The Furfurylation of Wood: A Nanomechanical Study of Modified Wood Cells

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Furfurylation of wood is of interest worldwide as an environmentally friendly modification process. It is widely assumed that low-molecular weight furfuryl alcohol (FA) can penetrate into wood cells and polymerize *in-situ* during the process, resulting in substantial improvement in the physical-mechanical properties and durability of wood. In this study, confocal laser scanning microscopy (CLSM) was used to visualize the microscopic distribution of polymerized FA resin in the Masson pine wood cavities, and a Nanoindenter was used to probe the mechanical properties of modified wood cells. The effects of catalysts (maleic anhydride and a mixed organic acid catalyst), FA concentration, curing time, and curing temperature on the nanomechanical properties of wood cell walls were investigated. An improvement in the indentation modulus and hardness of modified wood cells demonstrated indirectly but strongly that FA indeed penetrated wood cells during the modification process. Based on the results of the cell wall nanoindentation test, a combination of 50% furfuryl alcohol, 8 h curing time, and 95 °C curing temperature were proposed as the starting processing parameters for the development of a more practical and effective wood furfurylation process using a mixed organic acid catalyst.

Keywords: Furfurylation; Nanomechanical properties; Confocal laser scanning microscopy; Nanoindentation

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INTRODUCTION

Wood furfurylation is an environmentally friendly wood modification process that is attracting worldwide interest (Ermeydan *et al*. 2014). Many investigations have demonstrated that furfurylation is capable of significantly improving most of the physical-mechanical properties of treated wood (Baysal *et al*. 2004; Hadi *et al*. 2005; Esteves *et al*. 2011; Pfriem *et al*. 2012). Previous researchers also tried to understand the mechanism of wood furfurylation. Thygesen *et al*. (2010) studied the distribution of furfuryl alcohol (FA) polymer in wood using fluorescence spectroscopy and found a greater distribution of furfuryl alcohol resins in the lignin-rich parts of the compound cell wall, compared to the secondary cell wall. Lande *et al*. (2004) proposed that there might be a grafting reaction between lignin and furfuryl alcohol. Nordstierna *et al*. (2008) studied reactions between FA units and lignin model substances using nuclear magnetic resonance and found that chemical bonds can form between them.

The polymerization of furfuryl alcohol in wood is a complex chemical reaction, resulting in FA resins predominantly in wood cavities and cell walls (Herold *et al*. 2013).

Some conjugated chains form during the polymerization process of FA (Choura *et al*. 1996). Confocal laser scanning microscopy (CLSM) can measure the fluorescence emitted from these conjugated chains to detect the distribution of FA resins (Xue and Luo 2004). Additionally, Herold *et al.* (2013) found that a lower amount of maleic anhydride catalyst resulted in a lower degree of polymerization, in turn, leading to a lower weight percent gain (WPG) of furfurylated wood. It is clear that the distribution and degree of polymerization of FA in wood are key factors in determining the performance of modified wood. Lande *et al.* (2004) also suggested that the degree of modification in wood properties depends on the weight percentage gain and polymer content inside wood cell walls.

Furfuryl alcohol polymerization in microscopic cell cavities is easily detected using optical microscopy, whereas polymerization in wood cell walls is more difficult to ascertain. Nanoindentation is a popular technique, originally designed for testing the mechanical properties of thin films. It has been successfully used to characterize the mechanical properties of various plant cell walls (Wimmer *et al.* 1997; Wu *et al*. 2010; Yu *et al*. 2011; Rayón *et al*. 2013). Gindl *et al.* (2004) used nanoindentation to study the mechanical properties of wood that was penetrated with adhesives at the cell wall level and suggested that phenol-resorcinol-formaldehyde and melamine-urea-formaldehyde significantly increased cell wall hardness after penetration (Konnerth and Gindl 2006). Therefore, this method can serve as an indirect way to detect the existence of FA resin in wood cells. Furthermore, it is reasonable to assume that the micromechanical properties of modified cell walls are positively correlated with the extent of FA polymerization.

