case of the composites reinforced with particles of 0.2 mm, for which after UV exposure, a decrease in storage modulus was observed. A similar behaviour was noticed in the polypropylene matrix composites reinforced with wood particles of 0.25 mm in size (Terciu and Curtu 2012; Pothan et al. 2003; Romanzini et al. 2013). Prior to UV treatment, characteristic peaks at 50 Hz frequency loading were observed. These peaks show the effect of lignin components in oak particles (Villani et al. 2017). After UV treatment, the disappearance of the resonance peaks attributable to lignin was observed, confirming the chemical reaction, generating free radicals into the polyester resin.

Figure 2 shows the variation of the complex modulus E^* as a function of frequency in the range 1–50 Hz. On this graph, three zones of frequency were observed, namely between 1 and 5 Hz, between 5 and 10 Hz, and between 10 and 50 Hz. For all composites specimens the complex modulus increased from 1 to 5 Hz. In the second zone, the complex modulus is quite constant. In the third zone, again an increase in E^* modulus values was observed.

Regarding the viscous behaviour influenced by UV radiation, the most spectacular difference was observed for the composite with 1-mm particle, for which the loss modulus E'' increased by almost 77% after UV treatment. The smallest variation of the complex module was in the case of specimens reinforced with the smallest particles (0.04 mm) (Table 3).

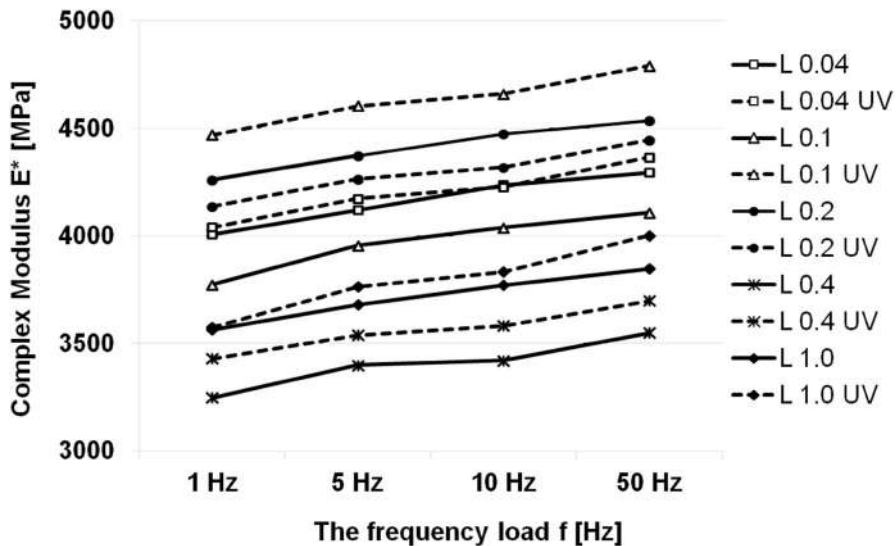


Fig. 2 Variation of the complex modulus E^* as a function of loading frequency, for UV exposure of specimens and for reference, untreated specimens

Table 3 Average values of loss modulus E'' for each loading frequency

Frequency (Hz)	Average value of loss modulus E'' (MPa)														
	L 0.04	L 0.04 UV	%	L 0.1	L 0.1 UV	%	L 0.2	L 0.2 UV	%	L 0.4	L 0.4 UV	%	L 1.0	L 1.0 UV	%
1	377	367	− 3	338	363	7	326	390	19	243	276	12	289	464	60
5	361	362	0	369	365	− 1	299	383	28	258	270	5	269	445	66
10	324	380	18	339	389	15	287	402	40	239	288	17	256	453	77
50	314	367	17	312	373	19	272	380	39	210	274	23	256	416	62

It can be recognized that variations in the storage modulus were determined by micro-structural modifications induced by cyclical loading. Given the fact that the specimens were subjected to dynamic bending, extreme tensions have been developed in the upper and lower layers. On these zones, the effect of UV radiation is significant and is due to cross-linking processes occurring in the polymer (Pepper 2016; Pothan et al. 2003).

Other interesting aspects of viscous-elastic properties of specimens are related to the variations in the internal friction as a function of time and temperature, as shown in Figs. 3 and 4.

As shown in Fig. 3, in general, for all studied specimens, after exposure to UV radiation, an increase in internal friction was observed with increasing particles size. Two exceptions are worth commenting. For specimens having very small wood particles (< 0.04 mm), the internal friction was firstly reduced after the specimen's photolysis, during the first 10 min. However, in the range 10–30 min, the internal friction increases with time. This phenomenon can be explained by the fact that the UV exposure accelerates the cross-linking processes on the polyester resin, the very small wood particles being included in polymer chains, determining a quasi-homogeneous structure of the composite. The larger the particles, the higher the deformation energy dissipated into the matrix and into the reinforcing elements, depending on the viscous-elastic characteristics of wood particles and polyester resin. However, as mentioned by Essabir et al. (2016) increasing loading frequency caused $\tan \delta$ decreases and therefore it can be seen that the material's capacity to absorb deformation energy decreases. On the other hand, with increasing loading duration, the internal frictions increase and the relaxation process is inhibited irrespective of the size of wood particles as noticed by Pothan et al. (2003) and Romanzini et al. (2013). The damping variation in case of the composites reinforced with particles of size 0.2–1 mm is clearly different (Fig. 3c, e).

The effect of thermal degradation

The effect of thermal degradation was studied in the temperature range between 30 and 120 °C. The effect of temperature on viscous-elastic behaviour of polyester composites reinforced with wood particles was observed on specimens exposed to five steps of temperature ranging from 30 to 120 °C, with a heating rate of 2 °C/min,

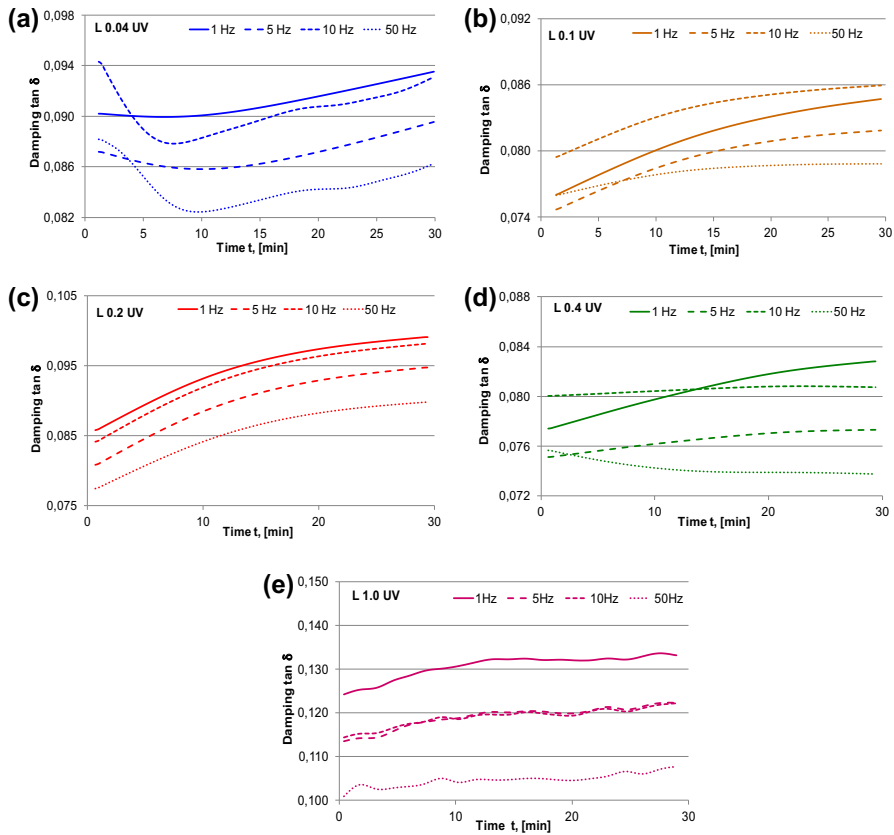


Fig. 3 Variation of internal friction expressed by $\tan \delta$ versus the time of loading, for photo-degradable specimens and for reference, untreated specimens, in frequency range 1 Hz, 5 Hz, 10 Hz and 50 Hz. Legend: **a** specimen L 0.04; **b** specimen L 0.1; **c** specimen L 0.2; **d** specimen L 0.4; **e** specimen L 1.0

for 45–50 min. The specimens were also subjected to a bending force of 6 N, with a frequency of 1 Hz. Figure 4 shows the variation of internal friction expressed by $\tan \delta$ as a function of temperature, for photo-degradable specimens and for reference, untreated specimens, in the temperature range between 30 and 130 °C.

It can be seen that the glass transition temperature increases for samples exposed to UV radiation compared to untreated specimens. With temperature increasing, three transition zones of damping were observed, namely: the first zone in temperature interval 30–60 °C, the second zone in the temperature interval 60–90 °C and the third zone within the interval 90–120 °C. It is noted:

1. In the first temperature zone, the damping curves are almost identical for both control specimens and UV-exposed specimens, irrespective of the size of wood particles (Fig. 4a–e). In this temperature range, the effect of UV radiation is not significant for the specimens reinforced with particles smaller than 0.4 mm. For composite having wood particle of 1 mm, the photo- and thermal degradation

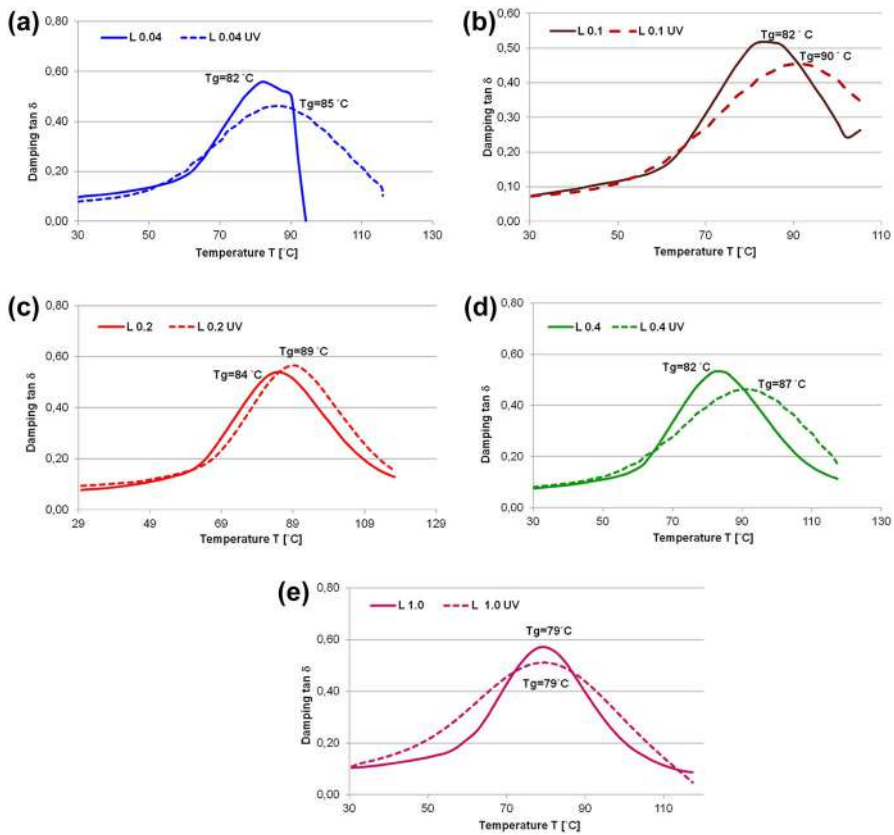


Fig. 4 Variation of internal friction expressed by $\tan \delta$ as a function of temperature, for photo-degradable specimens and for reference, untreated specimens, in temperature range between 30 and 120 °C. Legend: **a** specimen L 0.04; **b** specimen L 0.1; **c** specimen L 0.2; **d** specimen L 0.4; **e** specimen L 1.0

processes have a greater impact on the modifications of viscous-elastic behaviour of composites. UV-exposed samples have an increased slope. The matrix reacts differently with increasing temperature and UV radiation (Fig. 4e). Polyester resin loses its capacity to transmit internal adhesion forces to reinforcing elements. Bell-shaped zones on the diagram designate the relaxation behaviour of resin in its state of transition, when the matrix-reinforcing particles system starts the glass transition process (Terciu and Curtu 2012; Romanzini et al. 2013; Peng et al. 2014).

- In the second zone of temperature 60–90 °C, differences were observed on the slope of curves, on the values of damping coefficient and on the transition temperature. Modifications of glass transition temperature (Table 4) were induced by oxidative and thermal degradation of the polyester resin and shrinking phenomena of wood particles. UV treatment (dashed line) alternates the position of the peak, but the magnitude is not increased significantly.

3. A third creep zone is observed at temperatures above 90 °C, where the damping curve changes its slope. Thermal degradation process is illustrated by the significant drop of $\tan \delta$ values. Composites properties degradation is owed by transition temperature of the matrix and by thermal phenomena related to wood particles. Heating of the lignocellulosic composites leads to the evaporation of water in wood; the eliminated OH groups emphasize the production of oxidative reactions in the micro-structure of the composite. The deflection temperature (HDT, heat deflection temperature) is shown in Table 4.

Deflection temperature expresses thermal stability of the composite. It is worth mentioning Pepper (2016) and Essabir et al. (2016) who noted that for a specimen having particles of maximum 0.25 mm, the transition temperature is around 80 °C, which corresponds to the polyester resin transition temperature. The larger difference in glass transition temperature is observed in composites reinforced with particles of 0.1 mm (about 8 °C). This difference decreased with increasing particle size. It is interesting to point out that for untreated specimens, the transition temperature was the same for all the specimens reinforced with particles ranging from 0.04 to 0.4 mm, namely 82 °C. The increasing size of the wood particles from 0.4 to 1 mm introduced equilibrium between photolysis and thermal degradation processes of the polyester matrix. For example, the 1-mm UV-treated wood particle composite specimen has the same transition temperature as the non-treated specimen, 79 °C (Table 4). When comparing glass transition temperature of typical polyester resin (of 90 °C) with that of the composites reinforced with wood particles and the polyester matrix, it is noted that their transition temperature is lower by about 11–12%, which is in agreement with data of Guo et al. (2014) and Peng et al. (2014).

Figure 5 gives the variation of loss modulus E'' versus storage modulus E' (Cole–Cole diagrams) for all studied specimens. The influence of the reinforcing particle size is observed at the beginning of the loading (in the elastic field, if $E' < 1000$ MPa), when the slopes of the curves are characteristic of each type of specimens (Fig. 5a–e). Cole–Cole diagrams are asymmetric for all samples. This is

Table 4 Average values of glass transition temperature T_g , for each type of specimens before and after exposure to UV radiation

Samples	Before UV		After UV		$\Delta T_g = T_{g, UV} - T_g$, (°C)	Heat deflection temperature for untreated specimens, HDT (°C)	Heat deflection temperature for UV-treated specimens, HDT _{UV} (°C)
	T_g (°C)	Damping $\tan \delta$	T_g , (°C)	Damping $\tan \delta$			
L 0.04	82	0.558	85	0.461	3	79	79
L 0.1	82	0.519	90	0.455	8	77	81
L 0.2	82	0.538	89	0.565	7	83	82
L 0.4	82	0.533	87	0.456	5	80	78
L 1.0	79	0.570	79	0.510	0	80	77

in agreement with the fact that amorphous polymeric materials, at glass transition, exhibit several relaxation phenomena that can be attributed to molecular rearrangements (Bodîrlău et al. 2009; Chaochanchaikul et al. 2012).

Morphological structural modification analysis

Morphological structural changes due to UV radiation exposure are illustrated with images at the microscopic level with AFM. Figure 6 shows 3D images and phase contrast images for the surface of each analysed specimen before and after the exposure to UV radiation.

