

## Article

# The Viscoelastic and Hygroscopicity Behavior of Delignified and Densified Poplar Wood

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**Abstract:** The combination of alkaline delignification and densification was applied to improve wood mechanical strength. Poplar wood samples were subjected to alkali delignification with varying degrees of lignin and hemicellulose removal followed by hot pressing. Dynamic mechanical performances and dynamic sorption behavior of the untreated and densified wood were then evaluated. Results showed that appropriate removal of lignin can improve the stiffness of densified wood and reduce moisture sorption and the numbers of sorption sites. Fourier transform infrared (FTIR) microscopy along with X-ray diffraction (XRD) were used to explain the viscoelastic and hygroscopicity of delignified and densified wood. Hemicelluloses and lignin were selectively dissolved during alkali treatment. Wood crystallinity was increased after alkali treatment at a moderate concentration of 2%, beneficial to improving the dimensional stability and mechanical performance of delignified and densified wood. The crosslinking of cellulose chains through hydrogen bonding, the decreased content of free hydroxyl groups, and the increased crystallinity in the cell wall contributed to higher storage modulus and lower hydrophilicity. The results support mild delignification and densification as a feasible way towards extending the service life of wood products used as structural materials.

**Keywords:** delignification; densification; viscoelasticity; hygroscopicity; FTIR imaging microscopy



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## 1. Introduction

Wood, a complex hierarchical composite of cellulose (~45%), hemicelluloses (~22%), and lignin (~25%), has long been used as a structural material in the construction and furniture industries for its good strength and renewability [1]. Poplar wood can be grown on marginal land throughout the world. However, plantation woods have some undesirable properties, such as low dimensional stability and relatively low strength and stiffness, which limit their applications [2,3]. To improve wood utilization as a sustainable solution in a wide range of applications, different wood modification approaches, e.g., furfurylation, heat treatments, acetylation, and resin treatments, have been implemented [4]. Out of the multiple approaches available for wood modification, delignification followed by densification was recently demonstrated [4–6]. An aqueous alkaline treatment can result in an appreciable wood delignification [7,8]. The densified wood after alkaline delignification exhibits excellent mechanical properties due to the improved hydrogen bonding [5,8]. Bending strength and surface hardness showed 70% and 192% increase compared with untreated samples, respectively, due to the consolidation of cellulosic fibers, which substantially increased hydrogen bonding [7,8]. Therefore, the delignified and densified wood is suitable for scratch resistance and high bending strength sandwiched lightweight structures.

Wood is often subjected to various types of dynamic stressing and varying ambient humidity during its service life. The frequency-dependent behavior of wood in dynamic loading situations is of practical importance. Dynamic mechanical analysis (DMA) is a standard method for the characterization of materials that exhibits a significant change

in their viscoelastic behavior under various conditions [9]. It is well known that wood mechanical properties are sensitive to changes in moisture. This can be especially true for delignified wood due to the removal of hydrophobic lignin from cell wall to result in a more hydrophilic cellular structure. DMA measurements performed with moisture scans showed a moisture-induced softening of delignified aspen wood fibers due to the plasticization of glucuronoxylan [10]. Yet, understanding of the dynamic viscoelastic property of delignified and densified wood is very limited. Numerous studies have been conducted on the hygroscopic behavior of wood by using dynamic vapor sorption (DVS) to provide accurate isotherms over a wide range of relative humidity. Hailwood–Horrobin sorption theory was originally developed to analyze the adsorption part of the isotherm, which has been successfully applied to study the hygroscopicity of modified wood [11]. The hygroscopic structure of wood is attributed to the presence of different hydrophilic polymers that contain hydroxyl groups in the cell wall. Hemicelluloses are the most hydrophilic macromolecules in wood, followed by paracrystalline cellulose with lignin being the least hydrophilic. Furthermore, cellulose crystallinity can be affected by delignification at high temperatures, which could also affect the accessibility to hydroxyl groups and dynamic elastic modulus [12].

Chemical delignification using sodium hydroxide, sodium sulfite, or sodium chlorite, etc., or a mixture of these chemicals, removes lignin from wood by breaking the  $\beta$ -O-4 ether bonds among lignin molecules and the linkages between lignin and carbohydrates [13]. This process also degrades other wood cell wall components including cellulose to alter cell wall chemical composition and their spatial distributions within cell walls, in addition to affecting cell wall hydrophilicity and cellulose crystallinity. As a result, delignification can change wood viscoelasticity and hygroscopicity, and ultimately wood product mechanical performance and service life of wood products [12].

FTIR imaging microscopy has been developed for the characterization of spatial variations in chemical structure of biomaterials [14]. In comparison with other analyses, such as degradative chemical methods, separation, or isolation methods, FTIR microscopy imaging provides spatially resolved information about wood chemical composition and structural features in a visual and non-destructive manner. It has been applied to investigate fungal degradation of wood cell walls [15]. It can be equally applied to delignified wood to provide important information relevant to wood properties. By using FTIR microscopy imaging together with DMA and water sorption analysis, we aim to provide data for product service life evaluation of delignified and densified poplar wood. Our previous study [7] mainly conducted conventional mechanical testing without reflecting the delignification effect on wood strength and microstructure. The goal of the present study is to optimize the manufacturing process for improving the service life of wood products, and thereby increasing the utilization of plantation poplar wood as a sustainable structural material to reduce carbon footprint.

