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# Leachability of Fast-Growing Wood Impregnated with Low Concentrations of Furfuryl Alcohol

**He Sun [1], Yizhi Gong [2], Yuntian Yan [1], Changqing Fu [1], Ke Zhan [3], Chunlei Dong [1], Linkun Xie [1] and Taian Chen [1,*]**

[1] College of Materials Science and Engineering, Southwest Forestry University, Kunming 650224, China; hesun1993@163.com (H.S.); 15862231716@163.com (Y.Y.); cq292560@163.com (C.F.); dchunlei@swfu.edu.cn (C.D.); xielinkun@163.com (L.X.)
[2] China-ASEAN College of Marine Sciences, Xiamen University, Xiamen 361101, China; jrn1909366@xmu.edu.my
[3] College of Forestry, Wildlife and Environment, Auburn University, Auburn, AL 36849, USA; kzz0030@auburn.edu
* Correspondence: nfucta@sina.com

**Abstract:** Furfurylation can effectively improve the quality of fast-growing wood, but its leachability is unclear. In this study, fast-growing poplar (*Populus* sp.) and Chinese fir (*Cunninghamia lanceolata* (Lamb.) Hook.) were impregnated with low concentrations of 5%–20% furfuryl alcohol (FA), and the chemical and microscopic changes during leaching tests were analyzed by UV spectra and confocal laser scanning microscopy (CLSM). The results show that FA impregnation can regulate the weight percentage gain, but its effectiveness in regulating the cell wall bulking coefficient decreased as the impregnation concentration was increased. Impregnation with 15% and 20% FA showed no significant difference in the effect on volume swelling efficiency. The inverse relationship between the concentration of FA and the leaching rate was demonstrated by leaching tests, UV spectra, and CLSM. Notably, the leaching rate of poplar and Chinese fir wood was more than 30% when impregnated with 5% FA. Although the entirety of the furfuryl alcohol was deposited in the cell wall when impregnated with low concentrations of FA, the binding was not stable. The weight percentage gain of furfurylated Chinese fir was greater than that of poplar, but its leaching rate was lower, indicating that the cured furfuryl alcohol resin in poplar was not as stable as that in Chinese fir. Therefore, differences in tree species should be considered in low-concentration FA impregnation, as the improvement effect of concentrations below 10% on the properties of fast-growing wood is weak and the leaching rate of FA is significant.

**Keywords:** furfurylated wood; poplar; Chinese fir; leaching; furfuryl alcohol

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## 1. Introduction

Furfurylation is a common modification method in the field of wood science that can improve the properties of fast-growing wood species, reducing hygroscopicity and improving dimensional stability [1–5], decay resistance, subterranean termite resistance, density, and hardness [6–9]. During the modification process, due to the small molecular weight of furfuryl alcohol (FA), FA permeates the cell wall and undergoes a cross-linking reaction in the presence of acidity [10,11], resulting in the permanent expansion of the cell wall [12–15]. Typically, impregnation with high concentrations of FA results in substantial deposition within the cell lumen, which does not significantly improve the dimensional stability [16], whereas low concentrations of FA preferentially deposit within the cell wall [17]. Yu et al. performed FA modification via vapor phase furfurylation and obtained low-concentration-treated Chinese fir and poplar with weight percentage gains of 12.49% and 10.32%, respectively. They avoided the ineffective deposition of FA in the cell wall, as the FA-filled cell lumen did not directly affect the cell wall [18]. Therefore, high concentrations of FA in the cell lumen contributed less to the quality enhancement of furfurylated wood, while low concentrations of FA directly and effectively enhanced the properties of the cell wall.

Numerous scholars also studied the leachability of wood impregnated with FA, demonstrating that the use of furfurylated (e.g., leaching solution, burning performance) was environmentally friendly during the full life cycle [19–21]. Lin et al. found that the leachability of furfurylated wood with 30% FA was negligible due to the formation of hydrophobic FA resin, and the addition of FA reduced the leaching rate of fire-retardant additive guanylurea phosphate in modified wood [22,23]. Rahayu et al. found that the leachability of furfurylated wood with a weight percentage gain of 146.55% was significantly lower than that of wood modified by the combination of FA and nano-$SiO_2$, suggesting that the reaction between FA and the cell wall components resulted in a lower leachability [24]. Baysal et al. found that FA significantly inhibited the leaching of borates with the use of FA and borate modification [25]. Kong et al. concluded that the combination of FA and ammonium dihydrogen phosphate modification reduced the leaching of ammonium dihydrogen phosphate via furfurylation [26]. Morozovs et al. conducted hot-water/freeze-drying cycle tests on furfurylated wood with a weight percentage gain of 128%. Compared with untreated wood, the average water absorption rate and swelling of furfurylated wood decreased by 80% and 40%, respectively, which demonstrated the better modification effect of the high weight percentage gain. However, no studies have investigated low-concentration FA-modified cell walls in the optimization of furfurylated wood.

Leachability is a key index of furfurylated fast-growing wood and indicates the effectiveness of FA in the furfurylation of wood. For furfurylated wood, whose main market is indoor wood products, the advantages and disadvantages of high- and low-concentration FA impregnation should be integrated and balanced to produce wood with better dimensional stability, less weight percentage gain, moderate color, and lower glossiness. In addition, there are significant differences in the physicochemical properties of softwood and hardwood. Therefore, this study intends to use poplar and Chinese fir wood to explore the leachability of wood impregnated with low concentrations of FA to provide a reference for FA impregnation treatment parameters.

