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Study on Improving the Fixation Rate of Impregnated Poplar Wood with Maltodextrin and 1,3-Dimethylol-4,5-Dihydroxyethyleneurea

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Received: 11 July 2019; Accepted: 5 August 2019; Published: 8 August 2019



Featured Application: This paper paves the way for improving the fixation rate of impregnated wood and provides new insights into practical applications.

Abstract: The impregnation of poplar wood (*Populus adenopoda* Maxim) with 1,3-dimethylol-4,5-dihydroxyethyleneurea and maltodextrin and the effects of ZnCl₂ and curing at 103 °C and 120 °C on the fixation rate and the leaching resistance of modified samples were investigated (103 °C curing, ZnCl₂ + 103 °C curing, 120 °C curing, and ZnCl₂ + 120 °C curing are denoted as 103, ZC-103, 120, and ZC-120, respectively), with the aim of improving the modification effect. The results showed that ZC-103 had the highest fixation rate, and its weight leaching ratio was higher than that of 120. Fourier-transform infrared spectroscopy showed that ZnCl₂ did not affect the functional groups of the modified chemicals. The flexural strength and modulus and the compressive strength perpendicular to the grain were highest for ZC-103. In summary, ZC-103 exhibited the highest fixation rate, indicating that the hardener ZnCl₂ bridged and increased the interfacial properties between the chemicals and cell walls and therefore increased the potential for macromolecule polycondensation between the chemicals and cell wall materials. This research paves the way for improving the fixation rate of impregnated wood and provides new insights into practical applications.

Keywords: ZnCl₂; temperature; poplar; fixation rate; leaching cycle; wood properties

1. Introduction

Poplar wood is a green and environmentally friendly material that is recyclable and degrades naturally. It has the advantages of a fast growth rate, high yield, and a short harvesting period, which meets market demand, but has characteristics of low mechanical properties and dimensional stability, as well as low resistance to biocidal factors, which markedly affects its service life [1,2]. To date, many studies have been conducted on the chemical impregnation of wood: the functional improvement of the wood cell cavity or cell wall is achieved by treatments at a cell level or molecular level [3–6]. Water-soluble low-molecular-weight resin impregnation is a commonly used wood modification technique. Studies have shown that although in situ polymerization of monomers occurs inside the wood, it is difficult to improve the physical and mechanical properties of the wood because the polymer mainly fills the cell cavities and does not easily enter the cell walls: therefore, the wood bulk density cannot be increased significantly [5]. Improvements in the density and mechanical properties of wood

are closely related to weight percent gain (WPG), and the improvement of the dimensional stability of wood is closely related to the distribution ratio of the wood cell cavity/wall after resin impregnation [7].

The substance 1,3-dimethylol-4,5-dihydroxyethyleneurea (DM) is active with two nitrogen methylol groups and is commonly used in the textile industry [8]. The use of DM for wood modification has resulted in good performance and has improved the dimensional stability [9], durability [10], coating properties [11], and weathering resistance of wood [12,13]. Maltodextrin (MA) has been widely used in food [14], pharmaceutical [15], papermaking [16], and other industries because of its low sweetness, low viscosity, low odor, and low browning reaction [17]. Cai et al. used a combination of DM and MA for the impregnation of poplar wood and found that its antishrinkage efficiency increased by more than 60% and that mechanical properties were also improved. However, a leaching test indicated that the weight leaching ratio was 50% and increased with the MA concentration [18]. Subsequently, Cai et al. investigated drying characteristics during the curing process of DM/MA-impregnated wood materials, where it was found that the lower the deposition amount of the chemical, the more likely it was that the impregnated samples exhibited drying defects, including shrinkage and cross bending: When the amount of impregnation chemicals was higher, there was significantly less shrinkage, and fewer drying defects were observed [19]. Moreover, the higher the WPG of the modified material, the greater the functional improvement was [9]. Sun et al. studied the curing process of DM and found that the addition of 2% $ZnCl_2$ ensured the stability of DM under normal temperature (23 ± 2 °C) immersion conditions and ensured that the moisture discharge during the drying process of the impregnated material was compatible with the curing of the resin: the addition of $ZnCl_2$ ensured that the DM remained clear compared to other hardener, which facilitated observation during a subsequent immersion test, and also the addition of $ZnCl_2$ allowed for more chemicals to remain in the wood cell wall and cell cavity, making the modified wood more effective [20]. In addition, the curing temperature affects the degree of reaction between the modifier and the cell wall. He et al. [21] and Che et al. [22] investigated the effect of different curing temperatures on the WPG of impregnated material: it was concluded that a curing temperature of 120 °C was the most suitable temperature for DM. Yuan et al. investigated the effect of different curing temperatures on the static flexural strength of DM-modified wood. It was found that the mechanical properties were optimal when cured at 90 °C or 120 °C and that the mechanical properties deteriorated as the temperature increased [23].

In summary, it is important to improve the fixation rate and leaching resistance. Previous studies have shown that impregnated materials cured at a temperature of 103 ± 2 °C retain the modification effect [18,23]. In one study, modified poplar wood was impregnated with DM/MA, and the hardener $ZnCl_2$ was used at two curing temperatures (103 °C and 120 °C) to investigate the fixation rate, leaching resistance, surface wettability, and mechanical and thermal properties of the modified materials. It was expected that this method would improve the fixation rate and the leaching resistance of the DM/MA-modified system so that the poplar wood could be impregnated at a lower temperature to save on production costs.

2. Experiment

2.1. Materials

Poplar wood (*Populus adenopoda* Maxim) measuring 2000 mm × 150 mm × 25 mm (longitudinal × tangential × radial, L × T × R) was purchased from a local timber trading market (Harbin, China). The initial moisture content was 9.1%, and it was then processed to a specific experimental size and subsequently oven-dried at 103 °C for 24 h prior to use. Then, 1.5% $MgCl_2 \cdot 6H_2O$ was used as a catalyst and 2% $ZnCl_2$ was used as a hardener (the curing mechanism of $ZnCl_2$ is shown in Figure 1), and both were of analytical grade and were purchased from Guangfu Technology Development Co., Ltd. (Tianjing, China). MA was supplied by Jinyu Chemical Co., Ltd. (Shouguang, China), and it was used as an inflation agent. The crosslinkers consisted of a 60% solid mass fraction of DM, which was provided by Lanxiang Resin Co., Ltd. (Zhongshan, China).

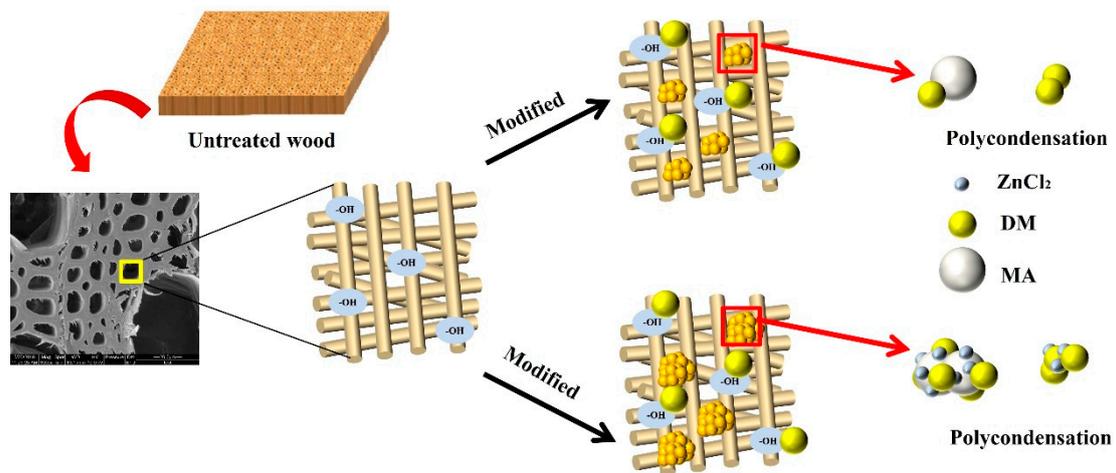


Figure 1. Curing mechanism of ZnCl₂.

