Melamine Formaldehyde Modified Furfurylation to Improve Chinese Fir's Dimensional Stability and Mechanical Properties

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Melamine formaldehyde modified furfurylation (MFMF) was developed in this investigation to overcome the issues encountered by traditional wood furfurylation, the strong acidic reaction condition and the high cost of furfuryl alcohol. In this study, the optimum ratio of melamine, formaldehyde, and furfuryl alcohol constituents and the optimum curing conditions were explored. Then, MFMF was applied to Chinese fir modification and its performance was evaluated by the weight gain rate (WGR), equilibrium moisture content (EMC), dimensional stability (anti-swelling efficiency [ASE]), and parallel-to-grain compressive strength. The results showed that MFMF took place at a pH close to neutral (6.8) and the formulas had good penetration of cell walls. The best stability and improvement to mechanical properties achieved by MFMF were: a WGR of 158.9%; a low EMC of 11.5% under 96% relative humidity conditions; an ASE in high humidity and water-soaked conditions of 58.5% and 64.2%, respectively; and an increase in parallel-to-grain compressive strength by 81.9%, when compared with the control.

Keywords: Furfuryl alcohol; Furfurylation; Chinese fir; Dimensional stability; Mechanical properties

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INTRODUCTION

The Chinese fir species (*Cunninghamia lanceolate*) has the largest planted area of any tree in southern China due to its rapid growth, straight texture, low presence of pests and diseases, ease of processing, and uniform plate structure (Chen and Wu 2000; Peng *et al.* 2006). Its mechanical properties and dimensional stability, however, are not good due to its poor resistance to moisture and wear, leading to limited practical applications in the wood industry (Peng *et al.* 2006). Thus, China's timber industry seeks a better and more efficient utilization of Chinese fir, as well as to increase its added value (Chen *et al.* 2014).

Furfurylation is a promising green and low-cost technology that improves the dimensional stability and mechanical properties of low-valued wood (Li *et al.* 2014). Furfural, a renewable chemical produced from bioresources, is obtained by the dehydration of pentosan from crop residues, such as bagasse, sunflower stalks, corn, rice bran, and cotton husk (Wang 2006). Furfuryl alcohol is a derivative of furfural through hydrotreatment (Wang 2006; Venås and Rinnan 2008). Furfuryl alcohol resin, a brown red viscous liquid formed by the polymerization of furfuryl alcohol under the action of acidic catalyst, is a kind of thermosetting polymer (Lande *et al.* 2004a). The reaction is an exothermic reaction itself, but the process is quite slow. The solidified furfuryl alcohol

resin has a good tolerance for acid, alkali, high temperature, water, fungi, and corrosion (Yuan *et al.* 2007). Previous studies reported that wood modification with furfuryl alcohol resin can effectively improve the quality and the durability of the wood, and the furfurylation does not harm the environment (Lande *et al.* 2004a; Lande *et al.* 2004b; Epmeier *et al.* 2007a; Epmeier *et al.* 2007b; Venås and Rinnan 2008; Pilgård *et al.* 2010; Esteves *et al.* 2011; He *et al.* 2012; Li *et al.* 2014, 2015).

Wood furfurylation is a complicated process. Currently, a three-stage production process is widely employed: pressure impregnation under vacuum conditions, resin curing, and product drying (He *et al.* 2012; Li *et al.* 2014; Li *et al.* 2015). The curing time ranges from a few hours to 20 hours, depending on the wood block size. However, the low pH of furfurylation is an issue that needs to be resolved because a lower pH ultimately affects the wood's properties due to degradation.