## 2. Materials and Methods

### *2.1. Materials*

Poplar (*Populus* sp.) and Chinese fir (*Cunninghamia lanceolata* (Lamb.) Hook.) trees were harvested from Shuyang, Jiangsu Province and Kaihua, Zhejiang Province, respectively. The trees were 20–23 years old, sawed into 3 cm-thick boards, and air-dried to a moisture content of about 12% in Kunming. The air-dried densities of poplar and fir were 480 $kg/m^3$ and 310 $kg/m^3$, respectively. Each sample was prepared using a sapwood section with a straight grain and no visible defects. The dimensions (tangential $\times$ radial $\times$ longitudinal) of the poplar and Chinese fir specimens were 35 $\times$ 15 $\times$ 10 mm, and more than 20 samples were prepared for each group. Furfuryl alcohol (FA), maleic anhydride, and borax were purchased from Tianjin Fengchuan Chemical Reagent Technologies Co., Ltd. (Tianjin, China), and deionized water was prepared in the laboratory.

FA, maleic anhydride, and borax were prepared at a mass ratio of 1:0.06:0.01, and the impregnation solvents with FA concentrations of 5%, 10%, 15%, and 20% were prepared with distilled water as the solvent. The impregnation treatment was as follows:

(1) Extraction: The samples were first subjected to benzyl alcohol extraction with a benzene:ethanol volume ratio of 1:2. The samples were dried in an oven at 45 °C until reaching a constant weight, placed in a Soxhlet extractor for 48 h, soaked in a water bath at 60 °C for 3 h, air dried to a constant weight, and finally placed in an oven at 103 °C for 24 h. The absolute dry mass and dimensions of the samples were measured with an accuracy of 0.0001 g and 0.01 mm, respectively.

(2) Furfuryl alcohol impregnation, curing, and drying: FA impregnation was performed using the full cell method [27]. Afterward, excess impregnation solution on the sample surfaces was wiped off, and the samples were wrapped with aluminum foil and

left to diffuse at room temperature for 72 h. The samples were cured in an oven at 103 °C for 6 h and then dried continuously at 50, 70, and 103 °C for 24 h.

The weight percentage gain (WPG) and bulking coefficient (BC) were calculated using the following equations:

$$WPG = (G_1 - G_0)/G_0 \times 100\% \quad (1)$$

$$BC = (V_1 - V_0)/V_0 \times 100\% \quad (2)$$

where $G_0$ and $G_1$ are the oven-dried weights (g) before and after FA treatment, while $V_0$ and $V_1$ are the oven-dried volumes ($mm^3$) before and after treatment, respectively.

The samples were, respectively, denoted as PW9, PW22, PW31, PW40, FW11, FW27, FW42, and FW54 according to the weight percentage gain of poplar and Chinese fir impregnated with 5%, 10%, 15%, and 20% FA.

### 2.2. Methods

#### 2.2.1. Leaching Procedure

(1) Water saturation: The wood samples were placed in the chamber, each group of samples was first treated under vacuum at −0.06 MPa for 30 min, then distilled water was added. The samples were further treated under pressure at 0.4 MPa for 60 min and finally treated under vacuum at −0.06 MPa for 30 min. The water uptake of the water-saturated sample (MC) and volume swelling efficiency (V) were calculated as follows:

$$MC = (G_2 - G_1)/G_1 \times 100\% \quad (3)$$

$$V = (V_2 - V_1)/V_1 \times 100\% \quad (4)$$

where $G_1$ and $G_2$ are the weights before and after water saturation, while $V_1$ and $V_2$ are the oven-dried volume and the swollen volume after water saturation, respectively.

(2) For the leaching process, the wood samples were placed in beakers containing distilled water at a volume ratio of 1:5 for 2 weeks of water immersion treatment. During this period, the water was changed 9 times in total: every 12 h on day 1, every 24 h on days 2–5, and every 48 h on days 7 to 14, i.e., the water was changed at the beginning of day 1, after 12 h, and at the beginning of days 2, 3, 4, 5, 7, 9, and 11. Each time the water was changed, the leaching medium was also collected [28–30]. The water uptake (MCWA) and volume swelling efficiency (VWA) after leaching tests were calculated as follows:

$$MC_{WA} = (G_3 - G_1)/G_1 \times 100\% \quad (5)$$

$$V_{WA} = (V_3 - V_1)/V_1 \times 100\% \quad (6)$$

where $G_3$ is the weight of the leached sample after 14 days and $V_3$ is the swollen volume after 14 days.

(3) Leaching rate and shrinkage rate: After the leaching tests, the wood samples were dried at 50 °C for 12 h, 70 °C for 12 h, and 103 °C for 24 h. The leaching rate ($M_L$) and shrinkage rate ($V_L$) were then calculated by the following equations:

$$M_L = (G_1 - G_4)/(G_1 - G_0) \times 100\% \quad (7)$$

$$V_L = (V_0 - V_3)/V_0 \times 100\% \quad (8)$$

where $G_4$ is the weight of the leached sample after 14 days, and $V_3$ is the oven-dried volume after 14 days.

