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Properties of densified poplar wood through partial delignification with alkali and acid pretreatment

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ABSTRACT

Poplar trees can be grown on marginal land to conserve water and recycle nutrients, but the wood has poor mechanical properties for structural applications. This study evaluated the feasibility of densifying poplar wood through delignification to improve mechanical properties. Delignification was conducted using a commercial soda pulping process under various NaOH concentrations of 0–6% with a reduced liquor-to-wood ratio of 3, along with a novel hydrotropic fractionation process using maleic acid. Delignified wood was pressed with or without stop bars at a low pressure of 1 MPa at 150 °C for 15 min or 100 °C for 2 or 10 h. Results indicate that wood density is the key variable dictating wood strength properties rather than extent of delignification. Pressing with stop bars resulted in similar wood densities for samples with different levels of delignification. Wood modulus of rupture (MOR), modulus of elasticity (MOE), and Brinell hardness (H_B) all increased linearly with wood density, in agreement with literature results from pure hydrothermal compression. When removing stop bars in pressing, MOR, MOE, and H_B were increased to 150 MPa, 20.7 GPa, and 43.2 MPa, respectively, from 88.5 MPa, 6.5 GPa, and 14.8 MPa for undensified poplar when wood density was increased to 0.81 g/cm^3 from 0.46 g/cm^3. Low-pressure densification with delignification is advantageous to significantly improve wood properties.

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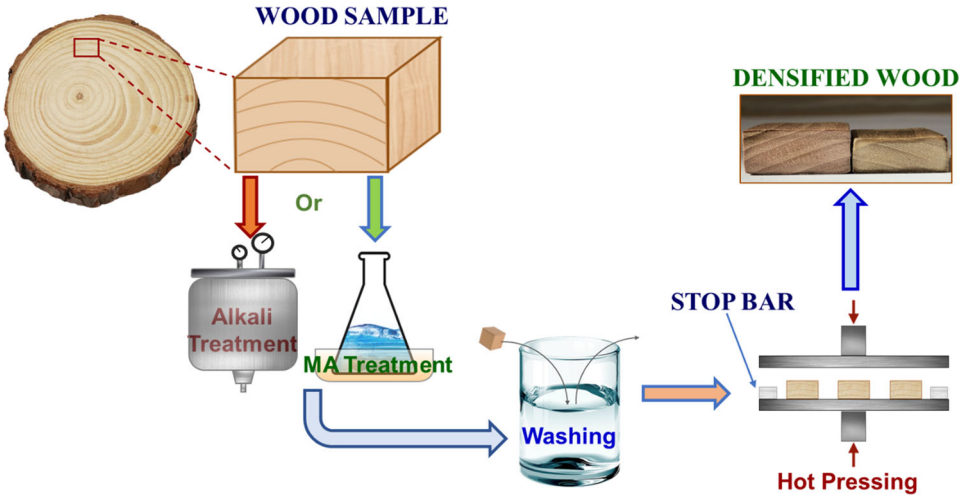
GRAPHICAL ABSTRACT



Introduction

Wood is a renewable structural material. Using wood for building and construction applications sequesters carbon. Furthermore, wood has a hierarchical structure with good porosity, resulting in lower density than metal, low thermal conductivity, and good strength. Recent interest in plant biomass resulted in mass plantation of short-rotation woody crops in many regions of the world [1]. Poplar trees can grow well on marginal land, spurring mass plantations to conserve water and recycle nutrients [2]. Despite much research on genetics, plantations [3, 4], and preprocessing [5–7], using short-rotation woody biomass such as poplar for economic biorefinery applications remains a challenge because of the low value of the main biorefinery products (fuels, sugars) and high costs of effective wood fractionation/deconstruction processes and enzymes/chemicals. Using poplar wood for structural materials with high value makes more economic sense. However, fast-growing plantation woods have poor physical properties compared with conventional wood, including low-dimensional stability, short fiber length, and high hygroscopicity [8]. The average density of air-dried poplar is approximately 0.4 g/cm^3 compared with 0.5, 0.65, 0.75 g/cm^3 for pine, birch, and oak, respectively. The modulus of rupture (MOR) and modulus of elasticity (MOE) of poplar are less than 40 and 8000 MPa, respectively [9]. Therefore, fast-growing poplar woods are not suitable for applications in construction and other engineering structures.