In this study, we used CLSM to visualize the microscopic distribution of polymerized FA resin in the wood cavities of Masson pine. Furthermore, nanoindentation was used to track changes in the nanomechanical properties of modified wood cells, from which the existence of FA polymerization in wood cells can be evaluated indirectly. Because the polymerization and grafting reactions of FA are closely correlated to the type of catalysts used, FA concentration, curing temperature, and curing time, the effects of these parameters on the hardness and indentation modulus of wood cell walls were investigated. Based on the results, a set of modification parameters were proposed for the future development of a more practical and effective wood furfurylation process using new catalysts or for new tree species.

EXPERIMENTAL

Furfurylation of Masson Pine Wood

Thirty-year-old Masson pine (*Pinus massoniana* Lamb.) wood was modified using a furfuryl alcohol solution initiated with two kinds of catalysts. The wood came from a fast-growing plantation located in the Fujian Province of China. Wood blocks with dimensions of 20 mm × 20 mm × 10 mm (Tangential × Radial × Longitudinal), were conditioned at 23 °C and 65% relative humidity for at least 30 days before furfurylation. The final moisture content of the wood blocks was 8~11%. Single-factor experiments were employed, as shown in Table 1. Two types of FA formulas with two different catalysts (*i.e*., F1 and F2) were prepared, which contained the same weight percentages of FA, sodium borate, catalyst, and water. The F1 formulation used a mixed organic acid catalyst solution composed of 2 parts citric acid and 1 part oxalic acid. This proportion was used to obtain an FA solution that allows a long pot life and enough

catalytic activity for polymerization. As a comparison, the F2 formulation used the widely known catalyst maleic anhydride. Chemicals were added in order and fully mixed with a magnetic stirring device. A custom-built reactor (PF-2) was used to impregnate FA into the wood using a full cell process, which was characterized by a segment of vacuum for 30 min followed by 3 h of 0.8 MPa pressure. The impregnated samples were then wrapped in aluminum foils to avoid the evaporation of solution during the curing stage. Polymerization of FA took place at this stage. The treated samples were further dried for 2 h at 60 and 80 °C, respectively, and later at 103 °C, until an oven-dried state was achieved.

Table 1. A Single-factor Variable Approach for Masson Pine Wood Furfurylation using Different Catalysts

Variable	FA concentration	Curing temperature	Curing time
Factors	%	℃	h
1	30	95	3
2	50	103	5
3	70	115	8
4		125	11
Constant factors	Curing time 5 h Curing temperature:103 ℃	FA Concentration: 50% Curing time: 5 h	FA Concentration: 50% Curing temperature:103 ℃

Sample Preparation for Nanoindentation

Furfurylated and untreated wood blocks were cut into small blocks with dimensions of 6 mm × 4 mm × 8 mm (Tangential × Radial × Longitudinal). To prevent epoxy resin from penetrating into wood cells, an un-embedding sample preparation procedure was adopted. Figure 1 shows the detailed procedure of sample preparation for nanoindentation.

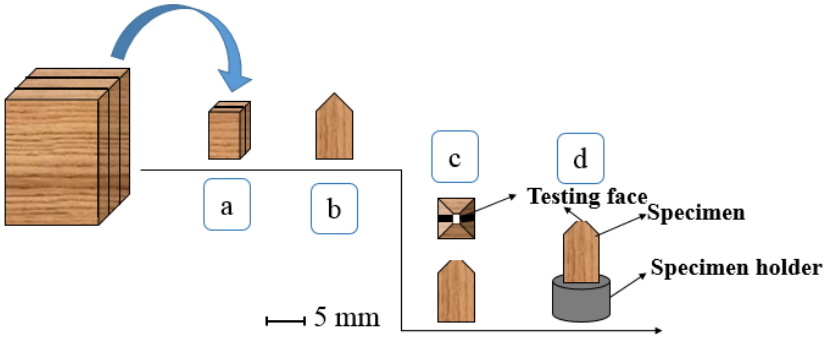

Fig. 1. Specimen preparation procedure for the wood block.

