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Wood Surface Changes of Heat-Treated *Cunninghamia lanceolate* Following Natural Weathering

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Abstract: To quickly clarify the effect of heat treatment on weatherability of *Cunninghamia lanceolate* (Lamb.) Hook., we investigated the surface degradation under natural exposure. A comparison between heat-treated and untreated samples was taken based on surface color changes and structural decay at each interval. Over four weeks of natural exposure, multiple measurements were carried out. Results show that color change decreased in the order of 220 °C heat-treated > untreated > 190 °C heat-treated. The results also indicate that the wood surface color stability was improved via the proper temperature of thermal modification. Low vacuum scanning electron microscopy (LVSEM) results expressed that thermal modification itself had caused shrinking in the wood surface structure. From the beginning of the weathering process, the heat treatment affected the surface structural stability. After natural exposure, the degree of wood structure decay followed the pattern 220 °C heat-treated > 190 °C heat-treated > untreated. Therefore, when considering the impact on the structure, thermal modification treatment as a protective measure to prevent weathering was not an ideal approach and requires further improvement.

Keywords: natural weathering; heat-treated; color change; wood anatomical; *Cunninghamia lanceolate*

1. Introduction

In recent years, the wood protection industry has been paying greater attention to environmentally friendly substitutes for traditional wood protection treatments. One existing environmentally conscious method is the thermal modification of wood. Modified wood does not impregnate the material with any harmful substances or chemicals and the finished material does not produce environmental pollution. In the heat-treatment process, the wood is heated to high temperatures, ranging from 160 °C to 260 °C, for various standing times based on the species and the desired material properties [1–4]. Thermal modification offers particular benefits. In general, it reduces the equilibrium moisture content, improves hydrophobicity, enhances dimensional stability, maintains uniform wood color, and offers improved protection, especially against damage caused by micro-organisms and insects. However, brittleness, cracking, and other forms of mechanical strength loss are the main disadvantages of heat-treated wood [1,3,5]. Thermally-modified wood has many applications for exterior structures, including terraces, fences, decks, cladding, garden furniture, doors, and windows; as well as interior uses, e.g., decorative panels, parquet, kitchen furniture, and saunas [3,6,7].

Weathering is the general term used to refer to the slow degradation of materials when exposed to the weather. It can be influenced by several factors, including sunlight, moisture, heat/cold, wind, air pollutants, and biological agents [8]. Weathering of wood surfaces can cause color, chemical, physical, mechanical, and microscopic changes. These changes occur in the wood surface at a depth of 0.05–2.5 mm during the initial weathering period [9].

Earlier research generally examined the resistance of heat-modified wood to artificial weather [10–16]. Heat-treated wood exhibits high physical characteristics and low mechanical properties during artificial weathering. Artificial weathering tests are generally considered to be a simulation of outdoor conditions, but this method includes only UV light and moisture cycles. There are many other degradation factors in the natural environment, such as microbes, air pollutants, chemicals, and biological agents [8]. Therefore, and artificial weathering experiment cannot fully substitute for a study of natural weathering, and it is still necessary to test the service life of wood. Research of natural weathering always takes many years. In fact, the surface changes of weathering characteristics begin from the moment the wood is exposed to the outdoor environment. It has been reported that the surface characteristics of wood can change significantly during a short exposure period [17]. Therefore, surface change analysis is a method that can evaluate the weatherability of wood over a short period of time.

The purpose of this study is to clarify the effect of heat treatment on the weatherability of *Cunninghamia lanceolate* (Lamb.) Hook. wood. We conducted an outdoor exposure experiment for one month and examined the anatomical and physical changes of wood surface. In order to attain these objectives, some techniques and methods for the study of wood surfaces were used such as a colorimeter for physical color changes and low vacuum scanning electron microscopy (LVSEM) for anatomical changes. These analytical tools provided accurate insight into the degradation process, which allowed a comparison between heat-treated and untreated Chinese fir exposed to natural conditions.

2. Materials and Methods

2.1. Preparation of Wood Samples

All the samples used in this study were taken from Chinese fir (*Cunninghamia lanceolate*) [18]. Samples were obtained from sapwood straight off the grain, and each was free of knots and visible defects. Samples were 10 (R) × 10 (T) × 10 (L) mm in size. Under drying conditions, three parts of the samples were cut with a hammer microtome. Lumber was heat-treated at 190 °C and 220 °C for 120 min, respectively, under steam. This range was chosen because 220 °C is a significant critical point for the heat treatment of Chinese fir [19]. From previous studies of Chinese fir [20], heat treatment at 190 °C and 220 °C was determined to be optimal temperatures for strength and corrosion resistance, respectively. Timbers were dried to a moisture content of 8% prior to the steam-heat treatments. About 4% moisture content was achieved after the steam-heat treatments. Samples were classified into three groups as follows: (1) untreated controls, (2) 190 °C heat-treatment, and (3) 220 °C heat-treatment.

