forests

MDPI

*Article*

# Artificial Weathering Effects on the Physical and Chemical Properties of *Paulownia tomentosa* and *Pinus koraiensis* Woods Heat-Treated in Oil and Air

**Intan Fajar Suri [1,2,†], Byantara Darsan Purusatama [3,†], Jong-Ho Kim [1], Wahyu Hidayat [2], Apri Heri Iswanto [4], Se-Yeong Park [1], Seung-Hwan Lee [1] and Nam-Hun Kim [1,*]**

[1] Department of Forest Biomaterials Engineering, College of Forest and Environmental Sciences, Kangwon National University, Chuncheon 24341, Republic of Korea; intanfajars@gmail.com (I.F.S.); kimjongho@kangwon.ac.kr (J.-H.K.); parksy319@kangwon.ac.kr (S.-Y.P.); lshyk@kangwon.ac.kr (S.-H.L.)
[2] Department of Forestry, Faculty of Agriculture, University of Lampung, Bandar Lampung 35145, Indonesia; wahyu.hidayat@fp.unila.ac.id
[3] Institute of Forest Science, Kangwon National University, Chuncheon 24341, Republic of Korea; byantara@kangwon.ac.kr
[4] Department of Forest Products Technology, Faculty of Forestry, Universitas Sumatera Utara, Medan 20155, Indonesia; apri@usu.ac.id
* Correspondence: kimnh@kangwon.ac.kr
† These authors contributed equally to this work.

**Abstract:** This study evaluated the effect of artificial weathering on the surface characteristics, physical properties, and chemical compositions of oil heat-treated (OHT) and air heat-treated (AHT) *Paulownia tomentosa* and *Pinus koraiensis* woods. The untreated and heat-treated samples at 180, 200, and 220 °C for 2 h were exposed to ultraviolet (UV) and water for artificial weathering for 168 and 336 h, respectively, according to ASTM G53-96. The weathering experiment comprised 2 h of UV-light irradiation followed by 2 h of condensation cycles. Color change, volumetric swelling, and chemical components of weathered samples were determined. In both species, heat-treated woods showed a significantly lower total color change and volumetric swelling than the untreated woods. The total color change and VS of OHT woods were significantly lower than those of AHT. Fourier transform infrared spectra indicated that the lignin peaks in untreated and AHT woods decreased after weathering exposure, whereas the peaks were stable in OHT woods. Oil heat treatment is an effective method to stabilize dimensional change and color quality during weathering.

**Keywords:** air and oil heat treatment; artificial weathering; color change; volumetric swelling; *Paulownia tomentosa*; *Pinus koraiensis*



**Citation:** Suri, I.F.; Purusatama, B.D.; Kim, J.-H.; Hidayat, W.; Iswanto, A.H.; Park, S.-Y.; Lee, S.-H.; Kim, N.-H. Artificial Weathering Effects on the Physical and Chemical Properties of *Paulownia tomentosa* and *Pinus koraiensis* Woods Heat-Treated in Oil and Air. *Forests* **2023**, *14*, 1546. https://doi.org/10.3390/f14081546

Academic Editor: Angela Lo Monaco

Received: 10 July 2023
Revised: 25 July 2023
Accepted: 27 July 2023
Published: 28 July 2023



## 1. Introduction

*Paulownia tomentosa* is a fast-growing species that is widely distributed worldwide. The wood has low density and shrinkage and high dimensional stability [1]. Therefore, *Paulownia* wood is widely used as a material for furniture, construction, pulp and paper, particleboard, handicrafts production, bioenergy applications, and in making musical instruments [1–5].

*Pinus koraiensis* is a native and major plantation tree species used commercially in Korea, with a high growth rate, low density, and shrinkage. These characteristics make the wood suitable for furniture, particleboard, fiberboard, and wooden boats [1,6]. However, both wood species have low aesthetic value due to their light creamy or pale brown color [1].

Some modification methods, such as chemical, thermal, and impregnation, can improve wood properties. Thermal modification represents a popular method and has been

generally used for wood modification [7,8]. Air, nitrogen, steam, oil, and vacuum are used as heating media for heat treatment [9–16].

Air heat treatment is a slow pyrolysis process between 180 °C and 260 °C under an oxidative atmosphere, resulting in higher hemicellulose degradation and a shorter time to alter the physical and chemical properties of wood. In addition, heat treatment in hot air is a low-cost method to improve the dimensional stability, hydrophobicity, durability, and color properties of wood [7,14,17–24]. Esteves et al. [23] reported that AHT *Pinus pinaster* wood at 170–200 °C had lower equilibrium moisture content and higher dimensional stability than steam heat-treated wood. In contrast, the mechanical properties of AHT wood were slightly lower than the steam heat-treated wood. Quirino et al. [24] reported that *Populus nigra* wood air heat-treated at 235 °C showed darker color than the wood heat-treated with water vapor and nitrogen.

Heat treatment with hot oil also has been commonly used for improving wood properties through the synergetic effects of oil and heat. During oil heat treatment, oil separates oxygen from wood and minimizes oxidative processes, which can slow down the weakening in the strength of the treated wood. In addition, oil heat treatment generates a fast and uniform heat transfer rate to wood and surface protection by the absorbed oil. Oil heat treatment can improve wood properties for outdoor use, such as uniformly darkening wood surfaces, improving fungal resistance, increasing density and compression strength, and reducing shrinkage [12,25–28]. Dubey et al. [29] explained that the weathering properties of oil-heat-treated (OHT) wood, such as color and dimensional stability, improved because the oil protected the wood surfaces from ultraviolet (UV) light and water absorption.

So far, the physical and mechanical properties of air- and oil-heat-treated *P. tomentosa* and *P. koraiensis* woods have been studied. Hidayat et al. [17,18] reported that the equilibrium moisture content and wettability of AHT *P. tomentosa* and *P. koraiensis* woods at 160, 180, 200, and 220 °C decreased, and the color of the wood surface became darker as the temperature increased, which was more preferred by consumers than the lighter colors of untreated wood. Kim et al. [19] explained that the lightness ($L^*$) of AHT *P. tomentosa* wood at 160, 180, 200, and 220 °C decreased with increasing temperature. The density and relative crystallinity of heat-treated *P. tomentosa* wood remained constant and increased slightly. Suri et al. [20–22] reported that OHT *P. tomentosa* and *P. koraiensis* woods showed a darker color, lower weight loss in abrasion and volume shrinkage, and higher density, compressive strength, and hardness than AHT woods.

Conclusively, compared to air heat treatment, oil heat treatment is a more effective method for darkening wood color and improving the dimensional stability, compression strength, and hardness of *P. tomentosa* and *P. koraiensis* woods [20–22]. To date, no information on the weathering properties of OHT and AHT *P. tomentosa* and *P. koraiensis* woods is available to fully understand the properties of both for exterior use. Therefore, we investigated the weathering properties of OHT and AHT *P. tomentosa* and *P. koraiensis* woods to provide valuable information for effectively using both wood species.

## 2. Materials and Methods

### 2.1. Materials

Table 1 lists the basic information about the sample trees. In the present study, three trees of each *P. tomentosa* (15–20 years old) and *P. koraiensis* (30–35 years old) were harvested from Kangwon National University (KNU) research forest, Chuncheon, Korea (N 37°77′, E 127°81′). Seven defect-free quarter-sawn boards, each from near the bark of both species, with dimensions of 160 mm (longitudinal) × 50 mm (radial) × 20 mm (tangential) were prepared for heat treatment. The samples were oven-dried and put in a conditioning room at 25 ± 5 °C under 60 ± 5% RH until equilibrium moisture content was established.

**Table 1.** Basic sample tree information.

| Common Name | Scientific Name | Age (Years) | D.B.H. (mm) | Air-Dried Density (g/cm$^3$) | Location |
|---|---|---|---|---|---|
| Royal paulownia | *Paulownia tomentosa* (Thunb.) Steud. | 15–20 | 280–330 | 0.30 (0.05) * | Chuncheon, Korea (37°77′ N, 127°81′ E) |
| Korean white pine | *Pinus koraiensis* Siebold & Zucc. | 30–35 | 280–320 | 0.42 (0.05) * | |

* Numbers in parentheses are standard deviations.