Melamine formaldehyde resin (MF) has been widely used in wood modification because it can react easily in acidic, alkaline, or neutral media. The present MF production process can be roughly classified into one-step and two-step methods. In the one-step process, the hydroxymethylation and etherification reactions are performed in an acidic medium, and completed in one pot. It has the advantages of a short production cycle, simple operation, easy control, and convenient production, but a shortcoming is that the product quality sometimes cannot meet the requirements. Therefore, most manufacturers presently use the two-step process that allows hydroxymethylation and etherification to occur separately. This process can be divided into two stages. In the first stage, formaldehyde reacts with melamine in an alkaline or neutral medium to produce a mixture of polymethylolated melamines (among those produced, ternary hydroxymethyl melamine is more stable than other species). Then, condensation of polymethylolated melamine is performed in an acidic medium and large branched or linear molecules are formed and linked by ether or methyl bonds. The storage time of the MF solution is short because it becomes a gel within several days; to improve its storage time, spray drying is usually employed to turn it into powder and to prevent contact with air. The MF powder is diluted into solution on site and then used for wood modification (Chen 2012).

In this investigation, melamine formaldehyde was explored to modify the furfuryl alcohol resin. The hydroxymethylation of melamine was first performed under alkaline conditions, then the hydroxymethylated solution combined with furfuryal alcohol was used to treat Chinese fir in impregnation. Finally, the copolymerization between hydroxymethylated melamine and furfuryl alcohol, and between themselves, took place during resin curing. The results showed that the MF modified furfurylation (MFMF) had good penetration of Chinese fir wood, and the copolymerization occurred at a pH close to neutral, rather than at the acidic condition of traditional furfurylation. This neutral furfurylation is believed to benefit the wood properties in the long run.

EXPERIMENTAL

Materials

Furfuryl alcohol (light yellow liquid, ≥ 98%) was purchased from Aladdin Co., Ltd. (Shanghai, China). Toluidine blue for wood staining was supplied by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Sulfomethylated lignin, reacting formaldehyde with the lignin reclaimed from the spent of softwood kraft pulping, was supplied by Jiefa Tech Co., Ltd. (Zhejiang, China). The common chemicals were all analytical grade and ordered

from Nanjing Chemical Reagent Co., Ltd. (Nanjing, China). All solutions were prepared with deionized water.

The fir wood used in this experiment was cut from Shunchang County, Fujian Province, China. The test materials used in the experiment were all from mature wood above chest height. The test specimens were prepared according to the Chinese National Standard GB/T1929 (2009): six samples sized 20 mm × 20 mm × 30 mm (T × R × L) for the parallel-to-grain compression strength test, and 12 samples sized 20 mm × 20 mm × 20 mm for the dimensional stability test. The specimens used had no knots, cracks, decay, oblique textures, or other defects.

Formula Optimization for Melamine Formaldehyde Modified Furfurylation

The constituents melamine, formaldehyde, furfuryl alcohol, and water were weighted and placed into a flask. The first step in the MFMF reaction was pre-reacting the melamine and formaldehyde into hydroxymethylated melamine. The reaction conditions were adopted from the literature addressed elsewhere (Chen 2012). The pre-reaction started when the pH of the medium was adjusted, with a 10% NaOH solution, to between 9.4 and 9.6, and the temperature was elevated to 98 °C and held for 10 min to 15 min. Then, the contents were discharged into a large beaker and cooled to ambient temperature. The stability of the formulas was observed, and, based on these observations, the ratio of constituents was optimized.

The second step in the MFMF reaction was the screening of the optimal formulas based on the curing time of resin. For those formulas that were kept stable and uniform after two weeks of storage at room temperature, their pH values were adjusted to approximately 6.8 by adding the catalyst citric acid, and then the specimens were placed in an oven at 100 °C to observe and record the resin curing time.

Chinese Fir Furfurylation

Three MFMF formulas selected based on the formula optimization were used for Chinese fir modification. Prior to the wood impregnation, the pre-reaction of melamine and formaldehyde was performed between the pH 9.4 and 9.6, and at the temperature of 98 °C for 10 min to 15 min, as addressed previously. After the formulations had been cooled, the pH of each of them was adjusted to approximately 6.8 by a catalyst called sulfomethylated lignin acid. The specimens were subjected to three steps for furfurylation: impregnation, curing, and drying. In impregnation, the specimens were first placed in an autoclave and a negative pressure was applied for 30 min to purge the air and non-volatile gases from the wood. Then, furfuryl alcohol formulations were inhaled into the system and the pressure of the autoclave was raised to 0.8 MPa by N_2 for 5 h, followed by impregnation for 18 h after the pressure was relieved. Finally, the specimens were removed from the device, using a gauze to absorb the liquid on the surface of wood blocks. For curing, the wood blocks were wrapped in aluminum foil and cured in an oven at 103 °C to avoid any evaporation of the furfuryl alcohol. After 7 h of curing, the aluminum foil was removed; the specimens were dried at 60 °C and 80 °C for 40 min each, and finally dried at 103 °C until bone-dry.

