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EFFECT OF PRESSURIZED HOT WATER TREATMENT ON THE MECHANICAL PROPERTIES, SURFACE COLOR, CHEMICAL COMPOSITION AND CRYSTALLINITY OF PINE WOOD

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ABSTRACT

The effect of a pressurized hot water treatment (PHWT) on the mechanical properties, chemical composition, surface color, and cellulose crystalline structure of *Pine* wood were examined in this study. The effects of PHWT of pine wood at 140, 160, 180, and 200°C for 1, 3 and 5 h were investigated in terms of changes in mechanical properties, chemical composition, surface color and cellulose crystallinity of pine wood by means of a GB/T standard, NREL LAP, Color Difference Meter, and X-ray diffraction (XRD). Both the temperature and treatment time showed significant effects. The results showed that the bending strength and elastic modulus decreased with an increasing temperature and duration. Changes in the chemical components and surface color occurred because of the degradation of the cellulose, hemicelluloses and lignin in the wood during the PHWT. Additionally, the relative degree of relative crystallinity of the samples increased. These findings demonstrated the potential of PHWT for the wood modification.

KEYWORDS: Pine wood, mechanical properties, chemical composition, surface color, crystallinity index, pressurized hot water treatment (PHWT).

INTRODUCTION

Heat treatment of wood is an effective and environmental friendly way to improve wood dimensional stability and durability. The effects of heat treatment on the technological properties of red-bud maple (*Acer trautvetteri* Medw.) wood have been examined (Korkut et al. 2008). The compression strength parallel to the grain, bending strength, elastic modulus, Janka hardness, impact bending strength, and tension strength perpendicular to the grain were determined. Compression combined with steam treatment was used to examine the changes in the porosity, chemical composition, and cellulose crystalline structure of spruce wood cell walls (Yin et al. 2017). However, compression combined with steam treatment required a long treatment time and only the surface of the wood was treated.

Silicone oil heat treatment (SOHT) was used by Okon et al. (2017) to examine the chemical composition, cellulose crystalline structure, thermal degradation, and contact angle of Chinese parasol wood. After SOHT was completed, chemical composition analysis, Fourier transform infrared (FTIR) spectroscopy, thermogravimetric analysis (TGA), and X-ray diffraction (XRD) analysis of the treated samples were conducted. In the case of oxygen isolation, hot oil was used for wood heat treatment by Sailer et al. (2000). The optimum heat treatment temperature was between 185°C and 205°C. After heat treatment, the corrosion resistance of the wood improved, but the mechanical properties decreased. Additionally, the heat treatment efficiency was higher. However, this treatment is expensive. Leppänen et al. (2011) extracted Norway spruce saw meal with pressurized hot water at 120°C to 240°C using a flow-through system. Only small amounts of hemicelluloses were extracted at 120°C and 160°C, and then dissolution was enhanced remarkably when higher extraction temperatures were applied.

Penttilä et al. (2013) used pressurized hot water extraction with a flow-through system to extract hemicellulose and lignin from birch sawdust. The structure of the extraction residue was studied at various levels. The PHWT was found to increase the lateral width of cellulose crystallites, which was determined through Wide-angle X-ray scattering (WAXS), whereas a small decrease in the crystallinity of cellulose was detected compared with native wood. Hosseinaei et al. (2011) performed a pressurized hot-water pretreatment on wood strands to investigate the effects of the extraction of hemicellulose under different temperatures and durations. The hydrolysate was analyzed by means of high-performance liquid chromatography. The effects of hemicellulose extraction on the wettability of wood strands were studied by measuring the contact angle and surface free energy. However, the mechanism of the treatment and the rearrangement of bio-molecules under compressive conditions were unclear. Changes in the physical and chemical structure at the molecular level have not been fully characterized and understood. It is therefore desirable to monitor the decomposition of the polymer structure in the cell wall and gain knowledge of property changes in treated wood. Additionally, wood is a cellular biomaterial with a complex multi-component structure. Its cell wall is primarily composed of cellulose, hemicelluloses, and lignin. Cellulose molecules form microfibril aggregates that are embedded in a soft matrix of hemicelluloses and lignin (Salmén and Burgert 2009). The properties of wood are highly dependent on its chemical composition, the orientation of the cellulose microfibrils, and the molecular interactions of the cell wall polymer assembly (Burgert 2006, Wei and McDonald 2016). Therefore, it is necessary to study the relationship between the duration and temperature of the PHWT and the effects on the treated material properties.