### 2.2. Heat Treatment

A commercial palm oil (Lotte Foods, Seoul, Korea) was used as heating media for oil heat treatment. The wood samples were fully soaked in a lab-scale oil bath with 5 L volume (C-WHT-S2; ChangShin Science, Seoul, Korea), and then the temperature was raised from 25 ± 5 °C to the target temperatures of 180, 200, and 220 °C using 2 °C/min heating rate. The target temperature was maintained for 2 h. The samples were removed from the oil bath after the bath naturally reached 25 ± 5 °C, and then the samples were drained in a room for 24 h.

For air heat treatment, the samples were treated in an electric furnace (Supertherm HT16/16; Nabertherm GmbH, Lilienthal, Germany). The temperature was raised from 25 ± 5 °C to 180, 200, and 220 °C at a heating rate of 2 °C/min and maintained at the target temperature for 2 h. The samples were removed from the furnace after the furnace chamber naturally reached room temperature (25 ± 5 °C). All heat-treated samples were oven-dried at 105 ± 3 °C for 24 h and then kept in a desiccator with silica gel for a week.

### 2.3. Artificial Weathering Test

The artificial weathering test was conducted according to the ASTM G53-96. Three wood samples 50 (L) mm × 50 (R) mm × 20 (T) mm dimensions for each treatment were prepared for the weathering test, as shown in Table 2. The AHT, OHT, and untreated wood were exposed to UV lamps in a QUV accelerated weathering tester (QUV/se Accelerated Weathering Tester, Q-LAB, Westlake, OH, USA) for 168 h and 336 h. The weathering cycle involved continuous light irradiation with UV exposure for 2 h and condensation for 2 h. The average irradiance for UV exposure was 0.83 W/m$^2$ at 340 nm wavelength at a constant chamber temperature of 60 °C. The condensation process was performed at 50 °C. After the weathering test, the exposed samples were stored in a room at 25 ± 5 °C until further evaluation.

**Table 2.** Heat-treated wood sample information for artificial weathering tests.

| Sample Dimension | Species | Heating Media | Temperature and Duration | Sample Number [1] | Total |
|---|---|---|---|---|---|
| 50 (L) × 50 (R) × 20 (T) mm$^3$ | *Paulownia tomentosa* (Thunb.) Steud. *Pinus koraiensis* Siebold & Zucc. | Oil and air | Control<br>180 °C for 2 h<br>200 °C for 2 h<br>220 °C for 2 h | 3 × 2<br>3 × 2 × 2<br>3 × 2 × 2<br>3 × 2 × 2 | 42 |

[1] Sample number = replication × species × heating media.

### 2.4. Color Change

The color before and after the weathering was evaluated with the CIE *L*a*b** system using a chroma meter (CR-10 Plus, Konica Minolta Inc., Tokyo, Japan). In addition, the color of each sample was measured at three points on the radial surface, as shown in Figure 1. The color change before and after the weathering test was measured with three replications and determined according to the following equation:

$$\Delta E^* = (\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2})^{1/2} \quad (1)$$

where $\Delta E^*$, $\Delta L^*$, $\Delta a^*$, and $\Delta b^*$ represent the changes in overall color, lightness, red/green chromaticity, and yellow/blue chromaticity, respectively.

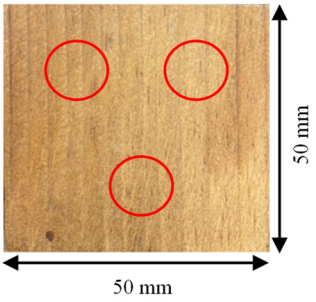


**Figure 1.** Color change measurements of samples were taken at three points (red circles).

### *2.5. Volumetric Swelling (VS) Measurement*

To measure VS, UV-exposed and oven-dried samples were immersed in water and weighed every 24 h until the weight was constant. VS was determined using the following formula:

$$VS = (V_1 - V_0)/V_0 \times 100\ (\%) \quad (2)$$

where $V_0$ and $V_1$ are the volume of the oven-dried specimens before water immersion ($mm^3$) and the volume of the specimens after water immersion ($mm^3$), respectively.

### *2.6. Fourier Transform Infrared Spectroscopy (FTIR)*

The wood powder was prepared from the surface of the wood using 800 grit sandpaper to investigate the chemical composition of each untreated and heat-treated sample before and after the artificial weathering tests. The spectra were measured with the attenuated total reflectance (ATR) method in the wavenumber of 400–4000 $cm^{-1}$ using an FTIR spectrometer (FT-IR, Nicolet Summit, Thermo Fisher Scientific, Waltham, MA, USA) installed at the Department of Forest Biomaterials Engineering at KNU.

### *2.7. Statistical Analyses*

In the present study, the color change and volumetric swelling experiment were performed with three replications. Differences in color change and volumetric swelling after the weathering test among heat treatment temperatures and between heat treatment methods were statistically analyzed at a 5% significance level using univariate analysis of variance, followed by post hoc Duncan's multiple range tests using SPSS (ver. 26, IBM Corp., New York, NY, USA).

## 3. Results and Discussion

### *3.1. Color Change after Artificial Weathering*

Figures 2 and 3 show the appearance of the heat-treated and untreated *P. tomentosa* and *P. koraiensis* wood, respectively, after the artificial weathering test. Macroscopically, both control and AHT woods at 180 °C showed a golden-yellow color after weathering. AHT *P. tomentosa* woods at 200 °C and 220 °C showed a grayish color, whereas AHT *P. koraiensis* woods at 200 °C and 220 °C showed dark-yellow color. In addition, the AHT woods at 200 °C and 220 °C showed an uneven color distribution after weathering exposure. In contrast, the color difference before and after the weathering of the OHT woods at all temperatures was negligible. As reported by Yildiz et al. [30], the weathered control woods (ash, Scots pine, and spruce) turned gray and dark, whereas the steam heat-treated woods turned silver-gray due to weathering. Furthermore, they mentioned that the light-colored woods generally tended to turn yellow or brown, and the dark-colored woods tended to bleach due to weathering. In the present study, OHT woods, after weathering exposure, showed a more uniform color than AHT woods, which could be due to heat treatment with oil providing even surface protection. As mentioned in previous studies,

oil as heating media in heat treatment generated a fast and uniform heating transfer and surface protection. In addition, linolenic acid in could protect the OHT wood surface from UV ray and water penetration during weathering [20,26,29].

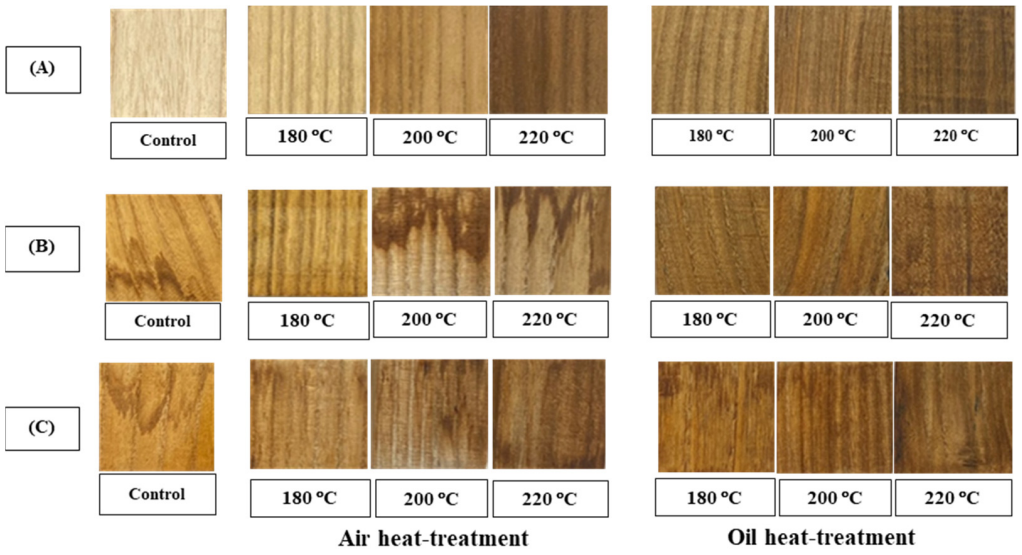


**Figure 2.** Appearances of air- and oil-heat-treated *P. tomentosa* wood after the weathering. Unexposed (**A**) and exposed to weathering for one (**B**) and two (**C**) weeks.