Basically, a cut was applied to ensure the parallel alignment of the bottom and top surfaces of the specimens. A pyramid was then formed with a sliding microtome (Leica SM2000, Germany). Then, an ultramicrotome (Leica UC7, Germany), equipped with a diamond knife, was used to cut off the tip of the pyramid to obtain a very smooth and small surface for indentation. Finally, the wood specimen was glued onto a metal holder,

keeping the sample's polished surface vertical to the indenting direction. Only the cell walls of latewood were selected for testing.

Nanoindentation Testing

A triboindenter (Hysitron, Minneapolis, MN), with a Berkovich diamond tip and a radius less than 100 nm, was selected for indenting. The temperature and relative humidity of the sample chamber were kept at 23 ± 0.5 °C and 45 ± 5%, respectively. Samples were put into the chamber at least 24 h before indenting, to minimize thermal shifts during testing.

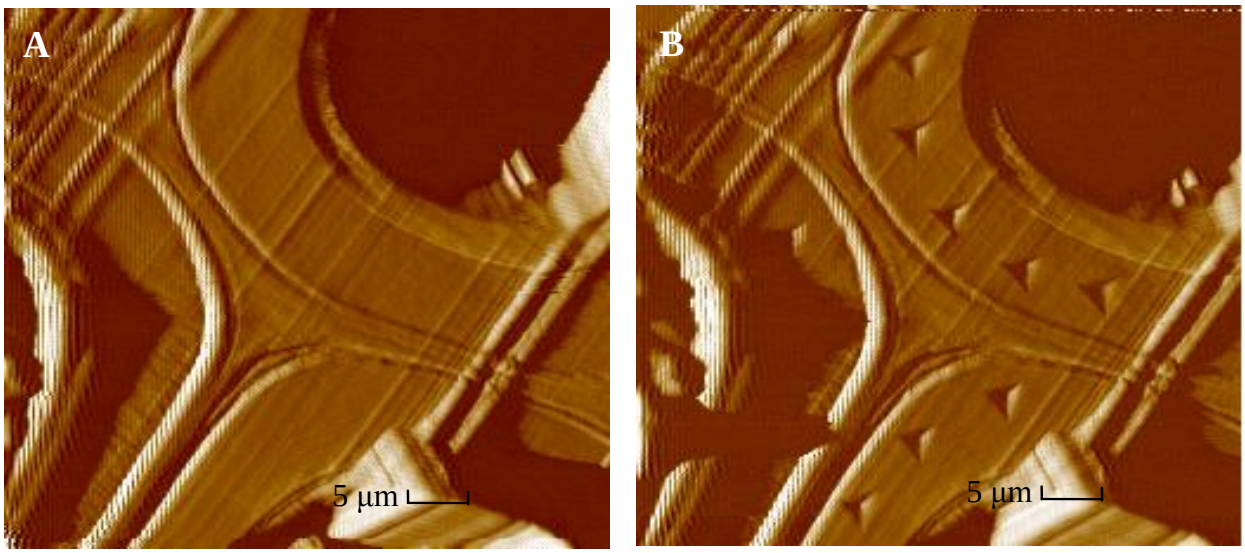

Fig. 2 The scanning size is 20 μm × 20 μm: A) scanned image of the cell wall before indentation; B) scanned image of the cell wall after indentation.