2.2. Preparation of Modified Wood

The impregnation components were 10% DM, 10% DM + 5% MA, 10% DM + 10% MA, 10% DM + 15% MA, and 10% DM + 20% MA. The wood samples were placed in a vacuum tank (1000 mm in diameter and 2000 mm in length) and kept below a liquid level of 50 mm. The instrument was turned on, and the samples were fully impregnated in a vacuum (0.01 MPa, 12 h) and under pressure (0.6 MPa, 48 h). Subsequently, the impregnated samples were air-dried at room temperature (23 ± 2 °C) for 24 h and were then preheated at 40 °C for 24 h, followed by curing at a specific curing temperature for 48 h (103 °C curing, ZnCl₂ + 103 °C curing, 120 °C curing, and ZnCl₂ + 120 °C curing are denoted as 103, ZC-103, 120, and ZC-120, respectively), and the experiment is shown in Figure 2. Deionized water was used throughout the study.

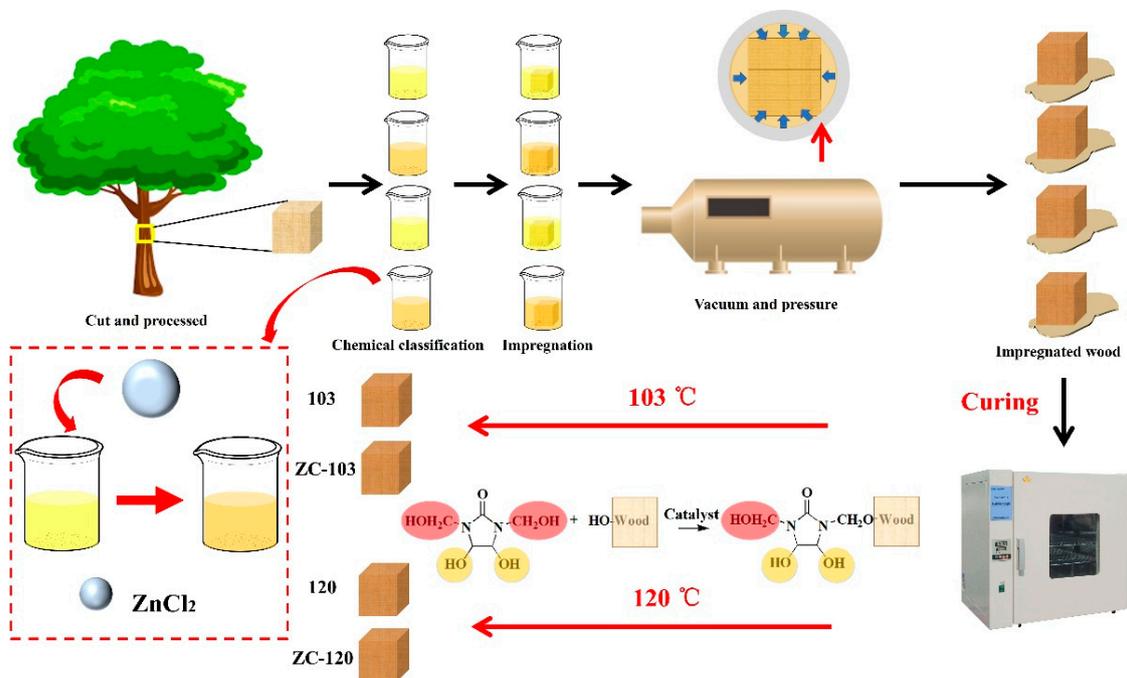


Figure 2. Experimental technology roadmap.

2.3. Characterization of Weight Percent Gain (WPG) and Weight Leaching Ratio (WLR)

The impregnated samples were subjected to oven-drying under different process conditions, and the mass (W_t) of each group was determined. The samples were then placed in several containers, which were filled with deionized water and were pressed down with barbed wire to prevent them from floating. All samples were leached with deionized water, which was changed daily for 10 d to remove the unreacted chemicals. The wood samples were oven-dried again, and the mass (W_w) was determined after a leaching test. Samples measuring 20 mm × 20 mm × 20 mm (L × T × R) and 20 replicates were used for each treatment. Equations (1) and (2) were used to determine the WPG and weight leaching ratio (WLR):

$$WPG = \frac{W_t - W_c}{W_c} \times 100\%, \quad (1)$$

$$WLR = \frac{W_t - W_w}{W_t - W_c} \times 100\%, \quad (2)$$

where W_t is the oven-dried mass after modification, W_c is the oven-dried mass before modification, and W_w is the oven-dried mass after leaching.

2.4. Leaching Cycle Test

To evaluate the fixation of the chemicals incorporated into the wood after treatment, three leaching cycles were performed: each included water-soaking for 7 d, followed by air-drying for 7 d and oven-drying at 103 °C for 48 h. During each cycle, the oven-dried weights of the samples were determined. The sample size was 20 mm × 20 mm × 20 mm (L × T × R), and 20 replicates were measured in each treatment. During the three leaching cycle tests, several liquid samples were obtained from the containers and characterized by a visible spectrophotometer (320–1100 nm, Model 722S, Shanghai Jingke Industrial Co., Ltd., Shanghai, China). In addition, a spectrophotometer was used for the first time to characterize the turbidity of the washed liquid: this represented a new method for a subsequent study of the leaching resistance of the impregnated material. Deionized water was used as a reference to calibrate the instrument. The test was conducted to measure the turbidity of the solution.

2.5. Fourier-Transform Infrared Spectroscopy

This experiment was performed on the chemicals and modified samples to investigate the effects of different temperatures and the addition of ZnCl₂ on the functional groups. The Fourier-transform infrared (FTIR) spectra of the wood powder (100–120 mesh) were recorded using KBr pellets at a resolution of 4 cm⁻¹ with 40 scans and a scanning range of 400–4000 cm⁻¹ (Magna-IR 560 apparatus, Thermo Nicolet, Beijing, China). The chemical compositions (group 1–6) of the test samples were as follows: 10% DM + 10% MA and 10% DM + 10% MA + ZnCl₂ at room temperature; 10% DM + 10% MA and 10% DM + 10% MA + ZnCl₂ cured at 103 °C for 48 h; and 10% DM + 10% MA and 10% DM + 10% MA + ZnCl₂ cured at 120 °C for 48 h. Six groups were tested. Among them, the test samples were as follows: untreated materials and 10% DM + 10% MA formulations in the 103, ZC-103, 120, and ZC-120 treatments and a total of 5 groups.

2.6. Morphological Analyses

The distribution of the chemicals in the wood before and after was observed by scanning electron microscopy (SEM) (FEI Company, Quanta200, Eindhoven, The Netherlands) at an accelerating voltage of 12.5 kV. The tangential section of the surfaces of the test samples was sliced with an SEM slicing knife. The fractured samples were then sputter-coated with a layer of gold for the SEM analysis. The untreated samples and the 10% DM + 10% MA samples were tested in the 103, ZC-103, 120, and ZC-120 treatments: 5 samples were tested.

2.7. Mechanical Tests

The bending resistance was tested using GB/T 1936.1–2009 and GB/T 1936.2–2009 standards. The sample dimensions were 300 mm × 20 mm × 20 mm (L × T × R). The horizontal grain compression was tested in accordance with the GB/T 1939–2009 and GB/T 1943–2009 standards, and the dimensions of the samples were 30 mm × 20 mm × 20 mm (L × T × R). Both tests were conducted using an electromechanical universal testing machine (CMT5504, MTS Systems Co., Ltd., Shanghai, China) with loading speeds of 2 mm/min and 0.5 mm/min, respectively. The impact strength was measured in accordance with the GB/T 1940–2009 standard. The dimension of the sample was 300 mm × 20 mm × 20 mm (L × T × R), and the pendulum energy was 4 J (XJC-15W, Chengde, China). Before carrying out these experiments, it was necessary to equilibrate the test samples at a relative humidity of 65% ± 5% and a temperature of 20 ± 2 °C to achieve an equilibrium moisture content of about 12%. The untreated samples and 10% DM + 10% MA were tested in the 103, ZC-103, 120, and ZC-120 treatments: 5 samples were tested and 20 replicates were used for each treatment.