Dimensional Stability and Mechanical Properties Test

Weight gain rate

The oven-dry weight of the Chinese fir specimens before and after furfurylation was recorded as m_0 and m_1, respectively. The weight gain rate was assessed by Eq. 1,

$$\text{WGR}\ (\%) = \frac{(m_1 - m_0)}{m_0} \times 100 \quad (1)$$

Equilibrium moisture content

Some oven-dried Chinese fir wood blocks were placed in a sealed desiccator with water. The relative humidity of the desiccator was measured as 96%. After a month of storage at this humidity, the blocks reached equilibrium and the equilibrium moisture content (EMC) of the wood blocks were calculated by Eq. 2, where m_2 and m_3 represent the weight before and after humidity storage.

$$\text{EMC}\ (\%) = \frac{(m_3 - m_2)}{m_2} \times 100 \quad (2)$$

Dimensional stability

In this investigation, the dimensional stability of Chinese fir was measured under high humidity and in water-soaked conditions, respectively. The dimensional stability of Chinese fir was characterized by anti-swelling efficiency (ASE). The modified and control specimens were oven-dried at 103 °C until bone-dry, then cooled to room temperature in a desiccator. The radial, tangential, and longitudinal sizes were recorded. Next, the specimens were placed in a sealed desiccator with water for one month, and, finally, soaked in water for a week. The radial, tangential, and longitudinal sizes of specimens were recorded and the coefficient of wet expansion (α) and ASE were calculated by Eqs. 3 and 4, respectively,

$$\alpha\ (\%) = \frac{(V_{\text{wet}} - V_{\text{dry}})}{V_{\text{dry}}} \times 100 \quad (3)$$

$$\text{ASE}\ (\%) = \frac{(\alpha_0 - \alpha_1)}{\alpha_0} \times 100 \quad (4)$$

where V_{wet} and V_{dry} are the volume of the specimens in the wet and dry state, respectively, and α_0 and α_1 represent the coefficient of wet expansion of the control and the modified specimen, respectively.

Parallel-to-grain compressive strength of wood

The parallel-to-grain compressive strength of wood was tested according to the Chinese National Standard GB/T1935 (2009). Specimens with dimensions of 20 mm × 20 mm × 30 mm (T × R × L) were loaded with a constant loading rate, and the maximum compressive load of the specimen, ensured for more than 90 s, was recorded as the parallel-to-grain compressive strength.

Methods

Fluorescent microscopy and scanning electron microscopy (SEM) examination

For fluorescent microscopy imaging, a small piece of wood from a specimen with the dimensions of 20 mm × 20 mm × 30 mm (T × R × L) was trimmed and cross-sectioned with a PowerTome XL ultramicrotome (RMC Boeckeler, Tucson, AZ, USA). Cross-sections of the slices with thicknesses of approximately 10 μm were collected and then stained with 0.5% toluidine blue. The slices were rinsed and then mounted on glass slides using glycerol to seal. Fluorescent microscopy was observed using a BX43 fluorescent microscope (Olympus Corp., Shanghai, China).

A small part of Chinese fir wood was sliced and its surface was smoothed. The specimens were freeze-dried for three days, then sputter-coated with an ultra-thin layer of Au prior to imaging (10 s by a 108 Cressington sputter coater, Watford, England). The scanning electron microscope (SEM) observation was made on a TM3000 Tabletop Scanning Electron Microscope (Hitachi Corp., Beijing, China).

RESULTS AND DISCUSSION

MFMF Formulas' Optimization

In the optimization of the MFMF formulas, different formulas with different molar ratios of melamine, formaldehyde, and furfuryal alcohol were prepared. The concentration of the formulations was 50%. The viscosity and pH of pre-reacted solutions, and the assessed curing time, are given in Table 1.