#### 2.2.2. Analysis of Leachates

The analysis of FA in the leaching medium of the water-saturated sample and each water change was performed using a UV spectrophotometer (UV-2600i, Shimadzu Scientific Instruments, Columbia, MD, USA): scanning range, 180–500 nm; reference sample, distilled water; scanning speed, 200 nm/min. All samples were tested under the same conditions [31,32].

2.2.3. Morphology and Microstructure

The samples were first processed into wooden blocks with dimensions (T × R × L) of 5 × 5 × 10 mm before and after the leaching tests, which were placed in a desiccator and evacuated at −0.06 MPa for 15 min, after which they were left to stand in water for 30 min and then removed immediately. The samples were sliced to a thickness of 10–12 μm along the longitudinal sections using a slicer (Leica SM2000R, Leica company, Weitzlar, Germany). Finally, the microstructure of furfurylated wood before and after the leaching tests was observed by confocal laser scanning microscopy (CLSM) under a 63× oil microscope (SP8, Leica company, Weitzlar, Germany) with 633 nm excitation and a detector range of 650–700 nm.

2.2.4. Statistical Analysis

Statistical analysis was employed to evaluate the effect of FA concentration on the modification of the wood cell wall, leaching rate, dry shrinkage, and water uptake during leaching tests in low-concentration FA-impregnated fast-growing wood. The data in each group were averaged and the standard deviation and significant differences were analyzed using SPSS statistics version 23 [33].

## 3. Results and Discussion

### *3.1. Analysis of the WPG and BC of Furfurylated Wood*

The WPG and BC of the furfurylated wood are listed in Table 1. The WPG was positively correlated with the concentration of FA, but there was a significant difference between the WPG of Chinese fir and poplar wood. The 10% furfurylated wood provided a WPG of ~28% for FW27 and ~22% for PW22. Increasing the concentration to 20% caused the WPG of FW54 and PW40 to reach ~54% and ~41%, respectively, which indicated that the WPG of Chinese fir was generally higher than that of poplar. Mulyosari et al. demonstrated that the WPG of furfurylated wood was related to differences in softwood and hardwood anatomical structure [34]. It has also been demonstrated that hardwood is easier to impregnate treatment than softwood [35,36]. Chinese fir has a simpler microstructure compared to poplar, while poplar is easier to impregnate compared to Chinese fir. However, the predominantly longitudinal permeability of small-sized wood for FA impregnation likely resulted in a lower WPG for the more permeable poplar wood.

**Table 1.** WPG and BC for Chinese fir and poplar with furfurylation (%).

| Sample | FA Concentration | 0% | 5% | 10% | 15% | 20% |
|---|---|---|---|---|---|---|
| Chinese fir | abbreviation | CTRL | FW11 | FW27 | FW42 | FW54 |
| | WPG | −0.15 e (0.08) | 11.69 d (0.01) | 27.96 c (0.02) | 42.38 b (0.05) | 54.15 a (0.04) |
| | BC | −0.20 e (0.14) | 5.47 d (0.01) | 8.00 c (0.02) | 9.51 b (0.02) | 11.61 a (0.03) |
| poplar | abbreviation | CTRL | PW9 | PW22 | PW31 | PW40 |
| | WPG | −0.37 e (0.01) | 9.41 d (0.01) | 22.07 c (0.02) | 31.40 b (0.04) | 40.98 a (0.05) |
| | BC | −0.46 d (0.06) | 3.80 c (0.01) | 6.48 b (0.01) | 8.52 a (0.01) | 9.07 a (0.01) |

The standard deviation is given in parentheses; the same letter after the mean indicates no significance at $p \leq 0.05$.

The BC of furfurylated poplar and Chinese fir generally increased with the concentration of FA, but this increase was not consistent (Table 1). The large change in BC from 5% to 10% FA impregnation in poplar and Chinese fir indicated that the FA resin was mainly deposited in the cell wall, which was significantly enlarged, while Kong et al. also observed a significant bulking of the cell wall by impregnation treatment with furfuryl alcohol concentration of more than 30% concentration for the cell wall [26]. However, with the increase in impregnation concentration, the change in BC gradually became smaller. The effect of 15% and 20% FA on the BC of poplar wood was not significantly different ($p > 0.05$), indicating that when the FA impregnation concentration was increased above 15%, the effect of FA concentration on the filling of the cell wall decreased.

### *3.2. Analysis of Leachate*

Table 2 shows the MC and V of poplar and Chinese fir after water saturation using the full-cell method. The MC of water-saturated poplar and Chinese fir decreased with the increase in impregnation concentration, which mainly due to the filling of pores by furfuryl alcohol, the covering of hydroxyl groups, and the hydrophobicity of the resin [37,38]. The V of poplar wood and Chinese fir decreased with the increase in impregnation concentration, which was attributed to the fixation effect of FA resin on the cell wall [39]. However, the greater the V of furfurylated wood, the greater the amount of FA resin that is lost, as more of the already cured FA resin is leached out due to dimensional changes. The V values of PW31 and PW40 were similar, which may be due to the close degree of deposition and densification of FA resin in the cell wall. The V of Chinese fir wood decreased with increasing modification concentration, indicating better dimensional stability, while there was no significant difference between the V values of FW42 and FW54.