## 2. Material and Methods

### 2.1. Materials

Poplar tree (*Populus deltoides* Bartr. ex Marsh  $\times$  *P. nigra* L.) was harvested in December 2018 from Hugo Sauer Nursery, USDA Forest Service, Northern Research Station, Rhinelander, WI, USA. Wood block samples with dimensions of 100 mm (longitudinal)  $\times$  20 mm (tangential)  $\times$  10 mm (radial) were cut from fresh wood logs. Wood materials within a radius of 10 mm from the center of each wood log were discarded to reduce the effect of heartwood on wood block properties.

Sodium hydroxide (NaOH, 98%) of ACS reagent grade was purchased from Sigma-Aldrich (Burlington, MA, USA).

### 2.2. Delignification

Aqueous NaOH solutions at 0, 2%, 6% concentrations were prepared by dissolving appropriate amounts of NaOH in water. Alkaline wood delignification was conducted

at 155 °C for 30 min using NaOH solutions with a liquor-to-wood ratio L/W = 3:1 in a 1 L bomb reactor as described previously [7]. These delignification runs were denoted as  $An$ , with  $n = 0, 2$ , or  $6$ , representing NaOH concentration in %.  $A0$  without NaOH is pure hydrothermal treatment. After delignification, all wood blocks were washed with water to remove chemicals.

### 2.3. Wood Densification

The wood blocks after washing were densified in radial (thickness) direction. The samples were compressed at a pressure of 1.0 MPa for 15 min at 150 °C, and the compression ratios of the samples ranged from 20% to 25%. After densification, the wood samples were dried in a climate chamber at 20 °C at 65% relative humidity for two weeks.

### 2.4. Characterizations

**Chemical compositional analysis.** Compositional analysis was carried out on ion chromatography (ICS-5000, Dionex, Sunnyvale, CA, USA) with amperometric detection (HPAEC-PAD) as described previously using Wiley-milled natural poplar and densified wood powders [16].

**Dynamic mechanical analysis (DMA).** Samples were vacuum dried under 60 °C until constant weight, i.e., reached zero moisture, before determination. The dynamic storage modulus ( $E'$ ), loss modulus ( $E''$ ), and loss factor ( $\tan\delta = E''/E'$ ) were determined using a dynamic mechanical analyzer (DMA 2980, TA Instruments, New Castle, DE, USA) in single cantilever bending mode at the frequency of 1 Hz. The temperature was increased from 30 °C to 250 °C at the rate of 2 °C/min. Triplicate samples were measured to ensure the reproducibility of results.

**Sorption experiments.** The moisture sorption behavior experiments were carried out using a dynamic vapor sorption apparatus (Advantage ET85, Surface Measurement Systems Ltd., Wembley, UK). The untreated, treated, and densified wood samples were maintained using a microbalance ( $\pm 0.1 \mu\text{g}$ ) at a constant temperature of  $25 \pm 0.1$  °C for approximately 3 days, starting at 0% relative humidity (RH) and increasing to 95% RH, then decreasing back to 0% RH. Sorption data were recorded in each increment or decrement of 10% RH. Samples were then maintained at a constant RH, until the weight change was less than 0.002% per 10 min. Data on weight change were acquired every 20 s.

**Sorption models.** The moisture adoption and desorption data were analyzed based on the Hailwood–Horrobin theory [17]. In this theory, adsorbed water exists in wood cell walls in two forms, one is hydrated water ( $M_h$ ), and the other is dissolved water ( $M_s$ ). They are related to the relative water vapor pressure, described as follows:

$$M = M_h + M_s \quad (1)$$

$$M = \frac{1800}{W} \times \left( \frac{k_1 \times k_2 \times RH}{100 + k_1 \times k_2 \times RH} \right) + \frac{1800}{W} \times \left( \frac{k_2 \times RH}{100 - k_2 \times RH} \right) \quad (2)$$

where  $M$  is the moisture content (MC) at a given RH.  $k_1$  is defined as the ratio of the activity of the hydrate to the product of the activities of the dissolved water in the polylayer and unhydrated wood at equilibrium.  $k_2$  is the equilibrium constant between dissolved water and the vapor in the atmosphere.  $W$  is the molecular weight of wood polymer at absorption site [11].

$$\frac{RH}{M} = \frac{W}{18} \times \left[ \frac{1}{k_2 \times (k_1 + 1)} \right] + \frac{W \times (k_1 - 1) \times RH}{1800 \times (k_1 + 1)} - \frac{W}{180,000} \times \left( \frac{k_1 \times k_2 \times RH^2}{k_1 + 1} \right) = A + B \times RH - C \times RH^2 \quad (3)$$

where:

$$A = \frac{W}{18} \times \left[ \frac{1}{k_2 \times (k_1 + 1)} \right] \quad (4)$$

$$B = \frac{W \times (k_1 - 1)}{1800 \times (k_1 + 1)} \quad (5)$$

$$C = \frac{W}{180,000} \times \left( \frac{k_1 \times k_2}{k_1 + 1} \right) \quad (6)$$

**FTIR imaging microscopy.** Chemical changes in wood cell walls were characterized using FTIR microscopic imaging in the mid-IR range. The transmission mode was applied in a Spectrum Spotlight 400 FTIR imaging system (Perkin-Elmer Inc., Shelton, CT, USA). Scanning was carried out using a specially designed array detector, which provides a pixel resolution of  $6.25 \mu\text{m} \times 6.25 \mu\text{m}$ . The spectra were recorded with a  $4 \text{ cm}^{-1}$  spectral resolution and 32 scans, between  $4000 \text{ cm}^{-1}$  and  $720 \text{ cm}^{-1}$ .

