

Article



Effects of Heat Treatment on Interfacial Properties of *Pinus Massoniana* Wood

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Abstract: Understanding the interfacial changes of wood during heat treatment can facilitate the improvement of the bonding and coating processes of heat-treated wood. Steam was used as the medium to modify *Pinus massoniana* wood through heat treatment at 160, 180, 200, and 220 °C. Changes to the surface characteristics after heat treatment were characterized by Fourier transform-infrared spectroscopy (FT-IR), X-ray diffraction (XRD), scanning electron microscope (SEM) and contact angle measurement. The results showed that: (1) hemicelluloses were the first to experience degradation at 160 °C, and this degradation was the most intense at 200 °C. The cellulose started experiencing obvious degradation at 200 °C, while there was less degradation of lignin at this temperature. (2) Oxygen-containing groups like hydroxyl and carbonyl were gradually reduced as temperature increased with deepened color and passivated surface. (3) Cellulose crystallinity presented a variable trend of increasing–decreasing–increasing. (4) Surface porosity and roughness of *Pinus massoniana* wood both increased after heat treatment. (5) The *Pinus massoniana* wood interface turned from hydrophilic to hydrophobic, and 180 °C was a turning point for the wettability of the *Pinus massoniana* wood interface.

Keywords: Pinus massoniana wood; heat treatment; interfacial properties; wettability; SEM

1. Introduction

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Artificial forests, which are characterized by short production cycles, high growth rates, and high yields, have relieved pressure on wood demand. Most plantations are fast-growing trees, such as *Populus alba*, *Cunninghamia lanceolata* (*Lamb.*) *Hook.*, *Larixgmelinii* (*Rupr.*) *Kuzen.*, *Eucalyptus robusta Smith*, *Pinus massoniana Lamb.*, and so on, all of which usually contain a high content of juvenile wood, along with numerous defects such as loose texture, low density, low strength, poor corrosion resistance, and inflammability [1–4], so it is especially important to conduct functional improvement of fast-growing woods in plantations. Wood modification methods mainly include acetylation, impregnation, compression, fire-retarding, and heat treatment, among which heat treatment-assisted wood modification has been extensively studied [5–15].

Hemicelluloses are degraded first during heat treatment, and the degradation products are mainly water, acetic acid, formic acid, methanol and furfural. With the increase of treatment temperature and time, the concentration of formic acid and acetic acid increased [16,17]. The thermal stability of cellulose was very high, but hemicelluloses degradation in acidic condition also had a certain influence on the stability of cellulose due to the intertwining of cellulose and hemicelluloses. The degradation products of cellulose were mainly levoglucosan. Lignin had good hydrophobicity and chemical reaction inertia due to the small content of hydroxyl groups, but it contained methoxy groups, so the ether bond in lignin was very easy to break during pyrolysis and degradation products were mainly



Citation: Wu, Z.; Deng, X.; Li, L.; Xi, X.; Tian, M.; Yu, L.; Zhang, B. Effects of Heat Treatment on Interfacial Properties of *Pinus Massoniana* Wood. *Coatings* 2021, *11*, 543. https:// doi.org/10.3390/coatings11050543

Academic Editor: Pierre Blanchet

Received: 23 March 2021 Accepted: 3 May 2021 Published: 5 May 2021

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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). carbonyl groups [18–22]. Gokhan found decreased compressive strength and hardness of hornbearn after heat treatment was correlated with the degree of density loss, and both compressive strength and hardness were reduced with increasing treatment temperature and lengthening treatment time [23]. Percin indicated that heat treatment resulted in large weight and density loss of Fagus longipetiolata, but contributed to improve dimensional stability [24]. Borůvka stated that increased treatment temperature reduced the strength of Betula platyphylla Suk., but improved its dimensional stability [25]. Obataya mentioned that the dynamic elasticity modulus, maximum bending stress, and bending strain of wood were gradually reduced with increased temperature and time [26]. Yildiz found that increased treatment temperature and time, parallel-to-grain compressive strength with temperature was a more significant influence than time [27]. Kamdem showed that heat treatment improved durability of wood, but reduced its mechanical strength, and hardwood was more sensitive to changes in heat treatment temperature than softwood [28]. Sundqvist found that the color change before the heat treatment of *Cunninghamia lanceolata* (*Lamb.*) Hook and pine was aggravated with the rising treatment temperature and lengthened treatment time [29]. Suleyma showed that wood density, water absorption, and surface roughness were reduced with the rise in treatment temperature and lengthening of treatment time [30]. Chu stated that heat treatment reduced the surface wettability of cottonwood, and increased the surface brittleness, which became more obvious with increased temperature [31]. Gérardin indicated that the heat treatment changed the acidity, wettability, and surface free energy of Cunninghamia lanceolata (Lamb.) Hook. and Fagus *longipetiolata* [32]. To sum up, heat treatment can not only improve the dimensional stability of wood but also enhance its corrosion resistance and durability, so it has been widely applied and welcomed to garden furniture in architectural engineering, windows and doors, musical instruments, the shipbuilding industry, and so on.