2.8. Thermal Tests

A thermal analyzer (TGA Q50, Bavaria, Germany) was used to detect the thermal stability of the modified samples during the heating process. Approximately 5 mg of the samples were placed in an aluminum pan. The samples were heated at a heating rate of 10 °C/min from 25 to 500 °C under a nitrogen atmosphere with a flow rate of 30 mL/min. The untreated materials and the 10% DM + 10% MA samples were tested in the 103, ZC-103, 120, and ZC-120 treatments.

2.9. Surface Wettability Tests

An automatic video-based microcontact angle (contact angle: CA) measuring instrument (OCA20, German DATA Physics) was used to detect the CA between the sample and the deionized water in a liquid phase environment at room temperature (23 ± 2 °C). The hydrophilic differences between the samples were determined. The sample dimensions were 20 mm × 20 mm × 20 mm. Before the test, it was ensured that the surface of the sample was smooth. The surface of each sample was measured 5–10 times in 5 positions, and each measurement lasted 30 s. The untreated samples and the 10% DM + 10% MA samples were tested in the 103, ZC-103, 120, and ZC-120 treatments: 5 groups were tested.

2.10. Water Absorption Tests

According to the GB/T 1934.1–2009 standard, the oven-dried samples were placed in containers of deionized water, and the samples were submerged in the water. The test was conducted at room temperature (23 ± 2 °C). The test samples were weighed after 6 h and subsequently every 1, 2, 4, and 8 d until the difference in moisture content was less than 5%. The dimensions of the sample were 20 mm × 20 mm × 20 mm (L × T × R), and the untreated samples and the 10% DM + 10% MA samples were tested in the 103, ZC-103, 120, and ZC-120 treatments with 10 replicates for each group. The water absorption (A_w) was determined using Equation (3):

$$A_w = \frac{W_i - W_t}{W_t} \times 100\%, \quad (3)$$

where W_t is the oven-dried mass after modification, and W_i is the wet mass at time i .

3. Results and Discussion

3.1. WPG and WLR Analysis

The results of the WPG and WLR are presented in Figure 3. The WPGs were positively correlated with the MA concentration in four treatments (Figure 3a). In general, the WPG of the samples in ZC-103 was higher than that of the other three groups at the same MA concentration. The addition

of ZnCl_2 in ZC-120 also increased the WPG. The results proved that the addition of the hardener ZnCl_2 increased the content of the DM/MA system modifier in the interior of the wood. This may have occurred because ZnCl_2 increased the permeability of the cell wall and wood samples were more conducive to immersion under pressure. It is also possible that ZnCl_2 acted as a modifier for cross-linking or grafting with the cell wall material to promote condensation of the molecules in the cell cavity to form macromolecules, which were immobilized in the wood. The WPGs of group C were the lowest, which may have been attributable to the high evaporation rate of the modifier at the high temperature of 120 °C, which resulted in a low fixation rate of the modifier.

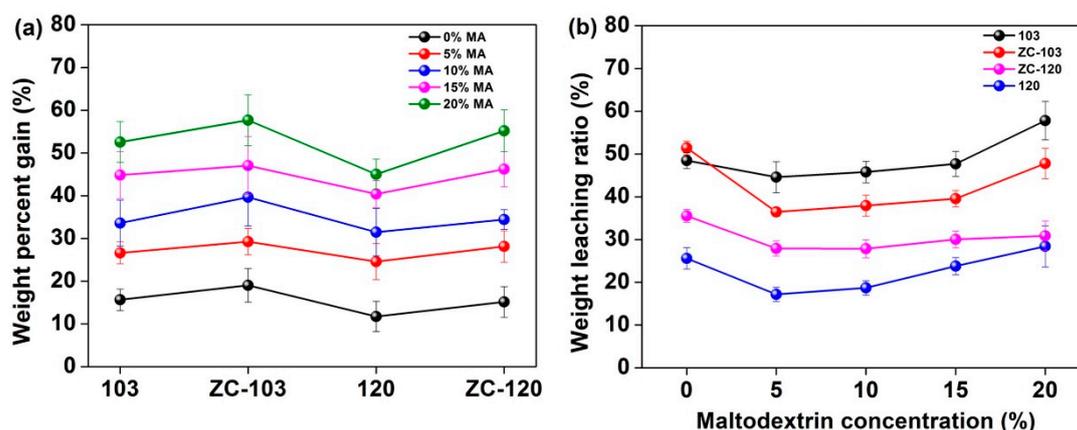


Figure 3. Weight percent gain (WPG) (a) and weight leaching ratio (WLR) (b) of wood treated with different methods and concentrations. Error bars represent the standard deviation of 20 replicates per treatment.

As shown in Figure 3b, the addition of 5% MA resulted in a reduction in the WLR of the samples compared to 0% MA of 3.87%, 14.99%, 8.42%, and 7.64% in the 103, ZC-103, 120, and ZC-120 groups, respectively: as the MA concentration increased, the WLR increased. The order of the WLR was 103 > ZC-103 > ZC-120 > 120. The curing efficiency of 120 was the highest, and the WLR was in the range of 17.18% to 28.40%. The reaction efficiency between DM/MA and the cell wall was better at 120 °C and remained permanently in cell cavities. In contrast, ZC-103 had a higher WPG, but the WLR was not satisfactory, and the WLR increased from 36.45% to 47.78%. This occurred because the fixation of the chemicals was limited at 103 °C and ZnCl_2 promoted the permeability of the wood in the capillaries, which resulted in the accumulation of chemicals that were encapsulated in macromolecules in the cell cavity after being washed with water. The standard deviation (STDVA) of the WPGs was in the range of 2.52% to 6.80%, indicating that the impregnation of the chemicals in the 20 replicate specimens was relatively uniform. The STDVA of the WLR was in the range of 1.03%–4.48%, demonstrating that the samples were saturated after immersion in water and that the differences between the groups were small.

In summary, the effective fixation rate of ZC-103 was the highest, and in the treatment of 10% DM + 10% MA, the WPG of ZC-103 increased by 15.33%, 20.69%, and 13.23% more than in 103, 120, and ZC-120, respectively. During the leaching test, 120 had the highest WLR, which was reduced by 27.08%, 19.25%, and 9.14% compared to the 103, ZC-103, and ZC-120 treatments, respectively.

3.2. Effect of Leaching Cycles on WPG

The effects of the water leaching cycles on the WPG are shown in Figure 4. The WPGs of the four treatments were basically the same after three washing cycles: the water saturation and oven drying caused a minor but steady decrease in the WPG over the three leaching cycles (Figure 4a–d). The rate of decrease in the WPG was more apparent for ZC-103 at high MA concentrations. A decrease in WPG during leaching experiments has also been observed in wood esterified by citric acid [24]

and succinic anhydride [25] and etherified by glutaraldehyde [26]: all compounds provided similar results. The average decreases in the WPG of 103, ZC-103, 120, and ZC-120 were 2.76%, 4.12%, 2.05%, and 3.29%, respectively. After three washing cycles, the WPG of the samples decreased by less than 5%, indicating that after the first leaching test, most of the chemicals that were incorporated and were present on the surface of the samples were washed out, and that in the remaining two washing cycles, the WPG decreased substantially. In general, the average decrease in ZC-103 was slightly higher than in the other groups. One reason may be that the initial presence of the chemicals was larger in ZC-103 than in the other groups. Another reason was that the chemicals were not completely fixed in the cell cavity at 103 °C, and the addition of ZnCl₂ increased the permeability: therefore, the outflow increased. The average decrease was lowest in 120, indicating that the modifier reacted with the cell wall at 120 °C and effectively immobilized it in the cell wall and cell cavity. The final WPG results after washing (Table 1) showed that, although the value of ZC-103 was higher than in the other groups, the final result was higher than in the other three treatments at the same MA concentration. It was greater than the amount of loss compared to the amount of fixing. In summary, although the addition of ZnCl₂ increased the loss rate to some extent, the relative loss rate was much smaller than in the other groups, and the samples treated at 120 °C exhibited stability during the washing cycles; however, the final fixation rate was lower than in the other groups. In addition, the STDVA of the WPG of the samples during the water cycle test was in the range of 0.60–4.47%, indicating that the response of the samples was similar.