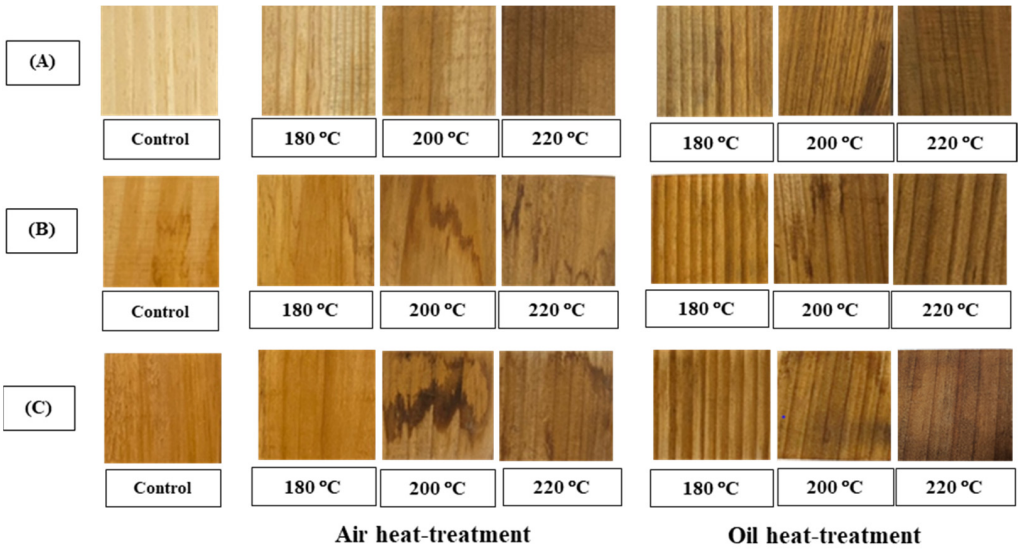


**Figure 3.** Appearances of air- and oil-heat-treated *P. koraiensis* wood after weathering. Unexposed (**A**) and exposed to weathering for one (**B**) and two (**C**) weeks.

Figures 4 and 5 show the lightness ($L^*$), red/green chromaticity ($a^*$), and yellow/blue chromaticity ($b^*$) of the OHT and AHT *P. tomentosa* and *P. koraiensis* woods after the artificial weathering tests. The $L^*$ values of untreated and heat-treated *P. tomentosa* woods at 180 °C decreased with increasing weathering duration (Figure 4). There was no significant difference in $L^*$ values of AHT and OHT *P. tomentosa* woods at 200 and 220 °C between before and after weathering exposure.

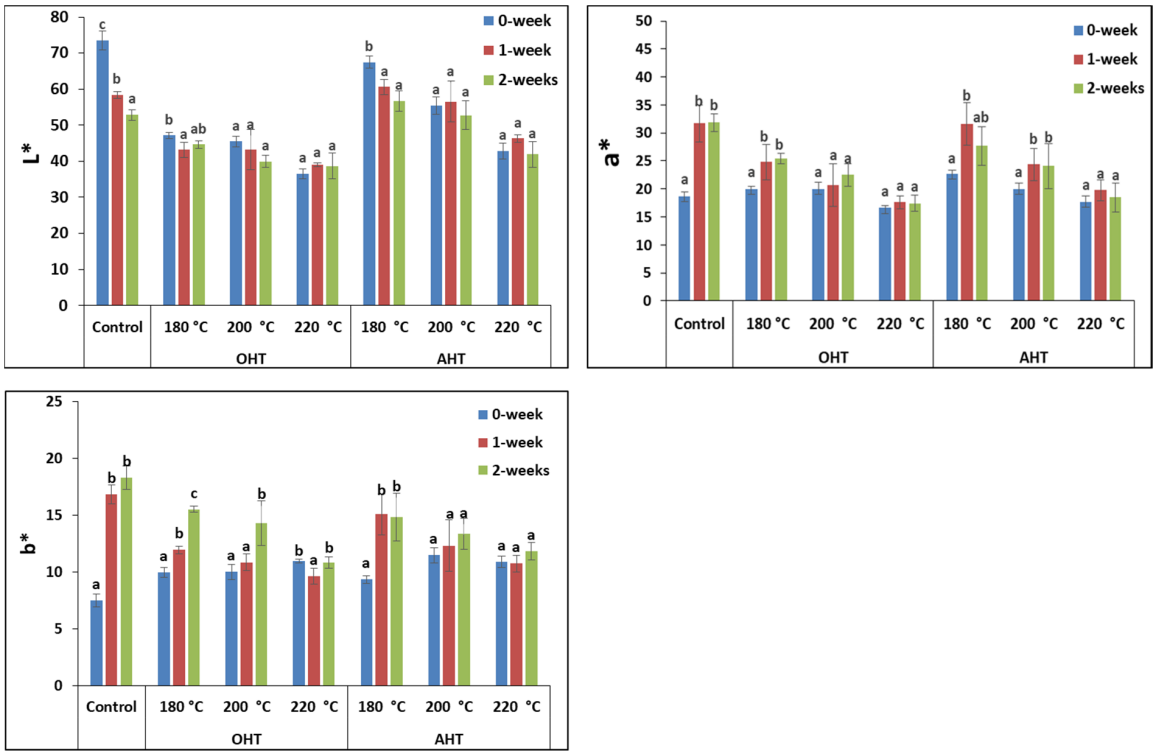


**Figure 4.** Color changes in oil heat-treated (OHT) and air heat-treated (AHT) *P. tomentosa* woods during the artificial weathering. (***L****), Lightness; (***a****), red/green chromaticity; and (***b****), yellow/blue chromaticity. The different letters on the histogram is a significant outcomes at a 5% significance level for comparisons between the samples using the Duncan's multiple range tests.

In *P. koraiensis*, the *L** values of untreated and AHT woods at 180 and 200 °C significantly decreased as the duration of weathering increased, whereas AHT woods at 220 °C showed no significant change in *L** values after weathering exposure. The *L** values of OHT woods at 180 °C significantly decreased with increasing weathering duration, whereas those of OHT woods at 200 and 220 °C hardly changed (Figure 5).

In both species, the *a** values of untreated and heat-treated wood at 180 °C significantly increased after weathering exposure. The *a** values of heat-treated woods at 200 and 220 °C hardly changed after weathering exposure.

The *b** value of untreated and heat-treated *P. tomentosa* wood at 180 °C significantly increased after weathering for one week. Furthermore, the *b** values of untreated and AHT woods at 180 °C were comparable between one and two weeks of weathering. There was no significant difference in the *b** values before and after weathering exposure of AHT woods at 200 and 220 °C. The *b** value of OHT *P. tomentosa* wood at 180 and 200 °C significantly increased with increasing exposure duration, whereas that of OHT *P. tomentosa* wood at 220 °C tended to remain constant with increasing weathering exposure. In *P. koraiensis*, the *b** value of untreated and heat-treated woods greatly increased after one week of exposure and became constant after two weeks.

Several studies support our results regarding the color change of heat-treated wood after artificial weathering. Nemeth et al. [31] reported that the dry heat-treated Pannonia poplar wood at showed a higher decrease in *L** value than the OHT wood after weathering for 40 h. Huang et al. [32] reported that the *L**, *a**, and *b** values of steam heat-treated *Pinus banksiana* wood slightly increased after weathering for 168 h and rapidly decreased after 336 to 1500 h of weathering.