In the present study, the effects of the PHWT on the bending strength, elastic modulus, surface color, chemical composition, and crystallinity of pine wood at different treatment temperatures (140°C, 160°C, 180°C and 200°C) and for different durations (1 h, 3 h and 5 h) were studied in details. The changes in mechanical properties, values of $L^*a^*b^*$ and ΔE^*, contents of cellulose, hemicelluloses, and lignin and cellulose crystallinity of the pine wood should be analyzed by means of GB/T 1936.1 (2009), GB/T 1936.2 (2009), Color difference meter, A NREL LAP and XRD.

MATERIALS AND METHODS

Materials

Small specimens 20 × 20 × 300 mm and 20 × 20 × 200 mm in the tangential (T), radial (R), and longitudinal (L) directions, respectively cut from pine wood were subjected to a PHWT in a laboratory-scale autoclave (Xingyu mechanical equipment Co., Ltd., Gangzhou, China). Afterwards, the treated specimens were cooled to room temperature inside the autoclave and conditioned to the equilibrium moisture content via storage in a conditioning room. The treated specimens were separated into three groups. Group 1 (20 × 20 × 300 mm) was subjected to a physical mechanics test according to GB/T 1929-2009. Group 2 (20 × 20 × 200 mm) was evaluated for color using the *CIE L*a*b**. Group 3 was sliced in the axial directions (0.3 g) to measure the wood polymer content according to the method in a NREL LAP. Each of the treated samples was sliced at the same height section and then milled into a powder for the X-ray diffraction (XRD) analysis.

Methods

NREL LAP

A NREL LAP was used to determine the cellulose, hemicelluloses, and lignin contents in the wood (Sluiter et al. 2008, Sluiter et al. 2010, Templeton et al. 2010). This method utilized acid hydrolysis and gas chromatography to determine the content of monosaccharides in the wood. The method can be mass-determined, and is widely used in international research institutions.

Determination of the mechanical strength of the wood

The wood was sawn according to the GB/T 1929 (2009) standard. Then, the bending strength of the wood was measured according to the GB/T 1936.1 (2009), and the elastic modulus of the wood was measured according to the GB/T 1936.2 (2009). Both mechanical tests were done on a universal mechanical testing machine (Li Ling test machine, Jinan, China). Additionally, 50 samples for each specimen, some of the specimens used in this experiment were pressurized in hot water, and some of them were untreated.

X-ray diffraction (XRD)

The XRD measurements were performed on an XRD instrument (D/MAX 2200, Rigaku, Boston, USA). The 2θ range was between 10° and 40° and was scanned at a rate of $4^{\circ}\cdot\mathrm{min}^{-1}$. Based on the peak height method developed by Segal et al. (1959), the XRD crystallinity index ($\mathrm{CrI}_{\mathrm{XRD}}$) was measured using the following height ratio:

$$CrI_{XRD} = \frac{I_{002} - I_{am}}{I_{002}} \times 100 \quad (\%) \tag{1}$$

where: I_{002} - represents both crystalline and amorphous parts and
I_{am} - represents only the amorphous part of the diffractogram.

Color difference meter

The color difference meter is developed and manufactured according to the international Commission Internationale Eclairage (CIE) (1931, 1976) standards. The working principle of the color difference meter is to automatically compare the color difference between the untreated and the treated wood samples, and output three sets of CIE-Lab data. At the same time, four sets of color difference data for *ΔE**, *L**, *a**, and *b** are also output (Bell et al. 2009, García-Mateos et al. 2015, Shukla and Vankar 2017).

RESULTS AND DISCUSSION

Mass loss

Tab. 1 indicates that the mass loss of the pine wood increased gradually with an increasing temperature and time. At 140°C, the mass loss rate increased slowly as the time increased. At this temperature, hemicelluloses degrade, whereas cellulose and lignin do not decompose. At 160°C, the mass loss rate increased significantly as the time increased. These results indicated that the chemical composition of the cell walls of the pine wood was changed. At 200°C for 5 h, the mass loss rate was 31.47%. Not only were the hemicelluloses degraded, but the lignin also reached the glass-transition temperature and was in the viscous flow state. As reported in the literature the chemical composition of wood changed obviously at about 165°C. The degradation rate of hemicelluloses is faster than that of cellulose and lignin (Leppänen et al. 2011, Shafizadeh et al. 1977, Kuriyama et al. 1967).

Tab. 1: Mass loss rate of the pine wood with different PHWT.