Heat treatment-based wood modification also has a great effect on the wettability of the wood surface, which influence wettability, spreading, diffusion, permeation, and adhesion on the wood surface. Good wettability of wood surfaces is a necessary precondition for realizing favorable adhesion properties [33,34]. Fast-growing *Pinus massoniana* wood was taken as the study object and water vapor as medium. The mainly study was focused on the changes in *Pinus massoniana* wood surface characteristics at different heat treatment temperatures. The novelty of this work is discussing in detail heat treatment temperatures range from 160–220 °C on the surface characteristics of *Pinus massoniana* wood from plantation forest, and the aim is to lay the foundation for the bonding and coating of *Pinus massoniana* glued wood structures.

2. Materials and Methods

2.1. Materials

Reagent grade 37% formaldehyde was obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). *Pinus massoniana* wood with a dimension of 2200 mm (length) \times 130 mm (width) \times 10 mm (thickness) and moisture content 10–14% was purchased from Rongjiang Guizhou, China, and after drying, knotless, and normally grown sapwood (without reaction wood, decay or insect or fungal damage) materials were selected. All other chemicals mentioned in this work were reagent grade.

2.2. Preparation of Melamine-Urea-Formaldehyde Resin

To lay the foundation for the later preparation of *Pinus massoniana* glued wood structures, melamine-urea-formaldehyde (MUF) resin was prepared and was to determine contact angle. MUF resin with a molar ratio (M + U)/F = 1:1.5 was prepared in the lab. Melamine accounted for 13% by weight. The MUF was prepared as follows: 121.6 parts of formaldehyde (37 wt %) was charged to a three-neck 500 mL flask equipped with a mechanical stirrer, thermometer and condenser, and the pH was adjusted to 9.0 with NaOH 30% solution. The first urea (42.72 parts) were then charged to the rapidly stirring solution, and then the temperature was increased and kept to 90 °C. The pH was adjusted to 5.0–5.2

with formic acid 10%, and 13.86 parts melamine were added to the mixture. After the water tolerance of mixture reached about 100%, the pH was adjusted to 9.0 immediately and cooled to 50 °C. The second urea (10.68 parts) was then charged and kept for 10min. The pH was adjusted to 8.0–8.5, and the resin was cooled to room temperature. The MUF resin had a solid content of 52% and viscosity of 12.26 s.

2.3. Preparation of Pinus Massoniana Heat-Treated Wood

Pinus massoniana wood with a size of 130 mm (length) \times 50 mm (width) \times 10 mm (thickness) without cracks, decay or allochromatic defects was chosen [35]. Steam (0.50 MPa) was the medium, and the wood samples were dried at 95 °C for 4 days before the heat-treatment. The dry-bulb temperature was raised to 85 °C and kept for 1h. Next, the temperature was increased to the target temperature (160 °C, 180 °C, 200 °C or 220 °C) at a rate of 10 °C/h and then kept for 1h, followed by cooling and humidity adjustment. The wet-bulb temperature was adjusted to 70 °C and then it was adjusted to and kept at 95 °C when the dry-bulb temperature exceeded 100 °C. The heat-treated wood was removed when the temperature was lower than 40 °C. The experiment was repeated five times for each temperature. The main chemical components of *Pinus massoniana* wood were measured according to previously described procedures [36].

2.4. Fourier Transform Infrared Spectroscopy (FT-IR)

1 mg of *Pinus massoniana* heat-treated wood power was mixed with 1g KBr to prepare a pill. The pill was then subjected to Fourier transform infrared spectroscopy (FT-IR; Scimitar1000, Varian, Palo Alto, CA, USA), and the data were acquired within the range of 400–4000 cm⁻¹ at 4 cm⁻¹ resolution using 32 scans. Five samples were analyzed for per treatment.