The overall color changes (Δ*E**) after the artificial weathering test for one and two weeks of *P. tomentosa* and *P. koraiensis* are shown in Figures 6 and 7, respectively. The Δ*E** values of the heat-treated woods after the weathering test were significantly smaller than those of the untreated woods. The Δ*E** value significantly decreased with increasing treatment

temperature. The OHT woods had significantly lower color change than the AHT woods after the weathering test, indicating higher color stability in OHT woods. In addition, heat-treated *P. tomentosa* wood showed a smaller total color change than heat-treated *P. koraiensis* wood. Deka et al. [16] reported that the total color change of thermally modified *Picea abies* wood after UV light irradiation for 400 h was noticeably lower than that of untreated wood. Ahajji et al. [33] also mentioned that the color of heat-treated *P. abies* wood in nitrogen circumstance at 210 °C to 250 °C for 1 h showed improved stability to UV radiation than that of untreated samples. Additionally, Dubey et al. [29] reported that the color of OHT *Pinus radiata* wood after the weathering test was more stable than that of the untreated sample. They explained that after oil heat treatment, the oil forms a protective layer on the wood surfaces and acts as a barrier for UV and water absorption during artificial weathering.

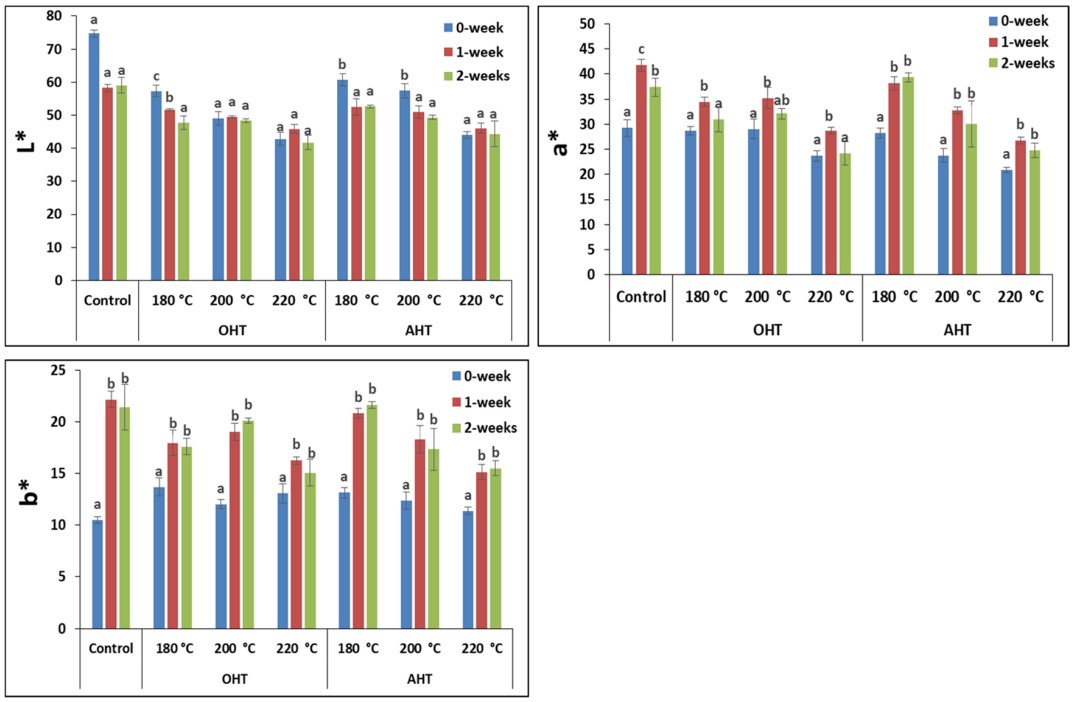


**Figure 5.** Color changes in oil-heat-treated (OHT) and air-heat-treated (AHT) *P. koraiensis* woods during the artificial weathering. (***L****), lightness; (***a****), red/green chromaticity; and (***b****), yellow/blue chromaticity. The different letters on the histogram is a significant outcomes at a 5% significance level for comparisons between the samples using the Duncan's multiple range tests.

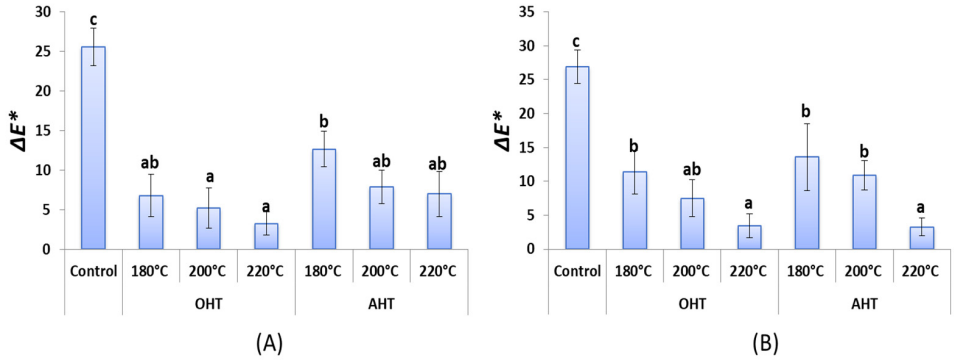


**Figure 6.** Overall color changes (Δ*E**) in *P. tomentosa* wood after weathering for one (**A**) and two (**B**) weeks. The different letters on the histogram is a significant outcomes at a 5% significance level for comparisons between the samples using the Duncan's multiple range tests.

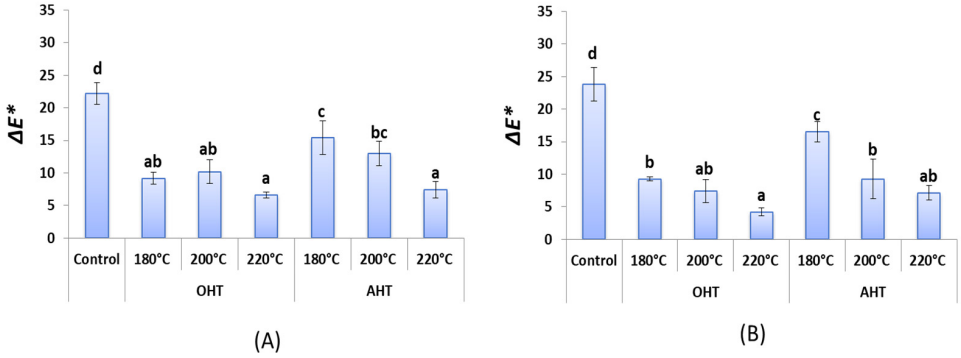


**Figure 7.** Overall color changes (Δ*E**) in *P. koraiensis* wood after weathering for one (**A**) and two (**B**) weeks. The different letters on the histogram is a significant outcomes at a 5% significance level for comparisons between the samples using the Duncan's multiple range tests.

### *3.2. VS in the Weathered Woods*

Figure 8 shows the VS in the heat-treated and untreated *P. tomentosa* and *P. koraiensis* wood exposed to artificial weathering.