Treatment temperature (°C)	Holding time (h)	Mass loss rate (%)
140	1	0.78
	3	3.73
	5	7.38
160	1	7.00
	3	11.88
	5	15.66
180	1	16.51
	3	21.27
	5	22.31
200	1	23.80
	3	27.54
	5	31.47

Chemical composition of the pine wood

Relative cellulose content

Tab. 2 shows the change in the cellulose content when the temperature and duration of the treatment were varied from 140°C to 200°C and 1 h to 5 h, respectively. After successive treatments at 140°C for 1 h, 3 h, and 5 h, the relative cellulose content of the wood remained unchanged compared with that of the untreated wood. At 160°C, the cellulose content was reduced. After treatments at 160°C for 1 h, 3 h, and 5 h respectively, the cellulose content decreased by 2.92%, 4.26% and 8.25%. Compared with the untreated material, the cellulose content loss was smaller. At 160°C to 200°C, the cellulose content decreased significantly with an increasing temperature and time. Then at 200 °C for 1 h, 3 h, and 5 h respectively, the cellulose content decreased by 20.46%, 29.17%, and 44.01%, which indicated that degradation of the cellulose in pine wood was intense. The trend of this change was consistent with that of the mass loss, which indicated that cellulose degraded obviously at about 200°C (Shafizadeh et al. 1977, Kuriyama et al. 1967).

Relative hemicelluloses content

Tab. 2 shows that the relative hemicelluloses content of the wood decreased gradually with an increasing treatment time and temperature. At 140°C for 1 h, 3 h, and 5 h respectively, the hemicelluloses content of the wood decreased by 7.23%, 12.15%, and 14.67%, compared with that of the untreated wood. This indicated that the hemicelluloses began to hydrolyze at 140°C. At 160°C for 1 h, 3 h, and 5 h, the hemicelluloses content of the wood decreased by 14.88%, 21.31%, and 28.53%, respectively. At 200 °C and for 1 h, 3 h, and 5 h, the hemicelluloses content decreased by 68.75%, 81.10%, and 93.68%, respectively. At the same treatment time and temperature, the hemicelluloses content decreased more than the cellulose content. In this process, the Acetyl group in hemicelluloses is cracked to form acetic acid, and carbohydrates are degraded to form formaldehyde and furaldehyde (Dirol et al. 1993, Sivonen et al. 2002, Kollman et al. 1965, Dietrich et al. 1978, Tjeerdsma et al. 2005).

Tab. 2: Relative contents of the chemical components with different treatments.

	Relative content of cellulose (%)			Relative content of hemicelluloses (%)			Relative content of lignin (%)		
Time	1 h	3 h	5 h	1 h	3 h	5 h	1 h	3 h	5 h
140°C	49.326	49.339	49.286	14.786	14.002	13.601	28.424	28.501	29.021
160°C	47.728	47.071	45.112	13.568	12.542	11.392	28.816	30.179	31.795
180°C	44.683	42.157	39.044	9.883	7.431	5.486	29.542	31.001	33.916
200°C	39.105	34.825	27.527	4.981	3.012	1.008	34.094	36.281	40.473
Untreated		49.166			15.939			28.401	

Relative lignin content

The relative lignin content in the wood increased gradually with an increasing treatment time and temperature. At 140°C for 1 h and 3 h, the lignin content of the pine wood was unchanged, and for 5 h, the relative lignin content increased by 4.02%. When the treatment temperature increased from 160°C to 200°C, the relative lignin content of the wood increased significantly. With a constant treatment time and temperature, the lignin in the pine wood degraded slowly, and the reduction in the lignin was smaller than that of the cellulose and hemicelluloses. The lignin degradation and cross-linking reaction occur simultaneously during heat treatment, however, the degree of degradation reaction is far greater than that of cross-linking reaction (Kamdem et al. 1999, Kamdem et al. 2002). The study of Funaoka et al. (1990) showed that the polycondensation of diphenylmethane occurs in lignin components during heat treatment. Demethoxy reaction was also accompanied by lignin degradation during heat treatment, and a large number of free radicals were produced to participate in the cross-linking reaction. These reactions have contributed to the increase of lignin content.