Enhancing the properties of fast-growing woods through cost-effective treatments is a value-added proposition. Different treatments [10], including impregnation, have been applied to improve mechanical strength and water resistance of wood [11–13]. Wood densification is another important method to improve the properties of low-density wood through heating/steaming and compression [14, 15]. The viscoelastic thermal compression (VTC) method uses elevated steam pressure to heat the wood above the lignin glass transition temperature (T_g) to densify wood [16], which enables the production of high-density wood without destroying wood microcellular structure. The VTC wood can be used in engineered structural composite materials [17]. Wood densification through pure thermal treatment, such as VTC, can achieve significant density improvement, especially for low-density fast-growing wood, but is often limited to a maximum of approximately 1 g/cm^3 in order to maintain the

integrity of wood cellular structure [17, 18]. Wood surface densification to compress only a few millimeters beneath the wood surface has also been developed to increase surface abrasion resistance and hardness [19, 20]. Increasing the surface density of wood is more efficient than densifying the whole cross section, because it reduces energy consumption [21] and retains the thickness or bulk that is important to out-of-plane (*z*-direction) stiffness. Laine et al. [22] elucidated the effects of pressing parameters on the micromorphology of the densified wood cell wall and the vertical density profile. They were able to increase the surface density and hardness of wood without damaging cell walls.

Chemical delignification [10], including using peroxide with acetic acid, was initially introduced to improve densification of resin-impregnated wood at low pressures [23]. Near-complete delignification using alkaline sulfite followed by peroxide bleaching was also applied to produce a transparent wood film by infiltrating a refraction-index-matching polymer followed by densification [24]. The resultant densified wood film had significantly improved mechanical properties. Partial delignification of approximately 50% using the same alkaline sulfite solution was later applied by the same group and achieved approximately tenfold increase in tensile strength of the densified wood [25]. Other studies on the subject include (1) delignification using peroxide with acetic acid followed by densification to improve wood mechanical properties and wood formability for manufacturing value-added products with different shapes [26, 27] and (2) soda pulping using NaOH and anthraquinone (AQ) as a catalyst for delignifying pine wood to produce strong wood through densification [28]. The study found that optimal delignification for achieving maximal strength for pine was at wood residual lignin content of 3.8% [28], substantially lower than the 11.3% for a hardwood [25]. Delignification using sulfite and Soda-AQ has major environmental impacts resulting from difficulties in sulfite recovery and carcinogenic potential using AQ, which is banned for food packaging [29]. Substantial lignin removal using peroxide is cost prohibitive because of the high peroxide dosage required for one-step wood delignification.

Because delignification represents a significant cost step with potential environmental impacts, studies on the extent of delignification using sustainable commercial delignification process are critically important. The objective of this study is to investigate commercial soda pulping using NaOH alone without AQ for poplar wood treatment with subsequent densification. The novelty of the study is to demonstrate that the extent of densification plays a more important role in densified wood performance than delignification. The study also evaluates recently developed acid hydrotropic fractionation using maleic acid (MA) for wood surface delignification and subsequent densification. MA is a FDA-approved indirect food additive (21CFR175-177) but can rapidly dissolve wood lignin at atmospheric pressure [30]. Lignin separation can be achieved simply by diluting the fractionated liquor to the minimal hydrotropic concentration (MHC) of approximately 25%. The acid can then be reused after re-concentration while dehydrating the dissolved hemicelluloses into furans using the MA in the liquor [30]. Compared with commercial alkali wood pulping, MA fractionation has significant advantages in terms of environmental impact, capital cost for chemical recovery, and valorization of hemicelluloses. Our goal is to obtain data and understanding for developing commercially viable process parameters for improving the mechanical properties of low-density fast-growing wood.

Material and methods

Materials

Poplar wood (*Populus deltoides* Bartr. ex Marsh × *P. nigra* L.) was harvested in December 2018 from Hugo Sauer Nursery, USDA Forest Service, Northern Research Station, Rhinelander, WI, USA. Wood block samples of 100 mm (longitudinal) by 10 mm (radial) by 20 mm (tangential) were cut from fresh wood logs (Fig. 1). Wood materials within a radius of 10 mm from the center of each wood log were discarded and not used for the study to eliminate the effect of juvenile wood on wood block mechanical properties.

Maleic acid (MA) and sodium hydroxide (NaOH, 98%) were ACS reagent grade and purchased from Sigma-Aldrich (Burlington, MA, USA).

Delignification

Poplar wood samples were dried to constant weight at 103 ± 2 °C before chemical delignification. NaOH

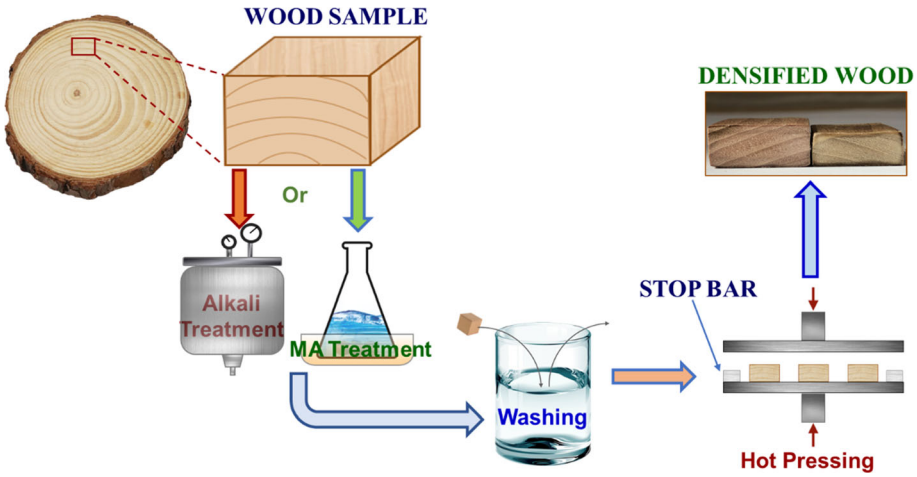


Figure 1 A schematic flow diagram showing wood block cutting, chemical delignification, and wood densification through hot-pressing.