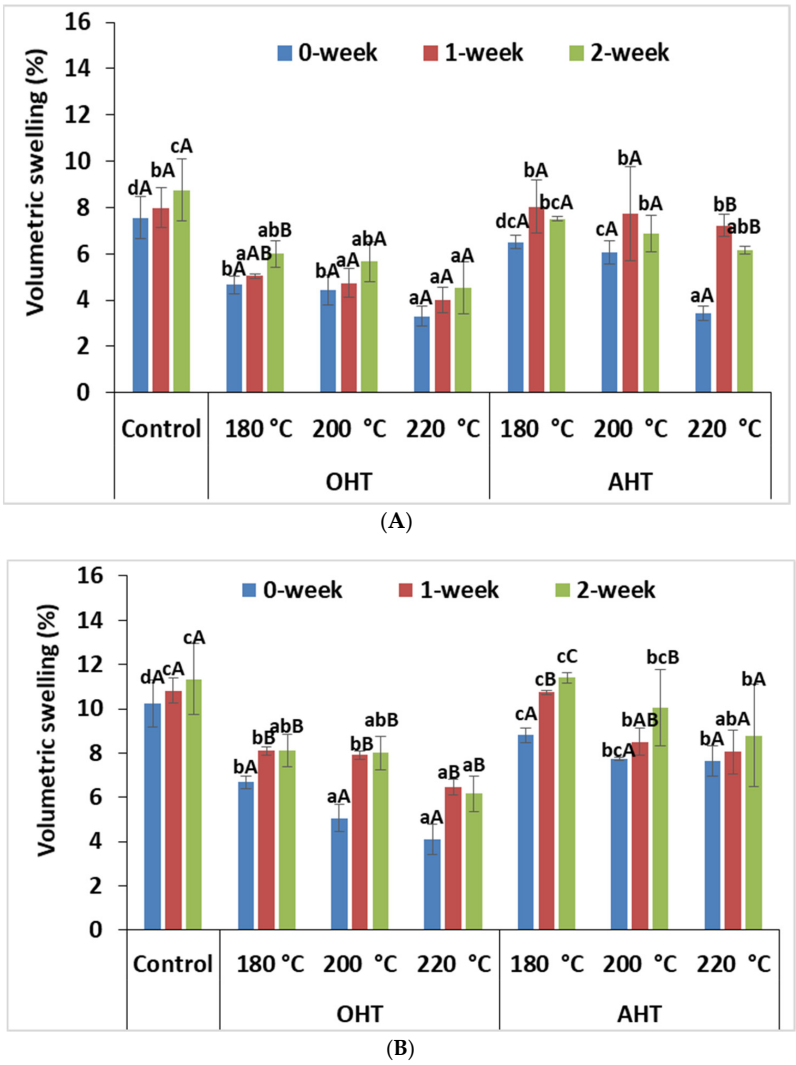


**Figure 8.** Volumetric swelling in water-immersed *P. tomentosa* (**A**) and *P. koraiensis* (**B**) woods exposed to artificial weathering. The same capital and lowercase letters on the histogram represent the insignificant

outcomes at the 5% significance level between weathering duration and between treatment conditions (AHT, OHT, and control), respectively.

In untreated woods of both species, VS tended to increase after weathering exposure, but the difference was not significant. The VS in AHT *P. tomentosa* wood at 180 and 200 °C increased after weathering exposure, whereas there was no significant difference before and after weathering. The VS in AHT *P. tomentosa* wood at 220 °C significantly increased after weathering exposure. In addition, there was no significant difference in VS of AHT *P. tomentosa* between one and two week exposure. The VS in AHT *P. koraiensis* wood at 180 and 200 °C significantly increased after weathering exposure, whereas there was no significant difference at 220 °C before and after weathering.

The VS in OHT *P. tomentosa* wood at 180 °C significantly increased after weathering exposure. The VS in OHT *P. tomentosa* wood at 200 °C and 220 °C increased after weathering, but the difference was not significant. The VS in OHT *P. koraensis* wood at all temperatures significantly increased after weathering exposure.

The VS in AHT, the untreated and AHT *P. tomentosa* woods after one week of weathering at all temperatures was comparable. After two weeks of weathering of AHT wood, the AHT *P. tomentosa* wood showed a significantly lower VS than the untreated woods, and the VS significantly decreased with increasing treatment temperature. After one and two weeks of weathering, the untreated and AHT *P. koraensis* wood at 180 °C showed a comparable VS, and the VS significantly decreased at 200 °C.

The OHT woods exposed to artificial weathering for one and two weeks showed significantly lower VS than the AHT woods, revealing higher dimensional stability in OHT wood. Among the OHT woods, the OHT wood at 220 °C showed the lowest VS, whereas there was no significant difference between the OHT woods at 180 and 200 °C.

In the present study, the OHT woods demonstrated better dimensional stability than the untreated and AHT woods, which is supported by several previous studies. Dubey et al. [29] reported that after accelerated UV weathering, the VS in OHT *Pinus radiata* wood increased; however, the increase was smaller than that in the untreated wood, indicating improved dimensional stability in the heat-treated wood samples. Bal et al. [34] reported that *Fagus orientalis* wood treated in hot sunflower oil showed significantly better dimensional stability than that treated in hot air. Yang et al. [35] observed the properties of the *Phyllostachys edulis* bamboo heat-treated in three different media, including air, nitrogen, and oil, at 150, 170, 190, and 210 °C for 1, 2, and 3 h, and revealed that heat treatment in oil was the most effective method to improve the dimensional stability of the bamboo.

There are some plausible explanations for the dimensional stability of OHT wood. Oil usually contains high levels of linolenic acid, which tends to dry quickly and can harden on the wood surface after heat-treatment with oil [36]. Linolenic acid preserves the OHT wood surface from UV ray and water penetration during weathering [20]. The higher dimensional stability of OHT wood after the artificial weathering test may be due to the increase in lignin stability due to condensation during the thermal modification process [16,29,36].

### 3.3. Chemical Composition

The FTIR spectra of heat-treated *P. tomentosa* and *P. koraiensis* woods before and after weathering are presented in Figures 9 and 10, respectively.

#### 3.3.1. Chemical Composition of AHT Woods before and after Weathering

AHT woods at 180 °C for both species showed comparable FTIR spectra to the untreated woods. The peaks at 1650 $cm^{-1}$ and 809 $cm^{-1}$ disappeared in AHT *P. tomentosa* wood at 200 and 220 °C, whereas the peaks were not detected in AHT *P. koraiensis* wood at 220 °C. The peak at 1157 $cm^{-1}$ of both AHT woods became smaller at 220 °C, whereas the peaks at 1105 $cm^{-1}$ and 1050 $cm^{-1}$ became greater at 200 and 220 °C. The lignin peak intensity at 1502 $cm^{-1}$ of both AHT woods, 1230 $cm^{-1}$ of AHT *P. tomentosa* wood, and 1260 $cm^{-1}$ of AHT *P. koraiensis* wood decreased at 220 °C.

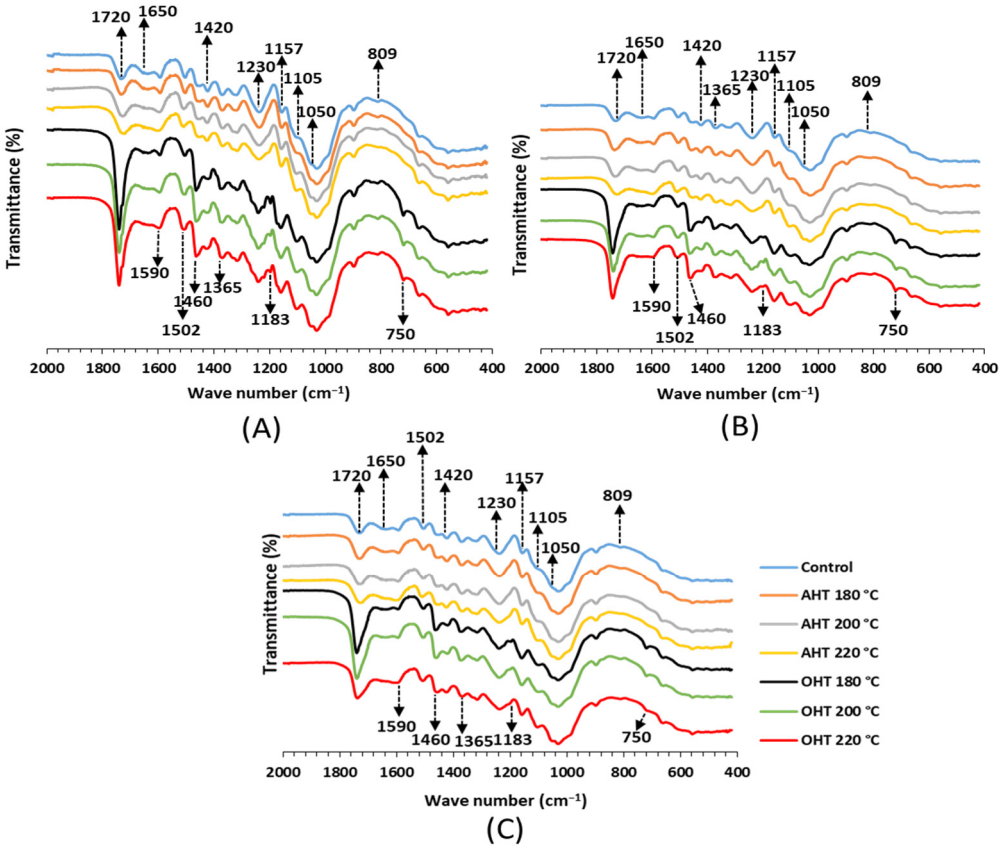


**Figure 9.** FT-IR spectra of air-heat-treated (AHT) and oil-heat-treated (OHT) *P. tomentosa* woods before and after weathering. Before weathering (**A**), one-week weathering (**B**), and two-week weathering (**C**).