Relative crystallinity degree of the cell walls of the wood

Crystalline structure of pine wood after treatments was studied by XRD. The XRD diffractograms of the cell walls of the untreated and treated pine wood (Fig. 2 and 3) clearly indicated changes in the signal intensities. The CrI_{XRD} values were lower after the treatment. These results were interpreted easily by the amorphous reduction of the hemicelluloses and cellulose in the high-temperature treatment process (Bhuiyan et al. 2000). The untreated wood displayed a typical native cellulose pattern that had a parallel upward arrangement of the cellulose chains. Typical peaks were observed at 16.8° and 22.45° (Guo et al. 2016a). The crystalline part of the cellulose microfibrils was not modified by the heat treatment, and so there were small shifts of the I_{am} and I_{002} values. The CrI_{XRD} of the samples that underwent the PHWT were larger than that of the untreated wood. At 160°C for 1 h, 3 h, and 5 h, the relative crystallinity index was calculated to be 52.09%, 54.67%, and 59.77%, respectively (Fig. 1a). Additionally, after treatments for 3 h at 140°C, 160°C, 180°C, and 200°C respectively, the relative crystallinity index was calculated to be 53.29%, 54.67%, 54.76%, and 63.91% (Fig. 1b).

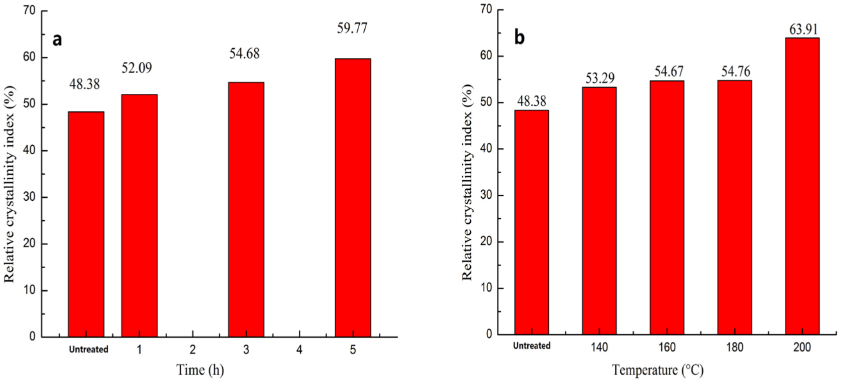

Fig. 1: Crystalline characteristics of the PHWT pine wood. (a)- Relative crystallinity index (%) as a function of time (h), (b) - Relative crystallinity index (%) as a function of temperature (°C).

It was clear seen that the relative crystallinity index was increased after treatment. This agreed with earlier results for CS-treated wood (Guo et al. 2015) and hydrothermal treated wood (Bhuiyan et al. 2000). The matrix substance was softened by the high temperature steam and became mobile during the treatment, which loosened the inner stress in the crystalline region of the cellulose (Kiemle et al. 2014, Tanahashi et al. 1989). Moreover, the various acids formed by the PHWT may have also diffused into the para-crystalline part of the cellulose, and the apparent crystalline moiety of the wood may have further increased because of their degradation. Therefore, the wood produced acetic acid and other acidic substances at 200°C, which resulted in an acidic environment in the pine wood. The hemicelluloses in pine wood was degraded severely, and the relative crystallinity increased significantly (Sivonen et al. 2002, Tjeerdsma et al. 2005).

Fig. 2 shows that after the treatment there was a significant increase in the intensity of the I_{002} reflection, especially for the wood treated at 200°C for 3 h. Interestingly, the I_{004} reflection experienced no change in the treated wood, which suggested that the cellulose molecular chains remained largely unaffected by the high-temperature steam and compression. The crystalline part of the cellulose microfibrils were not modified by the treatments. This meant that there were small shifts of the I_{am} and I_{002} values. Fig. 3 shows that for the wood treated at 160°C for 1 h, 3 h, and 5 h, the crystalline part of the cellulose microfibrils were not modified by the treatments. The increase of *CrI* was probably due to the fact that cellulose became more crystalline when wood was subjected to treatment. This was further supported by the indication that the native state of wood-cellulose was not-crystalline (Agarwal et al. 2016) and the increase of crystallinity index after treatment was mainly due to the increase or reordering in the crystalline region of cellulose using Wide-angle X-ray scattering (WAXS) method, but not from the degradation of amorphous domains (Guo et al. 2016b, Penttilä et al. 2013).

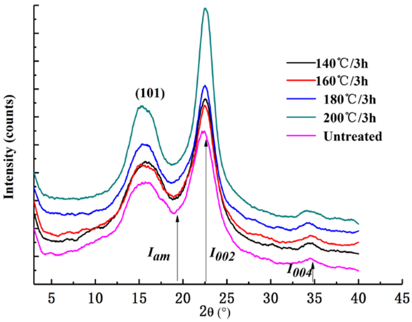

Fig. 2: XRD spectra of the untreated sample and samples PHWT at different temperature for the same time.