**X-ray diffraction (XRD) analysis.** XRD analysis was performed on a Bruker AXS D8-Advanced diffractometer equipped with Cu K $\alpha$  radiation generated using 45 kV and 40 mA. The scanning angle ( $2\theta$ ) ranged from  $5^\circ$  to  $45^\circ$ . The crystallinity index (*CrI*) was calculated using the Segal method [18].

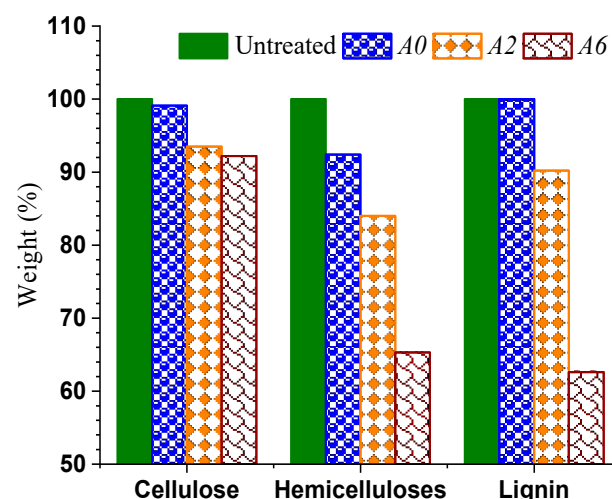
$$CrI (\%) = \frac{I_{200} - I_{para}}{I_{200}} \times 100 \quad (7)$$

where  $I_{200}$  is the maximum intensity of lattice diffraction angle (200), and  $I_{para}$  is the scattering intensity of paracrystalline diffraction at  $2\theta$  close to  $18^\circ$ .

### 3. Results and Discussion

#### 3.1. Chemical Composition

The poplar wood used in this study consists of 45% cellulose, 18% hemicelluloses, and 24% lignin. Pure hydrothermal pretreatment removed 8% of the hemicelluloses with no delignification. With increasing NaOH concentration in alkaline treatment, removal of both hemicelluloses and lignin was increased (Figure 1). However, cellulose dissolutions remained below 8% for all runs.

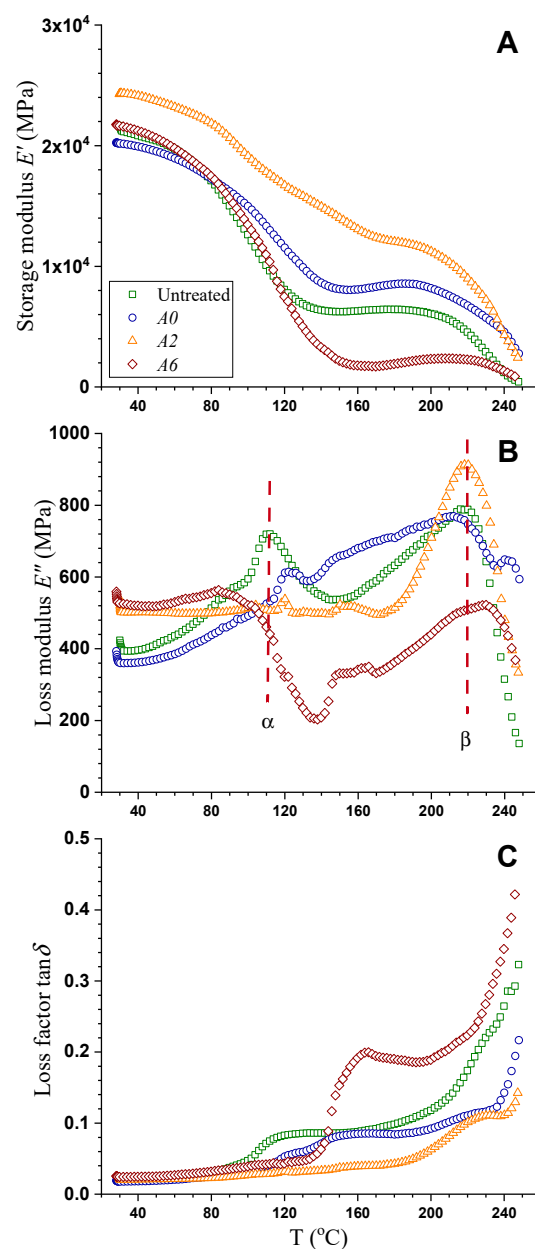


**Figure 1.** Wood chemical component yield after various pretreatments.

#### 3.2. Dynamic Mechanical Analysis

Considering the importance of bending properties at different service temperatures in practical applications, the dynamic thermal–mechanical properties of the materials were determined by DMA with a single cantilever mode. The results from DMA tests at 1 Hz are shown in Figure 2. The thermal-softening temperature of lignin, hemicelluloses and cellulose are  $30^\circ\text{C}$ – $205^\circ\text{C}$ ,  $150^\circ\text{C}$ – $220^\circ\text{C}$ , and  $200^\circ\text{C}$ – $250^\circ\text{C}$ , respectively [19]. The storage modulus  $E'$  is commonly used to evaluate the load-bearing capability of materials.