solutions of concentration 0, 1, 2, and 6 wt% and a MA solution at 50 wt% were prepared by dissolving appropriate amounts of NaOH or MA in water. Wood samples were delignified at 155 °C for 30 min using NaOH solutions at a liquor-to-wood ratio L/W = 3:1 in a 1-L bomb reactor placed in a 21-L rotating wood pulping digester heated by steam jacket, as described previously [31]. These delignification runs were denoted as A0 (without NaOH as pure hydrothermal treatment), A1, A2, and A6. Wood samples were also delignified using MA hydrotropic fractionation (MAHF) at 100 °C for 30 min in a flask on a glycerol heating bath. The MA treatment run is labeled as M50. After delignification, the samples were washed using tap water several times to a pH of approximately 7 ± 0.2.

Wood densification

The delignified wood samples were densified in the wood radial direction. Samples were compressed (Fig. 1) from an initial thickness of 10 mm to a final thickness of approximately 8 mm at a pressure of 1.0 MPa for 15 min at 150 °C by using two 8-mm-thick stop bars. These densified wood samples were labeled as AxT150t15 (Table 1), where x denotes NaOH concentration in alkali treatment. One set of wood samples, labeled as A2T150t15N (Table 1), treated with 2% NaOH was pressed without stop bars but at the same pressure of 1.0 MPa to achieve maximal densification at constant stress. In addition, two sets of samples also delignified with 2% NaOH were pressed under 1 MPa at 100 °C, one for 2 h and one for 10 h. The second set remained under load for an additional 14 h after heating. These two sets of samples were labeled as A2T100t2h and A2T100t24h, respectively (Table 1). After densification, the wood samples were conditioned in a climate chamber at 20 °C for two weeks at a relative humidity of 65%.

Table 1 List of wood delignification and densification conditions

Samples	Delignification			Densification process		
	T (°C)	*t* (min)	Stop bar	*P* (MPa)	*T* (°C)	*t* (min)
Control						
A0T150t15	155	30	Yes	1	150	15
A1T150t15	155	30	Yes	1	150	15
A2T150t15	155	30	Yes	1	150	15
A6T150t15	155	30	Yes	1	150	15
A2T100t2h	155	30	Yes	1	100	120
A2T100t24h	155	30	Yes	1	100	1440
A2T150t15N	155	30	No	1	100	15
M50T150t15	100	30	Yes	1	150	15

Mass loss (ML), compression ratio (CR), and density

Each wood sample was weighed before and after densification and conditioning. Mass loss (ML) by delignification was determined as

$$\mathrm{ML} = \frac{m_0 - m_1}{m_0}(\%) \quad (1)$$

where m_0 is the initial mass of the oven-dried sample before delignification and m_1 is the mass of the same sample after densification and oven drying.

The compression ratios (CRs) immediately after densification CR_1 and after conditioning CR_2 are defined as the percentages of change in wood sample thickness from its original sample thickness t:

$$\mathrm{CR}_N = \frac{t_0 - t_N}{t_0}(\%) \quad (2)$$

where t_0 and t_N are thicknesses of the initial and densified or densified and conditioned wood samples, with $N = 1$ immediately after densification and $N = 2$ after conditioning. A parameter to characterize wood sample rebound set-recovery (SR) or shrinkage (negative value) after conditioning can be expressed as

$$\mathrm{SR} = \frac{t_2 - t_1}{t_1}(\%) \quad (3)$$

Density (ρ) of the samples was calculated after conditioning in a climatic chamber (20 °C, 65% RH) until no change of weight. The densification ratio was defined as the density ratio of the densified wood over the original wood, i.e.,

$$\acute{\rho} = \frac{\rho_1}{\rho_0}(\%) \quad (4)$$

Chemical compositional analysis

Chemical compositions of the samples were determined by the Analytical Chemistry and Microscopy Laboratory at the USDA Forest Products Laboratory, Madison, WI, USA, using conventional two-step acid hydrolysis, as described previously [32]. In brief, the carbohydrates in wood samples were hydrolyzed into monomeric sugars in two steps using sulfuric acid and then analyzed for sugars by ion chromatography (ICS-5000, Dionex) with amperometric detection (HPAEC-PAD). The unsolubilized materials were measured gravimetrically. The amounts of ash were first determined from the remains after burning the unsolubilized materials at 560 °C for 3 h. The difference between the amounts of ash and the insoluble solids are considered to be Klason lignin.