The criteria for the optimization of the MFMF formulations were: (1) Formaldehyde content cannot be too high, because free formaldehyde is a major indoor pollutant; a lower formaldehyde can be fixed in the resin and without release into the atmosphere. (2) The viscosity of pre-reacted solutions cannot be too high because a high viscosity is not helpful for the formulation's penetration into wood when in impregnation. (3) The curing time must be in the range of 4 h to 8 h for easy and fast manufacturing. (4) The mass fraction of furfuryl alcohol cannot be too low, as low mass fractions do not achieve the desired effect of the furfuryl alcohol on wood modification.

Based on the above criteria, the molar ratio of melamine:formaldehyde:furfuryl alcohol was optimized to 1:2:2 and this ratio will be used for all formulas in the following experiments.

Table 1. Curing Time of Ternary Copolymerization of Melamine, Formaldehyde, and Furfuryl Alcohol with Different Ratios

Molar ratio			Viscosity (cP)	Medium pH	Curing time (h)
Melamine	Formaldehyde	Furfuryl alcohol			
1	1.8	0.5	22.5	9.5	10.0
1	0	1.8	—	—	—
1	1.0	1.0	—	—	—
1	1.0	2.0	—	—	—
1	2.0	1.0	14.5	9.6	1.0
1	2.0	0	11.0	9.4	0.3
1	2.0	2.0	13.0	9.5	5.2
1	2.5	1.0	13.5	9.4	0.8
1	3.0	1.0	12.5	9.4	0.7
1	3.0	2.0	11.5	9.7	7.0
1	4.0	1.0	12.0	9.4	3.7
1	4.0	2.0	15.0	9.4	5.3
1	4.0	3.0	26.5	9.4	5.5

Dimensional Stability and Mechanical Properties for Chinese Fir after Furfurylation

Prior to Chinese fir furfurylation, the selected formulation, the major constituents of which were melamine:formaldehyde:furfuryl alcohol with a molar ratio of 1:2:2, was applied to the Chinese fir impregnation and curing process. Firstly, the catalyst

sulfomethylated lignin acid was used to adjust the formula's pH to 6.8 (the usage was approximately 1.2%), but with varying curing times, 1 h and 2 h for wood furfurylation (WF-I and WF-II, respectively).

The physical properties of the oven-dry density *i.e.*, the weight gain rate (WGR) and EMC in 96% relative humidity, are shown in Table 2.

Table 2. Physical Properties of Chinese Fir after MFMF Furfurylation

Physical properties	Control	WF-I	WF-II
Adsorption rate	——	3.13	3.11
Density before furfurylation (g/cm^3)	0.34	0.37	0.35
Density after furfurylation (g/cm^3)	——	0.82	0.81
WGR (%)	——	153.86	158.93
EMC (%)	23.32	13.98	11.46

The oven-dried density of Chinese fir increased after furfurylation modification, which was related to resin infiltration (weight gain) into the wood. The higher the weight gain rate, the greater the dry density after modification. The wood specimens subjected to the WF-II process had the highest weight gain rate, 158.9%. However, the dry density, 0.81 g/cm^3 after modification, was not the highest; its increase to 0.46 g/cm^3 from 0.35 g/cm^3 was the greatest. The equilibrium moisture content in the 96% humidity environment of specimens subjected to the WF-II process was 11.5%, only approximately half of the control and also lower than WF-I. The longer curing time of WF-II, as compared to WF-I allowed the MFF resin to fill the wood cell's cell cavity, cell wall, pits, and other water infiltration paths, and to block more active groups that absorb moisture.

Compressive strength is an important index for wood's mechanical properties. The compressive strength of the modified Chinese fir is shown in Fig. 1. The parallel-to-grain compressive strength of the control and the wood modified by the MFMF of processes WF-I and WF-II were 53.7 MPa, 86.9 MPa, and 97.6 MPa, respectively. The parallel-to-grain compressive strength increments after Chinese fir wood furfurylation were increased by 61.8% and 81.9%, compared to the control. This trend was consistent with that of WGR, density change, and EMC.