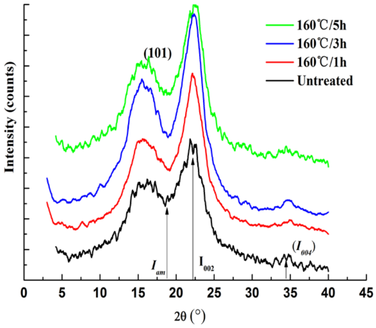

Fig. 3: XRD spectra of the untreated sample and samples PHWT at the same temperature for different times.

Mechanical properties of the pine wood

Fig. 4 and 5 show that after treatment for 1 h, the bending strength of the wood decreased less drastically. For the same duration at 140°C and 160°C, the bending strength of the wood decreased less as well. At 160°C and 200°C, the bending strength of the wood decreased significantly. At 140°C, the elastic modulus decreased less, while at 160°C and 200°C, the elastic modulus decreased significantly. As reported in the literature, PHWT and heat treatment has resulted in thermal degradation and structural changes in cellulose, hemicelluloses and lignin in wood. As a result, its mechanical strength decreases (Penttilä et al. 2013, Hosseinaei et al. 2011, Yin et al. 2017, Boonstra et al. 2006, Sailer et al. 2000, Kim et al. 1998).

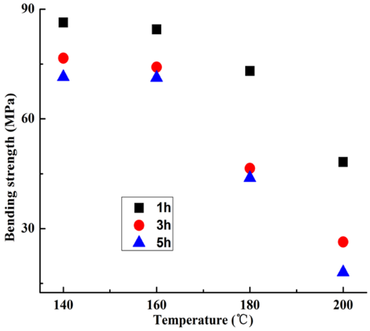

Fig. 4: The bending strength of the specimens after PHWT.

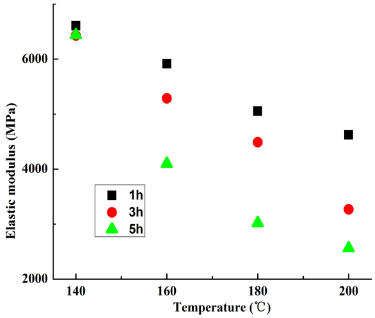

Fig. 5: The elastic modulus of the specimens after PHWT.

In the PHWT, the main chemical composition of the cell wall of the pine wood decreased gradually, which resulted in decrease in the wood density. This reduced the mechanical properties of the wood (Bekhta and Niemz 2003, Hou et al. 2012). During the heat treatment process, water acts as a catalyst to promote the hydrolysis rupture of the cellulose, lignin, and hemicelluloses molecular chains, and thereby accelerates the degradation of the wood polymer. Hydrolysis reduces the degree of polymerization of the cellulose and decreases the mechanical strength of the fiber. When the hydrolyzed cellulose becomes a powder, it completely loses its mechanical strength. At this stage, hemicelluloses are degraded and lose their adhesion in the cell wall. The strength of the cellulose and lignin junctions is weakened (Sailer et al. 2000). At the same time, it is easy for the cellulose chain to form an ether chain, and thus reduce the crystallinity of the cellulose. Lignin degradation also started to gradually lose the strength-supporting cellulose and contributed to significant changes in the mechanical properties of the wood.

Change of the wood surface color of the pine wood

Fig. 6 shows that the color of the pine wood deepened when the treatment temperature increased. At the same treatment temperature, the color of the pine wood deepened with an increase in the treatment time.

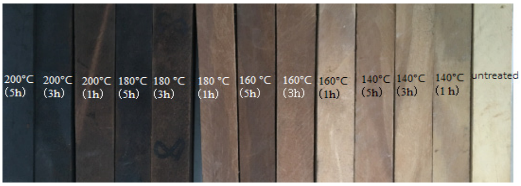

Fig. 6: Comparison between the PHWT samples and reference wood.

With different treatments of the wood, the color index changed significantly (Tab. 3). If treatment time was the same, the L^* of pine wood decreased gradually with the increase in treatment temperature. If treatment temperature was the same, the L^* of pine wood decreased gradually with the increase in treatment time. The decrease in the wood lightness (deepening of wood color) of the pine wood was because of the degradation of oxygen groups, such as acetyl and carboxyl groups, which resulted in an increase in the carbon content in the wood (Johansson et al. 2006, Ayadi et al. 2003, Bourgois et al. 1991). For the pine wood after the PHWT, the color index changes for a^* and b^* are presented in Tab. 3.