Static contact angle (CA) measurement

The static water contact angles (CAs) of control and densified samples were measured using the sessile drop method. For each sample, five drops of approximately 8 μL of distilled water were deposited manually by a chromatographic syringe on the wood surface at different locations. CA was measured by a microscope (Attention Theta, Biolin Scientific, Inc. Stockholm, Sweden) equipped with a goniometric head so that the scope's crosshair passed through the point of contact between the drop and the wood surface tangentially to the drop at that location. Measurements were made 5 s after the distilled water was dispensed to allow the drop to attain equilibrium on the surface of the sample. No fewer than five measurements were made to reduce uncertainty in the measured CA due to structural and chemical variations of the wood samples.

Mechanical testing

Modulus of rupture (MOR) and modulus of elasticity (MOE) were measured by three-point static bending tests using a modified standard procedure described in ASTM D4761-19 [33] on specimens with dimensions of approximately 100 mm (longitudinal) by 20 mm (tangential) by 8 mm (radial) at a crosshead speed of 5 mm/min using a universal mechanical testing machine with a span of 89 mm (Instron 5869, Grove, PA, USA). Mean and standard deviations of MOR and MOE were calculated from testing results of 10 replicate samples for each set of wood sample as

$$\mathrm{MOR} = \frac{3 \times F_{\max} \times l}{2 \times b \times t^2} \quad (5)$$

$$\mathrm{MOE} = \frac{l^3}{4 \times b \times t^3} K \quad (6)$$

where $F_{\max}$ is the peak load, l is the span of supports, b is the width of the sample, t is the thickness of the sample, and K is the slope of the load vs deflection curve between 20 and 40% of the maximum load achieved obtained from linear regression.

Wood hardness was characterized by the Brinell hardness test using European Standard EN 1534 [34]

with minor modifications, similar to that carried out in the literature [18, 35]. Specimens with dimensions 20 mm (longitudinal) by 20 mm (tangential) by 8 mm (radial) were tested using a universal mechanical testing machine (Instron 5896, Grove, PA, USA) with a ball of diameter D = 3.18 mm. During testing, the ball was penetrated to a depth h = 1.60 mm. At least six replicate samples were tested for each set to calculate mean and standard deviation. The Brinell hardness (H_B) in N/mm^2 was calculated as

$$H_B = \frac{F}{\pi \times D \times h} \quad (7)$$

where F is the applied load, D is the diameter of the indenter, and h = 1.6 mm is the measured depth of the indentation at the applied load.

Microscopic imaging

Images of cross sections of the control and densified wood samples were observed using a stereoscope (M205C, Leica, Wetzlar, Germany) equipped with a camera (FL3-U3-120S3C, FLIR System, Wilsonville, OR, USA) under 80 times magnification. The images were analyzed using Image J software (NIH, Bethesda, MD, USA).

Results and discussion

Wood yields and wood chemical compositions

Wood solids yields were greater than 95% for both pure hydrothermal (A0) and MA treatments. This was due to low dissolution of hemicelluloses (less than 10%) and near zero delignification in hydrothermal treatment using water (Table 2). MAHF can dissolve lignin and hemicelluloses but is only effective on fibers [30] or wood surface to result in a near zero delignification and minimal hemicellulose dissolution (less than 5%). Depending on the applied NaOH concentration, wood solids yield ranged from approximately 75 to 90%, while lignin and hemicellulose dissolutions ranged from approximately 10 to 35% by the three alkali treatment runs. Results clearly show that alkali treatment preserved cellulose well, with cellulose loss of only approximately 8% at the highest alkali dosage of 6%.

Effects of chemical treatment and pressing on compression ratio and wood density

The ML, measured CR, and $\acute{\rho}$ of the samples are presented in Table 3. ML after chemical treatment is 100− solids yield, as reported in Table 2. For alkali treatments including hot water, ML increased with treatment severity or NaOH dosage from 4.8 to 26% when NaOH concentration was increased from 0 to 6%. ML by MAHF was negligible, approximately 2%. The observed small variations in ML among all alkali-treated wood samples under the same condition but with different pressing conditions confirmed that changes in chemical composition or ML are minimal during densification [36].

The targeted CR for all samples was 20% by using stop bars of 8 mm in height during densification at 1 MPa. Run A2T150t15N was designed to achieve maximal densification under a relatively low pressure of 1 MPa without stop bars. Both compression ratios CR_1 and CR_2 among differently treated wood samples ranged from approximately 15 to 30%, except for pressing without the stop bars. The lowest CR of approximately 15% was achieved under MAHF, perhaps because wood chemical modification

Table 2 Solid yields and wood chemical compositions after chemical treatment and densification. Numbers in the parentheses are component yield