In the present study, AHT woods showed a noticeable change in the carbohydrate peaks with increasing temperature, which is consistent with previous studies. Lin et al. [37] reported that the peak intensity at 1730−1740 $cm^{-1}$ representing C=O stretching vibrations of acetyl, carbonyl, and carboxyl groups of heat-treated poplar and fir wood decreased with increasing temperature. Yildiz et al. [30] reported that the decrease in the water peak at 1650 $cm^{-1}$ for heat-treated pine and ash woods may be related to the acid-catalytic hydrolysis of wood polyose esters at elevated temperatures. Huang et al. [38] reported an increase in the C–O peak at 1103 $cm^{-1}$ after heat treatment due to the formation of new alcohols and esters, which could be related to the improvement of the hydrophobicity of wood.

After weathering exposure for 2 weeks, the lignin peak intensity at 1590 $cm^{-1}$, 1502 $cm^{-1}$, 1460 $cm^{-1}$, 1260 $cm^{-1}$, and 1230 $cm^{-1}$ of untreated and AHT woods at 180 and 200 °C decreased, whereas the lignin peaks of the AHT woods at 220 °C showed no noticeable change after weathering exposure. In this study, untreated and AHT woods showed a decrease in the peak of aromatic-skeletal vibration in lignin, which is consistent with a few earlier studies. Yildiz et al. [30] reported that lignin peaks at 1600 $cm^{-1}$ and 1510 $cm^{-1}$ decreased significantly due to UV irradiation during weathering in both untreated and heat-treated ash, iroko, Scots pine, and spruce woods. Huang et al. [38] reported that all lignin peaks at 1600 $cm^{-1}$, 1510 $cm^{-1}$, 1465 $cm^{-1}$, 1263 $cm^{-1}$, and 1103 $cm^{-1}$ in untreated and heat-treated *Pinus banksiana*, *Populus tremuloides*, and *Betula papyrifera* woods decreased significantly due to weathering.

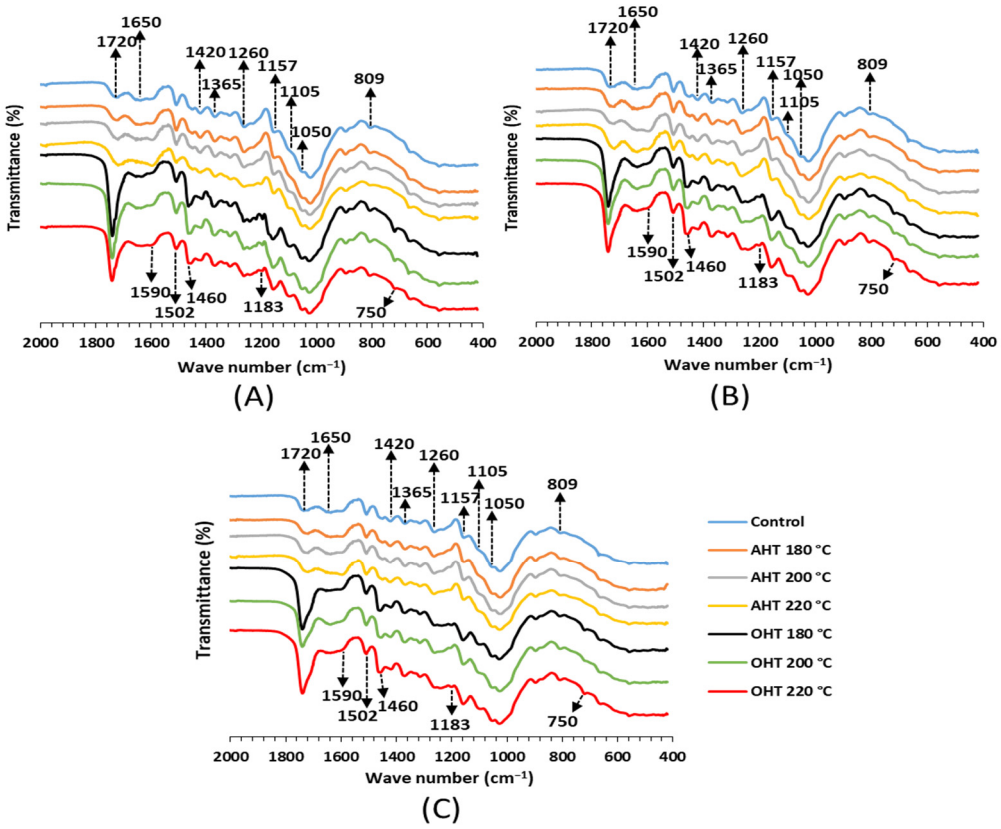


**Figure 10.** FT-IR spectra of air-heat-treated (AHT) and oil-heat-treated (OHT) *P. koraiensis* woods before and after weathering. Before weathering (**A**), one-week weathering (**B**), and two-week weathering (**C**).

3.3.2. Chemical Composition of OHT Woods before and after Weathering

The carbohydrate peaks at 1720 $cm^{-1}$, 1365 $cm^{-1}$, 1157 $cm^{-1}$, and 1105 $cm^{-1}$ in OHT woods of both species were noticeably higher than those in the untreated and AHT woods of both species. Additionally, the peaks of aromatic-skeletal vibration in lignin at 1460 $cm^{-1}$ in the OHT woods of both species were noticeably greater than those in the untreated and AHT woods of both species. Carbohydrate peaks at 1183 and 750 $cm^{-1}$ were detected in OHT woods, whereas they were absent in untreated and AHT woods. Some of the sharp peaks in the OHT woods could be related to the functional groups of edible palm oil. Some previous studies [39–42] have explained the contribution of functional groups of edible oil to FTIR peaks, such as carbonyl esters of the triglycerides at 1742 $cm^{-1}$, bending vibrations of the $CH_2$ and $CH_3$ aliphatic groups at 1465 $cm^{-1}$, symmetrical bending of $CH_3$ at 1377 $cm^{-1}$, stretching vibration of the C–O ester groups at 1238 and 1163 $cm^{-1}$,–C–O and CO stretching, $CH_2$ bending vibration at 1155 $cm^{-1}$, and methylene rocking vibration at 720 $cm^{-1}$.

In OHT *P. tomentosa* woods, the peak at 1650 $cm^{-1}$ disappeared at 200 °C and 220 °C, whereas the peak remained unchanged in OHT *P. koraiensis* wood. The carbohydrate peaks at 1157 $cm^{-1}$ and 890 $cm^{-1}$ and lignin peaks at 1502 $cm^{-1}$, 1230 $cm^{-1}$, and 1260 $cm^{-1}$ of OHT woods remained constant with increasing temperature. It seems that there was no significant change in FTIR spectra of OHT woods with increasing temperature due to the contribution of functional groups of edible oil to FTIR peaks, which confirmed the contribution of palm oil to the improvement of color and dimensional stability of OHT woods.