2.2. Natural Weathering Conditions

Untreated and heat-treated Chinese fir samples were placed in an outdoor environment for four weeks. The experiment was conducted during the summer season of 2018 in Fukuoka, Japan. The statistics mean temperature, humidity, duration of sunshine, total rainfall and wind speed were 30.01 ± 1.41 °C, 67.81% ± 6.31%, 9.13 ± 3.57 h, 1.68 mm, and 2.92 ± 0.80 m/s, respectively. They were orientated in a south-facing position at 45° relative to the horizontal (latitude 33° north) according to JIS K 5600-7-6 [21]. After one day of exposure, all the specimens were retrieved from the weathering racks, and measurements were taken in a laboratory, after which they were put back on the weathering racks. This was repeated after 2, 4, 7, 14, 21, and 28 days [22]. On each occasion, a puff of nitrogen was used to gently clear the surface of dust.

2.3. Color Measurements

Color measurements were used to evaluate the degree of color change on the sample surfaces after each period of natural weathering [22]. There were 10 replicates for each treatment group. A mathematical average was established based on 30 measurements for every data point of color measurement. For each sample, the color coordinates L*, a*, and b* were established both before and after exposure to weather. A handy colorimeter (Model NR-3000, Nippon Denshoku, Tokyo, Japan) was used to measure the color change, with a D65 standard illuminant and the 2° standard observer. The color difference values of ΔC*, ΔE*, and ΔH* were determined before and after the natural conditions. C* indicates chroma, while ΔC* is the chroma difference. The parameter ΔE* indicates the total difference value. ΔH* is the difference in hue [23,24]. Average values and standard deviation were computed for each sample. These parameters were then employed to establish ΔC*, ΔE*, and ΔH* based on the following formulae:

$$C^* = [(a^*)^2 + (b^*)^2]^{1/2} \tag{1}$$

$$\Delta C^* = C^* - C_o^* \tag{2}$$

$$\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2} \tag{3}$$

$$\Delta H^* = [(\Delta E^*)^2 - (\Delta L^*)^2 - (\Delta C^*)^2]^{1/2} \tag{4}$$

Positive values of ΔC* indicate greater vividness, whereas a negative value indicates a more faded hue in comparison to the initial color. A low ΔE* indicates that the color was not altered very much or remained the same, while a high value indicates obvious color change. ΔH* records the extent of the hue change.

2.4. Statistical Analysis

By statistical analysis of the color data before and after natural weathering, the color difference values of different exposure times did not conform to normal distribution. The rank sum test method of paired samples was selected in this experiment. With the change of exposure time, the color difference of 190 °C and 220 °C heat-treated wood was compared separately with that of untreated samples. The measurement index is the color difference values of ΔC*, ΔE*, and ΔH*, which were the quantitative data of the paired design. The rank of the contrast difference was reported in the results. The results of the Wilcoxon signed ranks test indicated the Z value, the approximate method was used to calculate the *p* value, and the statistical significance of the difference was determined.

2.5. Low-Vacuum Scanning Electron Microscopy (LVSEM)

During the natural weathering experiment, samples that had no coating were observed via low-vacuum scanning electron microscopy (LV-SEM, Model JSM-5600LV, JEOL, Tokyo, Japan). The microscopy conditions were as follows: a voltage of 15 kV, a pressure of approximately 10–30 Pa, and a working distance of 10–20 mm. This LVSEM method was deployed over the exact same area of wood surface before and after exposure. LVSEM was a valuable tool to observe the anatomical changes in the process of weathering [25,26].

3. Results

3.1. Discoloration of Wood Surfaces

Wood absorbs light, and polymeric compounds inside wood interact with photons. These factors lead to the deterioration and discoloration of wood. When wood is exposed to natural conditions, other factors such as moisture and microorganism growth also contribute to the degradation. The color of the exposed wood is influenced by light radiation, rain water, and temperature. UV light causes particularly remarkable color changes [24,27–29]. Color stability is an important parameter among the physical properties of wood.

After heat treatment, the color exhibited a notable change, and the colors visible to the naked eye became darker. L* (lightness) decreased, while a* (redness) increased. Different temperatures had effects on the color of wood. B* (yellowness) and C* (chroma) increased after 190 °C heat treatment, while these variables decreased after 220 °C heat treatment. These changes might be due to hydroxyl groups that were oxidized to carbonyl groups and carboxyl groups during heat treatment. If this is the case, then the wood color was darkened because the carbonyl groups belong to chromophric groups and the carboxyl groups to auxochromic groups [30].