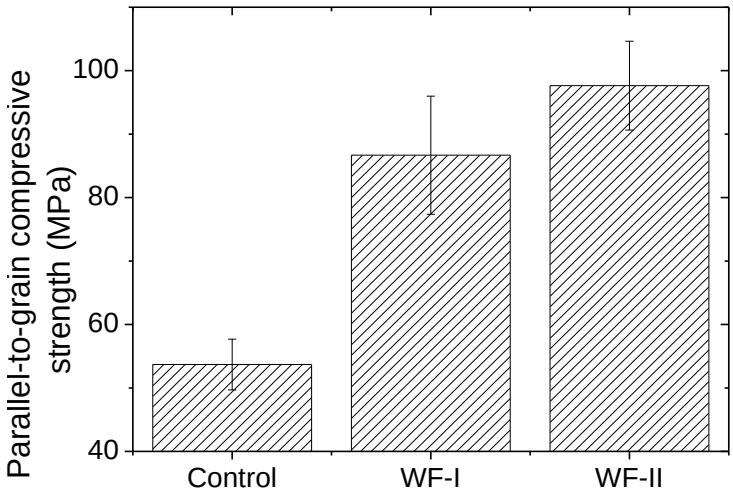

Fig. 1. Parallel-to-grain compressive strength of the control and wood modified by MFMF

The dimensional stability of Chinese fir under high humidity conditions and in aqueous conditions are shown in Table 3. The table shows that, after furfurylation, Chinese fir's swelling coefficient decreased, while the wet expansion coefficient increased. The greater the rate of weight gain, the higher the anti-wet expansion coefficient. The reason was previously addressed in detail in the relationship between WGR and EMC. Moreover, the anti-swelling performance in the grain direction of Chinese fir was notably better than in the radial and tangential directions. This performance was attributed to the anisotropic difference nature of wood.

Table 3. Swelling Coefficients and Anti-swelling Efficiency of Chinese Fir in High Humidity Conditions and Soaked in Water

Conditions	Specimen	SC, %			ASE, %			
		T	R	L	T	R	L	Volume
96% Humidity	Control	8.21	4.26	1.07	——	——	——	——
	WF-I	4.59	1.79	0.43	44.07	57.97	59.66	50.65
	WF-II	3.79	1.67	0.28	53.81	60.79	73.73	58.5
Soaked in water	Control	9.12	4.03	1.1	——	——	——	——
	WF-I	3.17	1.50	0.55	65.27	62.84	50.41	64.20
	WF-II	3.42	1.37	0.43	62.50	65.96	60.78	64.22

Imaging Observation by Microscopies

Two microscopies, SEM and fluorescent microscopy, were employed for observing the morphology change of Chinese fir and the resin distribution in wood after furfurylation, as presented in Figs. 2 and 3, respectively.

The cell wall distortion can be seen in Fig. 2a, but the phenomenon did not occur in other graphs. This distortion provided evidence that cell walls were strengthened by MFMF resin. In Fig. 2b, half of the cavities were empty and half of them were filled with resin; in Fig. 2c, more cavities were filled with resin. This difference was because the curing time of WF-II was longer than that of WF-I, which caused more complete curing in the former, and consequently less volatile FA was released when drying.