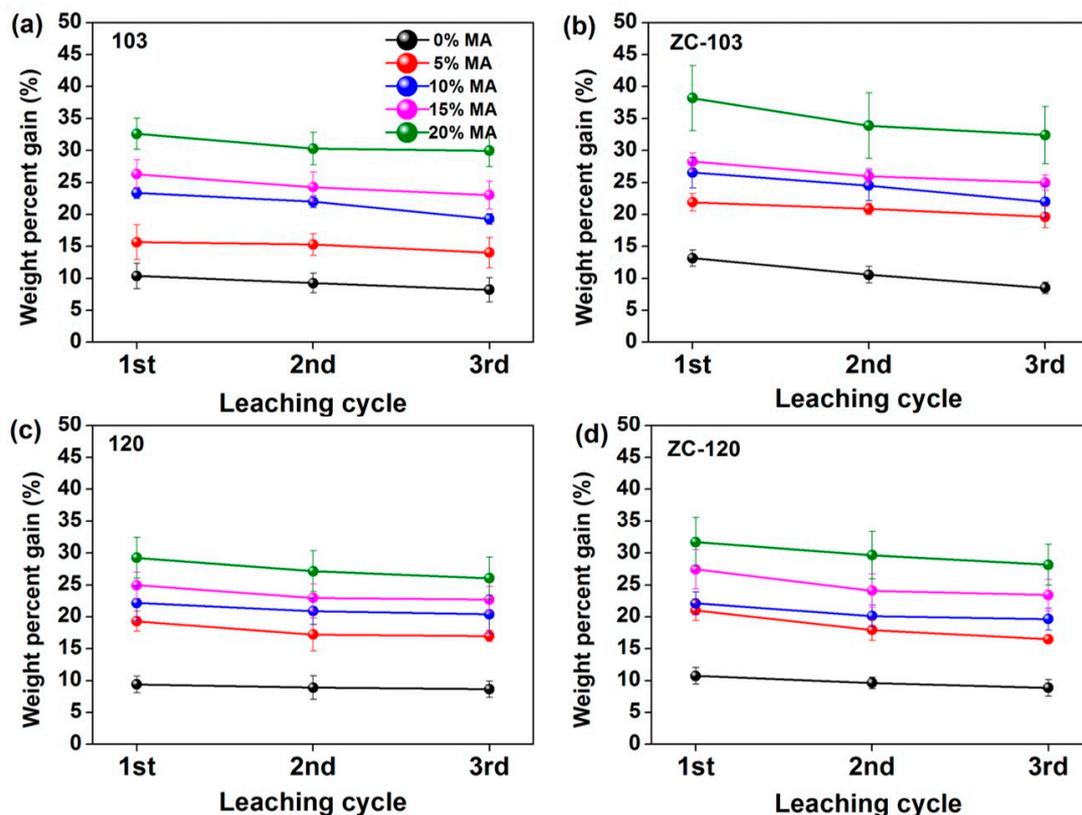


Figure 4. WPG of wood treated with different concentrations of maltodextrin (MA) and different treatments after three water leaching steps. The error bars represent the standard deviation of 20 replicates per treatment. (a) WPGs of 103 treatment after three leaching cycles; (b) WPGs of ZC-103 treatment after three leaching cycles; (c) WPGs of 120 treatment after three leaching cycles; (d) WPGs of ZC-120 treatment after three leaching cycles.

Table 1. WPG of wood for different groups after leaching cycles.

Methods	103 (%)	ZC-103 (%)	120 (%)	ZC-120 (%)
10% DM	8.21 ± 1.88	8.49 ± 0.87	8.65 ± 1.27	8.85 ± 1.28
10% DM + 5% MA	14.03 ± 2.38	19.61 ± 1.67	16.99 ± 0.85	16.48 ± 0.600
10% DM + 10% MA	19.28 ± 0.83	21.97 ± 2.49	20.39 ± 2.99	19.65 ± 1.72
10% DM + 15% MA	23.03 ± 2.19	24.97 ± 1.21	22.69 ± 2.00	23.42 ± 2.45
10% DM + 20% MA	29.95 ± 2.49	32.43 ± 4.47	26.07 ± 3.29	28.15 ± 3.19

All values are expressed as mean ± standard deviation (STDVA). DM: 1,3-dimethylol-4,5-dihydroxyethyleneurea; 103: 103 °C curing; ZC-103: ZnCl₂ + 103 °C curing; 120: 120 °C curing; ZC-120: ZnCl₂ + 120 °C curing.

Figure 5 shows the characterization of the immersion liquid after three water leaching cycles. Figure 5a–c shows that as the concentration of MA increased, the liquid became more turbid. The color of 103 treatment was darkest, 120 treatment had the lightest color, and the ZC-103 and ZC-120 treatments were lighter: this was in agreement with the results of the leaching experiment (Figure 3b). The spectrophotometer results in Figure 5d–f indicate that after three water cycles, the absorbance was similar for the groups and increased with the MA concentration. The order in terms of the absorbance was 103 > ZC-103 > 120 > ZC-120. In general, the absorbance decreased significantly between the first cycle and second cycle, but there was no significant change from the second to the third cycle, indicating that after one wash, most of the unreacted modifier was washed out. A visual assessment was consistent with these expectations.

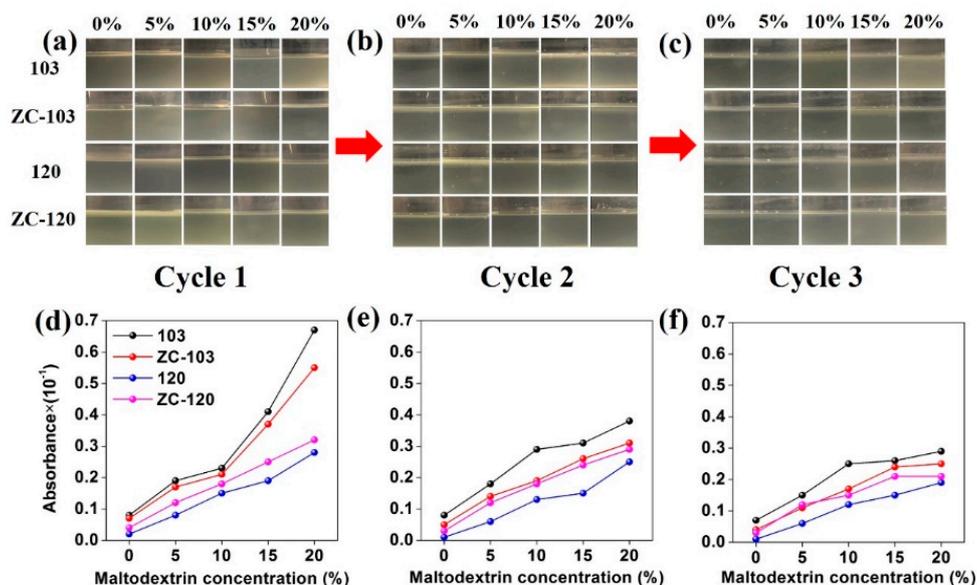


Figure 5. Changes in the immersion liquid after the leaching cycles (a–c); absorbance of the liquid after the leaching cycles (d–f).