In general, the values of  $E'$  for both the untreated and densified wood samples decreased when temperature increased due to the thermal degradation of wood components [2]. The temperature dependence of  $E'$  of the untreated poplar wood displayed a similar behavior to that of the hydrothermally treated and densified wood A0 in the range from 40 °C to 220 °C as shown in Figure 2A with A0 having a slightly higher  $E'$  in the range of 100 °C to 220 °C. This temperature dependence is attributed to the thermal softening of lignin in wood [20]. The alkali-treated and densified wood A2 had the highest  $E'$  among all the samples, higher than that reported in the literature for densified wood filled with epoxy [21]. The  $E'$  data reported here are also in agreement with the bending modulus data reported in our previous study [7]. However, increasing alkali concentration to 6% in delignification, the modulus  $E'$  of the resultant densified wood A6 was substantially decreased at high temperatures (>120 °C). Perhaps, this is due to the substantial removal of lignin as shown in Figure 1 and cellulose depolymerization [22].



**Figure 2.** Storage modulus  $E'$  (A), loss modulus  $E''$  (B), and loss factor  $\tan \delta$  (C) curves of the untreated and treated and densified wood samples.

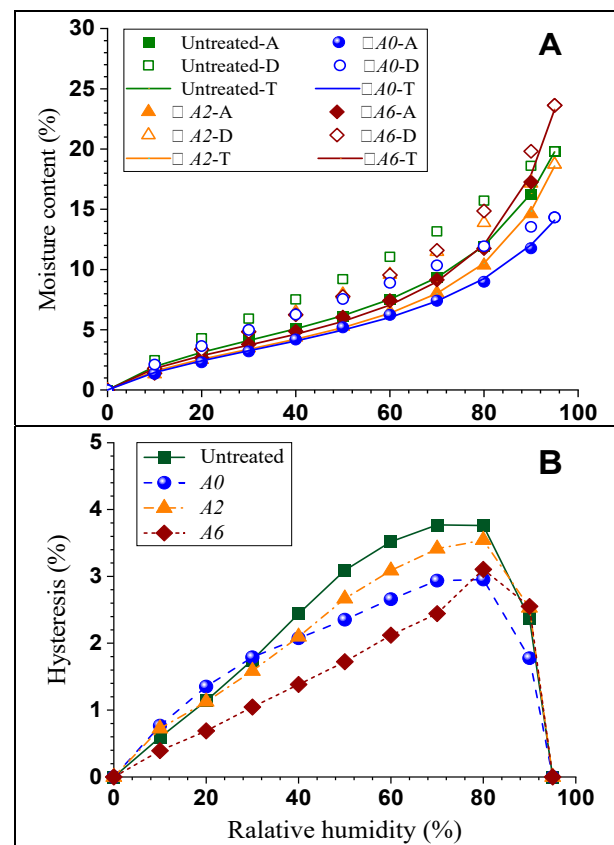
The changes in dynamic loss modulus  $E''$  are due to the viscous responses to changes in temperature, and generally reflect the amount of energy that was dissipated in wood [9,19]. Two main relaxation peaks occurred during a temperature scan were labeled as  $\alpha$  and  $\beta$ . Peak  $\alpha$  around 110 °C (Figure 2B,C) was observed from the untreated and hydrothermally treated (A0) wood samples, but not from the alkali-treated samples A2 and A6. This peak corresponds to the thermal softening of lignin [23]. Figure 2B revealed that the  $E''$  value of densified wood is decreased as compared to untreated wood around the  $\alpha$ -peak, representing a lower amount of energy dissipation associated with an increase in internal friction. A possible reason may be the change in crosslinking density of hydrogen bonds [24]. The relaxation peak  $\beta$  around 220 °C is due to the micro-Brownian motions of wood cell wall polymers in the paracrystalline region [25], which reflects cellulose chain consolidation and crystallization through pressing at elevated temperatures [26]. The  $\beta$ -peak of the alkali-treated and densified wood samples had a slightly higher temperature than that for the untreated poplar wood because hemicelluloses and paracrystalline cellulose were partially removed by alkali treatment (Figure 1) and cellulose are consolidated. The highest  $\beta$ -peak temperature was 226 °C for A2, with the lowest at 216 °C for A6, indicating that the delignification with 2% NaOH solution resulted in a stronger structure of densified wood, thereby enhancing the stress transfer under external force [27].

The damping capability of a wood sample is denoted by the loss factor  $\tan\delta$ , and was increased with scanning temperature. A high  $\tan\delta$  (0.20 at 160 °C for A6) indicates a more viscous (or damping) material due to the molecular rearrangements and other processes that decreased energy dissipation, while a low  $\tan\delta$  (0.04 at 160 °C for A2) indicates a more elastic material [28]. Among all samples, the alkali-treated wood A2 had the lowest damping or was most elastic, especially from 90 °C to 250 °C, and the  $\tan\delta$  peak shifted to a higher temperature due to consolidation of cellulose chains during high-temperature alkaline treatment, which resulted in the shift from viscoelastic to elastic. This suggests the increase in elastic modulus is more than the increase in loss modulus [29], and moderate delignification improves stiffness of densified wood. These data indicate that A2 has the longest service life [2], while A6 performed the worst. Perhaps, because the depolymerization of cellulose under the high NaOH concentration weakened wood mechanical performance. In summary, moderate alkaline delignification increased the interaction between cellulose fibers and facilitated greater stress transfer at the fiber matrix interface to result in a lower damping and higher  $E'$  value under 140 °C [30].