After weathering exposure, the peak intensity of aromatic-skeletal vibration in lignin in the OHT woods of both species did not exhibit a noticeable change, indicating an improvement in color and dimensional stability. Dubey et al. [21] reported that linolenic acid

in oil protects the surface of OHT wood from UV penetration and water absorption during weathering. The higher color and dimensional stability of OHT wood after the artificial weathering test may be due to the increase in lignin stability due to condensation during the thermal modification process [16,29,36]. The carbohydrate peaks at 1183 and 1157 $cm^{-1}$ in the OHT woods of both species decreased after weathering exposure, which could be related to oil degradation due to weathering exposure. As previously reported [39–42], these peaks may be due to the functional groups in edible palm oil. In OHT *P. koraiensis* wood, the peak at 1650 $cm^{-1}$ decreased after two weeks of weathering exposure, whereas the peak remained constant in OHT *P. tomentosa* wood. This decrease may be due to the leaching or water removal of previously formed oxidized compounds, such as quinones [42].

## 4. Conclusions

After weathering exposure, the color of untreated and AHT woods at 180 °C of both species changed from whitish to golden-yellow. AHT *P. tomentosa* woods showed a grayish color at 200 °C and 220 °C, whereas AHT *P. koraiensis* woods showed a dark-yellow color. There was no noticeable color difference in the OHT woods of both species after weathering. The AHT and OHT woods of both species had significantly lower total color change and VS than the untreated woods. However, OHT woods showed significantly higher color and dimensional stability than AHT.

In the FTIR spectra of AHT woods, the intensity of carbohydrate peaks noticeably changed with increasing temperature, whereas those peaks of OHT woods remained constant with increasing temperature. The peaks at 1720 $cm^{-1}$, 1365 $cm^{-1}$, 1157 $cm^{-1}$, and 1105 $cm^{-1}$ 1460, 1183 $cm^{-1}$, and 750 $cm^{-1}$ in OHT woods were sharper than those in AHT, which related to palm oil substances. The FTIR spectra of untreated and AHT woods of both species showed a noticeable decrease in lignin peak intensity after weathering exposure, whereas in OHT woods, the peaks were unchanged, exhibiting color and dimensional change stability. The intensity of some carbohydrate peaks in untreated and AHT woods increased after weathering exposure, but the peaks decreased in OHT *P. koraiensis* wood and remained constant in OHT *P. tomentosa* wood.

In conclusion, oil heat treatment at 200 °C and 220 °C effectively improved the color and dimensional stability of both *P. tomentosa* and *P. koraiensis* woods by weathering. These results will assist in determining the outdoor application and suitable heat treatment for woods of both species. In addition, to overcome the cost of palm oil, further study on the reusability of palm oil used for heat treatment should be considered for future research.

**Author Contributions:** Conceptualization, I.F.S. and N.-H.K.; methodology, I.F.S., S.-Y.P. and N.-H.K.; validation, N.-H.K.; formal analysis, I.F.S. and B.D.P.; investigation, I.F.S. and B.D.P.; resources, S.-Y.P. and N.-H.K.; data curation, I.F.S. and B.D.P.; writing—original draft preparation, I.F.S. and B.D.P.; writing—review and editing, B.D.P. and N.-H.K.; visualization, I.F.S. and B.D.P.; supervision, S.-Y.P., W.H., A.H.I. and N.-H.K.; project administration, J.-H.K.; and funding acquisition, S.-H.L. and N.-H.K. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF), funded by the Ministry of Education (NRF2016R1D1A1B01008339; NRF-2018R1A6A1A03025582), Science and Technology Support Program through the National Research Foundation of Korea (NRF) and funded by the Ministry of Science and ICT (MSIT) (NRF-2022R1A2C1006470), and the R&D Program for Forest Science Technology (Project Nos. 2021350C10-2323-AC03) by the Korea Forest Service (Korea Forestry Promotion Institute).

**Data Availability Statement:** The datasets generated and analyzed during the current study are not publicly available but are available from the corresponding author upon reasonable request.