3.3. Fourier-Transform Infrared Spectroscopy

The changes in the functional groups are shown in Figure 6. The FTIR spectra of 1–6 show that the peaks of the chemicals were basically the same at the same temperature (Figure 6a), indicating that the addition of ZnCl₂ did not affect the functional groups. When the temperature rose to 103 °C and 120 °C, the peaks at 3330 cm⁻¹ changed slightly in groups 3–6, indicating that the polycondensation reaction of the hydroxyl group (O–H) in the MA and DM was hardly promoted without the wood samples. The band at 1710 cm⁻¹ exhibited a shift for groups 3–6. The shift was more apparent at 103 °C, indicating that a O = C–N bond was generated in the chemicals. The absorption at 1457 cm⁻¹ exhibited no significant change in the peak of the C–N stretching vibration. As demonstrated in previous studies [18], the stretching vibration would only have been strengthened if a crosslink reaction

had occurred between the DM and wood: therefore, the chemicals did not crosslink. The absorption peak of C–O–C at 1157 cm^{-1} increased due to the condensation reaction of DM to form an ether bond. The highest absorption peak occurred at 1050 cm^{-1} and was caused by the stretching vibration of the alcohol and ether groups in the polysaccharide [11]. The peaks of groups 3–6 were significantly higher than the peaks of the groups that were modified at a normal temperature (group 1 and 2), but at $103\text{ }^{\circ}\text{C}$, the peak value was highest. This indicated that there were more alcohol and ether groups in the wood and that more chemicals remained in the wood at the $103\text{ }^{\circ}\text{C}$ curing treatment.

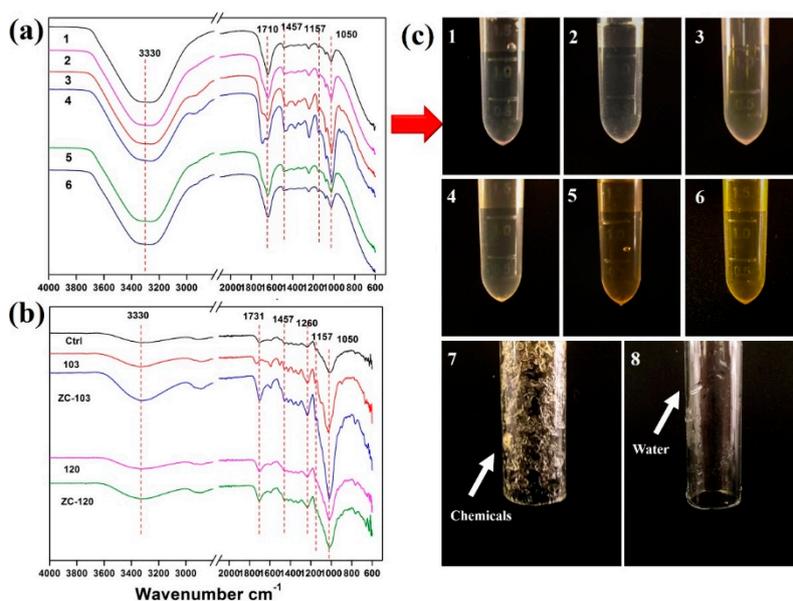


Figure 6. Fourier-transform infrared (FTIR) spectra of samples treated with different methods: (a) shows the FTIR of the samples in different treatments (Ctrl: untreated wood samples; group 1:10% DM + 10% MA; group 2:10% DM + 10% MA + ZnCl_2 ; group 3:10% DM + 10% MA, cured at $103\text{ }^{\circ}\text{C}$; group 4:10% DM + 10% MA + ZnCl_2 , cured at $103\text{ }^{\circ}\text{C}$; group 5:10% DM + 10% MA, cured at $120\text{ }^{\circ}\text{C}$; group 6:10% DM + 10% MA + ZnCl_2 , cured at $120\text{ }^{\circ}\text{C}$; group 7:10% DM + 10% MA, solidified at $120\text{ }^{\circ}\text{C}$ until the water evaporation was complete; group 8:10% DM + 10% MA + ZnCl_2 , solidified at $120\text{ }^{\circ}\text{C}$ until the water evaporation was complete. (b) Here, the FTIR spectra of the modified samples in different treatment groups are shown, and (c) shows the change in the color of the chemicals when heated to different temperatures at 10% MA.

As shown in Figure 6c, as the temperature increased, the color of the chemicals changed from no color to yellow, which further demonstrated that the high temperature contributed to the formation of alcohol and ether groups as a result of the reaction between MA and DM: this resulted in a strong absorption peak at 1050 cm^{-1} . After the water in the modifier without ZnCl_2 (7) was completely evaporated at $120\text{ }^{\circ}\text{C}$, it was found that a large amount of yellow solid particles adhered to the tube wall. In the modifier with ZnCl_2 (8), water droplets adhered to the tube wall, which indicated that the addition of ZnCl_2 decreased the volatilization of the chemicals. This may have occurred because ZnCl_2 facilitated the formation of large-particle polymers in the DM/MA system that did not degrade at the same temperature.

Figure 6b shows the FTIR of the modified wood samples and the untreated material. In the experimental group, the stretching vibration was strengthened at 3330 cm^{-1} , which occurred because DM contains three O–H per molecule: When reacting with poplar wood, O–H was introduced into the samples. Although DM underwent a polycondensation reaction with the O–H inside the wood, the added amount was greater than the consumption. The absorption peaks at 1731 cm^{-1} belonged to the acetyl and carboxyl groups of wood hemicellulose, nonconjugated ketones in lignin, carbonyl compounds, ester groups, etc. The absorption peaks at this point were shifted after the introduction of

DM, and an amide acetyl group ($O = C-N$) was formed in the wood samples. In addition, the increase in the peak of the $C-N$ bond stretching vibration at 1457 cm^{-1} also proved that DM reacted with the wood. At 1157 cm^{-1} , the absorption peak of $C-O-C$ gradually increased due to the crosslinking reaction between the wood and DM and the condensation reaction of DM to form an ether bond. The absorption peaks of the untreated wood at 1260 and 1224 cm^{-1} were attributed to the vibration of the carboxyl functional groups in xylan and other hemicelluloses [18,27]. In the experimental group, the stretching vibration was enhanced, indicating that wood modification occurred and that the chemicals not only filled the cell space between the wood cell and the intercellular space but that crosslinking had occurred with certain groups inside the wood to form carboxyl groups. The highest absorption peak of the infrared spectrum of the lanthanum-modified wood occurred at 1050 cm^{-1} and was caused by the stretching vibration in the alcohol and ether groups in the polysaccharide. The stretching vibrations in the treated samples were obviously strengthened by the vibration of various functional groups in the lignin, indicating chemical crosslinking with cellulose and DM in the wood. The peaks of 103 and ZC-103 were the largest, indicating the largest fixation rate of DM/MA inside the wood and a large amount of alcohol and ether. The peaks of the 120 and ZC-120 groups were lower than those of groups 103 and ZC-103 because the chemicals were more volatile at $120\text{ }^{\circ}\text{C}$, which was not conducive to the fixation of the chemicals.

In summary, the addition of $ZnCl_2$ had no significant effect on the functional groups of the modifier, indicating that no acidic substances able to affect the mechanical properties of the wood were generated in the high-temperature atmosphere. The samples cured at $120\text{ }^{\circ}\text{C}$ had excellent resistance to water leaching, but the amount of solidification inside the wood was lower than in the samples cured at $103\text{ }^{\circ}\text{C}$ because the modifier was more volatile and was not easily fixed at $120\text{ }^{\circ}\text{C}$.