Figure 1 shows the color modifications (L*, a*, b*, and c*) of untreated and heat-treated wood surfaces while exposed to natural conditions. Increases in a* (redness) were observed with the increase in exposure time during the first stages. Redness of heat-treated samples underwent an especially noticeable increase after the first weathering day. However, a slow increase in redness was also shown during the first 4 exposure days for untreated samples. After the first 4 days, the value of a* decreased quickly for both untreated samples. After the first 4 days, the value of a* decreased quickly for both untreated and heat-treated wood. Increases in b* (yellowness) and c* (chroma) were observed with increases in the number of natural weathering days. In particular, b* and c* exhibited rapid increases during the first week. Nevertheless, a slow increase in these values was also shown in the natural weathering experiment after the first week. This implies that the first week is a critical period for changes in yellow and intense chroma during the natural weathering. The L* (lightness) value of untreated wood demonstrated a decrease in each treatment, but the L* values increased as the number of days increased for wood that received heat treatment at 190 °C and 220 °C. As time increased during the first week, the value of L* changed rapidly. After one week, however, the value of L* changed incrementally. The darkening of untreated wood might be caused by high temperature inducing the migration of extractives to the wood surface. Several previous studies have reported similar results [11,12,31–33]. The surface of heat-treated wood became lighter during weathering as the extractives were degraded and removed. This lightening was mainly due to the photodegradation of lignin [12].