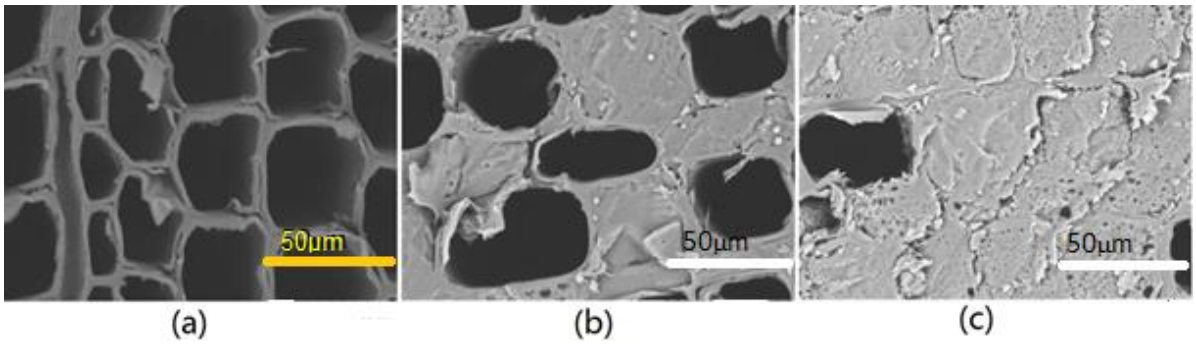

Fig. 2. SEM images of Chinese fir: (a) the control; and after MFF furfurylation by the process of (b) WF-I, and (c) WF-II

Fluorescent microscopy images of Chinese fir after MFMF furfurylation by process of WF-I, WF-II, and the control are presented in Fig. 3. The images show that the

fluorescence density in each graph was consistent with what was observed in the SEM images. In each graph, some tiny fluorescence spots, and even some cell walls, were obviously seen, indicating that the resin penetrated the cell walls, albeit the density was much weaker than that in the cavities.

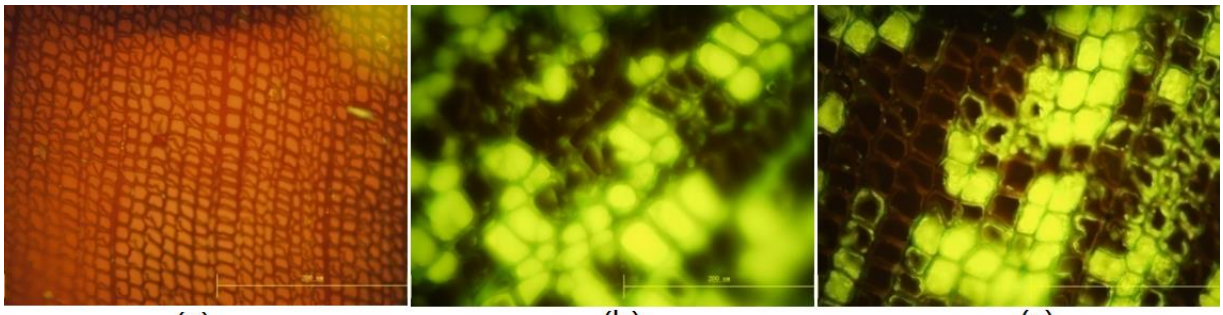

Fig. 3. Fluorescent microscopy observation of Chinese fir: (a) the control; and after MFMF furfurylation by the process of (b) WF-I, and (c) WF-II

Based on the discussion above, it was found that the MFMF formulas easily penetrated cell walls and the excess solution remained in the cavities. Therefore, further analysis of the study to reduce the impregnation time or reduce the concentration of MFMF to optimize the furfurylation process is needed.

CONCLUSIONS

1. The optimum formula for copolymerization of melamine, formaldehyde, and furfuryl alcohol was the molar ratio of 1:2:2, subjected to a pre-reaction at pH 9.4 to 9.6 at a temperature of 98 °C for 10 min to 15 min.
2. The condensation of melamine, formaldehyde, and furfuryl alcohol melamine occurred at near-neutral pH (approximately 6.8) during resin curing. Therefore, the wood after MFMF furfurylation had advantages in wood conservation over traditional furfurylation methods, whose condensation usually takes place in strongly acidic conditions.
3. The dimensional stability and mechanical properties of Chinese fir after MFMF furfurylation were improved substantially. The best performance after furfurylation in this investigation occurred when the equilibrium moisture content decreased to 11.5%; the ASE decreased to 58.5% and 64.2% for conditions of high humidity and soaked in water, respectively; and the compressive strength increased by 81.9%.
4. Melamine formaldehyde modified furfurylation formulations had good penetration into Chinese fir wood; the resin was retained in the cell walls, and it filled the empty cavities.