Phase contrast images for untreated specimens illustrate chemically a homogeneous surface, which is in contrast to the surface after UV exposure when some chemical compounds migrate to the specimen's surface. On the specimen's surface, some lignin black spots are observed, showing that its composition is non-homogeneous. This observation is in agreement with Chaochanchaikul et al. (2012). Lignin molecules are known to exhibit the greatest susceptibility to oxidative degradation (Saha et al. 2014; Cheng et al. 2015; Stanciu et al. 2016). The ATR-

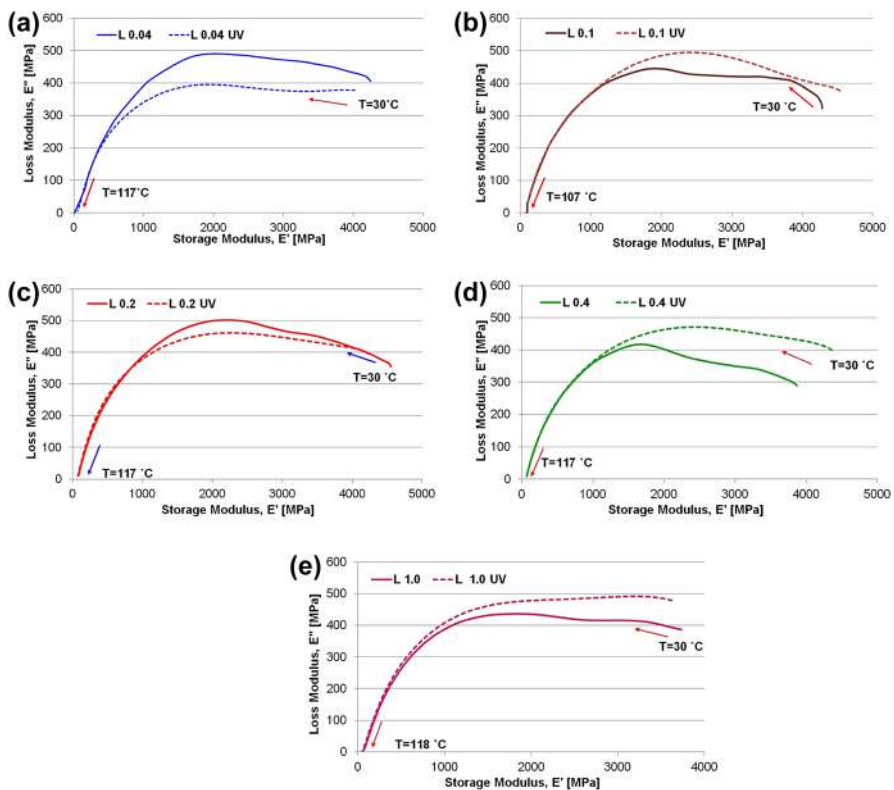


Fig. 5 Cole–Cole diagrams for each type of lignocellulosic composite specimens studied. Legend: **a** composites with 0.04-mm particles; **b** 0.1 mm; **c** 0.2 mm; **d** 0.4 mm; **e** 1 mm

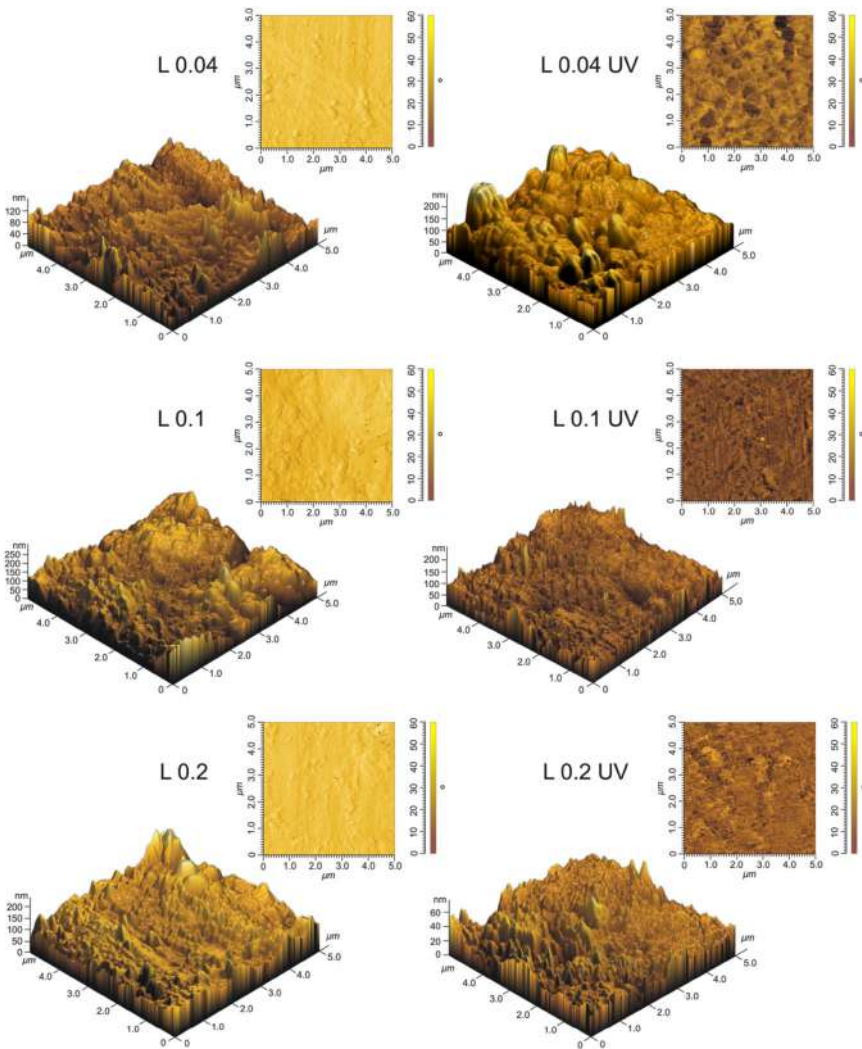


Fig. 6 Comparison among 3D images and phase contrast images for the surface ($5 \times 5 \mu\text{m}^2$) of each analysed specimen non-treated and exposed to UV radiation

FTIR spectroscopy analysis and FT-Raman spectroscopy performed by Cogulet et al. (2016) confirm that the wood colour evolves from yellow to brown (0–168 h), caused by the photo-sensitivity of α and β carbon in lignin (Fig. 7), as explained with the present model. The cleavage of β -O-4 linkage and the free rotating linkages give more flexibility to the macromolecule of lignin (Saha et al. 2014).

Surface roughness (R_q) was determined for each specimen with root-mean-square average of the roughness profile ordinates for a surface of 0.025 mm^2 (Fig. 8).

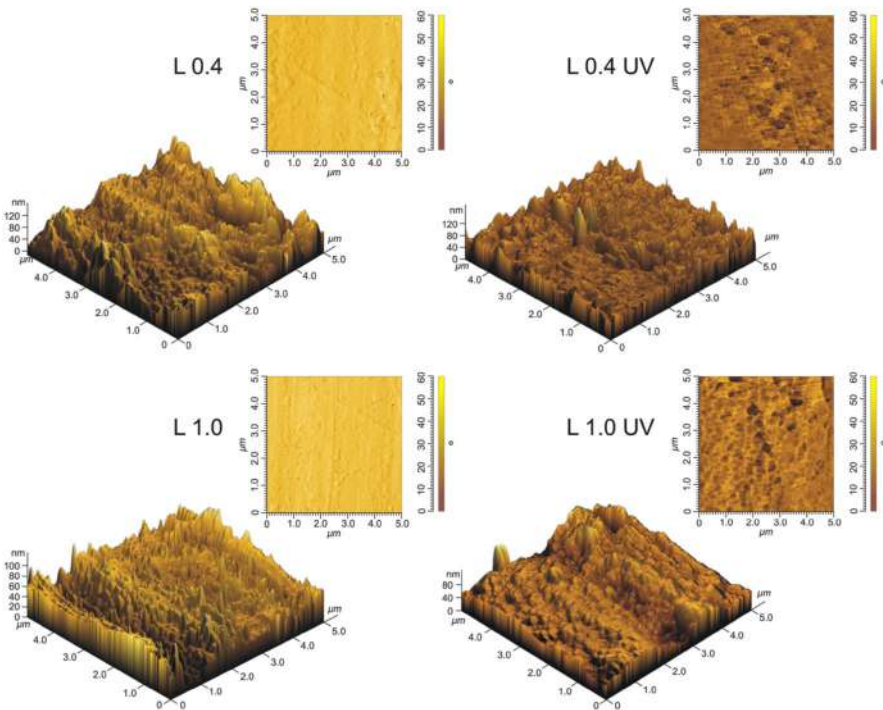


Fig. 6 continued

In general, two tendencies were observed. The first case is that of specimens whose roughness increased after the exposure to UV radiation, showing an oxidative degradation of the specimen surface reinforced with wood particles of 0.04 mm in size (L 0.04). The second case is that of specimens which recorded decreased roughness with tens of nanometres (nm) after exposure to UV. These specimens are morphologically unstable (L 0.1, L 0.2 and L 0.4). In the case of the present experiment, the most stable specimens are the specimens with polyester resin reinforced with 0.04- and 1-mm oak particles.

Conclusion

This study assessed the size effects of waste oak particles ranging from 0.04 to 1 mm on elasto-dynamical properties of a composite with two components, the oak particles and a polyester resin, submitted to UV radiation and to thermal degradation determined with DMA.

The size of the particles ranging between 0.04 and 1 mm has a small effect on the viscous-elastic behaviour of wood-based composites manufactured with these oak particles and polyester matrix and submitted to UV radiation. However, in this context, the highest effect of UV radiation on the complex module E^* was recorded

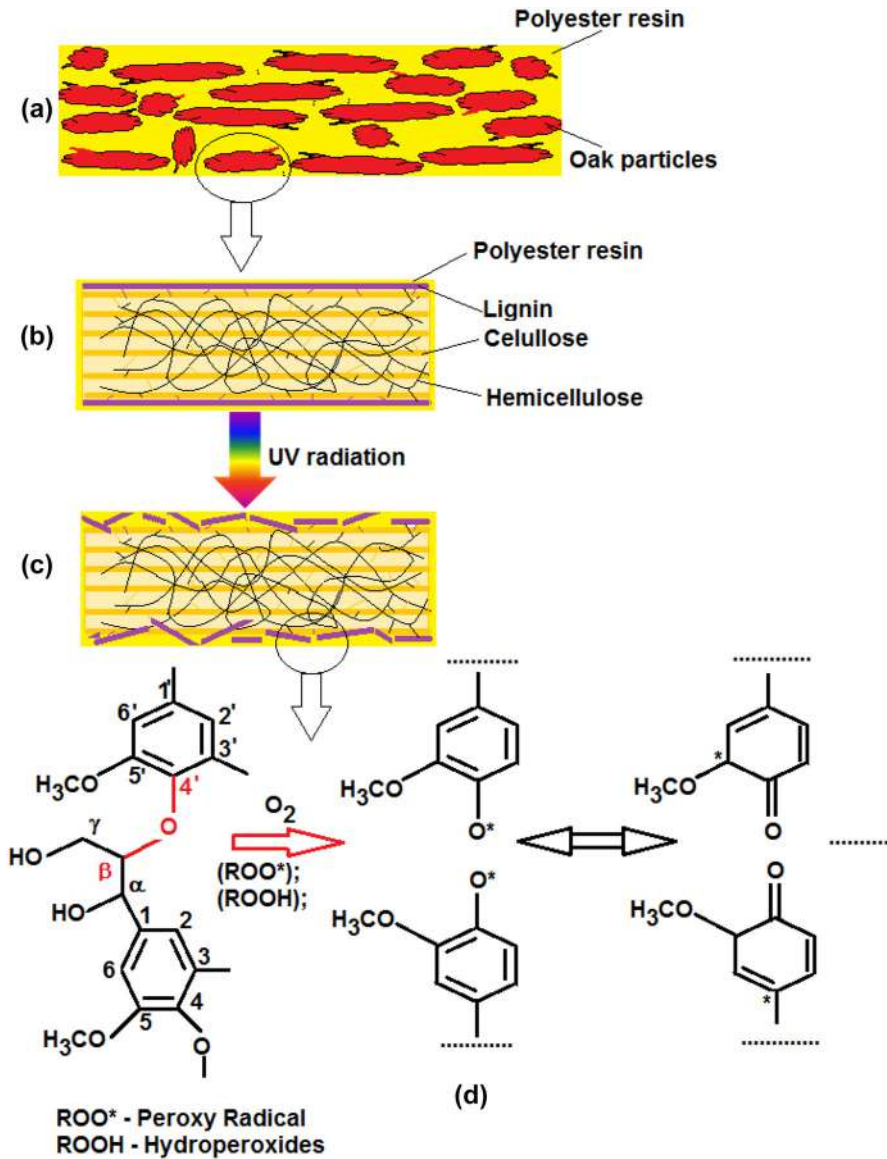


Fig. 7 Schematic representation of degradation induced by UV radiation on specimens composed of oak particles and resin. Legend: **a** principal constituents of the composites; **b** chemical constituents and the quality of specimen surface before treatment; **c** roughness of specimen surface after treatment; **d** chemical reactions

for composites made of 0.1-mm oak particles. This modulus is 20% higher than before exposure to UV. The most sensitive rheological parameter is the internal friction expressed by $\tan \delta$. After exposure to ultraviolet radiation, as the size of particles increases, the damping capacity of the specimens reinforced with particles

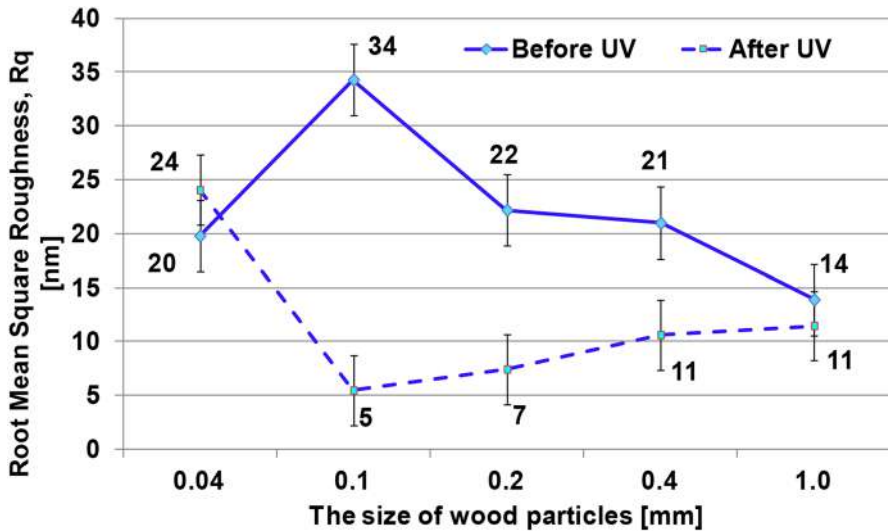


Fig. 8 Variation of root-mean-square roughness R_q of samples versus particle size

increased slightly, irrespective of the applied frequency of loading with DMA. The highest increasing damping effect (77%) after UV exposure was observed on specimens with 1-mm particles.

Thermal and UV degradations of the matrix determined increasing glass transition temperature T_g , which is the highest in the case of the composite with 0.1-mm oak particles. After UV exposure, increasing particle size in the composite induced decreasing glass transition temperature. UV radiation induced structural morphological instability at nanometric scale on the specimens' surface. From the morphological standpoint, the most stable to UV radiation and thermal degradation are specimens reinforced with 1-mm wood particles.

Acknowledgements This paper was supported by the programme Partnership in Priority Domains—PNIII under the aegis of Ministry of Research and Innovation and Executive Agency for Higher Education, Research, Development and Innovating Funding from Romania, project no. PN-III-P2-2.1-BG-2016-0017/85 SINOPTIC and project no. PN-II-PT-PCCA-2013-4-0656/59 STHEMOWTB. We are very thankful to Dr. Grahame Smith—Melbourne, Australia, for his very kind and effective contribution to the revision of the English version of this article. We are grateful to Professor Ioan Curtu (1942–2016) for a life dedicated to wood science, education and training of engineers and researchers in Romania.