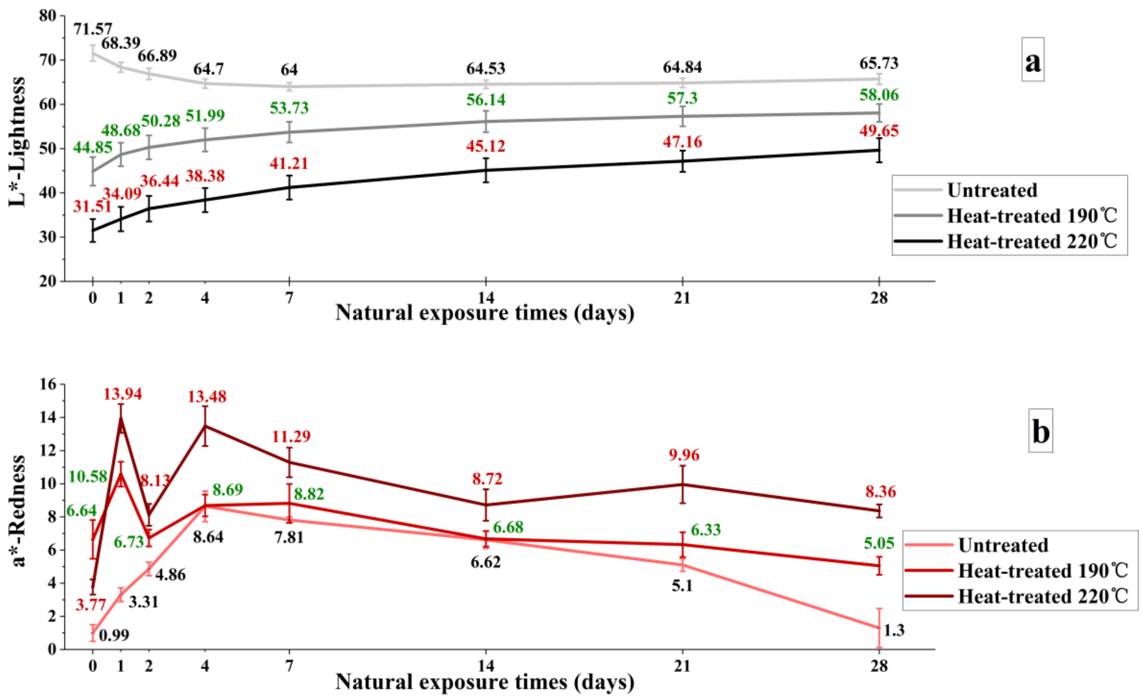


Figure 1. *Cont.*

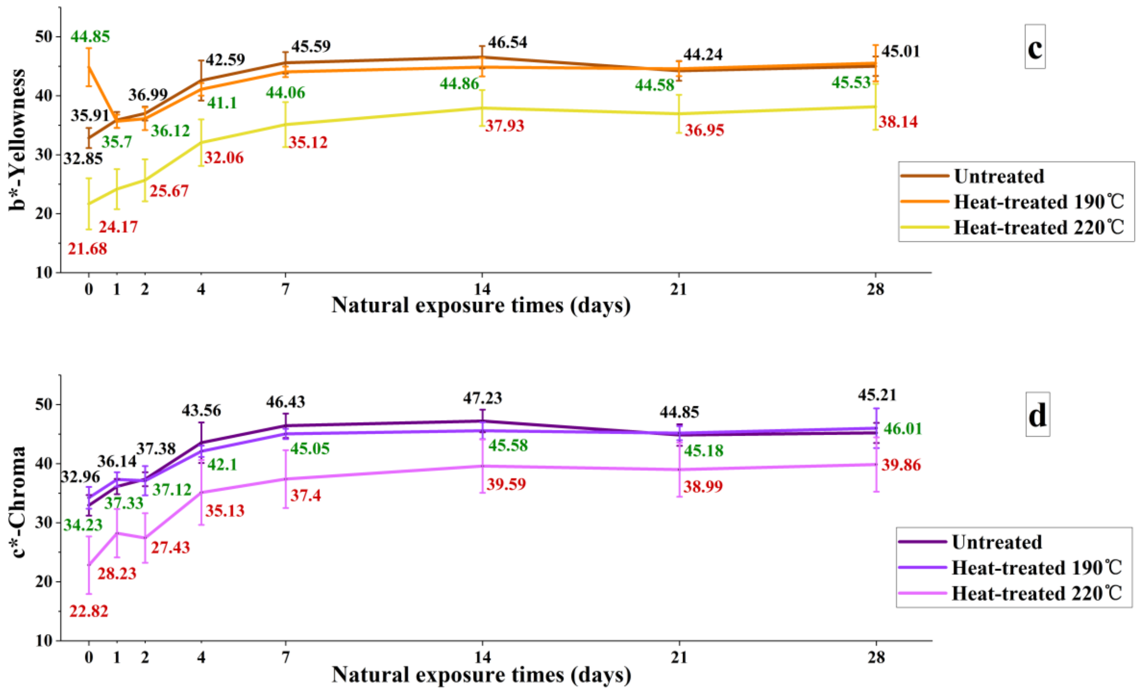
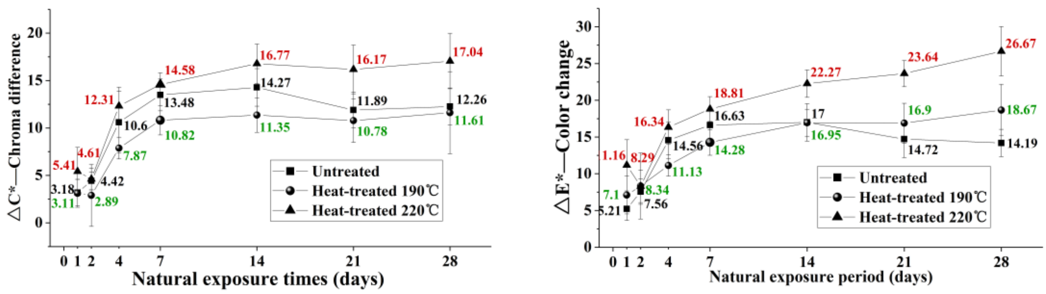


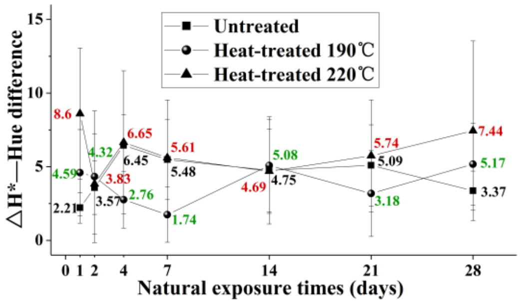
Figure 1. Color modifications for each of the four weeks of natural exposure: (**a**) Lightness L*; (**b**) redness a*; (**c**) yellowness b*; (**d**) chroma c*.

Figure 2 shows the effect of natural exposure on ΔC*, ΔE*, and ΔH*, revealing the color changes as a result of the effects of natural weathering on wood samples. The ΔC* (chroma difference) values in untreated and in heat-treated wood increased significantly in the first seven days, and the values then stabilized after the first week. The ΔC* value for 190 °C heat-treated wood was lower than other treatments. This result indicates that 190 °C heat-treatment could attenuate the chroma difference during the natural weathering process. The values of ΔH* (hue difference) exhibited insignificant changes during the four weeks of the experiment for both untreated and heated-treated wood (Figure 2c). Meanwhile, ΔE* (total color difference) values in untreated wood increased quickly over the initial seven-day period, and the values then started decreasing after two weeks. However, this phenomenon was not found in heat-treated wood. This implies that untreated and heat-treated samples exhibited different color change responses during the four weeks of natural weathering.



(**a**) (**b**)

Figure 2. *Cont.*



(**c**)

Figure 2. Color changes of wood samples subjected to natural conditions: (**a**) Chroma difference Δc*; (**b**) color change ΔE*; (**c**) hue difference ΔH*.

Wilcoxon signed ranks test statistics demonstrated significant differences in ΔC*, ΔE*, and ΔH* values during the four weeks of natural exposure for the untreated, 190 °C heat-treated, and 220 °C heat-treated wood samples (Table 1). The results illustrated that the surface chroma exhibited a significant negative difference for both the 190 °C heat-treated and untreated in the initial stage of natural weathering (Table 2). The 190 °C heat treatment clearly promoted the stability of chromaticity. The same results were also obtained for ΔE* (total color difference value) and ΔH* (hue difference), but the differences were not so significant. However, the 220 °C heat-treated wood exhibited a significant positive difference in ΔC*, ΔE*, and ΔH* when compared to untreated wood (Table 2). This shows that 220 °C heat treatment could not stabilize the color during the process of weathering. On the contrary, this treatment brings about greater color change (Table 1).