2.5. X-Ray Diffraction (XRD)

The crystalline structures of heat-treated *Pinus massoniana* were analyzed using an X-ray diffraction (XRD) spectrometer (Hitachi, Ltd., Tokyo, Japan) with Cu K α radiation (Cu K α , λ = 1.5406 Å) operated at 12.5 kV and 120 mA at the range of 5~80° with a scanning speed of 6° min⁻¹.

2.6. Scanning ElectronMicroscopy(SEM)

The surface of *Pinus massoniana* heat-treated wood was examined using a Hitachi S-3400N emission scanning electron microscope (SEM, Tokyo, Japan) operated at 12.5 kV to investigate the morphological features.

2.7. Contact Angle Measurement

A static droplet method was used to determine the contact angle of *Pinus massoniana* heat-treated wood [35]. A droplet of MUF resin liquid was dropped on a heat-treated wood, then the image of the droplet was immediately taken after 2 s using a JC2000A static drop contact angle measuring instrument from Zhongchen Digital Technology Equipment Co., Ltd. (Shanghai, China). Contact angle was analyzed by Newjce2000 software. The reported contact angle was the mean of 8–10 specimens, the maximum and minimum values were deleted, and then the rest of the samples were averaged. The standard deviation was less than 5%.

3. Results and Discussion

3.1. Effects of Heat Treatment on Contents of Pinus Massoniana Wood

The main components of wood are cellulose, hemicelluloses, and lignin, besides which other components account for 20–30% of mass, such as extractives, pigment, tannins, resins, and so on. The effects of heat treatment on the contents of cellulose, hemicelluloses, and lignin of *Pinus massoniana* wood are shown in Figures 1–3 and Table 1. As shown in Figure 1 and Table 1, the cellulose content in *Pinus massoniana* wood not treated and treated at 160 °C

were 42.6% and 41.2%, respectively, and the difference was not large, indicating that the thermal stability of cellulose structure was better at this temperature. The cellulose contents reached 39.0% and 33.5%, respectively, at 180 and 200 °C, showing that the cellulose started prominent pyrolysis when the temperature reached 200 °C. At 220 °C, the cellulose content was reduced to 29.4%, with the decrease in amplitude reaching as high as 31.0%, and the cellulose degradation was the most acute in this phase. As shown in Figure 2 and Table 1, hemicelluloses content in untreated Pinus massoniana wood were 13.1%. With the increase of temperature, the hemicelluloses content decreased linearly and were 11.3% and 8.8%, respectively, at 160 and 180 °C, with those at 200 and 220 °C 4.5% and 1.0%, respectively. This showed that the hemicelluloses structure, which was quite unstable, was prone to degradation during the heat treatment, and the degradation was the most acute within 200–220 °C. This was because hemicelluloses were heterogenous glycan consisting of different types of monosaccharide unit, with many branch structures; the bonding force between different monosaccharide units was weak, so they could be easily degraded in the heat treatment process; and the degradation products were mainly acids [16,19]. Seen from Figure 3 and Table 1, lignin content was gradually elevated with increased treatment temperature, the content was increased not obviously within 160–180 °C, but quite obviously within 200–220 °C.



Figure 1. Effects of heat treatment on cellulose content of Pinus massoniana wood.

Table 1. Effects of heat treatment on contents of Pinus massoniana heat-treated wood.

Cellulose/%	Hemicelluloses/%	Lignin/%
42.6 (3.3)	13.1 (1.2)	21.1 (3.2)
41.2 (2.5)	11.4 (0.9)	25.1 (3.9)
39.0 (3.7)	8.8 (0.8)	26.3 (3.6)
33.5 (2.5)	4.5 (0.5)	33.4 (3.5)
29.4 (3.1)	1.1 (0.3)	37.7 (3.3)
	Cellulose/% 42.6 (3.3) 41.2 (2.5) 39.0 (3.7) 33.5 (2.5) 29.4 (3.1)	Cellulose/%Hemicelluloses/%42.6 (3.3)13.1 (1.2)41.2 (2.5)11.4 (0.9)39.0 (3.7)8.8 (0.8)33.5 (2.5)4.5 (0.5)29.4 (3.1)1.1 (0.3)

Note: () means standard deviation.



Figure 2. Effects of heat treatment on hemicelluloses content of Pinus massoniana wood.