### 3.3. Moisture Sorption Analysis

The water vapor adsorption and desorption isotherms of the untreated and treated and densified wood samples are shown in Figure 3A. All the isotherms displayed a characteristic sigmoidal shape (IUPAC Type II) which is typically associated with wood-derived materials, i.e., with a linear line in the intermediate  $RH$  region and a convex curve in high  $RH$  range [31]. In accordance, a linear isotherm implies the decreased flexibility of cell wall polymers and thus higher stiffness due to densification [32]. Removing lignin by chemical treatment enriched hydroxyl-rich carbohydrates in the cell walls. Meanwhile, the acetyl group on the molecular chain of polyglucan was easily hydrolyzed so that the hydrophilic carbonyl group was reduced [33]. At the highest  $RH$  (95%), the MC of the A2 sample reached 18.7%, slightly lower than that of the untreated wood sample. At the moderate alkali concentration of 2%, a 16% hemicellulose removal resulted in slight enrichment of lignin and cellulose content along with a small decrease in hemicellulose content as reported previously [7], which perhaps reduced MC. While the MC of the A6 sample was as high as 23.6% due to a great extent of delignification that removed hydrophobic lignin (Figure 1) as evidenced by the low contact angle [7]. The desorption isotherms of untreated and hydrothermally treated (A0) wood samples were linear below 60%  $RH$  (Figure 3A), in agreement with an earlier study on pine wood densified in an open-press system at 150 °C for 1 h [34]. The experimental data in Figure 2 were replicated (Figure S1) with similar results.





**Figure 3.** Moisture content ((A): solid symbols indicate adsorption, open symbols indicate desorption, lines are theoretical predictions) and adsorption hysteresis (B) of the untreated and densified wood samples.

In addition to the differences in MCs, there were also differences in the degree of hysteresis as shown in Figure 3B. Hysteresis is a result of non-equilibrium excess sorption sites being occupied by water molecules according to the occupancy law [35]. All samples exhibited hysteresis over the entire RH region (Figure 3A), but the extent of hysteresis varied. Hysteresis of all the wood samples increased first and then decreased with increasing RH, but the highest hysteresis values varied from 2.5% to 3.5% at 80% RH, depending on the pretreatment process (Figure 3B). Lignin contributes to the phenomenon of hysteresis. The hysteresis of sample A6 was much lower than that of untreated wood because of the loss of free hydroxyl groups of wood due to hydrogen bonding by densification [32].

The water sorption data were fitted to the Hailwood–Horrobin model with fitting parameters listed in Table 1 and the model-predicted adsorption isotherms (Untreated-T, A0-T, A2-T and A6-T curves) are displayed in Figure 3A. All coefficients of variation ( $R^2$ ) were greater than 0.99.

**Table 1.** Coefficients of the Hailwood–Horrobin sorption model for the untreated and densified wood samples.

| Samples   | A    | B     | C     | $R^2$ | W (g/mol) | $k_1$ | $k_2$ | $M_h$ at 95% RH (%) |
|-----------|------|-------|-------|-------|-----------|-------|-------|---------------------|
| Untreated | 3.51 | 17.86 | 17.36 | 1     | 42690     | 7.09  | 83.51 | 3.58                |
| A0        | 5.22 | 18.63 | 17.93 | 0.998 | 48359     | 5.53  | 78.81 | 3.00                |
| A2        | 4.40 | 21.42 | 21.76 | 0.999 | 52233     | 6.64  | 86.28 | 2.91                |
| A6        | 3.68 | 21.14 | 21.81 | 0.998 | 49881     | 7.43  | 89.29 | 3.12                |

According to the Hailwood–Horrobin model, the moisture sorption isotherms can be divided into monolayer ( $M_h$ ) and multilayer ( $M_s$ ) water absorption regimes (Table 1 and Figure S2). As moisture absorption proceeds under dynamic equilibrium, water molecules gradually penetrate to result in a water-absorbed monolayer and continue to form a water polylayer through a secondary multilayer absorption process [36]. The  $M_h$  is of particular interest as it represents the water directly bound to the hydroxyl groups in the active sites. With further increase in  $RH$ , water preferentially adsorbs already hydrogen-bonded molecules to form clusters or a polylayer of water. Low moisture content in the monolayer is beneficial in maintaining the high dimensional stability of wood-based materials. The  $M_h$  of wood was slightly influenced by alkaline delignification and densification. The monolayer water adsorption at 95%  $RH$  decreased slightly after delignification and densification based on the fitted curve through data extrapolation (Table 1 and Figure S2) [11]. The  $M_h$  (2.91%) of A2 was slightly lower than the untreated wood (3.58%), which was attributed to increased hydrogen bonding through the removal of hemicelluloses, delignification, and densification, which reduced free hydroxyl groups, and a higher cell wall–water equilibrium constant ( $k_1$ ). Lignin and acetyl groups were partially removed during alkaline delignification. Therefore, monolayer saturation moisture content of alkaline delignified and densified wood decreased compared with untreated wood (Table 1 and Figure S2), though small variations in  $M_h$  are observed among wood samples treated differently. Similarly, the hygroscopicity and the dimensional stabilities of delignified and densified wood (A2) was improved, and set recovery was decreased. The  $M_h$  of A6 was higher than other densified wood samples with a higher water–water equilibrium constant  $k_2$ , perhaps due to a greater amount of lignin removal (Figure 1). A greater  $k_2$  indicated the increased activity of dissolved water in the microcapillaries [37].