References

- Azwa ZN, Yousif BF, Manalo AC, Karunasena W (2013) A review on the degradability of polymeric composites based on natural fibres. *Mater Des* 47:424–442
- Bagherpour S (2012) *Fibre Reinforced Polyester Composites*, Hosam El-Din M. Saleh (ed), Published: September 26, <https://doi.org/10.5772/48697>
- Beg MDH, Pickering KL (2008) Accelerated weathering of unbleached and bleached Kraft wood fibre reinforced polypropylene composites. *Polym Degrad Stab* 93:1939–1946
- Benini KCCC, Voorwald HJC, Cioffi MOH (2011) Mechanical properties of HIPS/sugarcane bagasse fiber composites after accelerated weathering. *Proced Eng* 10:3246–3251

- Bismarck A, Baltazar-Y-Jimenez A, Sarlkakis K (2006) Green composites as Panacea? Socio-economic aspects of green materials. *Environ Dev Sustain* 8:445–463
- Bodîrlău R, Teacă CA, Spiridon I (2009) Preparation and characterization of composites comprising modified hardwood and wood polymers/poly (vinyl chloride). *BioResources* 4(4):1285–1304
- Butylina S, Hyvärinen M, Kärki T (2012) A study of surface changes of wood-polypropylene composites as the result of exterior weathering. *Polym Degrad Stab* 97:337–345
- Cerbu C, Curtu I, Ciofoaia V, Rosca IC, Hanganu LC (2010) Effects of the wood species on the mechanical characteristics in case of some E-glass fibers/wood flour/polyester composite materials. *Mater Plast* 47:109–114
- Chaochanchaikul K, Jayaraman K, Rosarpitak V, Sombatsompop N (2012) Influence of lignin content on photodegradation in wood/HDPE composites under UV weathering. *BioResources* 7(1):38–55
- Cheng F, Hu Y, Li L (2015) Interfacial properties of glass fiber/unsaturated polyester resin/poplar wood composites prepared with the prepreg/press process. *Fiber Polym* 16(4):911–917
- Cipriano TF, Nazareth da Silva AL et al (2013) Rheological and morphological properties of composites based on polylactide and talc. *J Mater Sci Eng B* 3:695–699
- Cogulet A, Blanchet P, Landry V (2016) Wood degradation under UV irradiation: a lignin characterization. *J Photochem Photobiol B Biol* 158:184–191
- Coşniţă M, Cazan C, Duta A (2014) Interfaces and mechanical properties of recycled rubber polyethylene terephthalate wood composites. *J Compos Mater* 48(6):683–694
- Darie RN, Bercea M, Kozłowski M, Spiridon I (2011) Evaluation of properties of ldpe/oak wood composites exposed to artificial ageing. *Cell Chem Technol* 45:127–135
- Essabir H, Bensalah MO, Rodrigue D, Bouhfid R, Quiss A (2016) Structural, mechanical and thermal properties of bio-based hybrid composites from waste coir residues: fibers and shell particles. *Mech Mater* 93:134–144
- Gozdecki C, Wilczynski A (2015) Effect of wood particle size and test specimen size on mechanical and water resistance properties of injected wood-high density polyethylene composite. *Wood Fiber Sci* 47(4):1–10
- Guo G, Shi Q, Luo Y, Fan R, Zhou L, Qian Z, Yu J (2014) Preparation and ageing-resistant properties of polyester composites modified with functional nanoscale additives. *Nanoscale Res Lett* 9:215
- Kim JP, Yoon TH, Mun SP, Rhee JM, Lee JS (2006) Wood–polyethylene composites using ethylene–vinyl alcohol copolymer as adhesion promoter. *Bioresour Technol* 97:494–499
- Matuana LM, Kamdem DP (2002) Accelerated ultraviolet weathering of PVC/wood fibre composites. *Polym Eng Sci* 42:1657–1666
- Matuana LM, Jin Sh, Stark N (2011) Ultraviolet weathering of HDPE/wood-flour composites coextruded with a clear HDPE cap layer. *Polym Degrad Stab* 96:97–106
- Maxwell AS, Broughton WR, Dean G, Sims GD (2005) Review of accelerated ageing methods and lifetime prediction techniques for polymeric materials. NPL Report DEPC MPR016. National Physics Laboratory, Teddington, Middlesex, United Kingdom, Queen's Printer for Scotland
- Ndiaye D, Diop B, Thiandoume C, Fall PA, Farota AK, Tidjani A (2012) Morphology and Thermo Mechanical Properties of Wood/Polypropylene Composites. Polypropylene, INTECH. <https://doi.org/10.5772/3614>
- Ndiaye D, Verney V, Askanaian H, Commereuc S, Tidjani A (2013) Morphology, thermal behaviour and dynamic rheological properties of wood polypropylene composites. *Mater Sci Appl* 4:730–738
- Peng Y, Cao J (2016) Photochemical process of wood-thermoplastic composites. In: Rosu D (ed) Photochemical behaviour of multicomponent polymeric-based materials. Springer, Berlin, pp 291–346
- Peng Y, Liu R, Cao J (2014) Effects of antioxidants on photodegradation of wood flour/polypropylene composites during artificial weathering. *BioResources* 9(4):5817–5830
- Pepper T (2016) Polyester Resin. *Engineering Materials Handbook*. <http://home.engineering.iastate.edu/mkessler/MatE454/Constituent%20Materials%20Chapters%20from%20ASM%20Handbook/%285%29%20Polyester%20Resins.pdf> Accessed 10.10.2016
- Pothan LA, Oommen Z, Thomas S (2003) Dynamic mechanical analysis of banana fiber reinforced polyester composites. *Compos Sci Technol* 63:283–293
- Ratanawilai T, Nakawiro K, Deachsrija A, Homkhiew C (2014) Influence of wood species and particle size on mechanical and thermal properties of wood polypropylene composites. *Fiber Polym* 15 (10):2160–2168

- Romanzini D, Lavoratti A, JrHL Ornaghi, Amico SC, Zattera AJ (2013) Influence of fiber content on the mechanical and dynamic mechanical properties of glass/ramie polymer composites. *Mater Des* 47:9–15
- Saha P, Manna S, Roy D, Kim MC, Chowdhury S et al (2014) Effect of photodegradation of lignocellulosic fibers transesterified with vegetable oil. *Fiber Polym* 15(11):2345–2354
- Stanciu MD, Curtu I, Groza M, Savin A (2016) The evaluation of rheological properties of composites reinforced with hemp subjected to photo and thermal degradation. CONAT 2016 International Congress of Automotive and Transport Engineering (A. Chiru and N. Ispas Eds.). https://doi.org/10.1007/978-3-319-45447-4_62
- Stark NM, Berger MJ (1997) Effect of particle size on properties of wood-flour reinforced polypropylene composites. In: The fourth international conference on woodfiber-plastic composites, May 12–14, Madison, Wisconsin
- Teacă CA, Roșu D, Bođîrlău R, Roșu L (2013) Structural changes in wood under artificial UV light irradiation determined by FTIR spectroscopy and color measurements – a brief review. *BioResources* 8(1):1478–1507
- Terciu OM, Curtu I (2012) New hybrid lignocellulosic composite made of epoxy resin reinforced with flax fibres and wood sawdust. *Mater Plast* 49(2):114–117
- Varganici CD, Rosu D, Rosu L (2016) Life-time prediction of multicomponent polymeric materials. In: Rosu D (ed) Photochemical behaviour of multicomponent polymeric-based materials. Springer, Berlin, pp 227–258
- Villani V, Pucciariello R, Lavallata V (2017) Rheology of modified wood by means of pure solvent or solution treatments. *J Polym Environ* 25(2):479–486

Article

Mechanical and Rheological Behaviour of Composites Reinforced with Natural Fibres

Mariana D. Stanciu ^{1,*} , Horatiu Teodorescu Draghicescu ¹, Florin Tamas ²  and Ovidiu Mihai Terciu ¹

¹ Department of Mechanical Engineering, Transilvania University of Brasov, Eroilor 29, 500036 Brasov, Romania; draghicescu.teodorescu@unitbv.ro (H.T.D.); terciu.ovidiu.mihai@gmail.com (O.M.T.)

² Department of Civil Engineering, Transilvania University of Brasov, Eroilor 29, 500036 Brasov, Romania; florin.tamas@unitbv.ro

* Correspondence: mariana.stanciu@unitbv.ro

Received: 23 May 2020; Accepted: 17 June 2020; Published: 22 June 2020



Abstract: The paper deals with the mechanical behaviour of natural fibre composites subjected to tensile test and dynamic mechanical analysis (DMA). Three types of natural fibre composites were prepared and tested: wood particle reinforced composites with six different sizes of grains (WPC); hemp mat reinforced composites (HMP) and flax reinforced composite with mixed wood particles (FWPC). The tensile test performed on universal testing machine LS100 Lloyd's Instrument highlights the elastic properties of the samples, as longitudinal elasticity modulus; tensile rupture; strain at break; and stiffness. The large dispersion of stress–strain curves was noticed in the case of HMP and FWPC by comparison to WPC samples which present high homogeneity of elastic–plastic behaviour. The DMA test emphasized the rheological behaviour of natural fibre composites in terms of energy dissipation of a material under cyclic load. Cole–Cole plots revealed the connection between stored and loss heat energy for studied samples. The mixture of wood particles with a polyester matrix leads to relative homogeneity of composite in comparison with FWPC and HMP samples which is visible from the shape of Cole–Cole curves. The random fibres from the hemp mat structure lead to a heterogeneous nature of composite structure. The elastic and viscous responses of samples depend on the interface between fibres and matrix.

Keywords: natural fibre composites; mechanical properties; elastic behaviour; viscous response

1. Introduction

The natural fibres, vegetal, animal or mineral, consist of sustainable resources for composite materials used both in industrial applications and building structures. The source of vegetal fibres is different parts of plants such as bast for jute, hemp, flax, ramie, kenaf, leaf for sisal, banana and manila hemp (abaca), seeds in the case of cotton, coir and oil palm, wood and grass stem [1–4]. All vegetal fibres contain cellulose, hemicellulose and lignin in various proportions. For composite materials, reinforcement can be done with continuous fibres or with short fibres, in yarn or mat form. The ratio of mechanical properties and low weight, the possibilities to design different volumetric composition with effects on the mechanical, thermal, optical and electrical properties, and the environment protection and biodegradable properties of some natural composites are demonstrated by numerous pieces of research [5–7].

The main criteria for assessing new natural fibre composites were usually [8–10]: the degree of capitalization of the vegetal raw material and of other materials; the efficiency in use of raw material sources; volume or surface density; the limit values of the resistances to different mechanical stresses

(traction parallel and perpendicular to/on the surface of the plate, bending, shearing in different planes and directions, detachment, fatigue, etc.); the rigidity and elasticity of the products, expressed by the values of the longitudinal and transversal modulus of elasticity; the physical properties of lignocellulose composite materials (profile density, swelling coefficient and water absorption in different environments and periods, degree of penetration of different substances, humidity, content in crystalline substances, etc.); the ecological properties (volatile emissions, etc.); and biodegradation and recyclability. The natural fibre reinforced polymers are characterized by two stress–strain states: an elastic behaviour as a response to a fast applied force and a viscous behaviour as response to a slowly applied force. The fibre reinforcement plays an important role in elastic behaviour of polymeric composite, as the matrix contributes to the viscous behaviour. For instance, the most efficient volume fractions of fiber content is maximum 50–65 m% according to [11]. The tests to determine the flow and relaxation phenomena provide important information about the dimensional stability of the polymer [12,13]. Some studies have shown that the natural fibres used for reinforcement are thermally unstable above 200 °C, for which reason the used matrices are based on polyethylene (PE), PP, polyolefin, polyvinylchloride and polystyrene and thermosets (which can be cured below this temperature) [11–16].

Most studies on wood reinforced composites (plastic wood composites) have analysed either the influence of the particle volume fraction/resin, or the influence of the size of wood particles, or the influence of the fibre type used as reinforcing elements on the mechanical properties of composites [14,15]. Mechanical properties of wood plastic composites (WPC), determined by tensile and bending tests, show an increase of the elasticity modulus E and yield modulus at the same time with the increasing of the particle size between 0.1 mm and 0.2 mm. These mechanical parameters are lower for composites with larger particles (1.00–4.00 mm) [8,12–16]. The mechanical characteristics of plastic composites with wood sawdust as filler material were studied in previous research by [14–18]. They carried out a comparative analysis of the effects of water/seawater absorption on the degradation of mechanical properties obtained at bending, in the case of hybrid composites made of polyester resin reinforced with fiberglass E and wood flour as filler. Thus, the maximum flexural stress decreases by almost 33% after immersion in sea water of wood sawdust mixture and epoxy resin during 6572 h [15,16]. Other studies are addressed to degradation of lignocellulosic composites both by weathering, ageing or humidity, because, from a mechanical point of view, the exposure of lignocellulosic composites to different aggressive factors can produce modifications of the elastic characteristics, and can induce stress concentrations at the surface of the polymeric material (which can lead to its premature failure) [19–24]. The modifications of the elastic-dynamic properties of a composite made of small waste oak particles of various sizes and a polyester resin subjected to photo degradation by UV radiation and thermal degradations were studied by [16,25–31]. From the point of view of the change of the energy loss capacity (internal friction) after the exposure to UV radiations, the most stable are the specimens reinforced with 0.4 mm particles, whereas the most unstable are those reinforced with 1 mm particles [16]. Ref. [32] studied new lignocellulose composites with carbon nanotube, having improved the mechanical properties, stability and fire retardment. The mechanical behaviour of fibre-reinforced composites depends on the size of the fibres (diameter and length), their distribution in the composite structure, the strength and elasticity of the fibres, the chemical stability and thermal resistance of the matrix and the nature of the fibre-matrix interface. Depending on the main directions of stress in the final product, the layers can be oriented differently so as to ensure a multidirectional distribution of stress during applications [33,34]. Numerous studies have shown that the method of reinforcement, length and nature of the fibres influence the mechanical properties of the composite. There is a linear relationship between the increase of the fibre content and the increase of the elastic modulus of the composite [35–37]. The complexity of the composite behaviour consists of the differences between the rigidity of the components that lead to the development of shear stress at the interface between the matrix and the fibres [38–40]. The determination of the mechanical and dynamic properties of composites reinforced with natural fibres plays a key role in the different

structures and applications for both the proper design of the structures and the prediction of their lifetime cycle. The finished products from natural fibre reinforced composites obtained from wood waste or hemp or flax and polyester resin are exposed to environmental and technological risks such as high relative humidity, temperature, UV radiation, vibrations, etc., reducing their resistance to different loads. The mechanical and dynamical characterisation of lignocelluloses composites based on wood particles, flax woven and polyester resin have not been investigated yet.

The aim of this paper is to examine the mechanical and dynamical properties of three different types of three categories of composites (wood particle reinforced composites, hemp mat reinforced composites and flax reinforced composite with mixed wood particles). The mechanical characterization of natural fibre composites is very important from the design and analysis as well as from the life prediction point of view, and it was obtained by a uni-axial tension test according to SR EN ISO 527-4, where the longitudinal Young's modulus, tensile of rupture and strain at break are obtained. The polyester resin as a matrix in the studied composites is used for outdoor applications due to its high resistance to environment factors. The natural fibre composites proposed and studied in this piece of research have a good potential to be used in different parts of automotive structures as door panels, ornaments or for the indoor parts of boats. The effects of thermal degradation in terms of glass transition and heat deflection temperature were detecting by thermal dynamical mechanical analysis. Dynamic mechanical analysis (DMA) was carried out in order to provide quantitative information about the performance of material to cyclic stress and variation of temperature. Based on dynamic properties determined by DMA (stiffness, energy dissipation), the viscous-elastic properties of manufactured natural composites can be improved in order to increase the quality of composites. For the producers of composite materials and for the users of the products made from them, the present research offers information about the possibilities of use versus limitations depending on the determined mechanical properties.