Figure 2 shows images acquired before and after nanoindentation on an area of wood cell wall. The procedure started with selecting a target region under a light microscope, which is integrated in the instrument. The indenter tip was then used to acquire an image of the wood cell wall, from which the locations to be indented were carefully selected. The residual indentations were imaged again with the same tip. A three-segment load ramp was adopted. An advanced feedback force control mode was applied in this study to provide accurate control at the peak load. The target peak load and loading/unloading rates were 250 μN and 50 μN/s, respectively, for all of the tests. After attaining the peak load, the indenter was held at a constant load for 6 s. The holding segment was used to minimize the creep component in the following unloading segment. The indentation modulus of elasticity and hardness of the materials were calculated using Eqs. 1, 2, and 3 as follows,

$$E_r = \frac{\sqrt{\pi}}{2}\frac{S}{\sqrt{A_c}} \quad (1)$$

$$\frac{1}{E_r} = \frac{1-\nu^2}{E} + \frac{1-\nu_i^2}{E_i} \quad (2)$$

$$H = \frac{P_{max}}{A_c} \quad (3)$$

where E_i and v_i are the elastic modulus and Poisson ratio of the tips, respectively.

For the diamond tips, E_i was 1141 GPa and v_i was 0.07. E and v are the same properties of the samples. Here, 0.25 is adopted as the longitudinal Poisson ratio of the wood cell wall. E_r is called the reduced modulus, which can be obtained using Eq. 1. A_c is the maximum projected contact area during loading, which is calculated from the area function of the diamond tip used and the maximum contact indentation depth. P_{max} refers to the load measured at the maximum depth of penetrations in one indentation cycle.

Sample Preparation for the Confocal Laser Scanning Microscope

Untreated samples and samples impregnated with 70% FA cured for 5 h at 103 °C were selected for CLSM imaging. Microtomed sections with 25 μm in thickness were prepared with a sliding microtome. Then, the sections were immersed in a fluorescence quenching agent (Toluidine blue) solution (0.5%) to minimize the auto-fluorescence of lignin (Olmstead and Gray 1997). The sections were then rinsed in pure water several times, until no more Toluidine blue leached out. Then, the sections were placed on a glass slide, and one or two droplets of 50% glycerol aqueous solution were dropped around the samples. A thin cover glass was put on the top before being scanned with an inverted CLSM.

Confocal Laser Scanning Microscope Image Acquisition

A confocal scanning laser microscope (Meta 510 CLSM, Zeiss Inc., Germany) was applied for sample observation. Most of the images were obtained with a 63X immersion oil objective lens. The pinhole was set at 374 μm. The laser emission wavelength was 488 nm and 633 nm, respectively, for the untreated and treated samples.

RESULTS AND DISCUSSIONS

Mechanical Properties of Wood Cell Walls in Relation to FA Concentration

To detect the FA resin distribution in wood after modification, CLSM imaging was applied in both the treated and untreated samples. Figure 3A shows strong auto-fluorescence emitted from the lignin-rich middle lamella and cell corners of the undyed and untreated wood sample. It is widely known that toluidine blue can suppress the auto-fluorescence of lignin. Thus little fluorescence was observed when the sample was dyed with toluidine blue stain (Fig. 3B).

Figure 3C and D shows the images of the furfurylated Masson pine wood initiated with maleic anhydride (F2) and mixed acidic catalyst (F1), respectively. Both of the images show the predominant existence of FA resin in the cell cavities. In comparison, Fig. 3C shows higher fluorescence intensity than Fig. 3D, which is in line with the weight percent gain (WPGs) shown in Table 2.

The WPGs of the treated wood with F2 were greater than that treated with F1 under the same conditions of modification. This result can be explained by the fact that maleic anhydride has stronger acid sites than mixed organic acid, resulting in better polymerization in F2 modification. Due to the higher catalytic activity of maleic

anhydride, FA can polymerize in wood with faster speed and with less FA evaporation during the curing and drying stage.