**Table 2.** Full-cell water saturation of Chinese fir and poplar: MC and V before and after furfurylation.

| FA Concentration | | 0% | 5% | 10% | 15% | 20% |
|---|---|---|---|---|---|---|
| Chinese fir | MC | 294.10 a (0.24) | 225.07 b (0.13) | 150.86 b (0.20) | 105.53 d (0.13) | 85.20 e (0.13) |
| | V | 15.30 a (0.03) | 11.24 b (0.02) | 8.41 b (0.02) | 6.93 d (0.02) | 6.04 d (0.02) |
| poplar | MC | 196.81 a (0.24) | 167.65 b (0.11) | 141.53 b (0.10) | 115.68 d (0.10) | 100.16 e (0.09) |
| | V | 14.82 a (0.02) | 9.20 b (0.02) | 7.65 b (0.01) | 6.44 d (0.01) | 6.09 d (0.01) |

The standard deviation is given in parentheses; different letters after the two means represent significant differences at the significance level of $p \leq 0.05$.

The $MC_{WA}$ and $V_{WA}$ of the wood samples after 14 days of soaking tests are shown in Table 3. The MC of the control wood and FW11 after water saturation were lower than those prepared using the full-cell method, due to the low density of Chinese fir and the weak fixation effect of 10% FA on the cell wall. However, the $MC_{WA}$ of the other furfurylated samples increased after water soaking, as more water molecules penetrated the cell wall with the extension of soaking time. The loss of FA resin in the 14-day water soaking period increased the number of water molecules in the cell wall. There was no significant difference in the $V_{WA}$ of Chinese fir furfurylated with 10%, 15%, and 20% FA after 14 days of soaking tests, indicating that increasing the concentration did not significantly affect the reduction in $V_{WA}$ in the leaching tests (Table 3). The BC of furfurylated poplar was not significantly different at FA concentrations of 15% and 20%, which also suggests that increasing the concentration has less of an effect on the $V_{WA}$.

Table 4 shows the $M_L$ and $V_L$ of the furfurylated wood during the leaching tests. The lower the WPG of the poplar and Chinese fir, the greater the $M_L$, which is consistent with the color change in the leaching solution (Figure 1). Poplar and Chinese fir had the greatest $M_L$, with both exceeding 30% at 5% FA concentration, whereas the $M_L$ of both decreased as the concentration was increased to 20%. The WPG of Chinese fir wood was greater than that of poplar wood, but the $M_L$ was greater in poplar wood than in Chinese fir at all concentrations. This suggests that the FA resin in Chinese fir wood is more resistant to leaching and more stable than that in poplar wood. No significant difference in the $M_L$ of softwood and hardwood after FA modification was observed, which may be due to the selection of higher-concentration FA treatment [40]. Svensson et al. found that the release of organic compounds from wood in contact with water is related to its species and anatomical structure [41]. Numerous studies have demonstrated the existence of a chemical reaction between furfuryl alcohol and lignin [34,42], which leads to a tighter bonding and enhanced structural stability. Therefore, the differences in the leachability and $M_L$ of poplar and Chinese may be due to the higher pit aspiration and lignin content of Chinese fir wood cells, which makes FA resin more likely to retain and form macromolecules.

**Table 3.** MCWA and VWA of furfurylated wood after 14 days of soaking tests.

| FA Concentration | | 0% | 5% | 10% | 15% | 20% |
|---|---|---|---|---|---|---|
| Chinese fir | $MC_{WA}$ | 243.96 a (0.34) | 201.38 b (0.14) | 179.00 c (0.11) | 164.36 b (0.12) | 138.09 e (0.08) |
| | $V_{WA}$ | 15.55 a (0.03) | 11.15 b (0.02) | 7.76 c (0.03) | 6.90 cd (0.01) | 5.89 d (0.01) |
| poplar | $MC_{WA}$ | 203.12 a (0.21) | 177.15 b (0.16) | 154.59 c (0.13) | 125.95 d (0.10) | 113.77 e (0.12) |
| | $V_{WA}$ | 14.82 a (0.02) | 10.00 b (0.02) | 7.66 c (0.01) | 6.57 d (0.01) | 6.35 d (0.01) |

The standard deviation is given in parentheses; different letters after the two means represent significant differences at the significance level of $p \leq 0.05$.

**Table 4.** Leaching and shrinkage rates of furfurylated poplar and Chinese fir (%).

| FA Concentration | | 0% | 5% | 10% | 15% | 20% |
|---|---|---|---|---|---|---|
| Chinese fir | $M_L$ | 0.77 e (0.02) | 31.28 a (0.05) | 12.99 b (0.11) | 8.00 c (0.11) | 4.98 d (0.05) |
| | $V_L$ | 2.28 c (0.01) | 4.50 a (0.02) | 3.88 b (0.02) | 3.80 ab (0.01) | 3.52 b (0.01) |
| poplar | $M_L$ | 1.52 ab (0.01) | 37.67 a (0.05) | 16.88 b (0.02) | 12.71 c (0.02) | 8.04 d (0.01) |
| | $V_L$ | 2.95 ab (0.02) | 1.68 c (0.01) | 2.41 bc (0.01) | 2.02 a (0.02) | 2.40 b (0.01) |

The standard deviation is given in parentheses; different letters after the two means represent significant differences at the significance level of $p \leq 0.05$.