Table 1. Ranks heat-treated–untreated.

			N	Mean Rank	Sum of Ranks
ΔC*	190 °C heat-treated–untreated	Negative ranks	48 [a]	37.11	1781.50
		Positive ranks	20 [b]	28.23	564.50
		Ties	0 [c]		
		Total	68		
	220 °C heat-treated–untreated	Negative ranks	17 [a]	22.12	376.00
		Positive ranks	53 [b]	39.79	2109.00
		Ties	0 [c]		
		Total	70		
ΔE*	190 °C heat-treated–untreated	Negative ranks	39 [a]	30.74	1199.00
		Positive ranks	29 [b]	39.55	1147.00
		Ties	0 [c]		
		Total	68		
	220 °C heat-treated–untreated	Negative ranks	4 [a]	14.50	203.00
		Positive ranks	56 [b]	40.75	2282.00
		Ties	0 [c]		
		Total	70		
ΔH*	190 °C heat-treated–untreated	Negative ranks	41 [a]	35.30	1447.50
		Positive ranks	27 [b]	33.28	898.50
		Ties	0 [c]		
		Total	68		
	220 °C heat-treated–untreated	Negative ranks	28 [a]	30.20	845.50
		Positive ranks	42 [b]	39.04	1639.50
		Ties	0 [c]		
		Total	70		

[a] Heat-treated < untreated; [b] Heat-treated>untreated; [c] Heat-treated = untreated.

Table 2. Test statistics; [a] heat-treated–untreated.

	ΔC*		ΔE*		ΔH*	
	190 °C	220 °C	190 °C	220 °C	190 °C	220 °C
Z	−3.718 [b]	−5.071 [b]	−0.159 [b]	−6.083 [b]	−1.677 [b]	−2.323 [b]
Asymp. Sig. (2-talled)	**	**	0.874	**	0.093	*

[a] Wilcoxon signed ranks test; [b] Based on negative ranks. * Statistically significant $p < 0.05$; ** Statistically significant $p < 0.01$.

Other researchers [34,35] reported that cellulose remained relatively stable after heat treatment of Chinese fir. In hemicelluloses, the acetyl group was decomposed from molecular chains to acetic acid and degraded pyranose. A cross-linking occurrence had been formed among the aromatic units in the lignin. The observed that higher heat treatment temperatures intensified the reaction [19]. In the present study, there are two potential reasons for the favorable color stability under natural weathering of wood heat-treated at 190 °C. First, the heat treatment temperature of 190 °C may not have been enough to greatly change the chemical composition of wood because hemicellulose degradation was less 3% [34]. Second, color deepening after heat treatment could inhibit the color change to a certain extent [36,37]. As a result, the color change of wood during natural exposure was weakened and the color stability was improved after 190 °C heat treatment. The relative content of lignin in wood was significantly increased after heat treatment at 220 °C because of the degradation of hemicellulose [19,34]. The most important change in the process of weathering was the decomposition of lignin [24,27,38–41]. This directly results in the aggravation of weathering, and the color change was very significant. Therefore, selecting the appropriate thermal modification temperature played a substantial role in color stability during the weathering process.

3.2. Wood Structure Changes

The changes of wood surface structure accompany other physical changes taking place during the natural weathering. Heat treatment changes the characteristics of wood, including microscopic structural changes. In this study, low vacuum scanning electron microscopy (LVSEM) was used to investigate the wood structure degradation of heat-treated Chinese fir (*Cunninghamia lanceolate*) subjected to natural exposure. Both heat-treated and untreated wood surfaces were surveyed for comparison. LVSEM analysis of the three sections of heat-treated Chinese fir sapwood showed obvious microscopic structural changes that took place during the short-term exposure to conditions (Figures 3 and 4). It was found that microstructure did not change in the first two days of natural weathering, until after four days had a little change (shown in Figure 4g).