2. Materials

Because the aim of this study is to compare the mechanical characteristics of composites reinforced with natural fibres, the sample preparation is presented for each type of specimens: wood particle reinforced composites abbreviated as WPC, hemp mat and polyurethane resin abbreviated as HMP (in longitudinal and transversal direction of mat fibres), flax and wood particle reinforced composites (abbreviated as FWPC). The specimens have the specific shape and dimensions of tensile test composite materials, according to ASRO SR EN ISO 527 and were made by a hand lay-up process.

2.1. Natural Fibre Composites

2.1.1. Wood Particle Reinforced Composite (WPC)

The WPC specimens were obtained by mixing wood particles with polyester resin. The oak wood particles resulted from the mechanical processing of the wood logs from a Romanian factory. Oak particles were conditioned at 5–6% moisture content and their specific gravity was established by a pycnometer [41]. For the production of the lignocellulosic composites, in the first stage, the wood particles were sorted according to their size using granulometric sieves. Five classes of oak wood particles were obtained: less than 0.04 mm (coded WPC 0.04); between $0.04 \div 0.1$ mm (coded WPC 0.10); between $0.1 \div 0.2$ mm (WPC 0.20); between $0.2 \div 0.4$ mm ((WPC 0.40); between $0.4 \div 1$ mm ((WPC 1.00) and from 1 mm to 2 mm (WPC 2.00) (Table 1). From each type of grain sizes used as reinforcement, five specimens for the tensile test were prepared using the same volume fraction of 25% in a mixture with 440-M888 POLYLITE type polyester resin (Table 2), obtaining a total of 25 WPC type samples) (Figure 1a). For the DMA test, 2 specimens for the test with constant temperature and 2 specimens for the test with temperature variation (Figure 1b) were prepared from each type of wood particle reinforced composites. The physical features of WPC samples for the tensile test are shown in Table 1 and for the DMA test in Table 3.

Table 1. The physical characteristics of samples for the tensile test.

Samples	No. of Samples	No. of Layers	Thickness [mm]	Width [mm]	Area [mm ²]	Gauge Length [mm]
WPC 0.04	5	1	4.10 ± 0.10	10 ± 0.5	42 ± 1.5	50
WPC 0.10	5	1	4.10 ± 0.10	10 ± 0.5	42 ± 1.5	50
WPC 0.20	5	1	4.25 ± 0.25	10 ± 0.5	43 ± 1.5	50
WPC 0.40	5	1	4.20 ± 0.25	10 ± 0.5	42 ± 1.5	50
WPC 1.00	5	1	4.20 ± 0.20	10 ± 0.5	42 ± 1.5	50
WPC 2.00	5	1	4.30 ± 0.20	10 ± 0.5	43 ± 1.5	50
HMPL	5	1	1.80 ± 0.20	10 ± 0.5	18 ± 1.5	50
HMPT	5	1	1.80 ± 0.20	10 ± 0.5	18 ± 1.5	50
FWPC_L	5	6	6.80 ± 0.50	10 ± 0.3	69 ± 4.8	50
FWPC_T	5	6	6.60 ± 0.60	10 ± 0.4	68 ± 5.5	50

Table 2. The characteristics of the polyester resin type 440-M888 PolyLite, at 23 °C.

Properties	Units	Value	Tested Method
Brookfield Viscosity LVF	mPa·s(cP)	1100–1300	ASTM D 2196-86
Density	g/cm ³	1, 10	ISO 2811-2001
PH (max.)	mgKOH/g	24	ISO 2114-1996
Styrene content	% of weight	43 ± 2	B070
Curing time: 1% NORPOL PEROXIDE 1	Minutes	35–45	G020
Tensile Strength	MPa	50	ISO 527-1993
Longitudinal Elasticity Modulus	MPa	4600	ISO 527-1993
Elongation	%	1.6	ISO 527-1993
Bending strength	MPa	90	ISO 178-2001
Elasticity modulus at bending	MPa	4000	ISO 178-2001
The shock resistance P4J	mJ/mm ²	5.0–6.0	ISO 179-2001
Volume contraction	%	5.5–6.5	ISO 3521-1976
Glass transition temperature	°C	62	ISO 75-1993

Table 3. The physical characteristics of the samples for the DMA test (Legend: DMA operated under constant temperature T = const.; DMA operated under temperature variation T).

Samples	No. of Samples T = const./T var.	Thickness [mm]	Width [mm]	Gauge Length [mm]
WPC 0.04	2/2	4.10 ± 0.10	10 ± 0.2	40
WPC 0.10	2/2	4.10 ± 0.10	10 ± 0.5	40
WPC 0.20	2/2	4.25 ± 0.25	10 ± 0.5	40
WPC 0.40	2/2	4.20 ± 0.25	10 ± 0.5	40
WPC 1.00	2/2	4.20 ± 0.20	10 ± 0.5	40
WPC 2.00	2/2	4.30 ± 0.20	10 ± 0.5	40
HMPL	2/2	1.80 ± 0.20	10 ± 0.5	40
HMPT	2/2	1.80 ± 0.20	10 ± 0.5	40
FWPC_L	2/2	6.80 ± 0.50	10 ± 0.3	40
FWPC_T	2/2	6.60 ± 0.60	10 ± 0.4	40

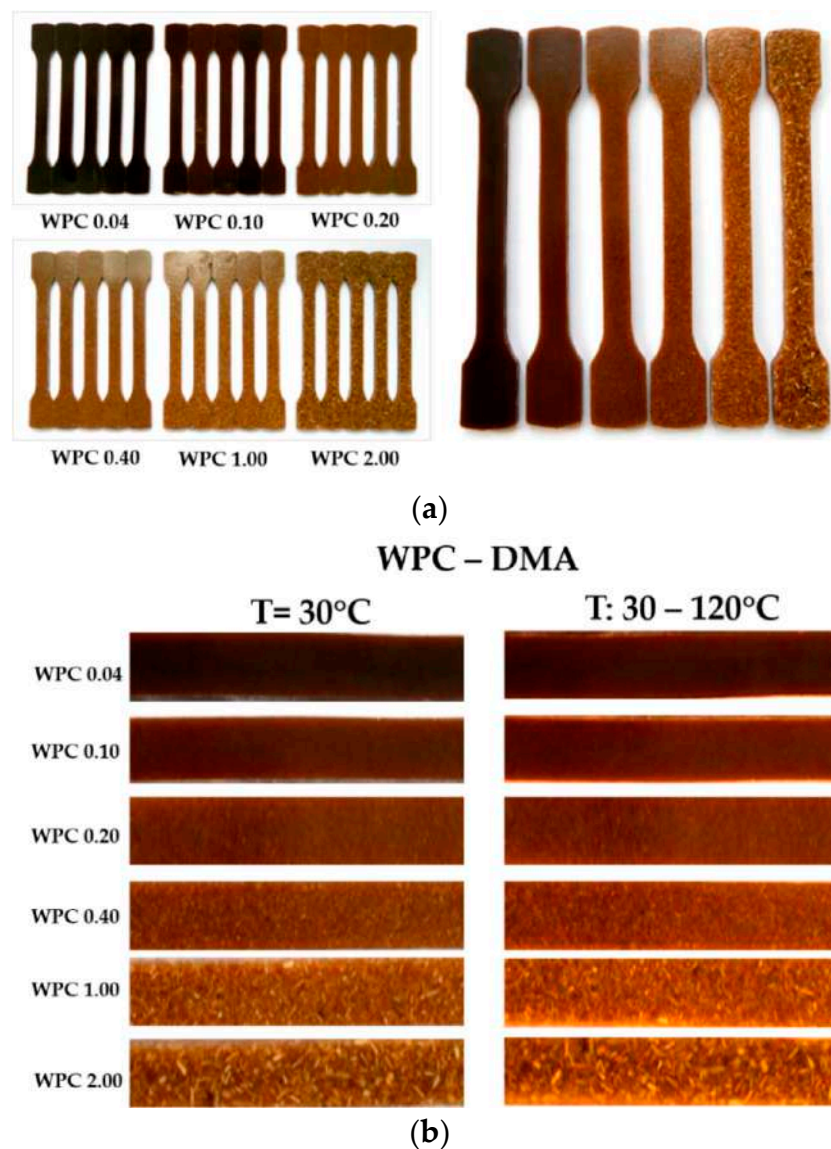


Figure 1. The specimens made from wood particles and polyester resin: (a) specimens for the tensile test; (b) samples for DMA.

2.1.2. Hemp Mat Reinforced Composites

The analysed composite material contains hemp mat and polyurethane resin (RAIGITHANE 8274/RAIGIDUR CREM), with 50% percent of reinforcing natural fibres. This type of natural fibre composite is used in the automotive industry for the interior panel of the car door. To evaluate the mechanical behaviour of composite reinforced with hemp fibres subjected to the tensile test, 5 samples on the longitudinal direction of the mat, coded HMPL were cut from the plate and 5 samples on the transversal direction of the mat, coded HMPT (Figure 2a). For the DMA test, 2 specimens for the test with constant temperature and 2 specimens for the test with temperature variation (Figure 2b) were prepared from each type of hemp mat reinforced composites. The physical features of hemp mat samples for tensile testing in Table 1 and for the DMA test in Table 3.

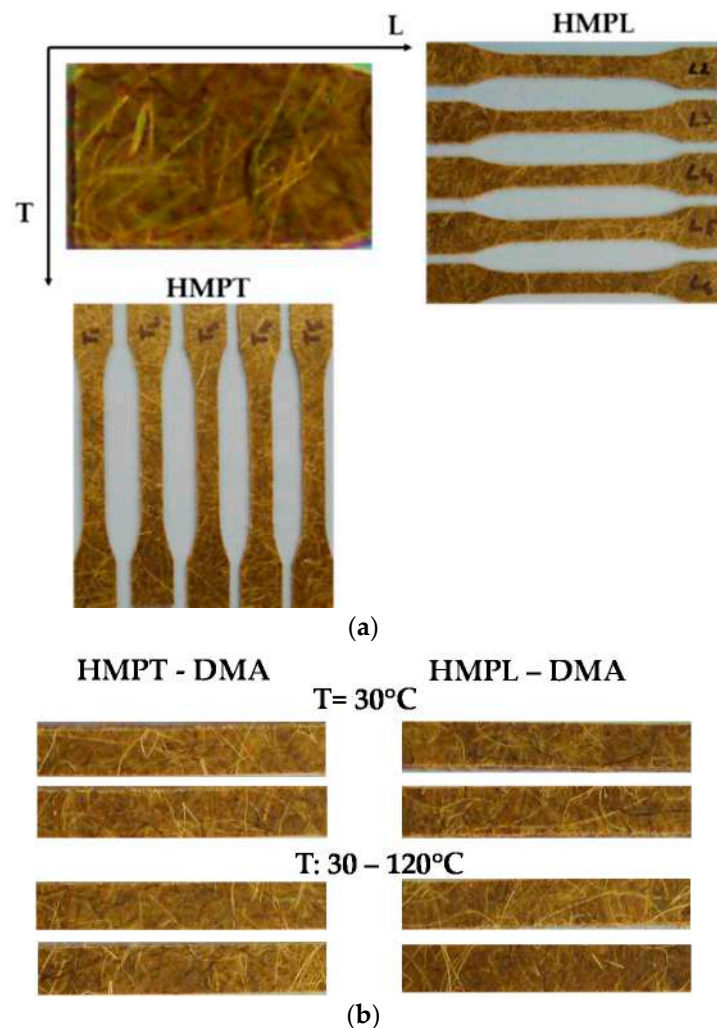


Figure 2. The specimens made from hemp mat reinforced and polyurethane resin: (a) geometry for tensile test: HMPL—sample cut in longitudinal direction; HMPT—sample cut in transversal direction; (b) geometry for the DMA test: HMPL—sample cut in longitudinal direction; HMPT—sample cut in transversal direction.

2.1.3. Flax Reinforced Composites

For these tests, the specimens were made of polyester resin reinforced with 6 layers of flax fabric and oak wood particles with dimensions between $0.1 \div 0.2$ mm, arranged between layers as it can be seen in Figure 3. The 6 layers of fabric have the same orientation of the warp and weft threads, respectively. The total volume percentage of reinforcement with natural fibres, in this case is approx. 30%. Samples for the tensile test were cut from the composite plate on the two main directions of the fabrics, respectively the warp direction (named FWPC_L) and the weft direction (named FWPC_T) (Figure 3a). For the DMA test, from each type of FWPC 2 specimens for the test with constant temperature and 2 specimens for the test with temperature variation were prepared (Figure 3b). The geometrical characteristics of FWPC for the tensile test are presented in Table 1 and for the DMA test in Table 3.

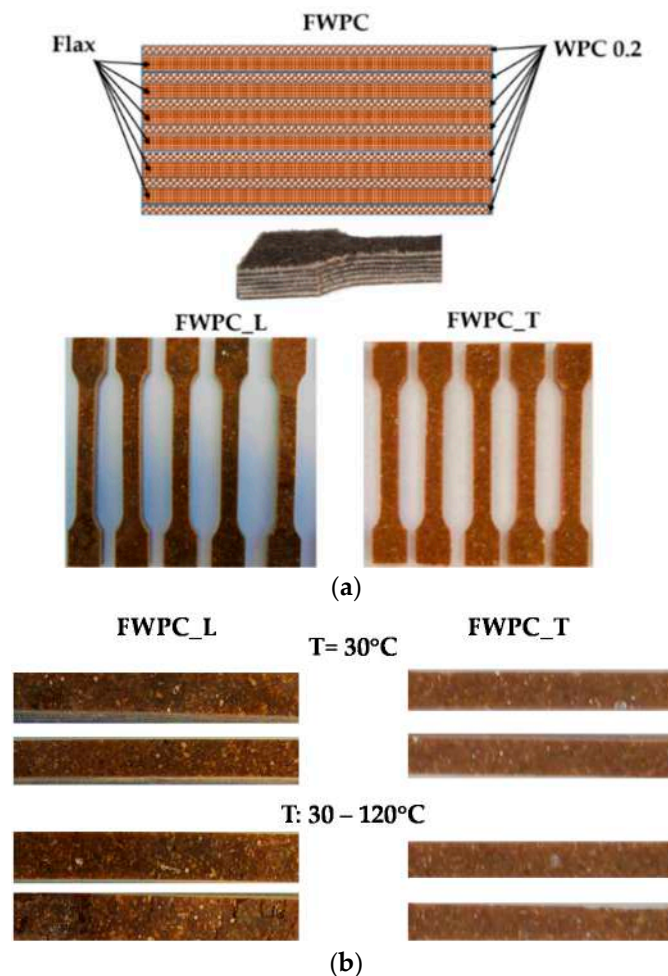


Figure 3. The specimens made from flax and wood particles reinforced and polyester resin: (a) samples for tensile test: FWPC_L—samples cut in longitudinal direction; FWPC_T—samples cut in transversal direction; (b) samples for DMA test.

2.2. Experimental Set-Up

2.2.1. Tensile Test

To determine the elastic characteristics of a material, the samples were subjected to a static tensile test. In this study, for the analysis of the mechanical behaviour of the composites, the specimens were tested on the universal testing machine LS100 Lloyd's Instrument belonging to the Mechanical Engineering Department of Transilvania University of Braşov. The specimens were loading with a constant speed of 1 mm/min until breaking. The elongation was measured simultaneously with loading using extension device (Figure 4a).

For data acquisition, the Nexygen Plus software was used. After the tensile tests (according to SR EN ISO 527-4), the characteristic curve, the specific deformation, the longitudinal elastic modulus, the rupture tension of each reinforced composite were determined, and on the basis of the load curves, the average deformation energy for each type of sample was calculated. The fracture of samples was analysed with optical devices.