**Figure 1.** Color change in furfurylated wood leaching solutions from water-saturated poplar and Chinese fir wood.

### *3.3. Analysis of Leached Water from Furfurylated Wood*

FA solution is soluble in water, and the C=C of FA solution can be detected by UV spectroscopy [32,33]. Impregnated FA cures into an insoluble resin in the cell wall under acidic conditions. FA that is not fully cured during the modification process can be blistered out by water. Therefore, the collected water from leaching tests can be examined by UV spectrophotometry to characterize the leachability of furfurylated wood.

Figure 2 shows the UV spectra of the leachate of furfurylated wood after water saturation. It can be seen that the absorption peak near 270 nm is from furfuryl alcohol [32]. The higher the concentration of FA used for the furfurylated wood, the lower the FA content of the leachate in the water-saturated treatment. The concentration of FA significantly affected the amount of FA leached out, with $M_L$ of FA being most pronounced at 5% concentration. This finding was consistent with the $M_L$ of furfurylated poplar and Chinese fir with low concentrations of FA.

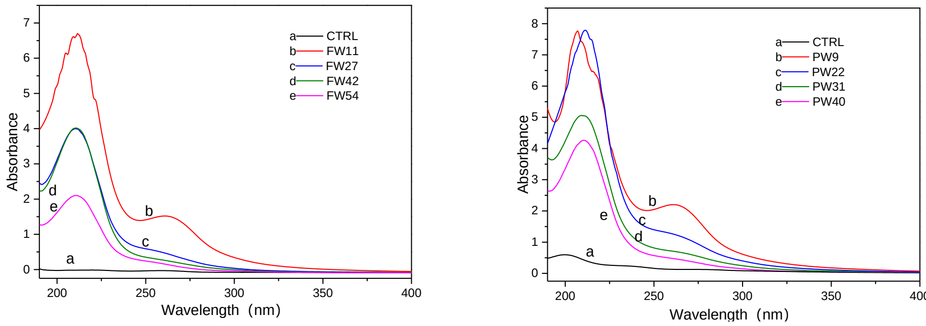


**Figure 2.** UV–vis spectra of saturated treatment leaching solution of poplar and Chinese fir.

The absorbances of FA in the leaching solutions at each water saturation stage of the leaching tests are shown in Table 5. The absorbances of FA in the leachate of FW11 and PW9 were significantly greater than at other concentrations in the water-saturated solution and after the first water change. The $M_L$ of furfurylated wood with 5% FA was higher, indicating weaker binding in the cell wall. As the number of water changes in the leaching tests increased, a higher impregnation concentration was found to result in a lower absorbance of FA in the leaching solution. Thus, impregnation at high FA concentrations did not show any significant leaching after soaking over long periods, indicating stronger bonding of FA impregnated in the cell wall.

**Table 5.** Furfuryl alcohol UV absorption peak (270 nm) at each stage of Chinese fir and poplar leaching tests.

| Sample | Chinese Fir | | | | | Poplar | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | CTRL | FW11 | FW27 | FW42 | FW54 | CTRL | PW9 | PW22 | PW31 | PW40 |
| Water saturation | 0.05 | 3.426 | 0.800 | 0.608 | 0.514 | 0.240 | 2.080 | 1.277 | 0.773 | 0.486 |
| 12 h | 0.305 | 4.554 | 1.434 | 1.060 | 0.801 | 0.261 | 5.652 | 2.519 | 1.706 | 1.218 |
| 24 h | 0.156 | 2.393 | 0.724 | 0.671 | 0.510 | 0.181 | 2.514 | 1.673 | 1.359 | 0.713 |
| 48 h | 0.199 | 2.381 | 1.295 | 1.039 | 0.870 | 0.061 | 1.807 | 0.503 | 0.923 | 0.679 |
| 72 h | 0.124 | 1.801 | 1.104 | 0.939 | 0.808 | 0.073 | 1.370 | 0.676 | 0.540 | 0.513 |
| 96 h | 0.121 | 1.485 | 0.889 | 0.667 | 0.693 | 0.056 | 1.452 | 1.016 | 1.005 | 0.771 |
| 120 h | 0.068 | 1.220 | 0.760 | 0.516 | 0.419 | 0.031 | 0.964 | 0.651 | 0.574 | 0.269 |
| 168 h | 0.085 | 1.322 | 1.016 | 0.707 | 0.521 | 0.063 | 1.248 | 1.029 | 0.909 | 0.636 |
| 216 h | 0.062 | 0.915 | 0.708 | 0.456 | 0.348 | 0.011 | 1.653 | 0.887 | 0.673 | 0.651 |
| 264 h | 0.050 | 0.807 | 0.642 | 0.468 | 0.315 | 0.028 | 0.906 | 0.748 | 0.989 | 0.736 |
| 312 h | 0.071 | 0.628 | 0.522 | 0.498 | 0.395 | 0.053 | 0.989 | 0.716 | 0.757 | 0.595 |

### *3.4. Morphology and Microstructure*

The distribution of FA resins in wood cell walls can be reflected by the intensity of their fluorescence under CLSM. Usually, a shorter polymerization length of FA in the cell wall results in weaker fluorescence in the cell wall than in the cell lumen [17]. Therefore, CLSM can be used to detect the leachability of furfurylated wood.