Figure 3. Effects of heat treatment on lignin content of Pinus massoniana wood.

Hemicelluloses were the first to degrade and could most easily experience pyrolysis during the heat treatment; the cellulose would undergo pyrolysis to a certain extent, too, but the lignin would not. According to the dynamic changes of cellulose, hemicelluloses, and lignin in *Pinus massoniana* wood during the heat treatment, the wood properties under the heat treatment could be forecast as follows: (i) the cell wall became thinner and cell cavity became large, which resulted in the density reduce and acidity increase of wood; (ii) the wood properties like toughness and flexural behaviors were degraded; (iii) the elasticity modulus and hardness of the wood were increased by a large margin (because the lignin content was positively correlated with the elasticity modulus and hardness of cell walls); (iv) the dimensional stability became better. *Pinus massoniana* wood belongs to *Pinaceae* plant from which many extracts such as resin, essential oil, and tannin can be extracted,

especially the high-content weak acid resin [4,21]. During heat treatment, these extracts may be degraded and oxidized into acids, which were migrated to the wood surface by virtue of high temperature and moisture, thus further enhancing the acidity of the wood.

3.2. Fourier Transform Infrared (FT-IR)Spectroscopy Analysis

Figure 4 shows the FT-IR results of *Pinus massoniana* wood before and after heat treatment. Peaks at 3393.3 cm⁻¹, 2918.8 cm⁻¹, 1733.6 cm⁻¹, 1647.6 cm⁻¹, 1510.4 cm⁻¹, 1459.2 cm⁻¹, 1317.5~1428.8 cm⁻¹, and 1265.7 cm⁻¹ were the O–H stretching vibration peak, C–H stretching vibration peak, non-conjugating C=O stretching vibration peak of hemicelluloses (xylose), conjugating C=O stretching vibration peak of lignin, C–C vibration peak of lignin benzene ring skeleton, C–H bending vibration peak of cellulose, C-H bending vibration peak of cellulose and hemicelluloses, and C–O bending vibration peak of lignin, respectively [36]. The ether bond C–O–C stretching vibration peaks of cellulose and hemicelluloses existed at 1060.2 and 1025.4 cm⁻¹, respectively. At 897.0 cm⁻¹ was the C–H bending vibration peak of cellulose and hemicelluloses and nemicellulose and nemicellulose and nemicellulose and nemicellulose and nemicellulose and nemicellulose existed at 1060.2 and 1025.4 cm⁻¹, respectively. At 897.0 cm⁻¹ was the C–H bending vibration peak of cellulose and hemicelluloses and nemicellulose and nemicellulose. At 811.0 cm⁻¹ was C–H out-of-plane bending



Figure 4. Fourier transform infrared (FT-IR) curves of *Pinus massoniana* heat-treated wood, (**a**) control, (**b**) 160 °C, (**c**) 180 °C, (**d**) 200 °C, (**e**) 220 °C.

The main components of hemicelluloses in *Pinus massoniana* are poly O-acetyl galactose glucose mannose and araban-4-O-methyl glucuronic acid xylose, where the content of the former is higher [37]. As shown in Figure 4, the hydroxyl absorption peak at 3393.3 cm⁻¹, carbonyl absorption peak at 1733.6 cm⁻¹, and mannose absorption peak at 811.0 cm⁻¹ presented weakened intensity. During heat treatment, (i) acetyl of hemicelluloses disconnect from the main chain to generate acetic acids, (ii) the hemicelluloses itself was degraded to generate acetic acids and propionic acids, (iii) the acids would go through esterification reactions with side lignin chains, and the hydroxyl content was reduced, and (iv) the water was dehydrated out between the hydroxyls on the molecular chain in the cellulose amorphous region, and so the quantity of free hydroxyls was reduced. After heat treatment, the *Pinus massoniana* wood surface would be passivated, in other words, the interaction between wood and resin was decreased.