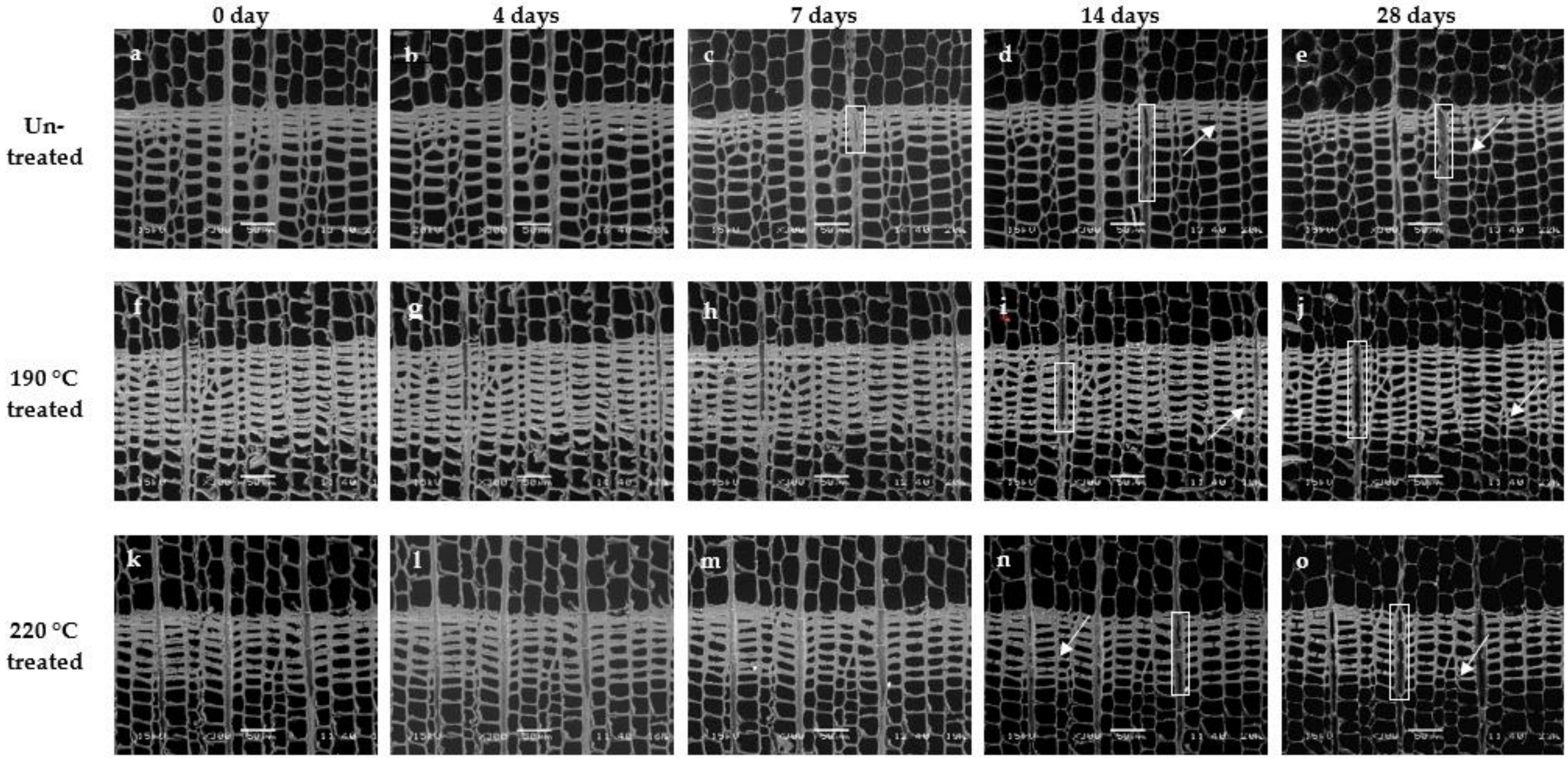


Figure 3. Scanning electron micrographs of cross sections of untreated and heat-treated wood before and after natural weathering.