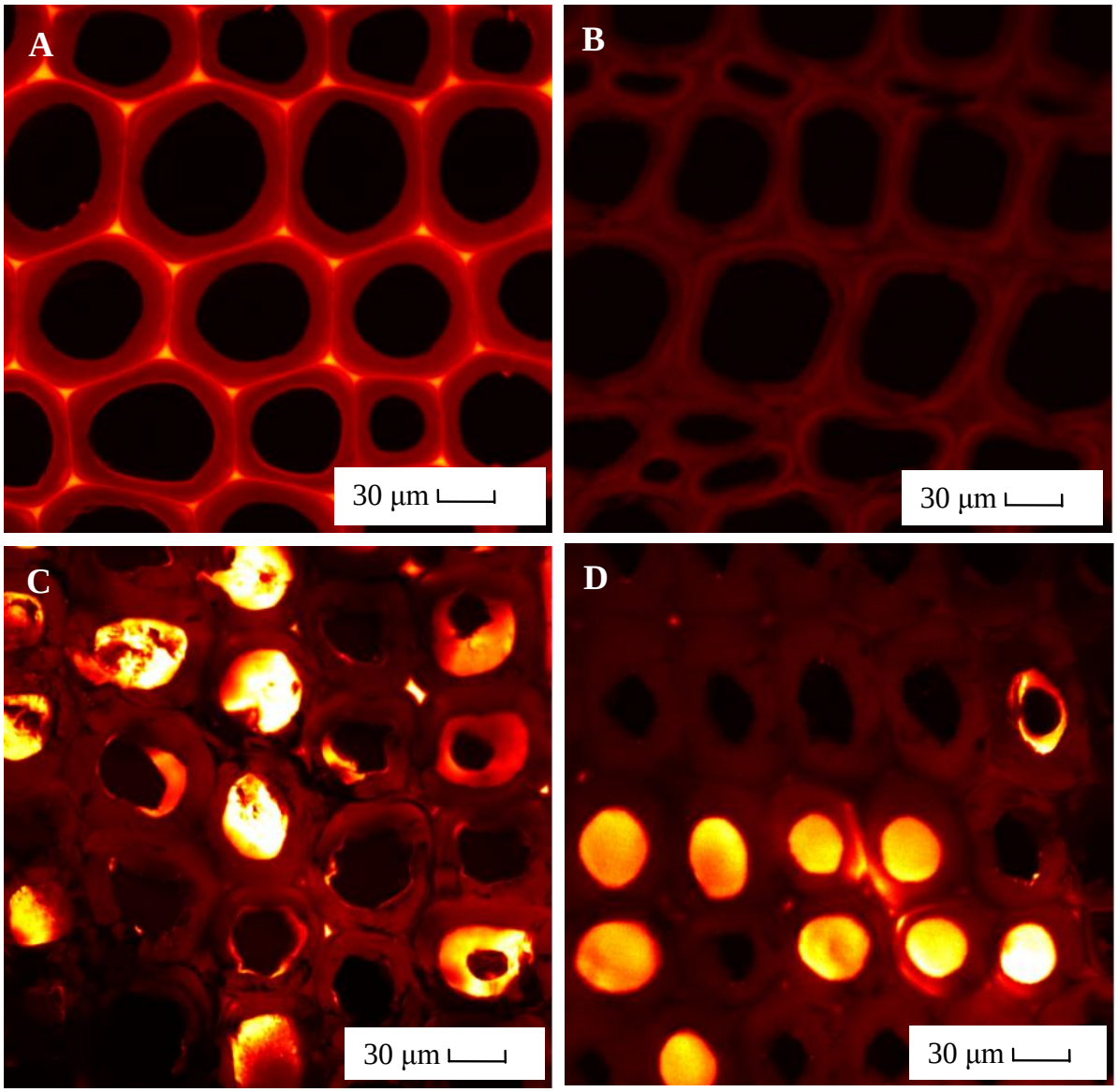

Fig. 3. Confocal laser scanning microscopy images of fluorescence. The excitation wavelengths and emission ranges were: A) 488 nm/ 500-550 nm, undyed wood, B) 488 nm/ 500-550 nm, dyed wood, C) 633 nm/ 650-700 nm, wood furfurylated with 70% F2, and D) 633 nm/ 650-700, wood furfurylated with 70% F1.