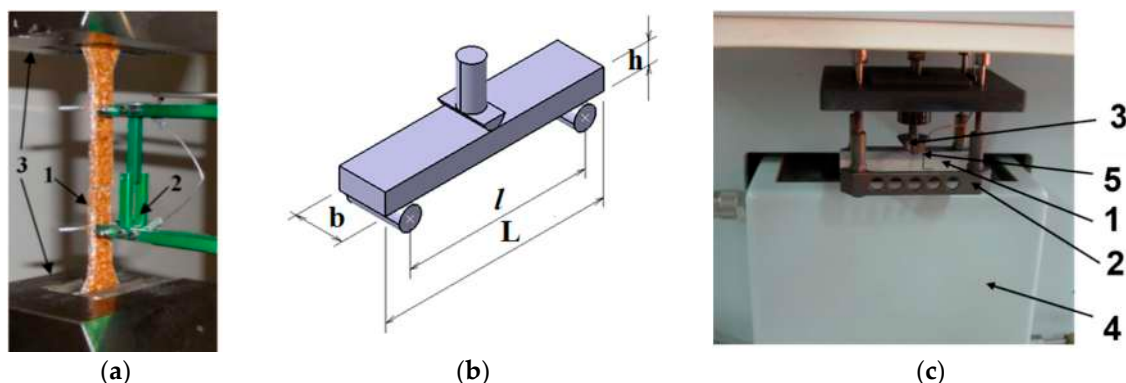


Figure 4. The experimental devices: (a) sample WPC 2.00 during the tensile test (Legend: 1—sample; 2—extension device for the elongation measurement; 3—tensile test machine jaws); (b) experimental set-up for the flexural test (3 points bending); (c) the DMA equipment (Legend: 1—sample; 2—sample supports; 3—loading device; 4—conditioner chamber; 5—temperature sensor).

2.2.2. Dynamic Mechanical Analysis

The rheological characteristics of the natural fibre composites were measured with the dynamic mechanical analysis by using the Dynamic Mechanical Analyzer DMA 242C Netzsch Germany at the Institute of Research and Development for Technical Physics in Iași. The method is based on ASTM D7028-07 which covers the procedure for the determination the glass transition temperature of polymer composites under the flexural oscillation mode. Thus, the complex modulus E^* , with its two components (the conservation modulus E' and the loss modulus E'') and the damping factor $\tan \delta$ were determined in two cases: under isothermal conditions ($T = 30^\circ\text{C}$) for 30 min and with temperature variation between 30 to 120°C , for 45 min. The specimens having the shape and geometry as it can be seen in Figure 4b were subjected to a flexural test. The input data were set up to 6 N for the applied force with frequency of 1 Hz. In Table 3, the specimen features for the DMA test are presented. For the DMA test, the samples have the same width and thickness as in the case of the tensile test and the length between supports is standard being set-up at 45 mm (Figure 4c).

3. Results and Discussion

The results in terms of qualitative and quantitative values of mechanical properties of natural fibre composites will be presented successively and then as a comparison. In the case of wood particle reinforced composites, it was noticed that, the smaller the reinforcing particles, the better the mechanical properties to traction. Nevertheless, the highest values of the elasticity modulus and of the tensile strength were obtained in the case of the composites reinforced with 0.2 mm particles. This is highlighted in the literature as well in the case of the polypropylene matrix composites (PP) [42]. The mechanical properties of the composites made of polypropylene and wood particles (WPC) in the case of tensile and bending tests show an increase in the values of the elasticity and resistance modulus simultaneous with the increase of the particle size between 0.25 and 2 mm, which is then followed by a slight decline of these values for larger particles (2–4 mm) [42]. The more elongated the particles, the more the mechanical properties increase because the contact between the reinforcing elements and the matrix occur over a larger surface. The first debonding of the matrix and the dispersed fibres occur near the breaking point. The characteristic curves for the same category of composites reinforced with wood particles did not display a large dispersion of values, the mixture between matrix and fibres being homogeneous (Figure 5).

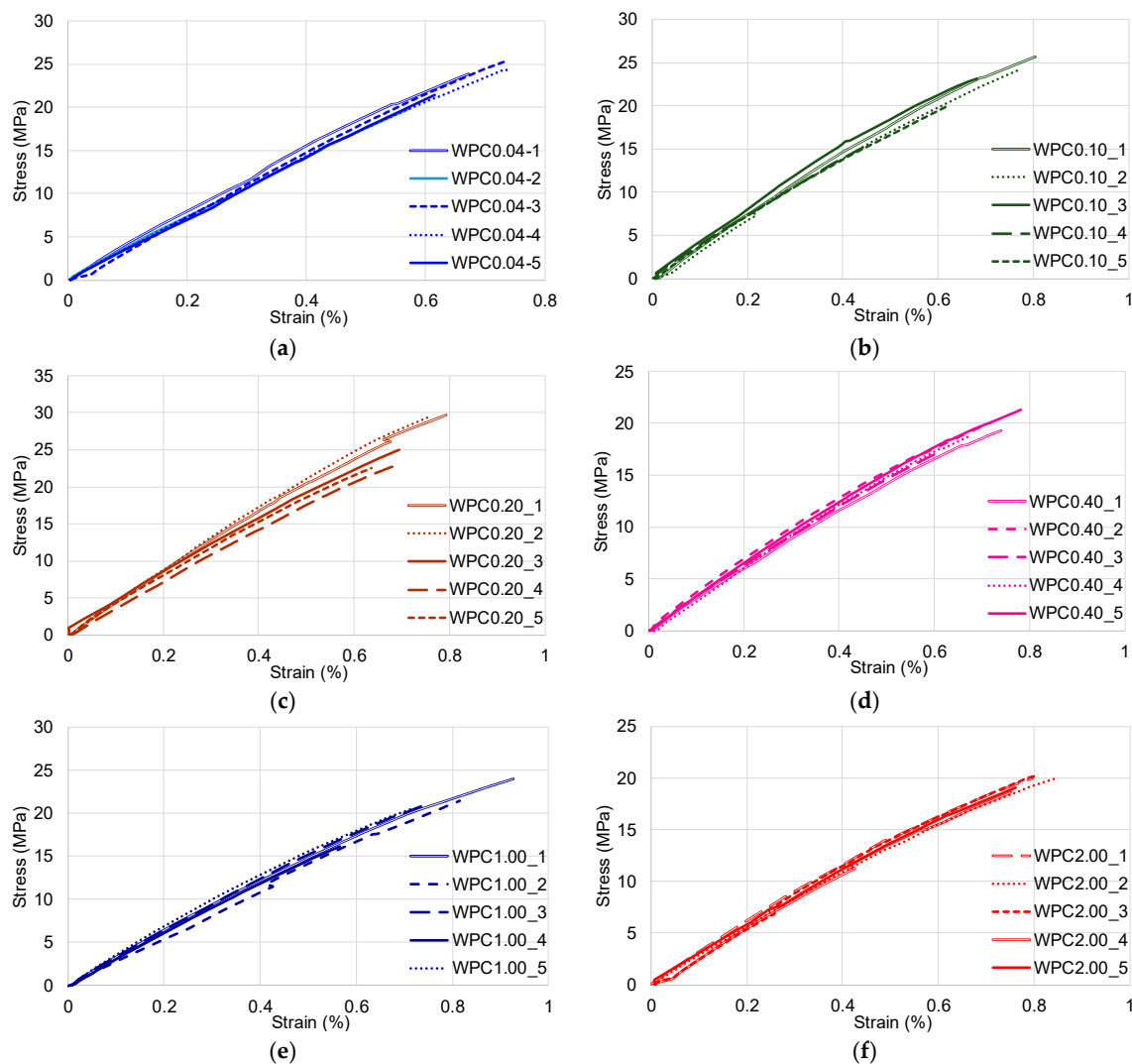


Figure 5. Characteristic curve stress–strain of wood particle reinforced composites: (a) stress–strain characteristic curves of WPC0.04 specimens; (b) stress–strain characteristic curves of WPC0.10 specimens; (c) stress–strain characteristic curves of WPC0.20 specimens; (d) stress–strain characteristic curves of WPC0.40 specimens; (e) stress–strain characteristic curves of WPC1.00 specimens; (f) stress–strain characteristic curves of WPC2.00 specimens.

Tensile tests performed by other researchers have shown that natural fibre fabric reinforced composite materials have major differences in the mechanical properties of traction in the direction of the warp and weft [42–45] as it can be seen in the case of HMP specimens (Figure 6a,b) and FWPC specimens (Figure 6c,d). It is known that the fibre mat is used as reinforcement to assure a quasi-isotropy of composite plates due to the random orientation of the fibres. Despite this assumption, the tests performed on hemp mat composites showed that there are significant differences between the tensile properties in the two directions of the mat (longitudinal and transversal direction). In the case of flax wood particle reinforced composites FWPC, the trend is similar to HMP regarding the mechanical properties in the weft and warp direction. Equally, it can be observed that HMP show a great spread of stress–strain curves in the longitudinal direction (Figure 6a) by comparison to FWPC which indicated a great dispersion of the curves in the transversal direction (Figure 6d).

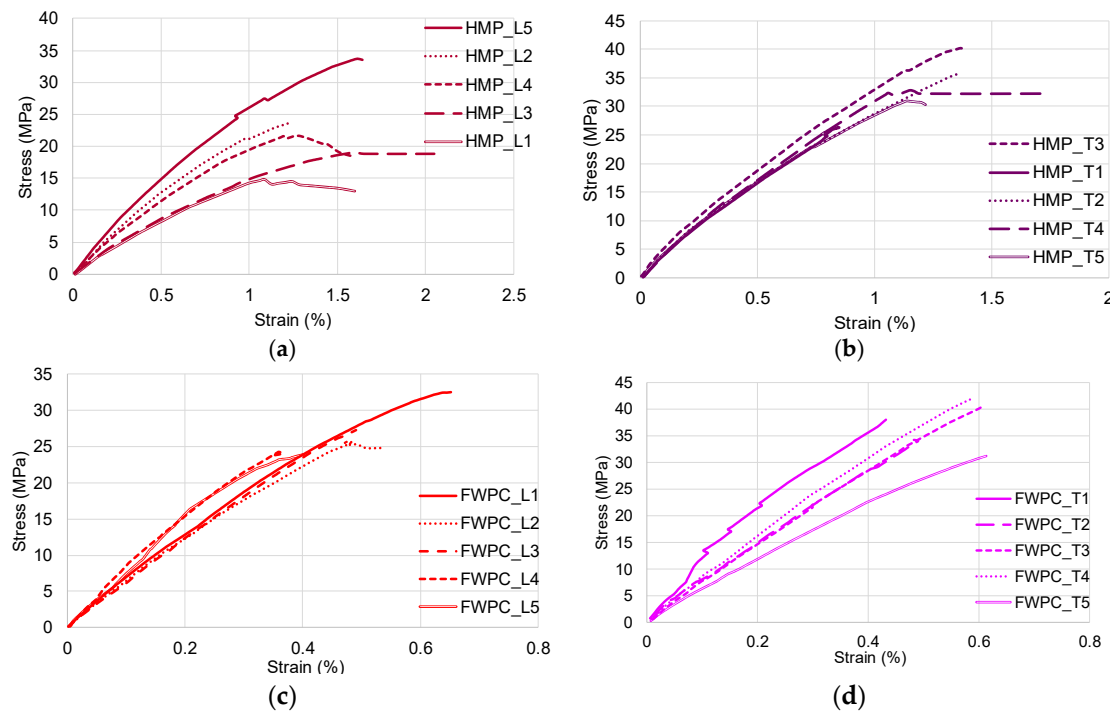


Figure 6. Characteristic curves stress–strain of natural fibres reinforced composites: (a) stress–strain curves for HMP_L samples; (b) stress–strain curves for HMP_T samples; (c) stress–strain curves for FWPC_L samples; (d) stress–strain curves for FWPC_T samples.

In Figure 7, it can be noticed that the FWPC samples present a rigid behaviour compared to the HMP_L samples which behave viscously. The WPC0.20 samples are also rigid by comparison to the other wood particle reinforced composite.

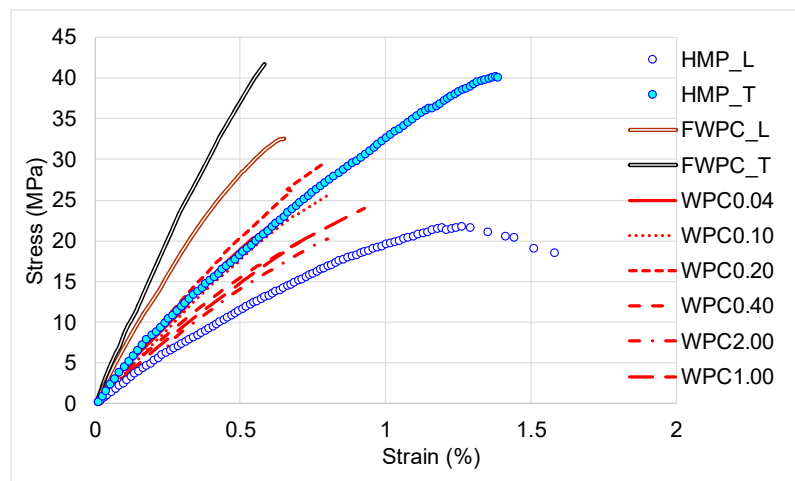


Figure 7. Comparison of stress–strain curves for tested samples.

The mechanical properties of tested samples in terms of the average values of the longitudinal elasticity modulus, stress at break, the strain and stiffness in percent are summarized in Table 4. In the case of WPC specimens, it can be observed that the modulus of elasticity varies from 2877 MPa, for the specimens reinforced with particles about $1 \div 2$ mm, up to the maximum value of 4012 MPa, for the specimens reinforced with particles about $0.1 \div 0.2$ mm. The minimum values of the tensile strength were noted for specimens reinforced with particles about $1 \div 2$ mm (WPC 2.0), being 19.5 MPa, and the maximum being 26 MPa, for specimens reinforced with particles from 0.1 to 0.2 mm (WPC 0.2).

For the HMP specimens cut in the longitudinal direction, an average tensile strength value of 26 MPa was obtained, and in the weft direction 32 MPa, approximately 23% higher than in the longitudinal direction. In the case of the longitudinal modulus of elasticity, it is observed that, in the transverse direction, its value is approximately 63% higher than in the longitudinal direction (Table 3). For the FWPC specimens cut in the warp direction, tensile strength values between 23.9 and 27.3 MPa were obtained, and in the weft direction between 31.4 and 42 MPa. The longitudinal elasticity modulus is higher in the transversal direction (weft) by almost 95% than in the warp direction (longitudinal). Although the mechanical properties of lignocelluloses samples are relatively low, they can be used in some applications as exterior and interior products, being valuable for the possibility of integrating wood residues from processing operations or from recycled wood in the form of chips and fibres.

Table 4. Average values of elastic characteristics obtained after the tensile test. Legend: E—longitudinal elasticity modulus; STDV—standard deviation; σ_r —tensile of rupture; ϵ_r —percentage strain at break; k—stiffness.

Samples	E (MPa)	STDV E (MPa)	σ_r (MPa)	STDV σ_r (MPa)	ϵ_r (%)	k (10^6 N/mm)
WPC 0.04	3626	218	23	2	0.920	0.003052
WPC 0.10	3693	181	22	4	1.261	0.003124
WPC 0.20	4012	328	26	4	0.011	0.003518
WPC 0.40	3109	138	19	2	0.014	0.002762
WPC 1.00	3041	260	21	3	0.011	0.002683
WPC 2.00	2877	85	20	1	0.010	0.002589
HMPL	3086	934	26	9	1.550	1.110
HMPT	5005	569	32	5	1.199	1.802
FWPC_L	8586	1247	27	3	0.377	7.397
FWPC_T	16700	3500	38	3	0.37	8.854

3.1. Dynamic Mechanical Analysis

3.1.1. Isothermal Conditions

The rheological characteristics of the natural fibre composites in terms of complex modulus E^* , with its two components (the storage modulus E' and the loss modulus E'') and the damping $\tan \delta$ were determined with the DMA. The storage modulus E' represents the capacity of materials to withstand the applied loading, being the expression of the elastic constant of the composite. The energy dissipation due to the internal friction of the material is called loss modulus E'' and it represents the viscous modulus. The ratio between the loss and storage modulus represents damping ($\tan \delta$). $\tan \delta$ is an indicator of how efficiently the material loses energy to molecular rearrangements and internal friction [46]. In Figures 8–10, the elastic and viscous responses of samples to dynamic loading with frequency of 1 Hz can be noticed. The capacity of WPC samples to store the deformation energy decreases slowly while increasing the time of loading. Similar behaviour is noticed in the case of the HMP samples with the mention that there are clear differences between the samples cut in the longitudinal direction compared to those cut in the transverse direction (Figures 8, 9 and 10b).