### 3.4. Imaging FTIR Spectra of the Cell Wall

The chemical structure of wood cell walls is a key factor to understand the physical and mechanical performance of wood-based materials. FTIR spectral microscopic images (Figure 4A–H6) of the untreated and treated and densified wood cell walls were obtained from absorbance bands to assess the spatial chemical composition distribution. The assignments of FTIR peaks are listed in Table 2 [38]. For natural poplar wood, higher lignin concentrations were found in the cell corners and middle lamella as shown in Figure 4B (1264  $\text{cm}^{-1}$ ), F (1506  $\text{cm}^{-1}$ ), and G (1596  $\text{cm}^{-1}$ ). The dramatic intensity declines at both 1232  $\text{cm}^{-1}$  and 1736  $\text{cm}^{-1}$  indicated the loss of unconjugated ester linkages in lignin–carbohydrate complexes (LCCs) for the densified wood samples A2 and A6 after alkaline delignification [39]. By comparing Figure 4B with B2 and B6, F with F2 and F6, and G with G2 and G6, the effect of delignification can be clearly seen from the changes in spectral images at 1264  $\text{cm}^{-1}$ , 1506  $\text{cm}^{-1}$  and 1596  $\text{cm}^{-1}$  that mainly represent the vibration of guaiacyl lignin ring and are the C=O stretch, aromatic skeletal vibration of lignin, and C=O stretching vibration in the aromatic rings of lignin, respectively, especially in the cell corner region [40]. This is in agreement with the chemical composition analyses shown in Figure 1. The observed significant decrease in the spectral image intensity of 1736  $\text{cm}^{-1}$  represents hemicellulose removal under alkaline condition [33], also in agreement with Figure 1. Spectral images represent cellulose at 1317  $\text{cm}^{-1}$  (assigned to crystalline cellulose, Figure 4C(C2,C6)) and 1336  $\text{cm}^{-1}$  (assigned to paracrystalline cellulose, Figure 4D(D2,D6)) [41] showed almost no changes for A2 sample (Figure 4(C2,D2)) and smaller changes for A6 sample (Figure 4(C6,D6)) compared with the changes in lignin and hemicelluloses discussed above.