Figure 3 shows CLSM images of furfurylated poplar and Chinese fir wood before and after leaching tests. The fluorescence of PW9 and FW11 impregnated with 5% FA were mainly distributed in the cell corners, i.e., the compound middle lamella. By contrast, the intensity of the cell wall fluorescence was significantly enhanced in FW40 and FW54 modified with 20% FA, indicating an increased amount of FA resin in the cell wall. In addition, the fluorescence of poplar wood was stronger than that of Chinese fir at the same concentration.

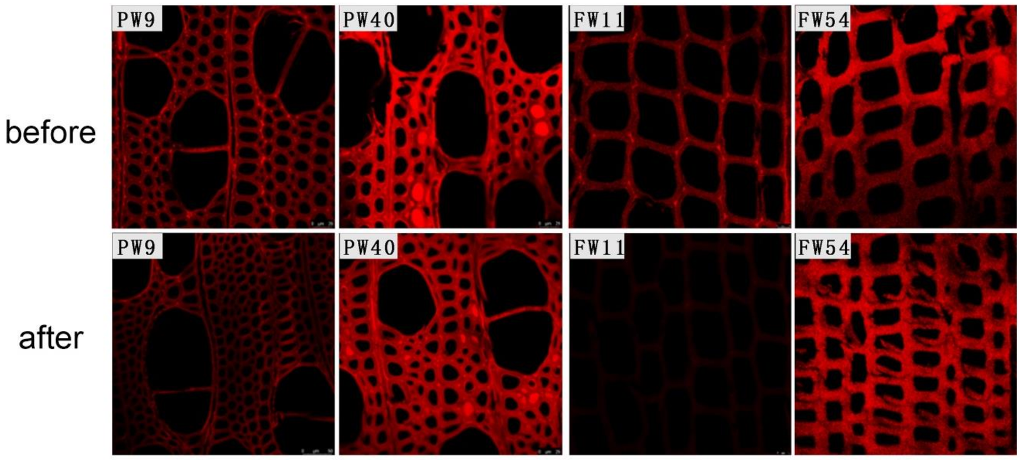


**Figure 3.** Changes in the microstructure of poplar and fir treated with low-concentration FA impregnation before and after leaching tests.

The overall brightness of the cell walls of poplar and Chinese fir wood impregnated with 5% FA darkened after leaching tests, but the change in the brightness of the cell walls of furfurylated wood with 20% concentration was not obvious. The modification of the cell walls with low concentrations of FA led to a higher leaching rate, which is consistent with the leaching rate, UV spectra, and color of leachate.

## 4. Conclusions

The WPG of furfurylated Chinese fir wood was greater than that of poplar at various concentrations. Increasing the impregnation concentration to 15% and 20% caused the effectiveness of FA concentration in regulating the cell wall bulking coefficient to decrease. The lower the FA concentration used for treatment, the higher the FA leaching rate. The leaching rate of poplar and Chinese fir after 5% FA impregnation was over 30%, indicating that 5% FA was not suitable for binding to the cell wall. The leaching rate of furfurylated Chinese fir was less than that of poplar, indicating that the cured FA resin in poplar was not as stable as that in Chinese fir. Thus, the differences in tree species should be considered for FA impregnation. Therefore, whether it is for indoor wood products or outdoor wood construction, the FA treatment concentration for furfurylated poplar and Chinese fir should not be less than 10%, and the minimum impregnation concentration of poplar wood should be higher than that of Chinese fir wood.