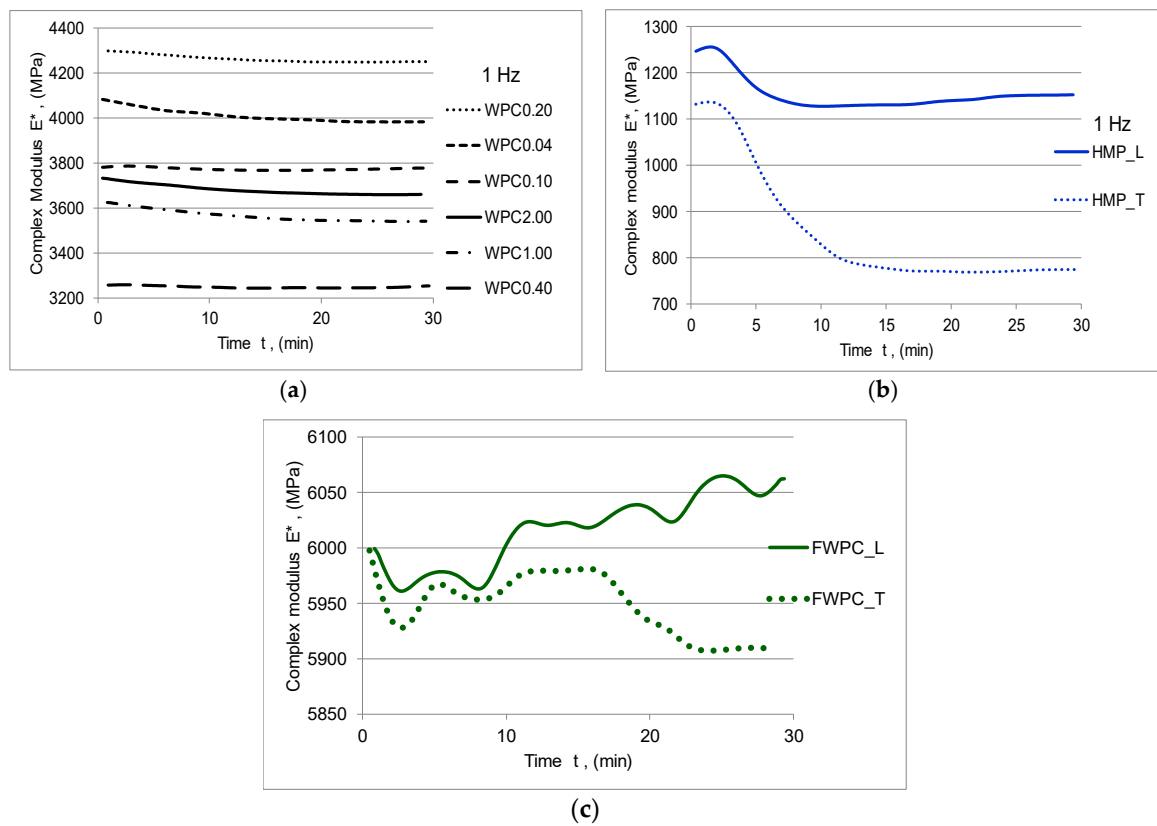


Figure 8. Variation of the complex modulus in time: (a) WPC samples; (b) HMP samples; (c) FWCP samples.

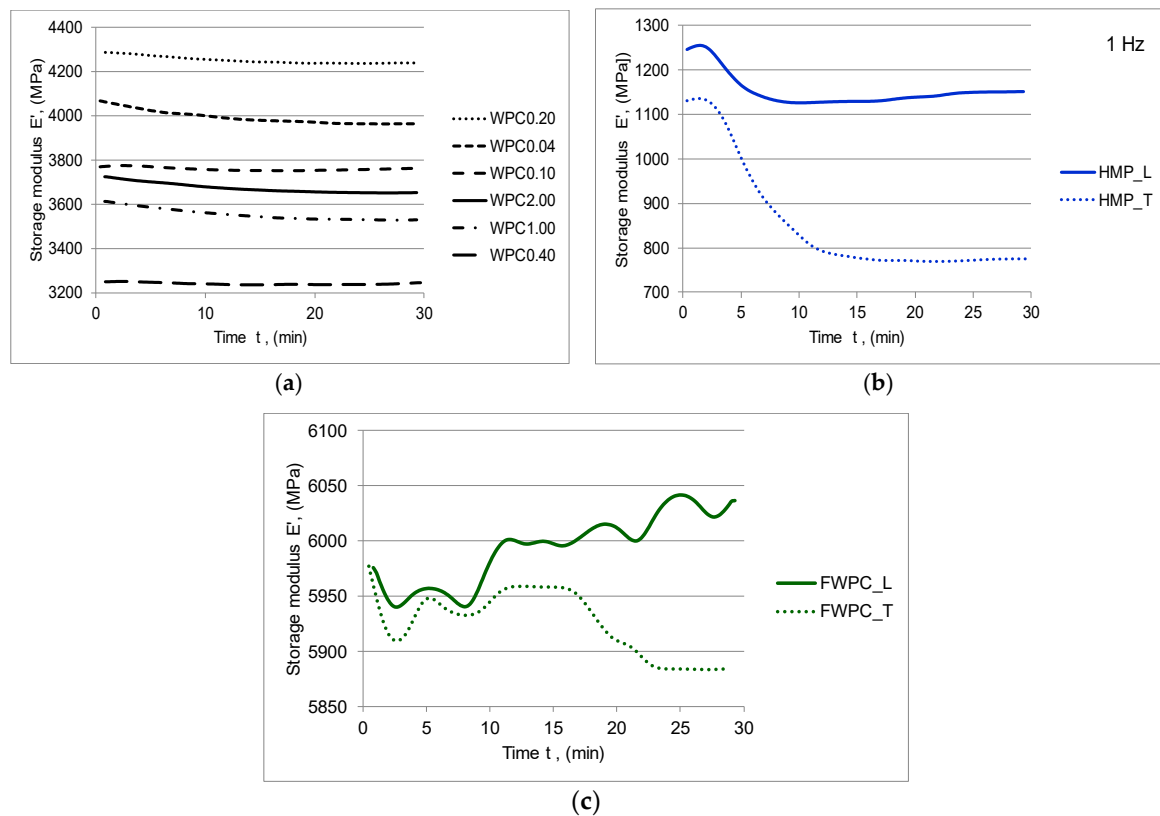


Figure 9. Variation of the storage modulus E' in time: (a) WPC samples; (b) HMP samples; (c) FWCP samples.

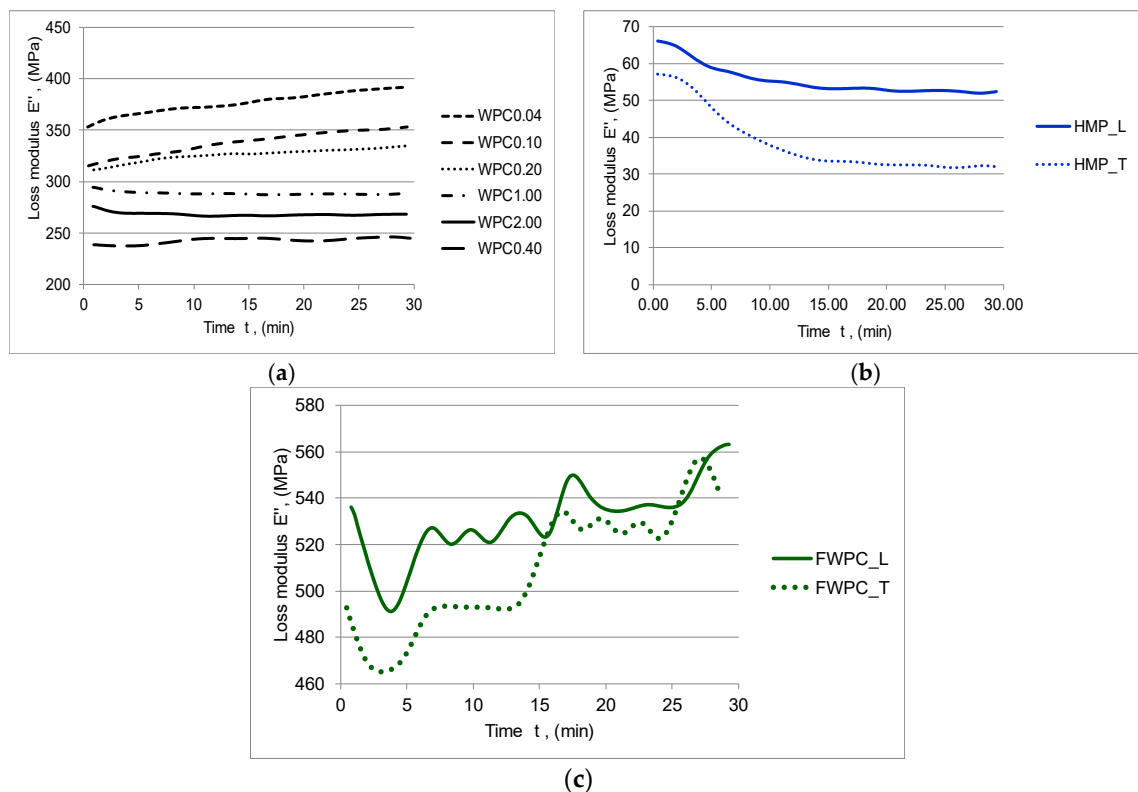


Figure 10. Variation of the loss modulus E'' in time: (a) WPC samples; (b) HMP samples; (c) FWPC samples.

Both types of samples have a similar viscous-elastic behaviour at the beginning, so that, after 10 min of stress, the samples cut in the longitudinal direction show a stiffening phenomenon compared to the samples cut in the transverse direction whose elastic behaviour decreases suddenly after 18 min of cyclic loading (Figures 8 and 9c). As far as the values of complex modulus and storage modulus for each type of the tested samples are concerned, it can be noticed that the lower values are noticed in the case of the HMP sample by comparison to WPC and FWPC. Initially, there are 1120–1260 MPa and, after 5 min, they decreased by 12.5% in the case of HMP_L maintaining constant value for remaining time exposure to cyclic loading. The HMP_T indicated a higher decreasing by almost 28% after 10 min and then a stabilization of the values at around 790 MPa. In the case of the WPC samples, the complex modulus ranges between 3250 MPa (WPC0.40) and 4270 MPa (WPC0.20). It can be noticed that the values for the flexural test in a dynamic regime are similar to Young's modulus values obtained in the tensile test. FWPC samples obtained the highest values for the dynamic modulus (5900–6060 MPa) in comparison to the other types of specimens. The loss modulus increases by increasing the time exposure to cyclic loading in the case of WPC and FWPC samples while the HMP samples indicated a decrease of this viscous component (Figure 10). This behaviour is due to the type of matrix: the WPC and FWPC, which contain as matrix polyester resin, indicated a slightly higher network density and it is slightly more cross-linked than the HMP sample based on polyurethane resin. The minimum values of energy dissipation due to internal frictions are indicated in the case of HMP samples. In the longitudinal direction (HMP_L), the viscous modulus decreases by 28% during the cyclic loading and, in the transversal direction (HMP_T), the decrease is 50%. For FWPC, the internal frictions increase by increasing the exposure time to loading; the overall value varied from minimum 465 MPa to maximum 560 MPa (in the case of FWPC_T) and from minimum 490 MPa to maximum 565 MPa (in the case of FWPC_L). For the WPC samples, the loss modulus varied in accordance with the wood particle sizes: the highest value of energy dissipation is recorded for smaller wood particles (WPC0.04). Regarding the variation of loss modulus, two groups can be noticed: WPC0.04, WPC0.10, and WPC0.20 indicated

an increase in internal friction and WPC1.00, WPC2.00, WPC0.40 indicated a slight decrease of the viscous modulus.

The damping $\tan \delta$ as a ratio between the loss and the storage modulus is an expression of the energy dissipation of a material under cyclic load, and it depends on the interface and adhesion between fibres and matrix. Any rigid material is characterized by a high damping value, whereas any ductile material indicates a low damping value [47]. In this sense, the damping $\tan \delta$ for the HMP samples tends to decrease by increasing the loading time, since, for the WPC and FWPC samples, the damping increases (Figure 11).

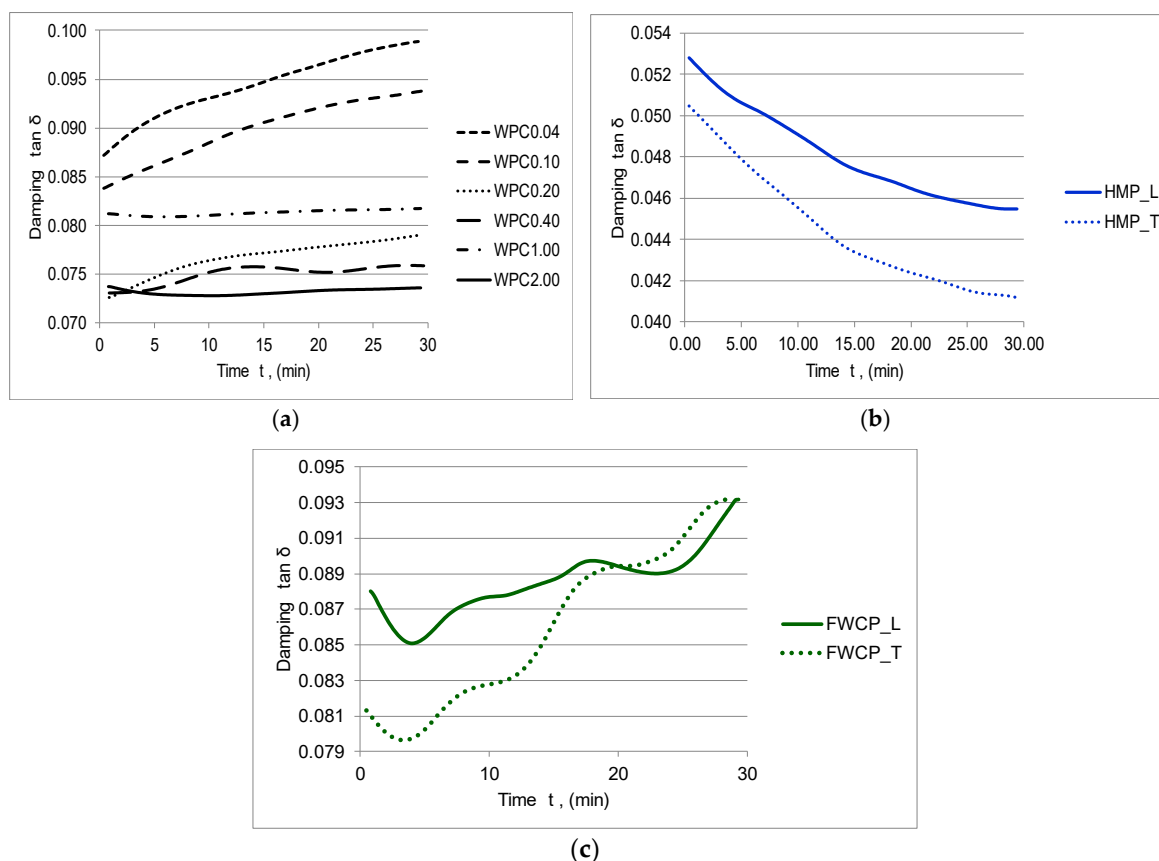


Figure 11. Variation of the damping $\tan \delta$ in time: (a) WPC samples; (b) HMP samples; (c) FWCP samples.