Tab. 3: Color CIE $L^*a^*b^*$ parameters for the pressurized hot water heat-treated pine wood.

	L^*			a^*			b^*			ΔE^*		
	1 h	3 h	5 h	1 h	3 h	5 h	1 h	3 h	5 h	1 h	3 h	5 h
140°C	59.97	57.33	43.11	11.97	10.55	11.96	26.87	25.37	22.86	14.33	17.15	31.57
160°C	47.49	44.08	36.83	10.55	10.84	10.36	25.37	19.62	17.30	27.64	31.55	39.15
180°C	34.94	30.88	25.32	10.17	7.36	5.83	16.23	12.12	7.40	41.30	46.66	53.76
200°C	27.28	24.53	23.03	6.36	3.64	3.39	9.60	5.71	4.88	51.02	55.42	57.17
Untreated		73.64			9.87			30.62				

At 140°C and 160°C, a^* of the wood color increased compared with that of the untreated material. At 140°C for 1 h, the chromaticity reached its highest value, which indicated that the color value was bright red. At 180°C and 200°C, a^* decreased. At this time, the color value changed to low luminance value. At 180°C for 5 h, the maximum decrease of a^* was 40.93% compared with that of the untreated wood. With increases in the treatment temperature, the yellow-blue (b^*) color index of the pine wood exhibited a decreasing trend. At 140°C for 1 h, the b^* of the pine wood was 12.26% lower than that of the untreated wood. At 160°C for 1 h, the b^* decreased by 29.02% compared with that of the untreated timber. As described in the literature, with increases in the treatment temperature and time, the color of wood turns black when the L^* value decreases gradually; and the change of a^* value and b^* value is the same as that of L^* value

(Gonzălez-Heńa et al. 2009, Bekhta et al. 2003, Brischke et al. 2007).

From Tab. 3, with increases in the treatment temperature and time, the ΔE^* value increases gradually, and the relative content of lignin is the same change. A positive relationship is obvious between ΔE^* value and the relative content of lignin, however a negative relationship is between ΔE^* value and the relative content of cellulose and hemicelluloses. The correlation between the change of wood color and the relative cellulose content of wood of any tree species is the weakest (Gonzălez-Heńa et al. 2009). According to the literature, Pinopyraldehyde group in lignin and the products of lignin oxidation are the main reasons for lignin color production (Johansson et al. 2006, Ayadi et al. 2003, Bourgois et al. 1991).

CONCLUSIONS

1. The treatment led to the decreasing of the hydroxyl and carbonyl groups in the cell walls of the treated wood. When the treatment temperature was 160°C to 200°C, the relative cellulose and hemicelluloses contents gradually decreased, however, the relative lignin content gradually increased.
2. The CI_{XRD} of the cellulose in the cell walls of the wood that had undergone the PHWT was increased because of crystallization that occurred in the semi-crystalline region, but the cellulose molecular chains in the crystalline region remained unaffected. Furthermore, increase in the CI_{XRD} was observed in the cell walls of the wood with increasing time and temperature treatments.
3. The bending strength and elastic modulus of the pine wood decreased, and the surface color of the pine wood gradually changed from pale yellow to dark brown with increasing time and temperature treatments.

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REFERENCES

1. Agarwal, U.P., Ralph, S.A., Reiner, R.S., Baez, C., 2016: Probing crystallinity of never-dried wood cellulose with Raman spectroscopy. Cellulose 23(1): 125-144.
2. Ayadi, N., Lejeune, F., Charrier, B., Ayadi, N., Lejeune, F., Charrier, B., Merlin, A., 2003: Color stability of heat-treated wood during artificial weathering. Holz als Roh- und Werkstoff 61: 221-226.
3. Bekhta, P., Niemz, P., 2003: Effect of high temperature on the change in color, dimensional stability and mechanical properties of spruce wood. Holzforschung 57(5): 539-546.
4. Bell, S.C., Nawrocki, H.D., Morr, K.B., 2009: Forensic discrimination of glass using cathodoluminescence and *CIE LAB* color coordinates: A feasibility study. Forensic Sci. Int. 189(1-3): 93-99.