Samples	Solids yield (%)	Ash (%)	Klason lignin (%)	Glucan (%)	Xylan (%)	Mannan (%)
Control	100	0.1	23.6 (100)	45.16 (100)	18.43 (100)	3.21 (100)
A0	95.2	0.1	25.0 (100.8)	47.01 (99.1)	17.88 (92.4)	3.34 (90.9)
A1	90.4	0.4	22.3 (85.6)	51.46 (103.0)	18.84 (92.4)	2.69 (85.2)
A2	86.7	0.2	24.6 (90.2)	48.71 (93.5)	17.86 (84.0)	2.26 (78.7)
A6	74.3	0.2	19.9 (62.6)	56.06 (92.2)	16.22 (65.3)	1.34 (57.1)
M50	98.0	0.5	24.5 (101.8)	50.51 (109.6)	18.18 (96.7)	3.57 (95.8)

Table 3 Average values and standard deviations of the compression and densification ratios of samples (conditioned in a climate chamber at 20 °C for two weeks at a relative humidity of 65% after densification)

Samples	ML (%)	CR_1 (%)	CR_2 (%)	SR (%)	$\acute{\rho}$	ρ (g/cm^3)
Untreated wood					1.00	0.463 ± 0.019
A0T150t15	4.8 ± 0.3	26.8 ± 3.0	29.1 ± 3.7	− 3.2 ± 1.6	1.20	0.554 ± 0.031
A1T150t15	9.6 ± 0.9	23.6 ± 1.7	23.5 ± 1.4	0.2 ± 1.4	1.11	0.511 ± 0.032
A2T150t15	14.0 ± 1.0	25.4 ± 1.6	26.0 ± 2.1	− 2.0 ± 0.9	1.16	0.536 ± 0.021
A6T150t15	26.0 ± 1.6	29.5 ± 2.6	31.1 ± 5.7	− 14.1 ± 6.1	1.24	0.569 ± 0.037
A2T100t2h	12.4 ± 1.1	25.0 ± 1.3	24.8 ± 2.1	0.2 ± 2.0	1.21	0.558 ± 0.034
A2T100t24h	14.8 ± 1.0	28.1 ± 1.4	26.4 ± 1.2	2.4 ± 0.6	1.17	0.541 ± 0.034
A2T150t15N	14.8 ± 0.9	58.7 ± 0.5	56.3 ± 0.6	5.9 ± 1.1	1.76	0.811 ± 0.038
M50T150t15	1.98 ± 0.4	15.3 ± 1.6	12.2 ± 4.6	3.7 ± 0.6	1.10	0.507 ± 0.022

was limited to near the sample surface under MAHF. Under the same pressing conditions at 150 °C for 15 min, removing the stop bars substantially increased CR to over 55%, as expected. The small variations in CR among wood samples under the same alkali treatment condition but pressed differently suggest that pressing conditions have limited effect on densification with stop bars. For example, a longer holding time of 24 h did not result in substantial improvement in CR. However, increasing alkali treatment severity, such as increasing alkali dosage, increased ML and CR (Table 3). SR is used to measure potential of set recovery or shrinkage of wood samples after conditioning. The small variations in $|SR|$ of $< 4\%$ for most runs, except A6T150t15 and A2T150t15N, suggest no significant set recovery or shrinkage after conditioning. However, severe treatment at alkali loading of 6% (A6) resulted in a large shrinkage of 14%, which can be attributed to the large mass loss of 26% (Table 3). Pressing without stop bars resulted in a set recovery of approximately 6%, as would be expected due to a large CR of over 55%. Dimensional stability is important for various applications, especially over time and under moisture conditions and needs to be further verified.

Hot-pressing reduced the thickness of wood samples and increased sample density. Comparing with the density of the control (untreated and unpressed) wood of 0.463 g/cm^3, pure hydrothermal treatment increased pressed wood density by approximately 20% (Table 2). Alkali treatment did not improve wood densification compared with hydrothermal treatment, with the highest wood density increase of 24% achieved with NaOH concentration of 6%. This is due to the restriction in pressing by the stop bars, despite the alkali treatment loosened wood structure. The loss of mass through dissolution of lignin and hemicelluloses by alkali (Table 1) also limits the increase in wood density. Extended pressing time only slightly improved densification due to the stop bars. Wood density was substantially improved when stop bars were removed in pressing, e.g., wood density was increased by over 75% to 0.81 g/cm^3 for A2T150t15N (Table 3). These results indicate that, whereas loosening wood structure through chemical treatment is important for wood densification, great densification can be achieved without severe treatment with proper control in pressing by using low or no stop bars in addition to pressure.