3.1.2. Temperature Variation

The viscous-elastic behavior of composites is emphasized by the temperature variation during cyclic loading. The stiffness and rigidity stability of composites at a certain temperature can be observed on the storage modulus curves. Thus, similar behavior between the WPC and FWPC samples can be noticed in Figure 12a,c: the glassy region presented between 30 °C and 40 °C characterized the rigidity of composites due to polymeric chains; in the second region (40–80 °C), the storage modulus decreases drastically because by increasing the temperature, the internal friction in polymeric chains is accelerated leading to a rubbery region. The HMP composite behavior differs, their stiffness being affected right from the start of the test and decreasing by temperature increase (Figure 12b). Despite this behavior, the reinforcement with hemp fibers and also the reinforcement with flax fabric lead to higher values of storage modulus by comparison to wood particle reinforced composites.

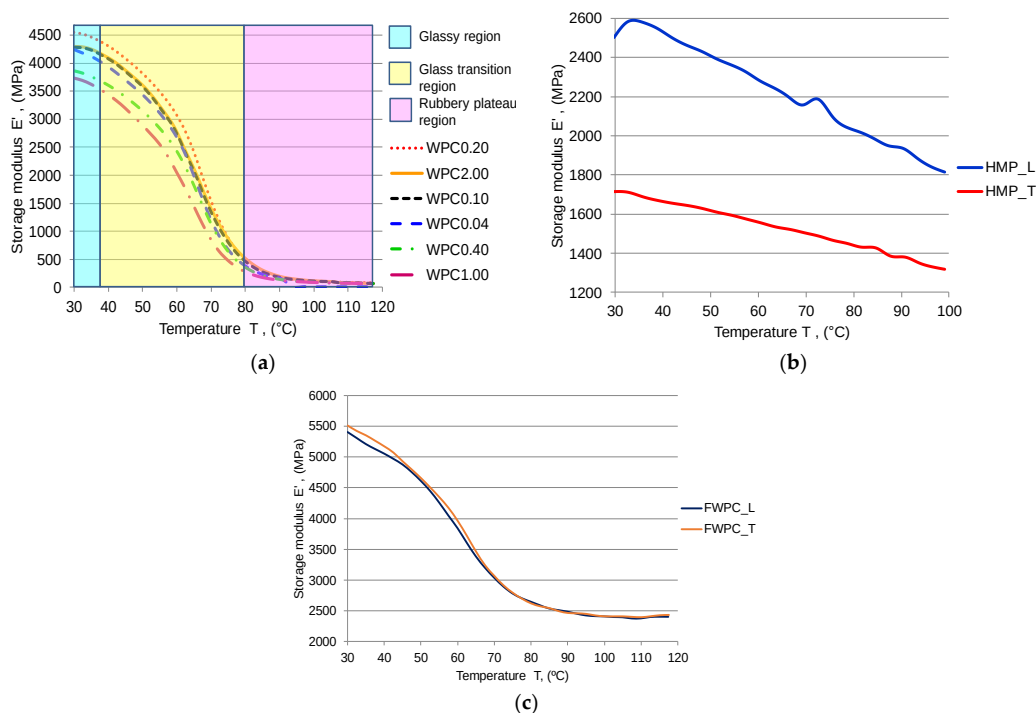


Figure 12. Variation of the storage modulus E' with temperature: (a) WPC samples; (b) HMP samples; (c) FWCP samples.

Figure 13 presents the effect of reinforcement on the damping as a function of temperature at 1 Hz frequency. From this type of chart, the glass transition temperature (T_g) can be extracted from the peak of damping variation curves.

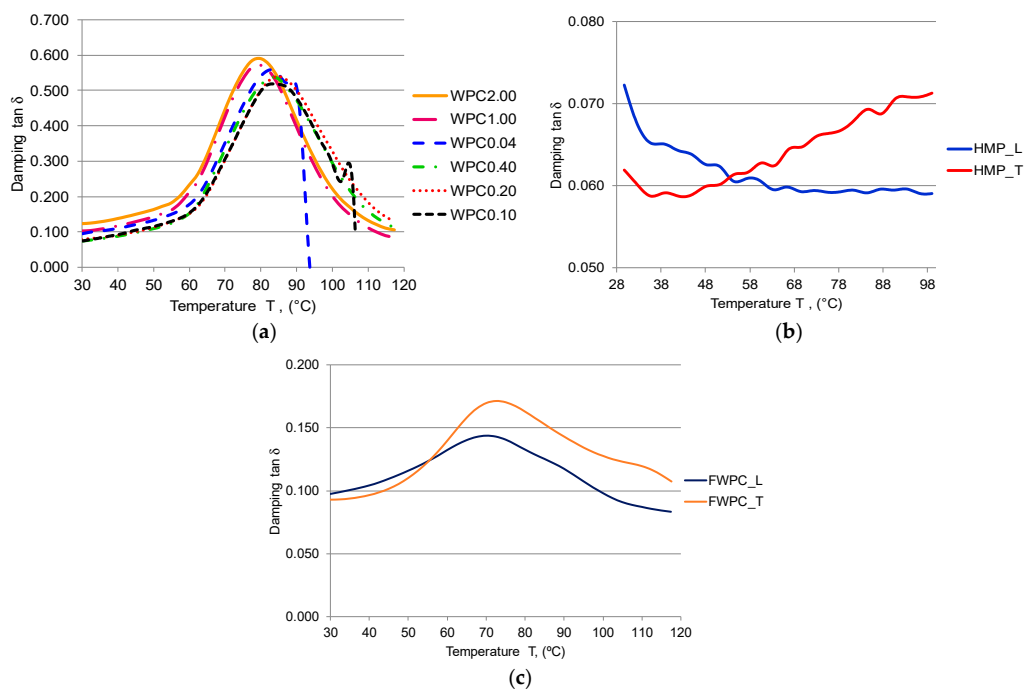


Figure 13. Variation of the damping $\tan \delta$ with temperature: (a) WPC samples; (b) HMP samples; (c) FWCP samples.

According to [48–50], lower damping values represent the improved interfacial interaction as it can be noticed in the case of FWPC and HMP (Figure 13b,c), while a higher damping value is recorded in the case of poor interfacial adhesion as it can be observed in Figure 13a—the WPC samples. Thus, the T_g for the WPC samples is around 78 °C (for 2.00 mm and 1.00 mm wood particle sizes) and 82 °C for smaller wood particles. The T_g for FWPC is lower than the one for WPC, being 70 °C. The HMP samples indicated a different behaviour. In Figure 14, the Cole–Cole charts are shown in order to analyse the connection between stored and loss heat energy for the studied samples. As [49–51] highlights, this kind of plot is useful to interpret the modification of viscous-elastic material with different reinforcement, as it is illustrated in Figure 14a—the WPC samples. The mixture of wood particles with polyester matrix leads to relative homogeneity of composite by comparison to the FWPC and HMP samples which is visible from the shape of Cole–Cole curves. The random fibres from the hemp mat structure lead to a heterogeneous nature of the composite structure.

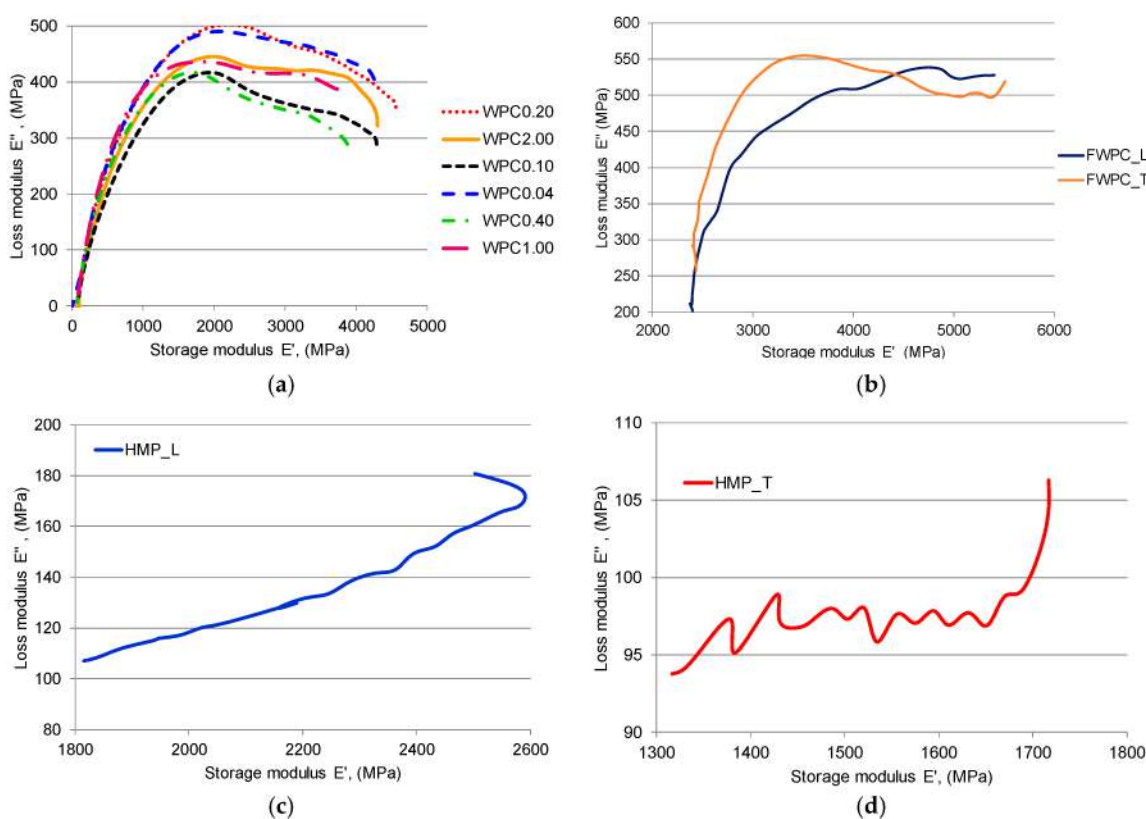


Figure 14. Cole–Cole plot: (a) WPC samples; (b) FWPC samples; (c) HMP_L sample; (d) HMP_T sample.

3.2. Fracture Analysing

In Figure 15, the ways of breaking of the tested composites are shown. Thus, it is noticeable that the breakage of the composite reinforced with wood particles (WPC) is produced through the simultaneous destruction of the matrix and of the dispersed fibres (Figure 15). In the case of the HMP samples, the matrix is fractured first; then, the dispersed fibres break. The plane of fracture is obtained on the area with the minimum resistance of the interface between the matrix and the fibres or in the area where the fibres are missing or do not have a good adhesion with the matrix. For the FWPC composites which contain both dispersed fibres (wood particles) and flax fabric, the fracture is produced first in the matrix mixed with wood particles and then the layers of flax fabric fail. It is appreciated that the use of a fabric structure (flax) doubles the tensile strength compared to mat reinforcement. The mechanism of failure differs between short fibres/particles reinforcement and long fibres [52,53]. The tension stress causes interface debonding. [53–56] considered that the final interface between the short fibres and the

matrix is easy to debond in the loading process. At the end of the final interface, the stress transfer from the matrix to the fibres depends on the shear stress only on the axial interface (Figure 16a). In the case of long fibre composites, the interface stress (shear stress) is higher due to the adhesion of resin to fibres (Figure 16b).

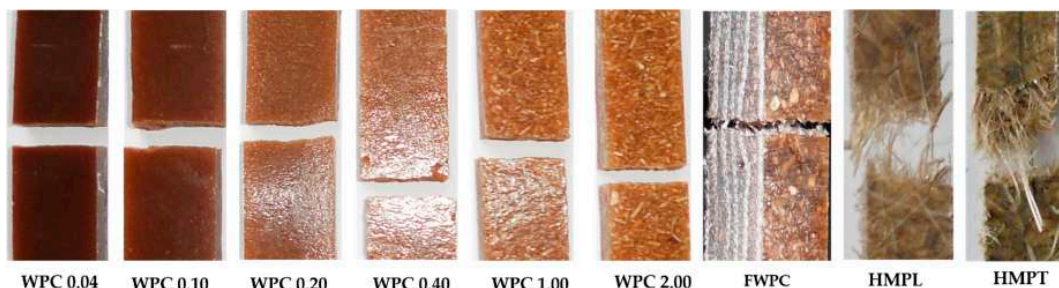


Figure 15. Modes of fractures recorded for all natural tested fibre reinforced composites.

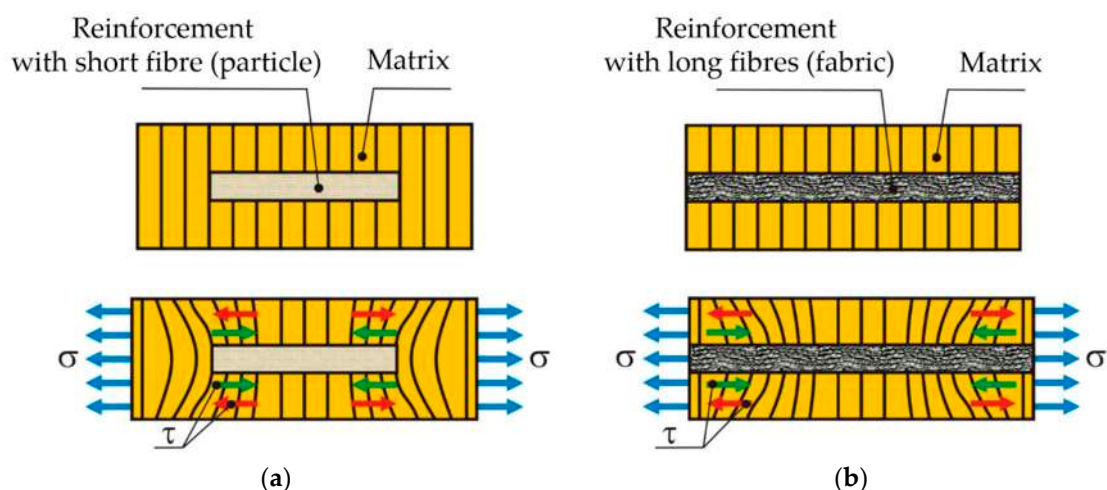


Figure 16. Mechanism of failure modes: (a) the case of short fibres reinforced composites; (b) the case of long fibres reinforced composites.

4. Conclusions

The mechanical behaviour of composite materials from three types of natural fibres was studied. The results demonstrated that both tensile and rheological behaviour depends on the size of fibres, disposition of fibres (randomly or fabric) and the type of matrix. The mechanical properties of natural fibres composites differ within the same type of composite. For instance, WPC0.20 recorded the higher values of Young's Modulus and tensile strength in comparison with WPC2.00 which have the lower values. It can be concluded that the best wood particles size is 0.20 mm from mechanical point of view. In case of HMP and FWPC, there is strong relation between direction of loading and weft/yarn direction. The longitudinal elasticity modulus is higher in the transversal direction (weft) by almost 80–95% than in the warp direction (longitudinal). The flax woven reinforcement in case of FWPC leads to the best mechanical properties from all types of tested composites.

Regarding DMA results, HMP and also FWPC present higher values of storage modulus by comparison to wood particle reinforced composites although the increasing temperature produces a decrease in viscous-elastic behaviour for all types of samples. The T_g for all tested natural fibres composite range between 65 and 85 °C, the matrix having the main role in modification of polymers stiffness.

The HMP presents a good capacity to absorb the energy of deformation, partially due to polyurethane resin and to the type of dispersed fibres. In the case of a structure made of lignocelluloses composite materials, consisting of layers reinforced with natural fibres as fabrics and layers reinforced

with wood particles, by adding an additional layer reinforced with wood particles on the visible surface of the panels. Thus, structures with superior aesthetic properties can be made which no longer require coating with other materials. Although the structure is no longer symmetrical, it has visible surfaces with natural textures whose colour can be changed by using wood particles of different species.