3.4. Morphological Analyses

The curing results of the wood samples before and after washing are shown in Figure 7. The lumen inside the untreated sample was clean, and the images of the pits were clean. The results of the 10% DM + 10% MA-treated samples in 103, ZC-103, 120, and ZC-120 showed that the chemicals almost filled the entire lumen of the catheter (Figure 7(a1–d1)). The WPGs were 33.59%, 39.67%, 31.47%, and 34.42%, respectively. The fixation of the chemical in the 120 treatment was significantly lower than in the other three groups, which was consistent with the results that are shown in Figure 3a, indicating that the curing treatment at $120\text{ }^{\circ}\text{C}$ easily volatilized the chemicals and affected the amount of immobilized modifier. After washing with water, the filling in the cell cavity was significantly reduced (Figure 7(a2–d2)), but the curing conditions of the catheter lumen (Figure 7(b2,d2)) were better when the hardener $ZnCl_2$ was used under the same conditions: there was only a thin layer of resin film attached to the cell wall (Figure 7(a2,c2)) because DM/MA was able to enter the cell wall of the wood and react with the main components of the cellulose, hemicellulose, and lignin. The main reaction was etherification with the hydroxyl groups in the wood and fixation in the cell wall of the wood. The substances in the cell cavity were mainly DM/MA substances that underwent a polycondensation reaction under the action of the catalyst and the high temperature so that macromolecular substances were formed and deposited in the cell cavity. Since $ZnCl_2$ increased the permeability of the wood cell wall and the reactivity of DM/MA, the polycondensation of large modified molecules helped the chemicals to adhere to the cell cavity. However, as shown in Figure 3b, the WLR at $120\text{ }^{\circ}\text{C}$ was relatively low compared to other groups, and it is also possible that the modifier sufficiently crosslinked and penetrated the cell wall so that the lumen of the catheter in Figure 7(c2) showed only a small amount of filler.

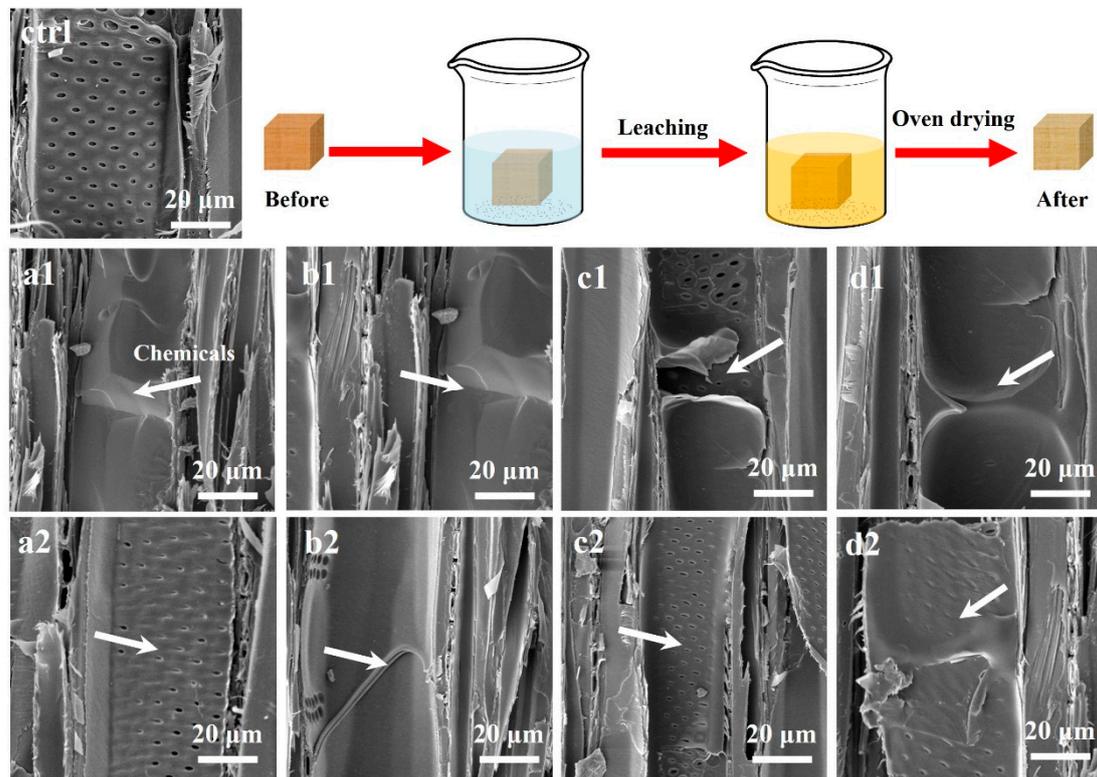


Figure 7. Micrographs of the tangential sections of the wood samples. The magnification is 20 μm , and the arrows point to the curing chemicals. Among the untreated wood samples (Ctrl), 10% DM + 10% MA were modified by 103, ZC-103, 120, and ZC-120 and are shown in (a1), (b1), (c1), and (d1). The micrographs of the resolidified products after the leaching test are shown in (a2), (b2), (c2), and (d2), which correspond to (a1), (b1), (c1), and (d1).

3.5. Determination of Mechanical Strength

The results of the flexural and transverse grain compression tests of the wood samples are shown in Figure 8. As shown in Figure 8a, there were significant differences in the results for the chemicals at the same concentration, and the flexural modulus values of the treatments were higher than those of the untreated samples. The flexural modulus values of 103, ZC-103, 120, and ZC-120 were 9.62, 10.06, 10.48, and 12.68 GPa, respectively, and the value of ZC-120 was 111.69% higher than the unprocessed sample (5.99 GPa). The smallest difference between a treatment and the control was observed for 103 (60.10%). In general, the addition of ZnCl_2 or an increase in temperature from 103 $^\circ\text{C}$ to 120 $^\circ\text{C}$ resulted in an increase in the flexural modulus. A high temperature and a relatively low agent fixation rate were more conducive to the rigidity of the wood samples, which was due to the DM/MA internal or external condensation reaction that deposited material in the lumen of the wood cell, causing the cell cavity of the wood to inflate. The deformation was lowest under the ultimate load. The flexibility of the wood originally produced by the empty spaces in the wood was reduced, resulting in increased rigidity [28]. In addition, due to the deposition of the modified chemicals in the cell wall of the wood, the free movement between the polysaccharide chains was reduced, and the rigid structure of the cell wall matrix was improved [9]. However, when the filling amount of the chemicals in the intercellular space reached a certain level, acidic hydrolysis of the catalyst MgCl_2 occurred: since the chemicals inflated the cell wall micropores, the water content in the cell wall was higher than in the sample under the same temperature and relative humidity conditions, and thus the plasticizing effect on the microfibrils was stronger under an external load, and the wood samples were more easily deformed [29]. In addition, the flexural strength was positively correlated with the change in the WPG (Figure 7a), although it decreased with increasing temperature; however, the flexural strength improved after adding ZnCl_2 ,

and the bending strength of 103, ZC-103, 120, and ZC-120 was 93.81, 97.29, 58.56, and 67.80 MPa, respectively. ZC-103 had a flexural strength value that was 39.90% higher than that of the untreated samples (69.54 MPa). When ZnCl_2 was added at 103 °C and 120 °C (ZC-103 and ZC-120), the bending strength was also slightly improved compared to the groups without ZnCl_2 (103 and 120) because more chemicals were deposited in the cell cavity and the intercellular layer of the cell wall. When the wood was subjected to an external force, the chemicals in the cell cavities and walls increased the compression resistance on the upper surface of the wood and acted as a tensile force on the lower surface of the wood: the change in the integrated stress manifested as an increase in the bending strength of the modified samples [26]. When the temperature was raised from 103 °C to 120 °C, a 37.58% decrease in the bending strength was observed (comparison of 103 and 120). The reason was that MA/DM acted as a modifier to crosslink with the macromolecules in the cell walls of the wood. The degree of activity and linkage of the active chemical groups in the wood changed, hydrogen bonding occurred, the connection between the microfibrils was broken, and the catalyst accelerated the hydrolysis of the hemicellulose: drying and high temperatures destroyed the linkage between the cellulose and resulted in a decrease in the bending strength [9,21]. The STDVAs of the modulus and the strength of the bending were in the range of 0.19–0.88 GPa and 1.54–3.87 MPa, respectively, indicating that the test results of the bending performance were uniform for the 20 replicates and that there was no significant difference between the individual tests.