Wood surface hydrophobicity

Wettability of the control and densified surfaces were assessed by measuring CA of water. A lower CA defines a surface with higher wettability. CA was decreased from 104° for the undelignified wood (control) to 84° for densified sample A6T150t15 (at 150 °C) (Fig. 2) with approximately 40% lignin removal (Table 2), because lignin is relatively

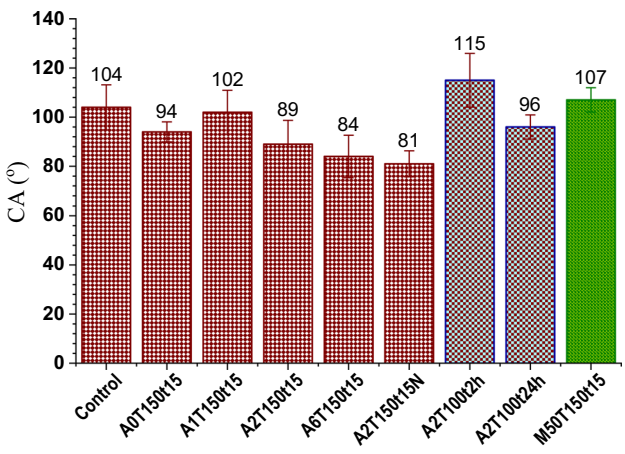


Figure 2 Average water CA of the control and densified wood samples.

hydrophobic. It appears that pressing at 100 °C for a longer time resulted in a more hydrophobic surface than pressing at 150 °C for only15 min. Longer pressing time promoted the exudation of lignin when pressing wet wood (with low lignin T_g) and any remaining extractives beneath wood surface after alkali treatment to produce a more hydrophobic wood surface [37]. MA treatment did not remove lignin (Table 2) and retained wood surface hydrophobicity with a CA similar to that of the control.

Physical and mechanical properties of densified wood

Our targeted application of densified poplar wood was flooring or wood veneers. Optical appearance is important. MAHF resulted in an appealing pinkish color, whereas alkali-treated wood samples showed a brownish color in comparison with the light color of the untreated poplar wood (Fig. 3). Both the pinkish and brownish colors of the treated wood samples are compatible with the color of most popular wood stains. Therefore, the two types of chemical treatments evaluated here did not negatively affect wood visual appearance.

A series of bending and hardness tests was performed on the control and densified wood samples. Figure 4 (Table S1) shows that MOR and MOE and H_B were all increased by densification after delignification. Their increases were all linearly proportional to the density of the densified wood. MOR of A2T150t15N increased to 150 MPa from 88 MPa of the control sample (or by 70%) when sample density was increased from 0.46 to 0.81 g/cm^3 (or by 76%) by removing stop bars in pressing. The increases in MOE and H_B are much more significant, i.e., MOE and H_B increased to 20.7 GPa from 6.5 GPa and 43.2 MPa from 14.8 MPa, respectively (or approximately by three fold).

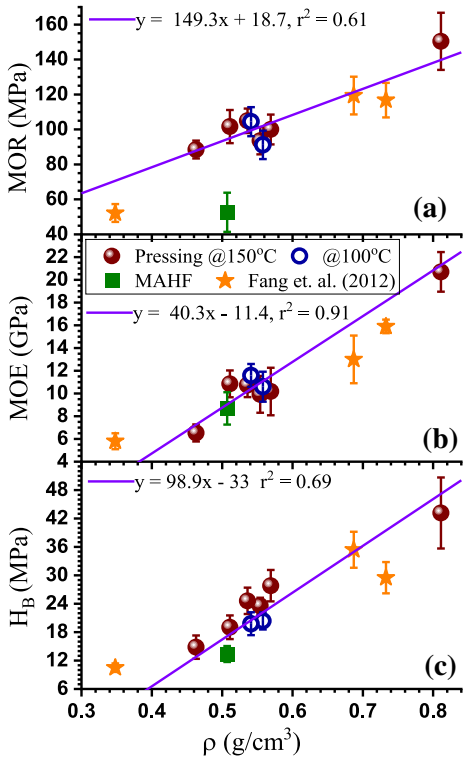


Figure 4 Effects of poplar wood density on densified wood mechanical properties: **a** MOR; **b** MOE; **c** H_B, in comparison with a literature work [18] using thermal treatment alone in densification. The literature data were not used in linear regression.

The densified wood samples prepared using stop bars during hot pressing showed no significant differences in mechanical properties among the samples with different chemical treatments and pressing conditions, because their densities are not much different. This suggests the strong dependence of wood mechanical properties on wood density. In other words, the effect of delignification on densified wood properties was mainly due to its effect on improving densification, i.e., increased delignification can achieve a greater densification under the same pressing condition even with stop bars (Table 3). To further illustrate the strong dependence of densified

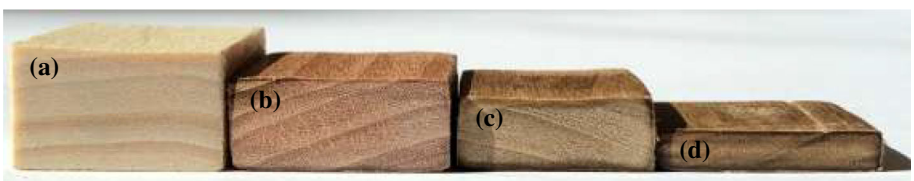


Figure 3 Photographs of untreated poplar wood and densified and conditioned wood samples. **a** Control; **b** MAT150t15; **c** A2T150t15; **d** A2T150t15N.