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

## References


1. Chong, S.H.; Park, B.S. *Wood Properties of the Useful Tree Species Grown in Korea*; National Institute of Forest Science: Seoul, Republic of Korea. (In Korean)
2. Akyildiz, M.H.; Kol, H.S. Some technological and uses of paulownia (*Paulownia tomentosa*) wood. *J. Environ. Biol.* **2010**, *31*, 351–355.
3. Lopez, F.; Perez, A.; Zamudio, M.A.M.; Alva, H.E.D.; Garcia, J.C. Paulownia as raw material for solid biofuel and cellulose pulp. *Biomass Bioenergy* **2012**, *45*, 77–86. [CrossRef]
4. Qi, Y.; Jang, J.H.; Hidayat, W.; Lee, A.H.; Lee, S.H.; Chae, H.M.; Kim, N.H. Carbonization of reaction wood from *Paulownia tomentosa* and *Pinus densiflora* branch woods. *Wood Sci. Technol.* **2016**, *50*, 973–987. [CrossRef]
5. Kang, C.W.; Jang, E.S.; Jang, S.S.; Cho, J.I.; Kim, N.H. Effect of heat treatment on the gas permeability, sound absorption coefficient, and sound transmission loss of *Paulownia tomentosa* wood. *J. Korean Wood Sci. Technol.* **2019**, *47*, 644–654. [CrossRef]
6. Son, Y.; Noh, N.J.; Kim, R.Y.; Koo, J.W.; Yi, M.J. Biomass and nutrients of planted and naturally occurring *Pinus koraiensis* in Korea. *Eur. J. For. Res.* **2007**, *10*, 41–50.
7. Hill, C.A.S. *Wood Modification: Chemical, Thermal and Other Processes*; John Wiley & Sons: Chincester, UK, 2006.
8. Esteves, B.M.; Pereira, H.M. Wood modification by heat treatment: A review. *BioResources* **2009**, *4*, 370–404. [CrossRef]
9. Tjeerdsma, B.F.; Militz, H. Chemical changes in hydrothermal treated wood: FTIR analysis of combined hydrothermal and dry heat-treated wood. *Holz als Roh- und Werkstoff.* **2006**, *63*, 102–111. [CrossRef]
10. Hakkou, M.; Pétrissans, M.; Zoulalian, A.; Gérardin, P. Investigation of wood wettability changes during heat treatment on the basis of chemical analysis. *Polym. Degrad. Stab.* **2005**, *89*, 1–5. [CrossRef]
11. Boonstra, M.J.; Acker, J.V.; Kegel, E.; Stevens, M. Optimisation of a two-stage heat treatment process: Durability aspects. *Wood Sci. Technol.* **2007**, *41*, 31–57. [CrossRef]
12. Dubey, M.K.; Pang, S.; Walker, J. Changes in chemistry, color, dimensional stability and fungal resistance of *Pinus radiata* D. Don wood with oil heat-treatment. *Holzforschung* **2012**, *66*, 49–57. [CrossRef]
13. Surini, T.; Charrier, F.; Malvestio, J.; Charrier, B.; Moubarik, A.; Castera, P.; Grelier, S. Physical properties and termite durability of maritime pine *Pinus pinaster* Ait., heat-treated under vacuum pressure. *Wood Sci. Technol.* **2012**, *46*, 487–501. [CrossRef]
14. Hidayat, W.; Jang, J.H.; Park, S.H.; Qi, Y.; Febrianto, F.; Lee, S.H.; Kim, N.H. Effect of temperature and clamping during heat treatment on physical and mechanical properties of Okan (*Cylicodiscus gabunensis* [Taub.] Harms) wood. *BioResources.* **2015**, *10*, 6961–6974. [CrossRef]
15. Esteves, B.; Ferreira, H.; Viana, H.; Ferreira, J.; Domingos, I.; Cruz-Lopes, L.; Jones, D.; Nunes, L. Termite Resistance, Chemical and Mechanical Characterization of *Paulownia tomentosa* Wood before and after Heat Treatment. *Forests* **2021**, *12*, 1114. [CrossRef]
16. Deka, M.; Humar, M.; Rep, G.; Kricej, B.; Sentjurc, M.; Petric, M. Effects of UV light irradiation on colour stability of thermally modified, copper ethanolamine treated and non-modified wood: EPR and DRIFT spectroscopic studies. *Wood Sci. Technol.* **2008**, *42*, 5–20. [CrossRef]
17. Hidayat, W.; Qi, Y.; Jang, J.H.; Febrianto, F.; Kim, N.H. Effect of mechanical restraint on the properties of heat-treated *Pinus koraiensis* and *Paulownia tomentosa* woods. *BioResources* **2017**, *12*, 7539–7551. [CrossRef]
18. Hidayat, W.; Qi, Y.; Jang, J.H.; Park, B.H.; Banuwa, I.S.B.; Febrianto, F.; Kim, N.H. Color change and consumer preferences towards color of heat-treated Korean white pine and royal paulownia woods. *J. Korean Wood Sci.* **2017**, *45*, 213–222. [CrossRef]
19. Kim, Y.K.; Kwon, G.J.; Kim, A.R.; Lee, H.S.; Purusatama, B.; Lee, S.H.; Kang, C.W.; Kim, N.H. Effects of Heat Treatment on the Characteristics of Royal Paulownia (*Paulownia tomentosa* (Thunb.) Steud.) Wood Grown in Korea. *J. Korean Wood Sci. Technol.* **2018**, *46*, 511–526. [CrossRef]
20. Suri, I.F.; Kim, J.H.; Purusatama, B.D.; Yang, G.U.; Prasetia, D.; Lee, S.H.; Hidayat, W.; Febrianto, F.; Park, B.H.; Kim, N.H. Comparison of the color and weight changes in heat-treated *Paulownia tomentosa* and *Pinus koraiensis* wood with hot oil and hot air. *BioResources* **2021**, *16*, 5574–5585. [CrossRef]
21. Suri, I.F.; Purusatama, B.D.; Lee, S.; Kim, N.; Hidayat, W.; Ma'ruf, S.D.; Febrianto, F. Characteristic features of the oil-heat-treated woods from tropical fast growing wood species. *Wood Res.* **2021**, *66*, 365–378. [CrossRef]
22. Suri, I.F.; Purusatama, B.D.; Kim, J.H.; Yang, G.U.; Prasetia, D.; Kwon, G.J.; Hidayat, W.; Lee, S.H.; Febrianto, F.; Kim, N.H. Comparison of physical and mechanical properties of *Paulownia tomentosa* and *Pinus koraiensis* wood heat-treated in oil and air. *Eur. J. Wood Prod.* **2022**, *80*, 1389–1399. [CrossRef]
23. Esteves, B.; Domingos, I.; Pereira, H. Pine wood modification by heat treatment in air. *BioResources* **2008**, *3*, 142–154. [CrossRef]
24. Quirino, R.L.; Richa, L.; Petrissans, A.; Teixeira, P.R.; Durrell, G.; Hulette, A.; Colin, B.; Petrissans, M. Comparative Study of Atmosphere Effect on Wood Torrefaction. *Fibers* **2023**, *11*, 27. [CrossRef]
25. Tang, T.; Chen, X.; Zhang, B.; Liu, X.; Fei, B. Research on the physico-mechanical properties of moso bamboo with thermal treatment in tung oil and its influencing factors. *Materials* **2019**, *12*, 599. [CrossRef] [PubMed]
26. Sailer, M.; Rapp, A.O.; Leithoff, H.; Peek, R.D. Upgrading of wood by application of an oil heat treatment. *Holz. Roh. Werkst.* **2000**, *58*, 15–22. [CrossRef]
27. Cheng, D.; Chen, L.; Jiang, S.; Zhang, Q. Oil uptake percentage in oil-heat-treated wood, its determination by soxhlet extraction, and its effects on wood compression strength parallel to grain. *BioResources* **2014**, *9*, 120–131. [CrossRef]
28. Okon, K.E.; Lin, F.; Lin, X.; Chen, C.; Chen, Y.; Huang, B. Modification of Chinese fir (*Cunninghamia lanceolata* L.) wood by silicone oil heat treatment with micro-wave pretreatment. *Eur. J. Wood Prod.* **2018**, *76*, 221–228. [CrossRef]

29. Dubey, M.K.; Pang, S.; Walker, J. Color and dimensional stability of oil heat-treated radiata pine wood after accelerated UV weathering. *For. Prod. J.* **2010**, *60*, 453–459.
30. Yildiz, S.; Tomak, E.D.; Yildiz, U.C.; Ustaomer, D. Effect of artificial weathering on the properties of heat-treated wood. *Polym. Degrad. Stab.* **2013**, *98*, 1419–1427. [CrossRef]
31. Nemeth, R.; Tolvaj, L.; Bak, M.; Alpar, T. Colour stability of oil-heat treated black locust and poplar wood during short-term UV radiation. *J. Photochem. Photobiol. A Chem.* **2016**, *329*, 287–292. [CrossRef]
32. Huang, X.; Kocaefe, D.; Kocaefe, Y.; Boluk, Y.; Pichette, A. Study of the degradation behavior of heat-treated jack pine (*Pinus banksiana*) under artificial sunlight irradiation. *Polym. Degrad. Stab.* **2012**, *97*, 1197–1214. [CrossRef]
33. Ahajji, A.; Diouf, P.N.; Aloui, F.; Elbakali, I.; Perrin, D.; Merlin, A.; George, B. Influence of heat treatment on antioxidant properties and colour stability of beech and spruce wood and their extractives. *Wood Sci. Technol.* **2009**, *43*, 69–83. [CrossRef]
34. Bal, B.C. Physical properties of beech wood thermally modified in hot oil and in hot air at various temperatures. *Cienc. Tecnol.* **2015**, *17*, 789–798. [CrossRef]
35. Yang, T.H.; Lee, C.H.; Lee, C.J.; Cheng, Y.W. Effects of different thermal modification media on physical and mechanical properties of moso bamboo. *Constr. Build. Mater.* **2016**, *119*, 251–259. [CrossRef]
36. Huang, X.; Kocaefe, D.; Kocaefe, Y.; Boluk, Y.; Pichette, A. Changes in wettability of heat-treated wood due to artificial weathering. *Wood Sci. Technol.* **2012**, *46*, 1215–1237. [CrossRef]
37. Gunstone, F.D. *Vegetable Oils in Food Technology: Composition, Properties, and Uses*; Blackwell: Oxford, UK, 2002.
38. Lin, B.J.; Colin, B.; Chen, W.S.; Petrissans, A.; Rousset, P.; Petrissans, M. Thermal degradation and compositional changes of wood treated in a semi-industrial scale reactor in vacuum. *J. Anal. Appl. Pyrolysis* **2018**, *130*, 8–18. [CrossRef]
39. Vlachos, N.; Skopelitis, Y.; Psaroudaki, M.; Konstantinidou, V.; Chatzilazarou, A.; Tegou, E. Applications of Fourier transform-infrared spectroscopy to edible oils. *Anal. Chim. Acta* **2006**, *573–574*, 459–465. [CrossRef] [PubMed]
40. Rohman, A.; Che Man, Y.B.; Ismail, A.; Hashim, P. Application of FTIR spectroscopy for the determination of virgin coconut oil in binary mixtures with olive oil and palm oil. *J. Am. Oil Chem. Soc.* **2010**, *87*, 601–606. [CrossRef]
41. Tomak, E.D.; Hughes, M.; Yildiz, U.C.; Viitanen, H. The combined effects of boron and oil heat treatment on beech and Scots pine wood properties. Part 1: Boron leaching, thermogravimetric analysis, and chemical composition. *J. Mater Sci.* **2011**, *46*, 598–607. [CrossRef]
42. Lim, S.Y.; Abdul Mutalib, M.S.; Khaza'ai, H.; Chang, S.K. Detection of fresh palm oil adulteration with recycled cooking oil using fatty acid composition and FTIR spectral analysis. *Int. J. Food Prop.* **2018**, *1*, 2428–2451. [CrossRef]