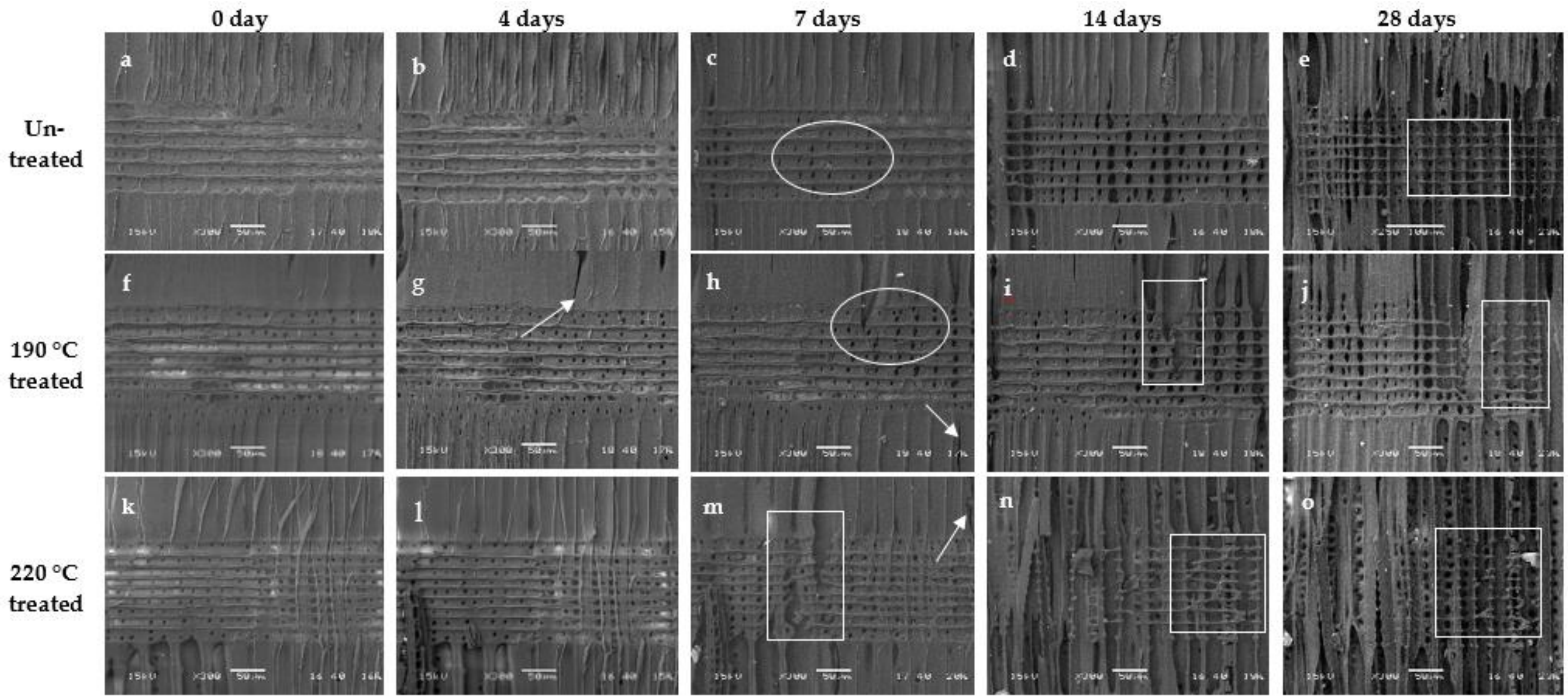


Figure 4. Scanning electron micrographs of radial sections of untreated and heat-treated wood before and after natural weathering.

3.2.1. Cell Wall

As shown in Figure 3a,f,k the microstructure of the heat-treated wood was rougher than the microstructure of untreated wood. Heat treatment caused the cell wall to become slightly plasticized [42]. The surface of the heat-treated Chinese fir wood was more brittle than the surface of untreated wood. In contrast, the 220 °C heat treatment had greater effects than the 190 °C heat treatment. After four weeks of natural weathering, the middle lamella and primary cell wall had substantially disappeared (as shown by the arrows in Figure 3e,j,o). Compared with the unexposed condition, the secondary cell wall became obviously thinner. The degradation of the secondary cell wall in heat-treated wood was more severe than untreated wood under natural weathering conditions. The comparison between the two heat treatment groups found that higher heat treatment temperatures produced more severe weathering erosion of the secondary cell wall (Figure 3).

The S1 layer comprises 30.0% cellulose, 51.7% lignin, and 18.3% hemicellulose. The S2 layer comprises 54.3% cellulose, 15.1% lignin, and 30.6% hemicelluloses. The S3 layer is composed of 13% cellulose, no or only negligible amounts of lignin, and 87% hemicelluloses [43]. The lignin content in wood exposed for four weeks is somewhat lower than the content in wood exposed for seven days. Compared with the untreated wood, the heat treatment caused significant degradation of hemicellulose and cellulose in the cell wall. Therefore, the lignin percentage was relatively increased. Chemical composition changes caused differences in the structure. As a result, the change in the material from exposure was more significant in heat treatment groups. However, there is a rupture phenomenon in the weathering stage due to the high level of lignin in the cell wall of the wood exposure for seven days. Previous studies on the heat treatment of Chinese fir showed that chemical changes increased with high temperature. The degree of wood plasticization increased with the proportion of hemicellulose and cellulose [7,19]. The results of this experiment are consistent with previous research conclusions that reported that heat treatment produced microstructural changes [12].

In the case of Chinese fir, the untreated and the heat-treated wood tended to show degradation in the primary cell wall and middle lamella when subjected to natural weathering after two weeks (as shown by the arrows in Figure 3d,i,n). According to the literature [43], the primary cell wall and middle lamella comprised primarily lignin (84%), a smaller percentage of hemicelluloses (13.3%), and a very small percentage of cellulose (0.7%). The disappearance of the primary cell wall and lamella in wood after four weeks of weathering evidenced that the most photosensitive component of the cell wall was lignin. This conclusion conformed to previous studies [12]. The lignin content in the cell walls of the heat-treated Chinese fir was much higher than that of the untreated control group, and higher heat treatment temperatures produced higher proportions of lignin in the cell wall [19,43]. The cell wall lignin content exhibited the following pattern: 220 °C treated > 190 °C treated > untreated. Structures with high lignin content were more seriously eroded during weathering due to the photodegradation of lignin. The degree of cell wall damage after weathering followed the pattern: 220 °C treated > 190 °C treated > untreated.