The further work will focus on simulation of mechanical behaviour of complex structures made from natural fibres composites using the elastic properties determined in experimental tests and predicting the stress and strain states of them.

Author Contributions: Conceptualization, M.D.S. and F.T.; methodology, H.T.D. and O.M.T.; software, H.T.D. and O.M.T.; validation, M.D.S. and F.T.; formal analysis, H.T.D. and O.M.T.; investigation, M.D.S. and O.M.T.; resources, F.T.; data curation, H.T.D.; writing—original draft preparation, O.M.T. and M.D.S.; writing—review and editing, H.T.D. and F.T.; visualization, M.D.S.; supervision, O.M.T.; funding acquisition, M.D.S. and F.T. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Sectorial Operational Program Human Resources Development (SOP HRD), financed from the European Social Fund and by the Romanian Government under the contract number POSDRU/88/1.5/S/59321 and Program partnership in priority domains PNII under the aegis of MECS UEFISCDI, project No. PN-II-PT-PCCA-2013-4-0656.

Acknowledgments: We are grateful to the manager Dorin Rosu, PhD and to the technical staff of S.C. Compozite S.A., Brasov, Romania, manufacturer of composite products for supplying the specimens for the experimental research of the present article. We are grateful to Savin Adriana, head of laboratory “Non-destructive tests” of the National Institute of Research and Development for Technical Physics in Iasi, for the DMA tests.

Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations and Notations

WPC	wood particle reinforced composites;
HMP	hemp mat and polyurethane resin;
FWPC	flax and wood particle reinforced composites;
DMA	dynamic mechanical analysis;
L	length of sample;
b	width of sample;
h	thickness of sample;
l	gauge length between bearings for 3 points bending;
E	longitudinal elasticity modulus;
STDV	standard deviation;
σ_r	tensile rupture;
ϵ_r	percentage strain at break;
k	stiffness;
E'	storage modulus;
E''	loss modulus;
$\tan \delta$	damping ratio;

References

1. Di Bela, G.; Fiore, V.; Valenza, A. Natural Fibre Reinforced Composites (Chapter 2). In *Fiber Reinforced Composites*; Cheng, Q., Ed.; Nova Science Publishers: New York, NY, USA, 2012.
2. Pamuk, G. Natural fibers reinforced green composites. *Tekstiler* **2016**, *59*, 237–243. [[CrossRef](#)]
3. Hristov, V.; Vasileva, S. Dynamic mechanical and thermal properties of modified poly (propylene) wood fiber composites. *Macromol. Mater. Eng.* **2003**, *288*, 798–806. [[CrossRef](#)]
4. Puglia, D.; Biagiotti, J.; Kenny, J.M. A review on natural fibre-based composites—Part II. *J. Nat. Fibers* **2005**, *1*, 23–65. [[CrossRef](#)]
5. Fajrin, J. Mechanical properties of natural fiber composite made of Indonesian grown sisal. *Infoteknik* **2016**, *17*, 69–84.
6. Terciu, O.M.; Curtu, I.; Teodorescu-Draghicescu, H. Effect of wood particle size on tensile strength in case of polymeric composites. In Proceedings of the 8th International Conference of DAAAM Baltic, Industrial Engineering, Tallinn, Estonia, 19–21 April 2012.

7. Stark, N.M.; Berger, M.J. Effect of particle size on properties of wood-flour reinforced polypropylene composites. In Proceedings of the Fourth International Conference on Woodfiber-Plastic Composites, Madison, Wisconsin, 12–14 May 1997.
8. Gozdecki, C.; Wilczynski, A. Effect of wood particle size and test specimen size on mechanical and water resistance properties of injected wood-high density polyethylene composite. *Wood Fiber Sci.* **2015**, *47*, 365–374.
9. Lilholt, H.; Sørensen, B.F. Interfaces between a fibre and its matrix. In *IOP Conference Series: Materials Science and Engineering*; IOP Publishing: Bristol, UK, 2017; Volume 219, p. 012030. [\[CrossRef\]](#)
10. Stanciu, M.D.; Curtu, I.; Groza, M.; Savin, A. The evaluation of rheological properties of composites reinforced with hemp subjected to photo and thermal degradation. In *CONAT 2016 International Congress of Automotive and Transport Engineering*; Chiru, A., Ispas, N., Eds.; Springer: Cham, Switzerland, 2016. [\[CrossRef\]](#)
11. Pickering, K.L.; AruanEfendy, M.G.; Le, T.M. A review of recent developments in natural fibre composites and their mechanical performance. *Compos. Part A* **2016**, *83*, 98–112. [\[CrossRef\]](#)
12. Terciu, O.M.; Curtu, I. New hybrid lignocellulosic composite made of epoxy resin reinforced with flax fibres and wood sawdust. *Mater. Plast.* **2012**, *49*, 114–117.
13. Patel, V.K.; Rawat, N. Physico-mechanical properties of sustainable Sagwan-Teak Wood Flour/Polyester Composites with/without gum rosin. *Sustain. Mater. Technol.* **2017**, *13*, 1–8. [\[CrossRef\]](#)
14. Stanciu, M.D.; Bucur, V.; Valcea, C.S.; Savin, A.; Sturm, R. Oak particles size effects on viscous-elastic properties of wood polyester resin composite submitted to ultraviolet radiation. *Wood Sci. Technol.* **2018**, *52*, 365–382. [\[CrossRef\]](#)
15. Cerbu, C.; Curtu, I.; Ciofoaia, V.; Rosca, I.C.; Hanganu, L.C. Effects of the wood species on the mechanical characteristics in case of some e-glass fibres/wood flour/polyester composite materials. *Mater. Plast.* **2010**, *47*, 109–114.
16. Cerbu, C.; Cosereanu, C. Moisture effects on the mechanical behaviour of Fir Wood Flour/Glass reinforced epoxy composite. *BioResources* **2016**, *11*, 8364–8385. [\[CrossRef\]](#)
17. Araújo, E.M.; Araújo, K.D.; Pereira, O.D.; Ribeiro, P.C.; de Melo, T.J. Fiberglass Wastes/Polyester resin composites: Mechanical properties and water sorption. *Polímeros Ciência e Tecnologia* **2006**, *16*, 332–335.
18. Sinha, A.; Narang, H.K.; Bhattacharya, S. Mechanical properties of natural fibre polymer composites. *J. Polym. Eng.* **2017**, *37*, 879–895. [\[CrossRef\]](#)
19. Tang, H.; Nguyen, T.; Chuang, T.; Chin, J.; Lesko, J.; Wu, F. Fatigue model for fiber-reinforced polymeric composite. *J. Mater. Civil. Eng.* **2000**, *12*, 97–104. [\[CrossRef\]](#)
20. Torabizadeh, M.A. Tensile, compressive and shear properties of unidirectional glass/epoxy composite subjected to mechanical loading and low temperature services. *Indian J. Eng. Mater. Sci.* **2013**, *20*, 299–309.
21. Degrieck, J.; Van Paepegem, W. Fatigue damage modelling of fibre-reinforced composite materials: Review. *Appl. Mech. Rev.* **2001**, *54*, 279–300. [\[CrossRef\]](#)
22. Pepper, T. Polyester Resin. Engineering Materials Handbook. Available online: <http://home.engineering.iastate.edu/~jmkessler/MatE454/Constituent%20Materials%20Chapters%20from%20ASM%20Handbook/%285%29%20Polyester%20Resins.pdf> (accessed on 10 October 2016).
23. Aramide, F.O.; Atanda, P.O.; Olorunniwo, O.O. Mechanical properties of a polyester fibre glass composite. *Int. J. Comp. Mater.* **2012**, *2*, 147–151.
24. Cerbu, C. Practical solution for improving the mechanical behaviour of the composite materials reinforced with flax woven fabric. *Adv. Mech. Eng.* **2015**, *74*, 1687814015582084. [\[CrossRef\]](#)
25. Prasad, A.V.R.; Rao, K.M. Mechanical properties of natural fibre reinforced polyester composites: Jowar, sisal and bamboo. *Mater. Des.* **2011**, *32*, 4658–4663. [\[CrossRef\]](#)
26. Thakur, V.K.; Thakur, M.K. Processing and characterization of natural cellulose fibers/thermoset polymer composites. *Carbohydr. Polym.* **2014**, *109*, 102–117. [\[CrossRef\]](#)
27. Ndiaye, D.; Diop, B.; Thiandoume, C.; Fall, P.A.; Farota, A.K.; Tidjani, A. Morphology and thermo mechanical properties of wood/polypropylene composites. In *Polypropylene*; INTECH: London, UK, 2012.
28. Ndiaye, D.; Verney, V.; Askanaian, H.; Commereuc, S.; Tidjani, A. Morphology, thermal behaviour and dynamic rheological properties of wood polypropylene composites. *Mater. Sci. Appl.* **2013**, *4*, 730–738.
29. Wambua, P.; Ivens, J.; Verpoest, I. Natural fibres: Can they replace glass in fibre reinforced plastics? *Compos. Sci. Technol.* **2003**, *63*, 1259–1264. [\[CrossRef\]](#)
30. Herrera, F.P.J.; Gonzalez, A. A study of the mechanical properties of short natural-fiber reinforced composites. *Compos. Part B* **2005**, *36*, 597–608. [\[CrossRef\]](#)

31. Gassan, J.; Bledzki, A.K. Possibilities to improve the properties of natural fiber reinforced plastics by fiber modification—jute polypropylene composites. *Appl. Comp. Mater.* **2000**, *7*, 373–385. [CrossRef]
32. Espert, A.; Camacho, W.; Karlsson, S. Thermal and thermomechanical properties of biocomposites made from modified cellulose and recycled polypropylene. *J. Appl. Polym. Sci.* **2003**, *89*, 2350–2353. [CrossRef]
33. Seldén, R.; Nyström, B.; Långström, R. UV Aging of Poly(propylene)/Wood-Fiber composites. *Polym. Compos.* **2004**, *25*, 543–553.
34. Gupta, M.K.; Bharti, A. Natural fiber reinforced polymercomposites: A review on dynamic mechanical properties. *Curr. Trends Fash. Technol. Text. Eng.* **2017**, *1*, 1–4. [CrossRef]
35. Ashok, R.B.; Srinivasa, C.V.; Basavaraju, B. Dynamic mechanical properties of natural fiber composites—A review. *Adv. Compos. Hybrid Mater.* **2019**, *2*, 586–607. [CrossRef]
36. Jiang, X.; Gao, Q. Stress-transfer analysis for fibre/matrix interfaces in short-fibre-reinforced composites. *Compos. Sci. Technol.* **2001**, *61*, 1359–1366. [CrossRef]
37. Teacă, C.A.; Roşu, D.; Bodîrlău, R.; Rosu, L. Structural changes in wood under artificial UV light irradiation determined by FTIR spectroscopy and color measurements—A brief review. *BioResources* **2013**, *8*, 1478–1507. [CrossRef]
38. Cosnita, M.; Cazan, C.; Duta, A. The influence of inorganic additive on the water stability and mechanical properties of recycled rubber, polyethylene terephthalate, high density polyethylene and wood composites. *J. Clean. Prod.* **2017**, *165*, 630–636. [CrossRef]
39. Mbarek, T.B.; Robert, L.; Hugot, F.; Orteu, J.J.; Sammouda, H.; Graciaa, A.; Charrier, B. Study of Wood Plastic Composites elastic behaviour using full field measurements. In Proceedings of the EPJ Web of Conferences, Poitiers, France, 4–9 July 2010; Volume 6, p. 28005. [CrossRef]
40. Varganici, C.D.; Rosu, D.; Rosu, L. Life-time prediction of multicomponent polymeric materials. In *Photochemical Behaviour of Multicomponent Polymeric-based Materials*; Rosu, D., Visakh, P.M., Eds.; Springer: Cham, Switzerland, 2016; pp. 227–258. [CrossRef]
41. Facca, A.G.; Kortschot, M.T.; Yan, N. Predicting the tensile strength of natural fibre reinforced thermoplastics. *Comp. Sci. Technol.* **2007**, *67*, 2454–2466. [CrossRef]
42. Romanzini, D.; Lavoratti, A.; Ornaghi, H.L., Jr.; Amico, S.C.; Zattera, A.J. Influence of fiber content on the mechanical and dynamic mechanical properties of glass/ramie polymer composites. *Mater. Des.* **2013**, *47*, 9–15. [CrossRef]
43. Panigrahy, B.S.; Rana, A.; Chang, P.; Panigrahi, S. Overview of flax fibre reinforced thermoplastic composites. *Am. Soc. Agric. Biol. Eng.* **2006**, *6*–165, 1–12. [CrossRef]
44. ISO 527-1:2012 Plastics—Determination of Tensile Properties. Available online: <https://www.iso.org/standard/56045.html> (accessed on 1 August 2019).
45. ASTM D7028-07. *Standard Test Method for Glass Transition Temperature (DMA Tg) of Polymer Matrix Composites by Dynamic Mechanical Analysis (DMA)*; ASTM International: West Conshohocken, PA, USA, 2015; Available online: www.astm.org (accessed on 10 December 2019).
46. Arputhabalan, J.; Palanikumar, K. Tensile properties of natural fiber reinforced polymers: An overview. In *Applied Mechanics and Materials*; Trans Tech Publications Ltd.: Stafa-Zurich, Switzerland, 2015; Volume 766, pp. 133–139.
47. Menard, K.P. *Dynamic Mechanical Analysis. A practical Introduction*; CRC Press–Taylor & Francis Group: New York, NY, USA, 2008.
48. Cheng, F.; Hu, Y.; Li, L. Interfacial properties of glass fiber/unsaturated polyester resin/poplar wood composites prepared with the prepreg/press process. *Fiber Polym.* **2015**, *16*, 911–917. [CrossRef]
49. Saba, N.; Safwan, A.; Sanyang, M.; Mohammad, F.; Pervaiz, M.; Jawaid, M.; Alothman, O.; Sain, M. Thermal and dynamic mechanical properties of cellulose nanofibers reinforced epoxy composites. *Int. J. Biol. Macromol.* **2017**, *102*, 822–828. [CrossRef] [PubMed]
50. Devi, L.U.; Bhagawan, S.; Thomas, S. Dynamic mechanical analysis of pineapple leaf/glass hybrid fiber reinforced polyester composites. *Polym. Compos.* **2010**, *31*, 956–965. [CrossRef]
51. Jesuarockiam, N.; Jawaid, M.; Zainudin, E.S.; Thariq Hameed Sultan, M.; Yahaya, R. Enhanced thermal and dynamic mechanical properties of synthetic/natural hybrid composites with graphene nanoplateletes. *Polymers* **2019**, *11*, 1085. [CrossRef]
52. Alothman, O.Y.; Alrashed, M.M.; Anis, A.; Naveen, J.; Jawaid, M. Characterization of date palm fiber-reinforced different polypropylene matrices. *Polymers* **2020**, *12*, 597.

53. Awaja, F.; Zhang, S.; Tripathi, M.; Nikiforov, A.; Pugno, N. Cracks, microcracks and fracture in polymer structure: Formation, detection, autonomic repair. *Prog. Mater. Sci.* **2016**, *83*, 536–573. [[CrossRef](#)]
54. Dhakal, H.N.; Méner, E.L.; Feldner, M.; Jiang, C.; Zhang, Z. Falling weight impact damage characterisation of flax and flax basalt vinyl ester hybrid composites. *Polymers* **2020**, *12*, 806. [[CrossRef](#)] [[PubMed](#)]
55. Stanciu, M.D.; Şova, D.; Savin, A.; Iliş, N.; Gorbacheva, G. Physical and mechanical properties of ammonia-treated black locust wood. *Polymers* **2020**, *12*, 377. [[CrossRef](#)] [[PubMed](#)]
56. Saba, N.; Jawaid, M.; Alothman, O.Y.; Paridah, M.T. A review on dynamic mechanical properties of natural fiber reinforced polymer composites. *Constr. Build. Mater.* **2016**, *106*, 149–159. [[CrossRef](#)]



© 2020 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/>).