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

## References


1. Jiang, X.; Wang, J.; Wang, Z.; Hua, F.; He, S.; Lu, B.; Wang, X.; Zhang, X.; Leng, W. Microstructural and thermo-mechanical characterization of furfurylated douglas fir. *Polymers* **2022**, *14*, 4641. [CrossRef] [PubMed]
2. Liu, M.; Li, W.; Guo, F.; Wang, H.; Zhang, X.; Yu, Y. Dimensionally stable and highly durable bamboo material prepared through a simple surface furfurylation. *Constr. Build. Mater.* **2021**, *276*, 122156. [CrossRef]
3. Liu, M.; Lyu, S.; Peng, L.; Fan, Z.; Cai, L.; Huang, Z.; Lyu, J. Study on properties of radiata pine wood treated with furfuryl alcohol as fretboard materials for string instruments. *Eur. J. Wood Wood Prod.* **2022**, *80*, 1185–1200. [CrossRef]
4. Zheng, Z.; Chen, C.; Huang, Y.; Ou, R.; Hu, C.; Wang, X.; Zhou, Q.; Tu, D. Developing a unilaterally surface-densified wood composite with excellent performance through surface impregnation of furfuryl alcohol resin. *ACS Appl. Polym. Mater.* **2022**, *4*, 5308–5318. [CrossRef]
5. Shen, X.; Yang, S.; Li, G.; Liu, S.; Chu, F. The contribution mechanism of furfuryl alcohol treatment on the dimensional stability of plantation wood. *Ind. Crop Prod.* **2022**, *186*, 115143. [CrossRef]
6. Hadi, Y.S.; Mulyosari, D.; Herliyana, E.N.; Pari, G.; Arsyad, W.O.M.; Abdillah, I.B.; Gérardin, P. Furfurylation of wood from fast-growing tropical species to enhance their resistance to subterranean termite. *Eur. J. Wood Wood Prod.* **2021**, *79*, 1007–1015. [CrossRef]
7. Zhang, L.; Wang, W.; Chen, J.; Cao, J. Dimensional stability and decay resistance of clay treated, furfurylated, and clay-reinforced furfurylated poplar wood. *Chem. Phys. Technol. Wood* **2022**, *76*, 256–267. [CrossRef]
8. Hadi, Y.S.; Herliyana, E.N.; Mulyosari, D.; Abdillah, I.B.; Pari, R.; Hiziroglu, S. Termite resistance of furfuryl alcohol and imidacloprid treated fast-growing tropical wood species as function of field test. *Appl. Sci.* **2020**, *10*, 6101. [CrossRef]
9. Skrede, I.; Solbakken, M.H.; Hess, J.; Fossdal, C.G.; Hegnar, O.; Alfredsen, G.; Master, E.R. Wood modification by furfuryl alcohol resulted in a delayed decomposition response in rhodonia (postia) placenta. *Appl. Environ. Microbio.* **2019**, *85*, e00338-19. [CrossRef]
10. Xu, J.; Hu, D.; Zheng, Q.; Meng, Q.; Li, N. The distribution and polymerization mechanism of polyfurfuryl alcohol (pfa) with lignin in furfurylated wood. *Polymers* **2022**, *14*, 1071. [CrossRef]
11. Shen, X.; Guo, D.; Jiang, P.; Li, G.; Yang, S.; Chu, F. Reaction mechanisms of furfuryl alcohol polymer with wood cell wall components. *Holzforschung* **2021**, *75*, 1150–1158. [CrossRef]
12. Mantanis, G.I. Chemical modification of wood by acetylation or furfurylation: A review of the present scaled-up technologies. *Bioresources* **2017**, *12*, 4478–4489. [CrossRef]
13. Esteves, B.; Nunes, L.; Pereira, H. Properties of furfurylated wood (*Pinus pinaster*). *Eur. J. Wood Wood Prod.* **2011**, *69*, 521–525. [CrossRef]
14. Buchelt, B.; Dietrich, T.; Wagenführ, A. Testing of set recovery of unmodified and furfurylated densified wood by means of water storage and alternating climate tests. *Hfsg* **2014**, *68*, 23–28. [CrossRef]
15. Lande, S.; Westin, M.; Schneider, M. Properties of furfurylated wood. *Scand. J. For. Res.* **2011**, *19*, 22–30. [CrossRef]
16. Li, W.; Wang, H.; Ren, D.; Yu, Y.; Yu, Y. Wood modification with furfuryl alcohol catalysed by a new composite acidic catalyst. *Wood Sci. Technol.* **2015**, *49*, 845–856. [CrossRef]
17. Thygesen, L.G.; Barsberg, S.; Venås, T.M. The fluorescence characteristics of furfurylated wood studied by fluorescence spectroscopy and confocal laser scanning microscopy. *Wood Sci. Technol.* **2010**, *44*, 51–65. [CrossRef]
18. Liu, M.; Guo, F.; Wang, H.; Ren, W.; Cao, M.; Yu, Y. Highly stable wood material with low resin consumption via vapor phase furfurylation in cell walls. *Acs Sustain. Chem. Eng.* **2020**, *8*, 13924–13933. [CrossRef]
19. Lande, S.; Westin, M.; Schneider, M.H. Eco-efficient wood protection. *Manag. Environ. Qual. Int. J.* **2004**, *15*, 529–540. [CrossRef]
20. Vetter, L.; Pilgård, A.; Treu, A.; Westin, M.; Acker, J. Combined evaluation of durability and ecotoxicity: A case study on furfurylated wood. *Wood Mater. Sci. Eng.* **2009**, *4*, 30–36. [CrossRef]
21. Lande, S.; Eikenes, M.; Westin, M. Chemistry and ecotoxicology of furfurylated wood. *Scand. J. For. Res.* **2004**, *19*, 14–21. [CrossRef]
22. Lin, C.; Kim, I.; Mantanis, G.I.; Karlsson, O.; Jones, D.; Sandberg, D. Leach-resistant fire-retardant treated furfurylated wood by incorporating guanyl-urea phosphate. *Wood Mater. Sci. Eng.* **2021**, *16*, 429–431. [CrossRef]
23. Lin, C.; Karlsson, O.; Kim, I.; Myronycheva, O.; Mensah, R.A.; Försth, M.; Das, O.; Mantanis, G.I.; Jones, D.; Sandberg, D. Fire retardancy and leaching resistance of furfurylated pine wood (*Pinus sylvestris* L.) Treated with guanyl-urea phosphate. *Polymers* **2022**, *14*, 1829. [CrossRef] [PubMed]
24. Rahayu, I.S.; Wahyuningtyas, I.; Zaini, L.H.; Darmawan, W.; Maddu, A.; Prihatini, E. Physical properties of impregnated ganitri wood by furfuryl alcohol and nano-$SiO_2$. *Iop Conf. Ser. Earth Environ. Sci.* **2021**, *891*, 012012. [CrossRef]
25. Baysal, E.; Ozaki, S.K.; Yalinkilic, M.K. Dimensional stabilization of wood treated with furfuryl alcohol catalysed by borates. *Wood Sci. Technol.* **2004**, *38*, 405–415. [CrossRef]
26. Kong, L.; Guan, H.; Wang, X. In situ polymerization of furfuryl alcohol with ammonium dihydrogen phosphate in poplar wood for improved dimensional stability and flame retardancy. *ACS Sustain. Chem. Eng.* **2018**, *6*, 3349–3357. [CrossRef]
27. Pu, H.; Chen, T.; Li, Y. Influences of furfurylation modification on the wood properties of rubberwood. *J. For. Eng.* **2014**, *4*, 50–53.
28. *CEN 2020: SS-EN 84:2020*; Wood Preservatives—Accelerated Ageing of Treated Wood Prior to Biological Testing—Leaching Procedure. CEN: Brussels, Belgium, 2020.
29. Beck, G. Leachability and decay resistance of wood polyesterified with sorbitol and citric acid. *Forests* **2020**, *11*, 650. [CrossRef]