3.2.2. Rays

Figure 3a,f,k show that the heat treatment apparently did not alter the microstructure of the wood rays. After natural weathering over 28 days, ray parenchyma cells exhibited a much higher the degree of degradation in the heat treatment groups and untreated groups than surrounding tracheids (as shown by the square area in Figure 3e,j,o). It is well known that parenchyma cells only possess very thin primary cell walls and no secondary walls. The chemical constituents of these cell walls are mostly lignin [14]. After heat treatment, these cell walls are still mainly composed of lignin. The attenuation of the cell wall in the parenchyma cells during the weathering process was obvious. This provides more evidence that the photosensitivity of lignin was particularly prominent.

3.2.3. Cross-Field

SEM pictures of the cross-field structure on the radial section of untreated and heat-treated samples displayed certain differences (Figure 4). Serious structural damage was found at the cross-field after heat treatment at 220 °C (shown in Figure 4m). Longer exposure times produced the more obvious damage. After 28 days of weathering, the cell walls of the ray parenchyma at the cross-field position were significantly degraded (as shown by the square area in Figure 4e,j,o). Compared with the thickness of cross-field tracheid walls after weathering, the degradation of ray parenchyma cells is obvious. These cells only possess primary walls and do not contain secondary walls. Therefore, their main components were lignin [14,43], and lignin was highly degraded during weathering. The degradation degree of tracheid cell walls also increased with higher heat treatment temperatures.

In SEM micrographs of the cross-field pits of Chinese fir, it can be seen that the pits did not suffer damage due to the heat treatment process (Figure 4f,k). The edges of the bordered pits were destroyed after 1 week of weathering and cracked along the direction of the microfibril (as shown by the circle area in Figure 4c,h,m). Higher heat treatment temperatures produced higher plasticity. During the process of weathering, cracking was more likely to occur under the influence of shrinkage and swelling.

3.2.4. Tracheids

Micrographs of the radial surface of untreated and heat-treated wood demonstrated that the natural weathering process caused degradation of the wood surface. After only a week, severe longitudinal micro-cracks appeared on the tangential surface tracheids of the heat-treated wood (as shown by the arrows in Figure 4h,m). Cellulose is responsible for wood strength, hemicelluloses and lignin compose the matrix system in wood, and lignin provides wood with rigidity or stiffness. During the process of weathering, the change of humidity and the loss of lignin in the secondary cell wall caused serious surface shrinkage and made the wood crack more easily. After heat treatment, plasticization exacerbated the cracking.

4. Discussion

In summary, it can be seen that the more serious deterioration during the natural weathering process was caused by the anatomical position of high lignin content. Lignin was always the most sensitive chemical component in weathering, and this is consistent with the results of previous studies [24,27,38–41]. Relative lignin content depended more on the degradation of hemicellulose at higher treatment temperatures [30,34]. The more obvious the decay phenomenon happened in the high lignin content anatomical position under natural exposure. We conclude that heat treatment of wood could not improve structural stability; on the contrary, it would aggravate the decline of the anatomical structural structure. Both 190 °C and 220 °C heat treatments accelerated the aging phenomenon, and these results differ only in degree. These trends were contrary to the results of color stability.

Heat-treated wood, considered comprehensively, can enhance the dimensional stability of wood, maintain uniform wood color, and, most importantly, prevent degradation caused by microorganisms and insects [1,3,5]. These advantages play a very positive role in the natural weathering of wood. In particular, reducing the damage caused by microorganisms and insects greatly improves the degradation resistance of the wood itself, and it mitigates the effects of natural weathering caused by decay. However, because heat treatment reduces the mechanical strength and structural stability of wood, heat treatment as a means of wood weatherproofing should be comprehensively evaluated first. In the process of heat treatment, the changes of mechanical strength and structural stability should be considered and serve as the focus of future research. Making full use of the advantages of improving corrosion resistance and reducing the loss of mechanical strength and structural stability, heat-treatment technology is better applied to the environmentally friendly modification of wood weathering prevention, and the utilization rate of wood is thus improved.

5. Conclusions

Heat-treated and untreated *Cunninghamia lanceolate* samples were exposed to natural conditions for one month. The physical and anatomical changes were examined on wood surfaces by different analysis methods.

After 190 °C heat treatment, the color change of the Chinese fir surface was significantly restrained in the process of natural weathering. Heat treatment played a positive role in maintaining the physical properties of wood.

The LVSEM study indicated that heat treatment aggravated the degradation of the wood structure in Chinese fir subjected to natural conditions. Thermal modification was not conducive to the maintenance of structural stability.

The effect of heat treatment on the weatherability of Chinese fir wood was beneficial for aesthetic properties and harmful for structural properties. If heat treatment is deployed as an anti-weathering treatment method, practitioners should comprehensively consider the advantages and disadvantages of thermally modified wood.

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