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REFERENCES CITED

Chen, C. (2012). *Study on the Synthesis and Applications of Melamine Formaldehyde Resin*, Master's Thesis, Zhengzhou University, Zhengzhou, China.

Chen, J., Moa, Y., Zheng, C., Fan, R., Zhou, S., and Chen, Y. (2014). "Effect of thinning on growth and timber outturn in *Cunninghamia lanceolata* plantation," *Forest Research* 27(1), 99-107. DOI: 10.1021/tx400350b

Chen, R., and Wu, C. (2000). "Study on physical and mechanical properties of middle cutting wood of *Cunninghamia lanceolata* in Fujian province," *Journal of Northeast Forestry University* 28(4), 41-43.

Epmeier, H., Johansson, M., Kliger, R., and Westin, M. (2007a). "Bending creep performance of modified timber," *Holz als Roh-und Werkstoff* 65(5), 343-351. DOI: 10.1007/s00107-007-0189-1

Epmeier, H., Johansson, M., Kliger, R., and Westin, M. (2007b). "Material properties and their interrelation in chemically modified clear wood of Scots pine," *Holzforschung* 61(1), 34-42. DOI: 10.1515/HF.2007.007

Esteves, B., Nunes, L., and Pereira, H. (2011). "Properties of furfurylated wood (*Pinus pinaster*)," *European Journal of Wood and Wood Products* 69(4), 521-525. DOI: 10.1007/s00107-010-0480-4

GB/T1935 (2009). "Wood physical mechanics test and sample cutting method," Standardization of Administration of China, Bejing, China.

He, L., Yu, Y., Yu, Y. -S., Tian, G. -L., and Wang, H. -K. (2012). "Stability and mechanical performance of furfurylated Chinese fir," *China Wood Industry* 3, 22-24, 28.

Lande, S., Eikenes, M., and Westin, M. (2004a). "Chemistry and ecotoxicology of furfurylated wood," *Scandinavian Journal of Forest Research* 19(sup5), 14-21. DOI: 10.1080/02827580410017816.

Lande, S., Westin, M., and Schneider, M. (2004b). "Properties of furfurylated wood," *Scandinavian Journal of Forest Research* 19(sup5), 22-30. DOI: 10.1080/0282758041001915

Li, W. -J., Wang, H., An, X. -J., Wang, H. -K., and Yu, Y. (2014). "Effects of furfurylation on the physical, mechanical, and mold proof performance of bamboo," *Journal of Beijing Forestry University* 36(2), 133-138. DOI: 10.13332/j.cnki.jbfu.2014.02.003

Li, W., Wang, H., Ren, D., Yu, Y., and Yu, Y. (2015). "Wood modification with furfuryl alcohol catalysed by a new composite acidic catalyst," *Wood Science and Technology* 49(4), 845-856. DOI: 10.1007/s00226-015-0721-0.

Peng, W. X., Wu, Y. Q., Zhang, Z. F., Zhang, D. Q., and Li, N. C. (2006). "Situation and developing trends of Chinese fir," *World Forestry Research* 19(5), 54-58.

Pilgård, A., de Vetter, L., Van Acker, J., and Westin, M. (2010). "Toxic hazard of leachates from furfurylated wood: Comparison between two different aquatic organisms," *Environmental Toxicology and Chemistry* 29(5), 1067-1071. DOI: 10.1002/etc.132

Venås, T. M., and Rinnan, Å. (2008). "Determination of weight percent gain in solid wood modified with *in situ* cured furfuryl alcohol by near-infrared reflectance spectroscopy," *Chemometrics and Intelligent Laboratory Systems* 92(2), 125-130. DOI: 10.1016/j.chemolab.2008.02.002.

Wang, Z. (2006). "Applied to the technology of loading prevention decay wood in wood industry," *Forestry Science & Technology* 1, 41-43.

Yuan, Y. -M., Sun, J. -L., Chen, X. -B., Zhang, H. -B., and Zhu, H. -Y. (2007). "Quick inspection of formaldehyde in furfuralohol resin of an aeronautic casting sand mould agglutinant," *Foundry Technology* 2, 290-291.

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