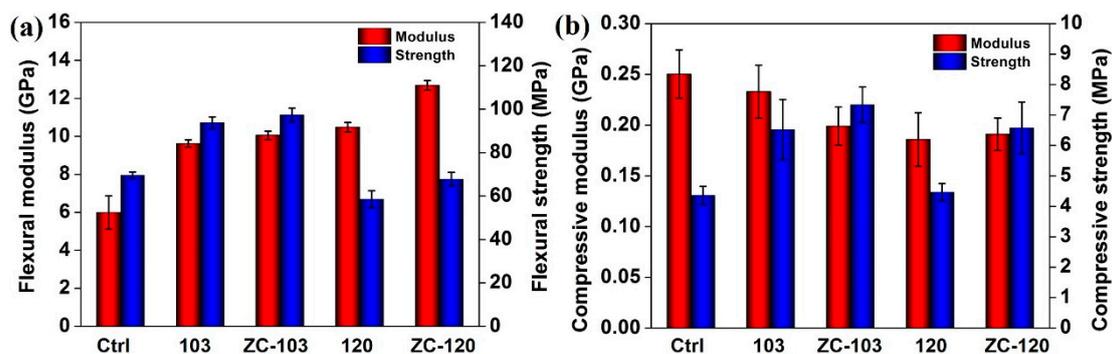


Figure 8. Flexural strength and modulus (a) and transverse compressive strength and modulus (b) of the wood samples after treatment with 10% DM + 10% MA in 103, ZC-103, 120, and ZC-120 treatments.

As shown in Figure 8b, the transverse compressive modulus of elasticity was significantly reduced in the treated compared to the untreated samples, and the values of 103, ZC-103, 120, and ZC-120 were 0.23, 0.19, 0.18, and 0.17 GPa, respectively. The value was lowest for 120 cured at 120 °C, which was 28.00% lower than in the untreated samples. The addition of ZnCl_2 (ZC-120) resulted in a negative effect, indicating that there was more MgCl_2 in the samples. MgCl_2 is a Lewis acid that does not provide oxygen ions during hydrolysis but accepts the free electron pair provided by the oxygen atom on the MA glycosidic bond: It polarizes the bond, making it more susceptible to attack by hydronium ions. The greater the concentration of hydrogen ions, the more easily the hydrolysis occurs, resulting in a decrease in the strength of the cellulose without the protection of hemicellulose [30]. In contrast, the compressive strengths of the cross-grain were 6.52, 7.33, 4.47, and 6.58 MPa (103, ZC-103, 120, and ZC-120, respectively): the value of group B was 68.12% larger than that of the untreated samples (4.36 MPa). In general, an increase in temperature reduced the compressive strength of the grain, whereas the addition of ZnCl_2 increased the compressive strength. The compressive modulus and strength were in the range of 0.16×10^{-1} – 0.26×10^{-1} GPa and 0.29–0.99 MPa, respectively.

The results of the impact strength test are shown in Figure 9. As shown in Figure 9a, the impact strengths of 103, ZC-103, 120, and ZC-120 were 15.74, 12.31, 13.58, and 8.01 KJ/m^2 , respectively. In general, the curing temperature of the modified samples and the addition of ZnCl_2 reduced the impact strength: The minimum value occurred in ZC-120 and was 4.05 times lower than that of the untreated material. The value of 103 was 2.21 times lower. Therefore, the loss of the impact strength

was higher at 103 °C than at 120 °C. The reduction in impact strength was attributed to the hydrolysis of the polymer inside the wood and the cross-linking reaction of the modifier in the cells. During this process, the moisture content inside the cell wall decreased, the brittleness of the wood increased, and the deposition amount of the modifier increased [31,32]. More hydronium ions were produced by MgCl₂, resulting in a larger amount of cellulose being hydrolyzed. Figure 8b shows the fracture surfaces of the samples after the impact test. The poplar sample was not broken into two pieces, but a fiber bundle was generated on the surface. In contrast, the modified samples were brittle, the sections were relatively smooth, and there was no fiber bundle. The cross-sections were black, indicating that the cellulose was degraded by high-temperature catalysis. The STDVA was in the range of 1.09–2.62 KJ/m², indicating that there were no differences in the 20 replicates.

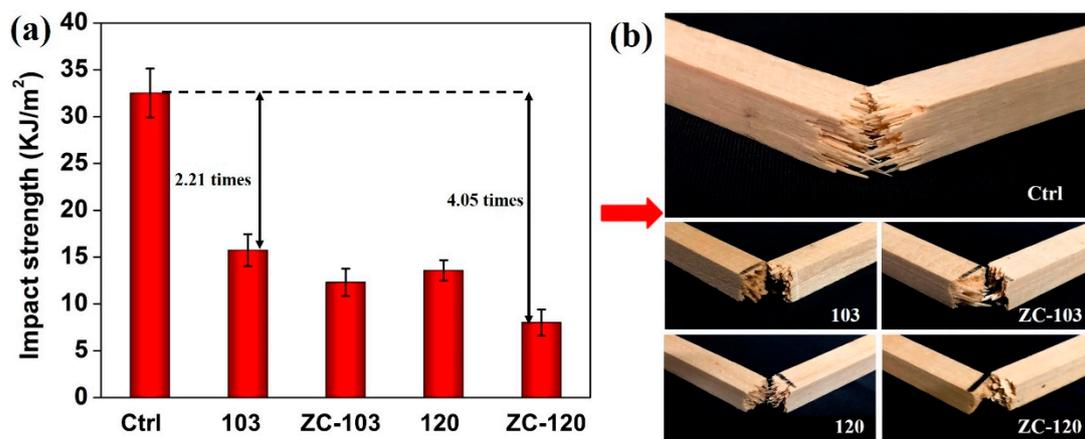


Figure 9. The impact strength of the wood samples after the four treatments 103, ZC-103, 120, and ZC-120 (a); fracture surfaces of the samples after the impact test (b).

3.6. Thermogravimetric Analysis

Thermogravimetric analysis (TGA) was used to examine the thermal stability of the different wood samples: the TGA and differential thermogravimetric (DTG) curves are shown in Figure 10a,b, respectively. The curves could be divided into three regions, which was consistent with previous studies [33,34]. Water evaporation occurred in the range of 50–150 °C and represented high-temperature evaporation of the bound water in the wood cells. The active pyrolysis zone was around 200–400 °C, and there were two peaks in this area, representing the degradation of cellulose and hemicellulose. The passive degradation zone, which represented lignin degradation, occurred in the range of 400–500 °C, and no peaks were observed.

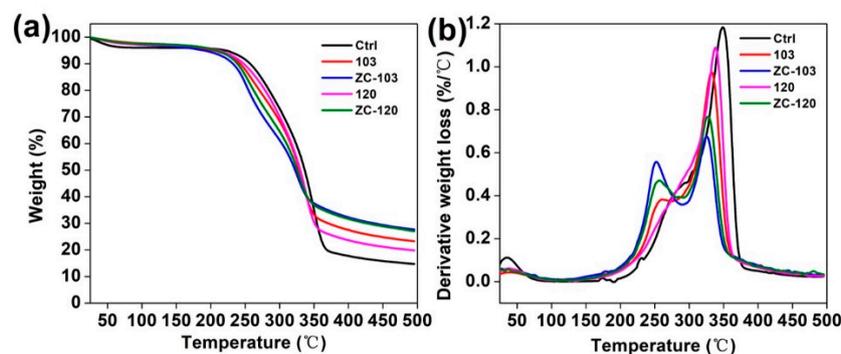


Figure 10. TGA (a) and differential thermogravimetric (DTG) (b) curves of the 10% DM + 10% MA-treated samples in different groups.