wood properties on wood density, data from densified poplar wood veneers with thermal treatment alone from Fang et al. [18] are overlaid in Fig. 4 (also Table S4). Fang et al. [18] used steam (140–220 °C) injected from the press to treat wood under a pressure profile of 4.5–9 MPa for 30 min to densify wood, compared with pressing at a much lower constant pressure of only 1 MPa at 150 °C min for 15 min in the present study. The data points of Fang et al. [18] shown in Fig. 4 were in the order of density: unpressed and pressed at 160 and 200 °C in the x coordinate. Results indicate that the present data set is in agreement with the data of Fang et al. [18]. However, the achieved density, 0.73 g/cm^3, was lower for wood veneers 4.3 mm thick using thermal treatment alone, even with much higher pressures and steamed at 220 °C, than the achieved density of 0.81 g/cm^3 in the present study with samples 10 mm thick using pressing pressure of only 1 MPa at 150 °C with 10% lignin removal (Table 2).

Statistical ANOVA analysis was conducted to illustrate the significance of the dependence of mechanical properties of densified wood on densification. Apparently, the effects of stop bars on MOR, MOE, and H_B were all significant ($0.000 \leq \text{sig} < 0.0001$ in Table S2) for the two sets of samples treated at the same alkali charge of NaOH = 2% and both pressed under 150 °C for 15 min but one with (ρ = 0.811 g/cm^3) and the other without (ρ = 0.536 g/cm^3) stop bars. When analyzing the dependence of mechanical properties of four sets of wood samples pressed under the same condition of 150 °C for 15 min but treated with different alkali concentrations between 0 and 6%, it was found that the dependences of MOR (sig = 0.02 < 0.05) and H_B (sig = 0.00 < 0.05 with a confidence level of 99%) on alkali were significant, but the dependence of MOE (sig = 0.49 > 0.05) on alkali was insignificant (Table S3). The dependence of wood density on delignification or alkali charge was also found significant (sig = 0.00 < 0.05, Table S3) from ANOVA for these four sets of wood samples pressed under the same condition, suggesting that the effects of delignification on wood mechanical properties were because delignification improved densification.

It is interesting to note that the MOE and H_B of the MA-treated sample follow the density correlation shown in Fig. 4, but not MOR. This suggests that cellulose depolymerization occurred in the MA treatment, affecting wood sample bending strength.

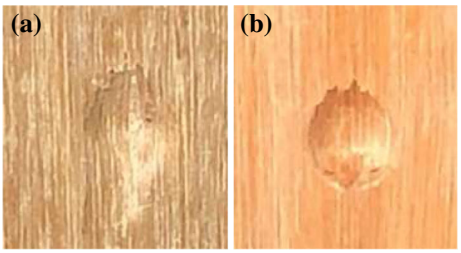


Figure 5 Photographs of hardness tested samples: **a** A2T150t15; **b** M50T150t15.

Pictures of wood samples after hardness testing using the same ball pressed to the same depth shown in Fig. 5 indicate that fibers at the edge of the hemispherical indent were broken on the wood sampled treated by MA, but not on the control or the sample treated by alkali. This suggests that MA treatment resulted in brittle cellulosic fibers, which reduced MOR.

Microstructure of densified wood

Optical microscopic imaging was used to examine changes in wood anatomic microstructure along with potential cracks through delignification and densification. Figure 5 shows the microstructure of the untreated and densified wood samples in the cross-fiber direction under the same magnification. Although it is difficult to see the deformation and collapsing of lumen and buckling of ray cells, the compression effect can be clearly seen from the deformation and collapsing of vessel elements by comparing the control sample (Fig. 6a) with the densified wood samples (Fig. 6b–h). Standfest et al. [38] used a computed microtomographic technique and showed that compression mainly took place in vessels, with ray cell buckling and collapsing of lumens, in densifying hybrid poplar using VTC under 5.5 MPa with steam at 170 °C. This is because poplar has thin-walled vessels. It can be expected that the lumens and ray cells are also greatly deformed and collapsed in the present study after certain levels of delignification, especially the removal of easily accessible lignin in the middle lamella, which weakened the integrity of the cell walls. Laine et al. [22] showed the micromorphology of a softwood using SEM and found substantial deformation of earlywood cells due to their thin cell walls but not of latewood cells. With minor differences between earlywood and latewood cells in poplar wood, a