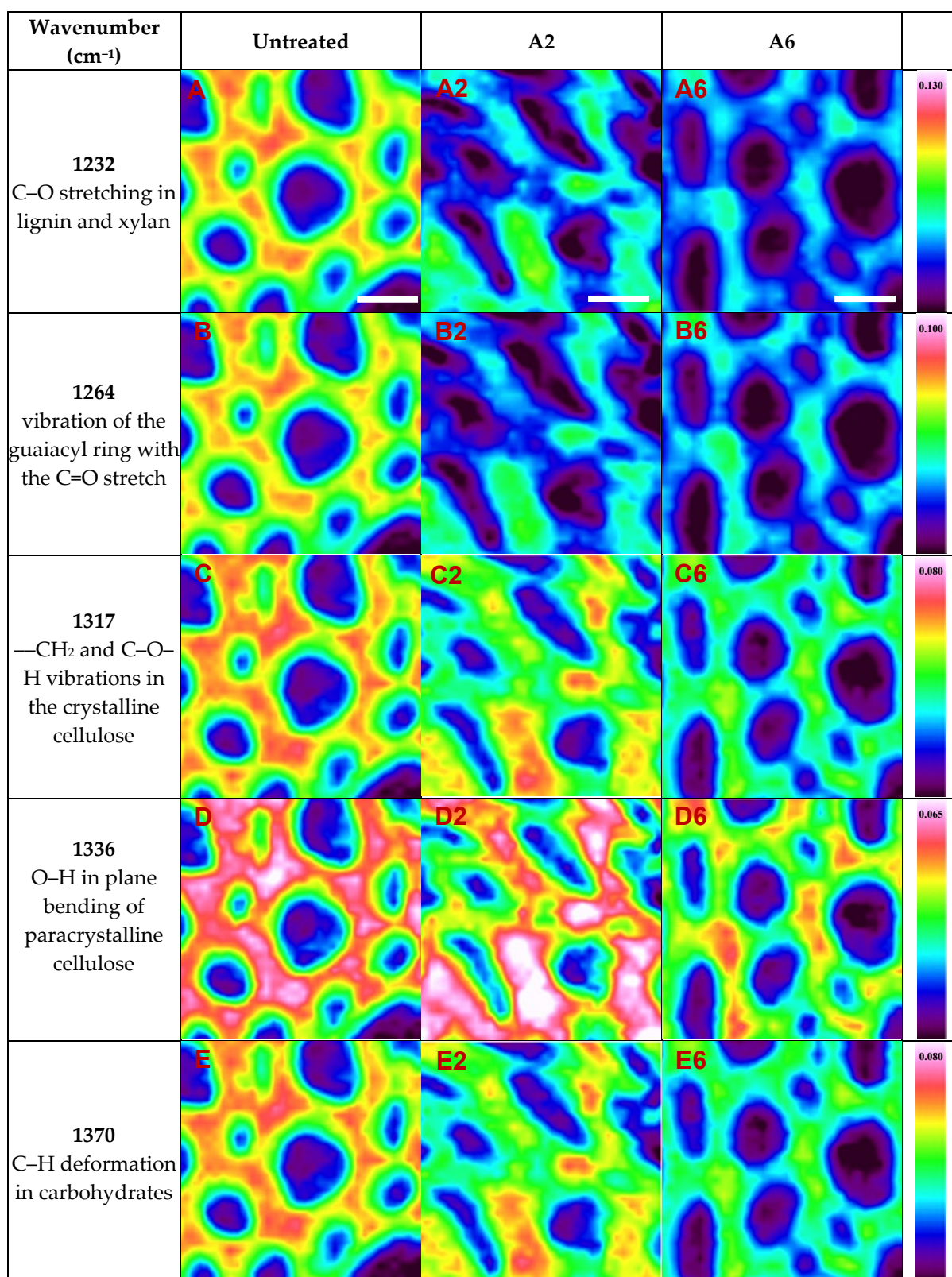
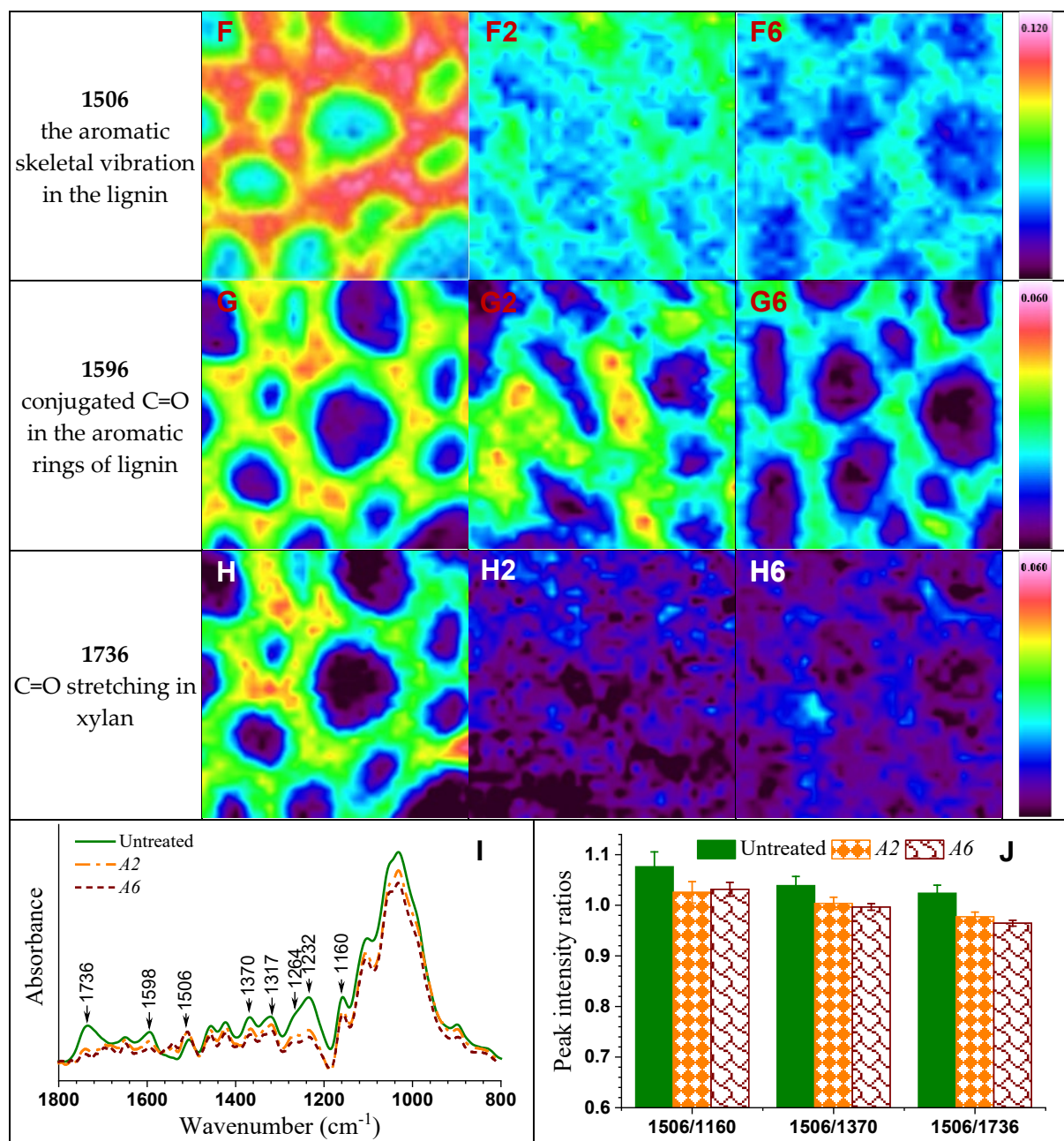


Figure 4. Cont.



**Figure 4.** False-color FTIR spectral images of the untreated wood (left column (A–H)), A2 (middle column (A2–H2)), and A6 (right column (A6–H6)). Scale bar = 12 μm. (I) Average FTIR absorbance spectra of the untreated, A2, and A6 samples. (J) Spectral intensity ratio of selected bands.