In Table 2, the T_{onset} of the samples that contained $ZnCl_2$ was higher, which may be because of the brittleness of the wood samples. The addition of $ZnCl_2$ changed the particle size of the modified sample powder, and DM/MA had a smaller particle size and was more easily dispersed in the wood matrix: the good interface between the chemicals and the wood matrix made the samples more sensitive to temperature changes [35,36]. The main degradation of carbohydrates in the wood occurred in the range of 200–400 °C, while the T_{max} of the untreated samples was 348.21 °C, indicating that the degradation occurred earlier than in the untreated group (Table 2). As the temperature continued to rise, the residual mass of each group changed little. The order of thermal stability from strong to weak was ZC-103 > ZC-120 > 103 > 120 > Ctrl: the two groups (ZC-103 and ZC-120) with $ZnCl_2$ exhibited better thermal stability, and the residual mass values were 27.65% and 26.97%, respectively. The untreated wood samples had the worst thermal stability, and the residual mass was 14.72%, which might have been caused by the proportion of water in the wood. The proportion of water in the mass lost was relatively higher than in the other samples. In general, these results indicated that the addition of $ZnCl_2$ improved the thermal stability of the modified samples and the quality of the residual mass because $ZnCl_2$ acted as a dehydrator at that time and caused the aromatization of carbon [37,38]. In addition, $ZnCl_2$ affected the physical bonding and enhanced the interaction between the chemicals and the matrix, thereby forming a barrier that minimized the volatility of the pyrolysis process of the DM/MA-modified samples.

Table 2. Thermal properties of the 10% DM + 10% MA-treated samples in different groups. T_{onset} : decomposition onset temperature; T_{max} : maximum decomposition rate temperature; T_{end} : decomposition termination temperature.

Methods	T_{onset} (°C)	T_{max} (°C)	T_{end} (°C)	Residual Mass (%)
Ctrl	221.36	348.21	494.23	14.72
103	203.68	332.42	495.49	23.25
ZC-103	187.80	323.96	495.34	27.65
120	210.85	337.45	495.50	19.82
ZC-120	205.75	325.01	495.40	26.97

3.7. Determination of Surface Wettability and Water Absorption

The surface CA and water absorption of the modified samples are shown in Figure 11. The CA is a convenient indicator to evaluate the hydrophilic–hydrophobic nature of the surface, and the hydrophobicity of the wood surface is of great significance for practical applications [39–41]. The CA results showed significant differences between the four treatments (Figure 11b). The CAs of the 103, ZC-103, 120, and ZC-120 treatments after equilibrium were 36.20°, 56.10°, 37.10°, and 47.35°, respectively, indicating that the CA was largest for ZC-103 with $ZnCl_2$ cured at 103 °C, 36.65° larger than in the untreated samples (19.45°). ZC-120 had the second largest CA, indicating that the addition of $ZnCl_2$ resulted in an increase in the CA of the wood surface: this was attributed to the proportion of chemicals entering the wood. As shown in Figure 11a, in untreated wood, the deionized water penetrated into the interior of the wood through channels such as pits, and hydrophilic groups such as hydroxyl groups on the surface combined with water molecules to form oxygen bonds and were diffused [41], which resulted in a small CA of the untreated wood and strong hydrophilicity. In contrast, the channels of the modified wood were filled with chemicals, which hindered the infiltration of moisture. The results show that the larger the filling amount, the larger the CA was. In addition, the DM/MA also reacted with hydrophilic groups on the surface of the wood, rendering the surface hydrophobic. However, the unreacted DM monomer also contained two hygroscopic hydroxyl groups, which generated hydrogen with water molecules. The combination of the bonds made the surface of the wood somewhat hydrophilic, but since most of the modifiers underwent polycondensation into macromolecules inside the wood, in general the wood surface was still hydrophobic.

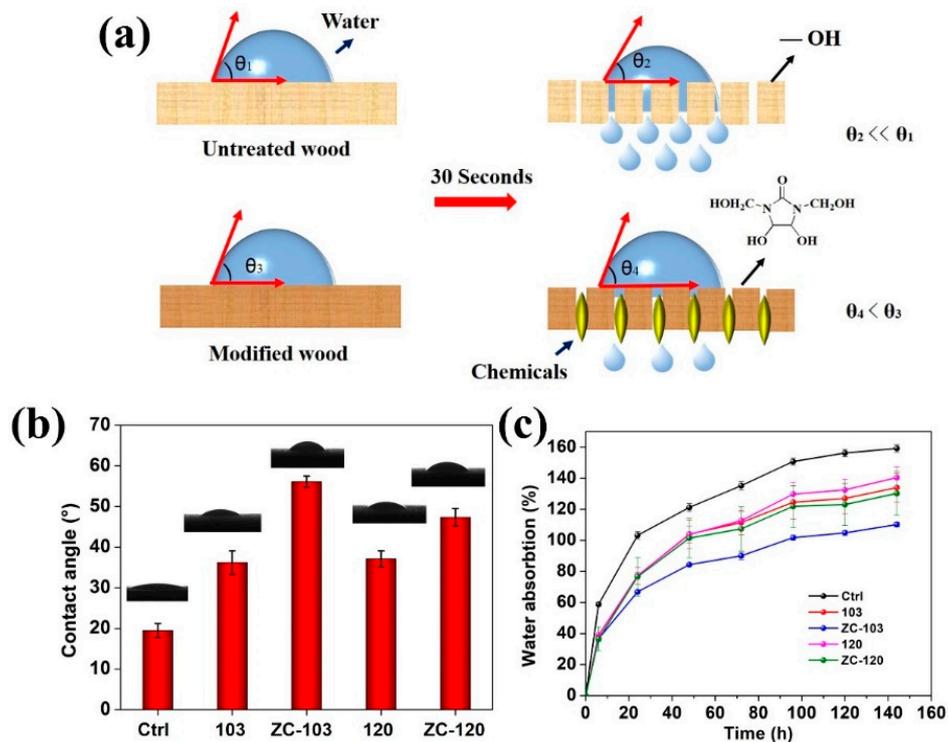


Figure 11. Schematic diagram of the permeation of the deionized water on the surface of the wood samples (a); the surface contact angle of the untreated and treated samples (b); the water absorption of the untreated and treated samples (c).

As shown in Figure 11c, the water absorption of the samples was also related to the amount of fixation agent in the wood. The maximum water absorption values of the 103, ZC-103, 120, and ZC-120 treatments were 133.96%, 110.17%, 140.41%, and 139.23%, respectively, and the water absorption in all groups was lower than in the untreated wood. The STDVA of the CA was in the range of 1.40° to 2.90° , indicating that the left and right CAs and the characteristics of the wood surface were relatively uniform. In addition, the STDVA of water absorption was in the range of 0.16% to 14.15% and increased with increasing water absorption, but both were within the allowable range. In summary, the CA was the largest for the group with ZnCl_2 cured at 103°C , which proved that these conditions greatly improved the hydrophobicity of the wood.

4. Conclusions

1,3-dimethylol-4,5-dihydroxyethyleneurea (DM) and maltodextrin (MA) were used as modifiers for wood impregnation, and the effects of the hardener ZnCl_2 on the fixation rate and performance of the modified samples at 103°C and 120°C were investigated. In this study, ZC-103 treatment with the modified samples exhibited the best fixation effect, and the mechanical properties, thermal stability, and surface hydrophobicity also improved. These findings offer researchers an environmentally friendly method for wood modification.

In future research, it is necessary to study the release of formaldehyde under this curing condition, which can provide an important basis for establishing a complete and environmentally friendly modification process.

Author Contributions: M.C. conceived of and designed the experiments; M.C. and Z.F. performed the experiments; M.C., Z.F., and Y.C. analyzed the data; M.C. wrote the paper, with revisions by Z.F., Y.C., and Y.Z.; M.C. and Y.Z. edited numerous drafts.

Funding: This research was funded by the National Natural Science Foundation of China (Grant No. 31670562).

Acknowledgments: This work was financially supported by the National Natural Science Foundation of China (Grant No. 31670562).

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

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