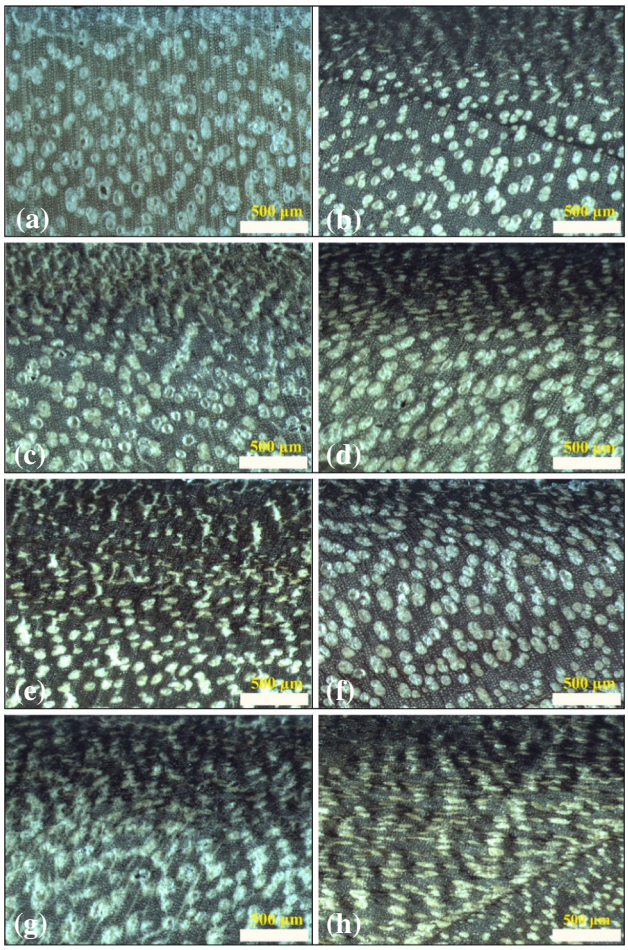


Figure 6 Optical micrographs of sample cross section fiber longitudinal direction. **a** Control; **b** A0T150t15; **c** A1T150t15; **d** A2T150t15; **e** A6T150t15; **f** M50T150t15; **g** A2T100t2h; **h** A2T150t15N. All scale bars = 500 µm.

uniform densification of poplar is expected in the present study, as shown by Standfest et al. [38]. The collapsing of vessels and lumens and buckling of ray cells reduced the void volume in wood and increased wood density to improve its mechanical properties.

Increasing treatment severity by increasing alkali concentration from 0 to 6%, increased the compressed depth from the top surface (Fig. 6b–e) compared with the control without compression (Fig. 6a). At 6% alkali concentration, the observable compressed area covers more than 50% of the wood sample height (Fig. 6e). Furthermore, deformation in the vessel elements is much more severe. The high lignin removal at 6% NaOH resulted in a much lower lignin content of less than 20% in the treated wood (Table 2), which reduced the compression strength of the wood [39]. Certainly, lower lignin removals resulted in less wood structure deformation in samples treated with lower alkali dosages. Deformation is much less visible for the MA-treated sample (Fig. 6f) due to near zero delignification and mass loss (Table 2). Increasing pressing time at a relatively low temperature of 100 °C increased the depth of deformed area for wood treated under the same conditions, as can be clearly seen from Fig. 6g in comparison with Fig. 6d, in agreement with Rautkari et al. [40]. The fact that no observable differences in mechanical properties between these two samples, A2T150t15 (Fig. 6d) and A2T100t2h (Fig. 6g), suggests that surface densification (Fig. 6d) can be as effective as bulk densification (Fig. 6g).

Removing stop bars in pressing not only substantially increased the depth of the deformation area to cover almost the entire sample height, but also reduced vessel element size (Fig. 6h), which resulted in a substantially higher density of 0.81 g/cm^3 and mechanical strength (Fig. 4). Overall, no cell-wall fractures were observed under tested pressing conditions, as expected from VTC of poplar wood under a much higher pressure of 5.5 MPa [38] than the 1 MPa applied in the present study, which ensured the improved wood mechanical properties of the densified samples [22].

Conclusions

Wood delignification can substantially facilitate wood densification to increase wood density at low pressures, such as 1 MPa in this study, to preserve the integrity of wood cells. Wood microstructure imaging analysis indicated that surface densification achieved using short pressing times is just as effective in improving wood mechanical properties as whole cross section densification achieved using longer pressing times. The extent of delignification, however, is not critical to densification. Desired densification can be achieved by using stop bars of proper thicknesses at low levels of delignification. Commercial soda pulping can be used to achieve sufficient wood delignification for poplar wood at a very low alkali concentration (1%) with a lower liquor-to-wood ratio (3:1) than in pulping. Wood mechanical properties increased linearly with wood density, in agreement with pure thermal densification, but at reduced densification pressure. With lignin removal below 7%, densification under 1 MPa for 15 min can

increase bending strength and hardness by as much as 70% and 190%, respectively. Compared with alkali treatment, MA treatment that removed insignificant amount of lignin and resulted in minimal densification (less than 10%) reduced wood bending strength though increased wood hardness. The optical appearance of the densified wood samples after both alkali and MA treatments was desirable and compatible with the colors of popular wood stains. Because alkaline wood pulping is widely practiced commercially, the present study has significant importance to upgrade low-grade wood, such as short-rotation woody crops, for high-value structural material applications in furniture, packaging, and construction using the existing wood pulping infrastructure.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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