3.3. XRD Analysis

Cellulose crystallinity represents the percentage occupied by the crystalline region of the cellulose microfiber and can reflect the degree of crystal formation during the cellulose condensation. Crystallinity is closely related to elasticity modulus, impact toughness, and mechanical properties. The effects of heat treatment on the 2θ diffraction angle and degree of crystallinity of *Pinus massoniana* wood are shown in Figure 5 and Table 2. Within the scanning interval of $0-80^{\circ}$, two significant peaks appeared on the curve, where the first one was located at about $2\theta = 18^{\circ}$, representing the scattering intensity of the diffraction angle in the amorphous region. The second one appeared near $2\theta = 22^{\circ}$, denoting the maximum strength (I002) of the diffraction angle in the crystalline region. The I002 diffraction angles of untreated Pinus massoniana wood and that going through heat treatment were both about 22°, indicating that this heat treatment condition did not generate any obvious effect on the crystalline region of the wood. The degree of crystallinity of untreated Pinus massoniana wood cellulose was 45.8%. At the treatment temperatures of 160, 180, 200, and 220 °C, the degrees of crystallinity of cellulose were 46.5%, 47.3%, 44.8%, and 50.5%, respectively, which were increased by 0.7%, 1.5%, -2.8%, and 4.7%, respectively, manifesting that the degree of cellulose crystallinity presented the variation trend of increasing-decreasingincreasing with the increase in the heat treatment temperature. This result was consistent with the research conclusions of Mehnet [38] and Li [39].



Figure 5. X-ray diffraction (XRD) curves of Pinus massoniana heat-treated wood.

able 2. Diffraction angle and relative dep	gree of crystallinity of <i>Pinus</i>	massoniana heat-treated wood.
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Treatment Temperature	2 θ/°	Relative Degree of Crystallinity/%
control	22.5	45.8%
160 °C	22.3	46.5%
180 °C	22.0	47.3%
200 °C	22.1	43.8%
220 °C	22.1	50.5%

Hemicelluloses were the first one to degrade, and could most easily experience pyrolysis during the heat treatment, the acids generated by the pyrolysis or the hot would degrade the amorphous region of cellulose and even microfibril in the crystalline region, and degrade the glucose units into a short-chain structure, so the degree of cellulose crystallinity was reduced. Meanwhile, the water would be dehydrated between hydroxyls on the molecular chain of the amorphous region of cellulose to generate an ether bond, and as a result, the microfibrils in the amorphous region were rearranged in an orderly and crystallized manner, and then the degree of cellulose crystallinity was elevated.

The hydrolysis of cellulose was not acute within the temperature range of 160–180 °C, what mainly took place during this process was transformation of amorphous region of cellulose into crystalline region, so the degree of crystallinity was increased in this phase. At 200 °C, the hemicelluloses degradation became acute, the generated acids would exert an effect on degrading the whole cellulose chain (the reduction amplitude in degree of cellulose crystallinity caused by this was much higher than that caused by the transformation of amorphous region into crystalline region) and, consequently, the degree of crystallinity was the minimum in this phase. The degree of cellulose crystallinity was increased at 220 °C, and the degree of crystallinity at the time was the highest in comparison with those at other treatment temperatures, which might be ascribed to the following aspects: (1) poly O-acetyl galactose glucose mannose and araban-4-O-methyl glucuronic acid xylose in hemicelluloses were degraded and crystallized; (2) the degraded microfibrils in the amorphous region of cellulose were crystallized again; (3) under the high-temperature environment, the water vapor might generate a certain degrading effect on lignin, and the lignin after all acetyls were stripped off become a monocrystal.

3.4. Color Change of Pinus Massoniana Wood

Wood color is directly related to its chemical components. Specifically, wood color is associated with unsaturated functional groups of chemical compounds, which, under visible light, will generate absorption peaks and result in the color development of chemical compounds, including vinyl, carbonyl, phenol, quinone, and diaromatic rings [29,32,40]. Lignin is the main source of wood color, followed by extractives, pigment, tannins, and resins. As shown in Figure 6, wood color was gradually darkened with increased treatment temperature, which was ascribed to the following aspects: (1) cellulose, hemicelluloses, and lignin experienced degradation to different degrees, and oxygen-containing groups like acetyl and carboxyl were gradually degraded, leading to increased carbon content; (2) Pinus massoniana wood extract contained various phenolic substances. Accompanied by the degradation of hemicelluloses and cellulose, these phenolic substances would go through redox reactions with increasing concentration in the heat treatment process, and as a result, the wood color was darkened; (3) As the heat treatment temperature was elevated, the lignin would be degraded and thus experience condensation reactions, the color chromophore groups in the conjugate of lignin were lengthened, and increased in quantity.



Figure 6. The appearance of Pinus massoniana heat-treated wood.