30. Miyauchi, T.; Mori, M.; Imamura, Y. Leaching characteristics of homologues of benzalkonium chloride from wood treated with ammoniacal copper quaternary wood preservative. *J. Wood Sci.* **2008**, *54*, 225–232. [CrossRef]
31. Ehmcke, G.; Koch, G.; Richter, K.; Pilgård, A. Topochemical and light microscopic investigations of non-enzymatic oxidative changes at the initial decay stage of furfuryl alcohol-modified radiata pine (*Pinus radiata*) degraded by the brown rot fungus Rhodonia placenta. *Int. Biodeterior. Biodegrad.* **2020**, *154*, 105020. [CrossRef]
32. Xie, W.; Chen, Q.; Wang, H.; Zhang, J. Rapid determination of furfural and furfuryl alcohol contents through UV spectra. *China Pulp Pap. Ind.* **2018**, *39*, 11–14.
33. Boneka, A.S.; Uyup, M.K.A.; Hua, L.S.; Siam, N.A.; Salim, S.; Ashaari, Z. Sorption isotherm and physico-mechanical properties of kedondong (*Canarium* spp.) Wood treated with phenolic resin. *Constr. Build. Mater.* **2021**, *288*, 123060. [CrossRef]
34. Mulyosari, D.; Hadi, Y.S.; Herliyana, E.N.; Pari, G.; Pari, R.; Abdillah, I.B. Physical properties of furfurylated mangium (*Acacia mangium* willd.) And pine (*Pinus merkusii* jungh et de vriese) woods. *Iop Conf. Ser. Mater. Sci. Eng.* **2020**, *935*, 12009. [CrossRef]
35. Emaminasab, M.; Tarmian, A.; Oladi, R.; Pourtahmasi, K.; Avramidis, S. Fluid permeability in poplar tension and normal wood in relation to ray and vessel properties. *Wood Sci. Technol.* **2017**, *51*, 261–272. [CrossRef]
36. Wang, X.; Zhou, Y.; Fu, Z.; Gao, X.; Zhou, F.; Fu, F. Effects of microwave treatment on microstructure of Chinese fir. *Forests* **2020**, *11*, 772. [CrossRef]
37. Beck, G.; Hill, C.; Cocher, P.M.; Alfredsen, G. Accessibility of hydroxyl groups in furfurylated wood at different weight percent gains and during rhodonia placenta decay. *Eur. J. Wood Wood Prod.* **2019**, *77*, 953–955. [CrossRef]
38. Thygesen, L.G.; Engelund, E.T.; Hoffmeyer, P. Water sorption in wood and modified wood at high values of relative humidity. Part i: Results for untreated, acetylated, and furfurylated norway spruce. *Holzforschung* **2010**, *64*, 315–323. [CrossRef]
39. Chen, T.; Luo, P.; Xu, Z.; Luo, X.; Hu, Z. Effects of furfuryl alcohol impregnation on physical and mechanical properties of densified poplar wood. *J. For. Eng* **2016**, *1*, 21–25.
40. Pilgård, A.; Treu, A.; Albert, N.; Zeeland, V.; Richard, J.; Westin, M. Toxic hazard and chemical analysis of leachates from furfurylated wood. *Environ. Toxicol. Chem.* **2010**, *29*, 1918–1924. [CrossRef]
41. Svensson, H.; Marques, M.; Kaczala, F.; Hogland, W. Leaching patterns from wood of different tree species and environmental implications related to wood storage areas. *Water Environ. J.* **2014**, *28*, 227–284. [CrossRef]
42. Martha, R.; Mubarok, M.; Batubara, I.; Rahayu, I.S.; Setiono, L.; Darmawan, W.; Akong, F.O.; George, B.; Gérardin, C.; Gérardin, P. Effect of furfurylation treatment on technological properties of short rotation teak wood. *J. Mater. Res. Technol.* **2021**, *12*, 1689–1699. [CrossRef]