5. Bhuiyan, M.T.R., Hirai, N., Sobue, N., 2000: Changes of crystallinity in wood cellulose by heat treatment under dried and moist conditions. J. Wood Sci. 46(6): 431-436.
6. Boonstra, M.J., Tjeerdsma, B., 2006: Chemical analysis of heat treated softwoods. Holz als Roh- und Werkstoff. 64: 204-211.
7. Bourgois, J., Janin, G., Guyonnet, R., 1991: The color measurement: A fast method to study and to optimize the chemical transformations undergone in the thermically treated wood. Holzforschung 45: 377-382.
8. Brischke, C., Welzbacher, C.R., Brandt, K., Rapp, A.O., 2007: Quality control of the thermally modified timber: Interrelation ship between heat treatment intensities and *CIE L a b* color data on homogenized wood samples. Holzforschung 61(1): 19-22.
9. Burgert, I., 2006: Exploring the micromechanical design of plant cell walls. Am. J. Bot. 93(10): 1391-1401.
10. Dietrich, H.H., Sinner, M., Puls, J., 1978: Potential of steaming hardwoods and straw for feed and food production. Holzforschung 32: 193-199.
11. Dirol, D., Guyonnet, R., 1993: The improvement of wood durability by rectification process. IRG WP: International Research Group on Wood Preservation 24. Orlando, Florida, USA, 4: 1-11.
12. Funaoka, M., Kako, T., Abe, I., 1990: Condensation of lignin during heating of wood. Wood Sci.Technol. 24: 277-288.
13. García-Mateos, G., Hernández-Hernández, J.L., Escarabajal-Henarejos, D., Jaén-Terrones, S., Molina-Martínez, J.M., 2015: Study and comparison of color models for automatic image analysis in irrigation management applications. Agr. Water Manage 151: 158-166.
14. GB/T 1929-2009: Wood physical and mechanical test sawing and sample intercepting methods.
15. GB/T 1936.1 - 2009: Wood bending strength measuring method.
16. GB/T 1936.2 - 2009: Wood flexural modulus of elasticity measuring method.
17. Gonzălez-Heńa, M., Hale, M.D.C., 2009: Color in the thermally modified wood of beech, Norway spruce and Scots pine: Part 1. Color evolution and color changes. Holzforschung 63(4): 385-393.
18. Guo, J., Guo, X., Wang, S., Yin, Y., 2016a: Effects of ultrasonic treatment during acid hydrolysis on the yield, particle size and structure of cellulose nanocrystals. Carbohyd. Polym. 135: 248-255.
19. Guo, J., Rennhofer, H., Yin, Y., Lichtenegger, H.C., 2016b: The influence of thermo-hygro-mechanical treatment on the micro- and nanoscale architecture of wood cell walls using small and wide-angle X-ray scattering. Cellulose 23(4): 2325-2340.
20. Guo, J., Song, K., Salmén, L., Yin, Y., 2015: Changes of wood cell walls in response to hygro-mechanical steam treatment. Carbohydrate Polymers 115: 207-214.
21. Hosseinaei, O., Wang, S., Rials, T.G., Xing, C., Zhang, Y., 2011: Effects of decreasing carbohydrate content on properties of wood strands. Cellulose 18(3): 841-850.
22. Hou, X., Smith, T.J., Li, N., Zong, M.H., 2012: Novel renewable ionic liquids as highly effective solvents for pretreatment of rice straw biomass by selective removal of lignin. Biotechnol. Bioeng. 109(10): 2484-2493.
23. Johansson, D., Morén, T., 2006: The potential of colour measurement for strength prediction of thermally treated wood. Holz als Roh- and Werkstoff 64: 104-110.
24. Kamdem, D.P., Pizza, A., Guyonnet, R., 1999: Durability of heat-treated wood. IRG WP: International Research Group on Wood Preservation 30. Rosenheim, Germany, Pp 1-15.