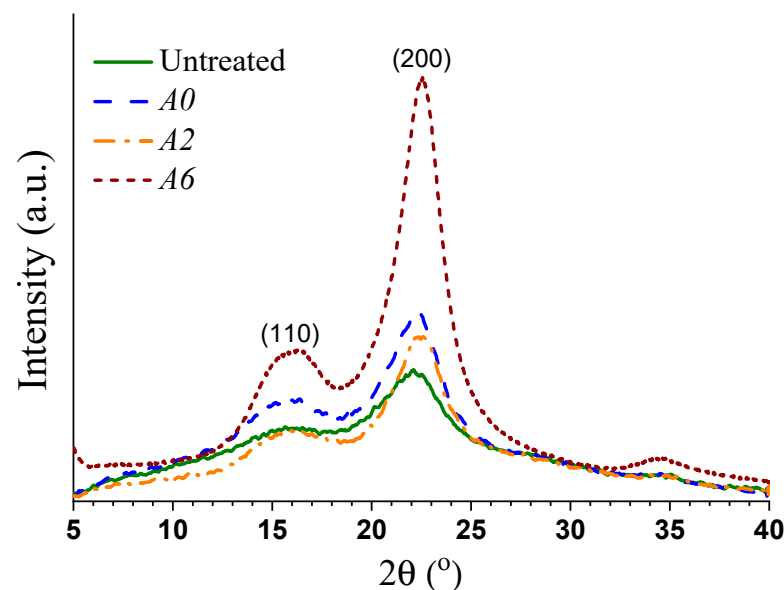
The spatially averaged FTIR spectra are shown in Figure 4I with spectral band intensity ratios in Figure 4J. The lignin/carbohydrate ratios (1506/1370 and 1506/1736) were decreased with increasing alkali concentration due to the contribution from phenolic extractives. These results indicate that the degradation of hemicelluloses and lignin was more pronounced than the degradation of cellulose through alkaline delignification, in agreement with chemical composition analysis shown in Figure 1.

**Table 2.** Spectral band assignments of the main spectral peaks observed in wood FTIR spectra.

| Wavenumber (cm <sup>−1</sup> ) | Functional Group                                                   |
|--------------------------------|--------------------------------------------------------------------|
| 1160                           | C–O–C bond in carbohydrates                                        |
| 1232                           | C–O stretching in lignin and xylan                                 |
| 1264                           | vibration of the guaiacyl ring with the C=O stretch                |
| 1317                           | –CH <sub>2</sub> and C–O–H vibrations in the crystalline cellulose |
| 1336                           | O–H in plane bending of paracrystalline cellulose                  |
| 1370                           | C–H deformation in carbohydrates                                   |
| 1506                           | the aromatic skeletal vibration in the lignin                      |
| 1596                           | C=C skeletal vibration in aromatic ring and C=O stretch            |
| 1736                           | C=O stretching in acetoxy group of hemicellulose                   |

### 3.5. Wood Crystallinity

During hot pressing, most wood components, except crystalline cellulose, are plasticized and can undergo a great extent of deformation. The elastic strain energy stored in paracrystalline microfibrils and amorphous lignin in wood is the principal reason for thermal fixation to improve wood dimensional stability of compressed wood [42]. The cellulose crystalline structures of the untreated natural poplar wood and the densified wood were evaluated using XRD. As shown in Figure 5, the characteristic cellulose diffraction peaks, 16.3° and 22.5°, corresponding to the (110) and (200) planes [43], suggest that the cellulose I crystal structure was well preserved in all the untreated and densified wood samples. Alkaline solutions with low sodium hydroxide (A2) only had a slight effect on the crystal structure of cellulose, which remained dominated by cellulose I, and the content of cellulose II was negligible.

**Figure 5.** X-ray diffractograms of untreated and densified poplar wood samples.

Segal method-determined *CrI*s are listed in Table 3. *CrI* was increased to 66% or by approximately 50% after treatment with NaOH at 6%. This increase in *CrI* can be attributed to the rearrangement/consolidation of less-ordered cellulose molecules after heat and alkali treatment [26]. After treatment with an alkaline solution, lignin and hemicelluloses in poplar wood were partially removed, and the accessibility of cellulose increased [44], which facilitated crosslinking of cellulose chains through hydrogen bonding during subsequent hot pressing. The increase in the *CrI* of the densified wood (Table 3) could contribute to the increase in the elastic modulus [45]. However, crystalline cellulose with its highly ordered and rigid structure might break more easily than paracrystalline cellulose, which is less



stiff. Therefore, a dramatic rise in *CrI* such as sample A6 might have a negative impact on the toughness of densified wood [46].

**Table 3.** Cellulose crystallinity of untreated and densified wood.

| Groups    | <i>CrI</i> (%) |
|-----------|----------------|
| Untreated | 34.4           |
| A0        | 44.9           |
| A2        | 50.9           |
| A6        | 66.3           |

#### 4. Conclusions

The effects of delignification on dynamic mechanical properties and dynamic vapor sorption of subsequent densified wood were evaluated. No major cellulose degradation occurred in alkaline wood delignification at 2% NaOH concentration; however, cellulose degradation can be significant at high NaOH concentrations of 6%, despite cellulose loss being lower compared with losses of lignin and hemicelluloses based on chemical composition analyses. A higher storage modulus and lower damping of densified wood with moderate delignification at NaOH concentration of 2% were obtained as a result of hemicelluloses and paracrystalline cellulose removal. Meanwhile, the reduced hygroscopicity of cell walls in densified wood at a higher *RH* was observed. The restricted mobility of the cell wall polymers due to the crosslinking of cellulose chains through hydrogen bonding, the decreased content of free hydroxyl groups, and the increased crystallinity in the cell wall contributed to higher storage modulus and lower hydrophilicity. Mild delignification and densification are promising for the improving the utility and value of plantation wood. This study provides a pathway for the developing short rotation wood as structural materials with a longer service life.

**Supplementary Materials:** The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/f14091721/s1>. Figure S1: Moisture content of the untreated and densified wood samples. Figure S2: Monolayer and multilayer calculated using the Hailwood–Horrobin model of the untreated wood (A), A0 (B), A2 (C), and A6 (D).

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