3.5. SEM Analysis

The apparent morphologies of untreated *Pinus massoniana* wood and treated *Pinus massoniana* wood at heat treatment temperatures of 160 (b) and 220 °C (c) are shown in Figure 7. As shown in Figure 7, the surface of untreated *Pinus massoniana* wood was smooth with clear and compact texture, and greasy pits could also be clearly observed (A). At 160 °C, the surface of *Pinus massoniana* wood started becoming rough, accompanied by slight fiber tearing phenomenon (B). At a temperature of 220 °C, the fiber tearing phenomenon was very apparent (C) on the surface of *Pinus massoniana* wood, the resin

particles in the pits were obviously degraded or dissolved and migrated, and the pit membranes were exposed and cracked, so the pits became hollow, narrow and long with decreasing pore diameter (D). During the heat treatment, the degradation of cellulose, especially hemicelluloses, reduced the toughness of *Pinus massoniana* wood, the internal stress would be released from the wood during the moisture migration, so the surface of cell walls went through the fiber tearing phenomenon; the cell walls became thinner and the cell cavity was enlarged, giving rise to the collapse and shrinking of the pit border of the cell walls. In conclusion, the porosity and roughness of the surface of *Pinus massoniana* wood were obviously observed after the heat treatment.



Figure 7. Scanning electron microscopy (SEM) of *Pinus massoniana* heat-treated wood, (**a**) control; (**b**) 160 °C; (**c**) 220 °C.

3.6. Contact Angle Analysis

The contact angle is useful for judging the wettability of wood. The larger the contact angle, the poorer the wettability will be. Generally speaking, the wettability of solid surfaces is poor, and the liquid cannot wet the solid when the contact angle is larger than 90° [41]. Contact angle measurements of MUF resin on Pinus massoniana wood are displayed in Figure 8. Under the heat treatments of 160 and 180 °C, the contact angles were 81.5° and 86.5°, respectively, indicating that the surface of *Pinus massoniana* wood was hydrophilic, and the MUF resin spread on the surface and permeated into the wood. When the treatment temperatures were 200 and 220 °C, the contact angleswere 98.0° and 110.5°, respectively, and the surface became hydrophobic. The change of MUF-based contact angles on Pinus massoniana wood is consistent with that for water-based contact angles [33,42,43]. Therefore, the heat treatment temperature 180 °C was a turning point for the interfacial wettability of *Pinus massoniana* wood. Below the temperature of 180 °C, the interface was hydrophilic, and it could be effectively bound by conventional wood adhesives—formaldehyde-based resins. However, when the temperature was above 180 °C, the interface became hydrophobic, which would change alternative adhesives. The interface could be fully glued only by using phenolic resin, isocyanate and polyurethane, but their preparation cost was higher.





4. Conclusions

Heat treatment endowed wood with superior dimensional stability, corrosion resistance and durability. Therefore, understanding the interfacial changes of wood during the heat treatment can facilitate the improvement of bonding and coating processes of heat-treated wood. The novelty of this work was discussing in detail heat treatment temperatures ranging from 160 to 220 °C on the surface characteristics of *Pinus massoniana* wood from plantation forest, and the aim was to lay the foundation for the bonding and coating of *Pinus massoniana* glued wood structures. The results showed that hemicelluloses were the first to experience degradation at 160 °C, the cellulose experiencing obvious degradation at 200 °C, while there was less degradation of lignin. *Pinus massoniana* wood turned darkened color and passivated surface (accompanied with porosity and roughness). The *Pinus massoniana* wood interface turned from hydrophilic to hydrophobic, and 180 °C was a turning point for its wettability.

Author Contributions: Z.W. contributed the analysis of the results and the design of the experiment, X.D. and L.L. contributed the preparation of the samples and the testing of FT-IR and XRD, X.X. and M.T. contributed the testing and the analysis of contact angles, L.Y. and B.Z. contributed the edit of the paper and the analysis of the SEM results. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by Science-technology Support Foundation of Guizhou Province of China (Nos. [2019]2308, ZK [2021]162, [2020]1Y125 and NY [2015]3027), Cultivation Project of Guizhou University of China (No. [2019]37), Forestry Department Foundation of Guizhou Province of China (No. [2018]13).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Informed consent was obtained from all subjects involved in the study.

Data Availability Statement: All the data are provided in the manuscript.

Acknowledgments: The authors highly appreciate the program from Science-technology Support Foundation of Guizhou Province of China (No. [2019]2325). The authors also thank the anonymous reviewers for their invaluable comments and suggestions to improve the quality of the paper.

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

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