25. Kamdem, D.P., Pizzi, A., Jermannaud, A., 2002: Durability of heat-treated wood. Holz als Roh-and Werkstoff 60: 1-6.
26. Kiemle, S.N., Zhang, X., Esker, A.R., Toriz, G., Gatenholm, P., Cosgrove, D.J., 2014: Role of (1,3) (1,4) - β-glucan in cell walls: Interaction with cellulose. Biomacromolecules 15(5): 1727-1736.
27. Kim, G.H., Yun, K.E., Kim, J.J., 1998: Effect of heat treatment on the decay resistance and bending properties of Radiata pine sapwood. Material und Organismen 32(2): 101-108.
28. Kollman, F., Fengel, D., 1965: Changes in the chemical composition of wood by thermal treatment. Holz als Roh- and Werkstoff 23: 461-468.
29. Korkut, S., Kök, M.S., Korkut, D.S., Gürleyen, T., 2008: The effects of heat treatment on technological properties in Red-bud maple (*Acer trautvetteri* Medw.) wood. Bioresource Technol. 99(6): 1538-1543.
30. Kuriyama, A., 1967: On changes in the chemical composition of wood within the temperature range up to 200°C. Material 16(69): 772-776.
31. Leppänen, K., Spetz, P., Pranovich, A., Hartonen, K., Kitunen, V., Ilvesniemi, H., 2011: Pressurized hot water extraction of Norway spruce hemicelluloses using a flow-through system. Wood Sci. Technol. 45(2): 223-236.
32. Okon, K.E., Lina, F., Chen, Y., Huang, B., 2017: Effect of silicone oil heat treatment on the chemical composition, cellulose crystalline structure and contact angle of Chinese parasol wood. Carbohyd. Polym. 164:179-185.
33. Penttilä, P.A., Kilpeläinen, P., Tolonen, L., Suuronen, J.P., Sixta, H., Willför, S., Serimaa, R., 2013: Effects of pressurized hot water extraction on the nanoscale structure of birch sawdust. Cellulose 20(5): 2335-2347.
34. Sailer, M., Rapp, A.O., Leithoff, H., Peek, R.D., 2000: Upgrading of wood by application of an oil-heat treatment. Holz Roh. Werkst. 58(1-2): 15-22.
35. Salmén, L., Burgert, I., 2009: Cell wall features with regard to mechanical performance. A review COST Action E35 2004-2008: Wood machining - Micromechanics and fracture. Holzforschung 63(2): 121-129.
36. Segal, L.C., Creely, J.J., Martin Jr., A.E., Conrad, C.M., 1959: An empirical method for estimating the degree of crystallinity of native cellulose using the X-ray diffractometer. Text. Res. J. 29: 786-794.
37. Shafizadeh, F., Chin, P.P.S, 1977: Thermal deterioration of wood. In: Wood Technology Chemical Aspects (ed. Goldstein LS). ACS Symposium Series 43: 57-81.
38. Shukla, D., Vankar, P.S., 2017: 4B - Dyeing application of newer natural dyes on silk with fastness properties, *CIE lab* values and shade card. The textile Ins. Book Series, Elsevier. Natural Dyes for Textiles, Pp 141-166.
39. Sivonen, H., Maunu, S.L., Sundholm, F., Jämsä, S., Viitaniemi, P., 2002: Magnetic resonance studies of thermally modified wood. Holzforschung 56: 648-654.
40. Sluiter, A.D., Hames, B.R., Ruiz, R.O., Scarlata, C., Sluiter, J., Templeton, D., Crocker, D., 2008: Determination of structural carbohydrates and lignin biomass (NREL/TP-510-42618). National Renewable Energy Laboratory, Golden, CO.
41. Sluiter, J.B., Ruiz, R.O., Scarlata, C.J., Scarlata, A.D., Sluiter, A.D., Templeton, D.W., 2010: Compositional analysis of lignocellulosic feedstocks. 1. Review and description of methods. J. Agr. Food Chem. 58(16): 9043-9053.
42. Tanahashi, M., Goto, T., Horii, F., Hirai, A., Higichi, T., 1989: Characterization of steam-exploded wood. III. Transformation of cellulose crystals and changes of crystallinity.

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43. Templeton, D.W., Scarlata, C.J., Sluiter, J.B., Wolfrum, E.J., 2010: Compositional analysis of lignocellulosic feedstocks. 2. Method uncertainties. J. Agr. Food Chem. 58(16): 9054-9062.
44. Tjeerdsma, B.F., Militz, H., 2005: Chemical changes in hydrothermal treated wood: FTIR analysis of combined hydrothermal and dry heat-treated wood. Holzforschung 1(63): 102-111.
45. Wei, L., McDonald, A.G., 2016: A review on grafting of biofibers for biocomposites. Materials 9(4): 303.
46. Yin, J., Yuan, T., Lu, Y., Song, K., Li, H., Zhao, G., Yin, Y., 2017: Effect of compression combined with steam treatment on the porosity, chemical composition and cellulose crystalline structure of wood cell walls. Carbohyd. Polym. 155(2): 163-172.

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