The indentation modulus and hardness of the cell wall as a function of different catalysts and FA concentration are shown in Fig. 4. The indentation modulus of cell walls treated with F1 (mixed acid catalyst) and F2 (maleic anhydride catalyst) increased by 27% and 22%, respectively, when the concentration of FA increased from 0 to 30%. That suggests that low-molecular furfuryl alcohol can easily penetrate wood cell walls and polymerize *in-situ*.

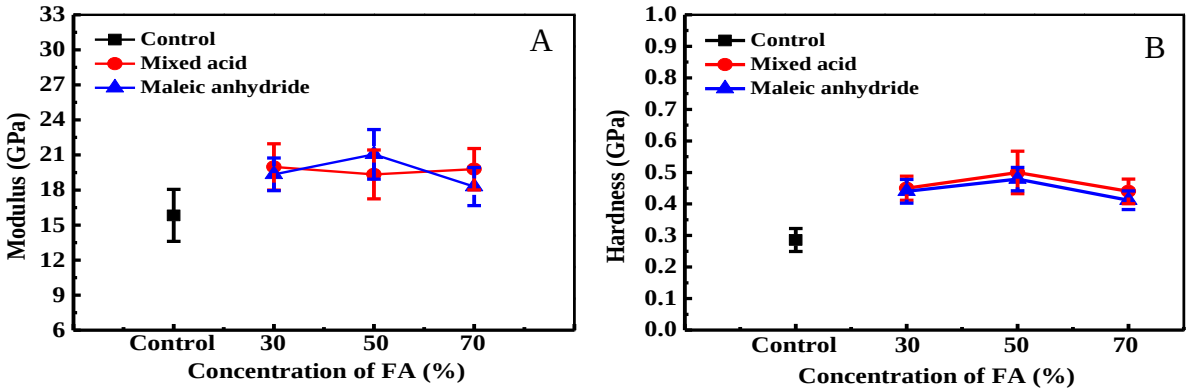

Fig. 4 (A) Indentation modulus and (B) hardness of furfurylated Masson pine wood treated with various FA concentrations

Lukowsky (2002) suggested that molecular weight is the key factor in determining where resins can be deposited in wood. Furuno *et al.* (2004) found that the resin with the low and medium molecular weight from 290 to 480 could penetrate into wood cell walls, but those with higher molecular weight mainly remained in the cell lumen. Much lower improvement in both modulus and hardness were achieved when the concentration of FA was further increased from 30 to 70%. This phenomenon can be partly explained by the fact that wood cell walls have only limited porosity to accommodate limited FA resins. Although higher FA concentration can augment the WPGs of FA resin in wood, most of this was located in the cell lumens. Furthermore, too much penetration of resin might even destroy the integration of wood cell walls, which could partly explain the slight decrease of cell wall modulus and hardness when 70% FA concentration was adopted. It therefore seems 50% FA concentration is high enough to reach a full modification of Masson pine wood cell walls. It's also worth noting that both the indentation modulus and hardness of cell walls in furfurylated wood using different catalysts exhibited small differences, while the WPG of the treated wood with F1 are much smaller than that of the wood treated with F2. (Shown in Table 2: Groups A, B, and C).

Table 2. Weight Percent Gain of Furfurylated Wood

Group	Concentration of FA/%	Curing time/h	Curing temperature/℃	F1	F2
A	30	5	103	24.7±5.65	36.4±3.75
B	50	5	103	41.7±4.45	78.8±4.02
C	70	5	103	59.0±4.76	70.8±5.38
D	50	5	95	44.1±4.89	74.8±4.99
E	50	5	115	38.5±4.85	69.2±5.75
F	50	5	125	53.3±5.10	64.0±6.49
G	50	3	103	41.8±3.55	77.6±5.27
H	50	8	103	62.1±3.35	74.1±3.38
I	50	11	103	69.2±6.94	77.6±3.36

Mechanical Properties of Wood Cell Walls in Relation to Curing Temperature

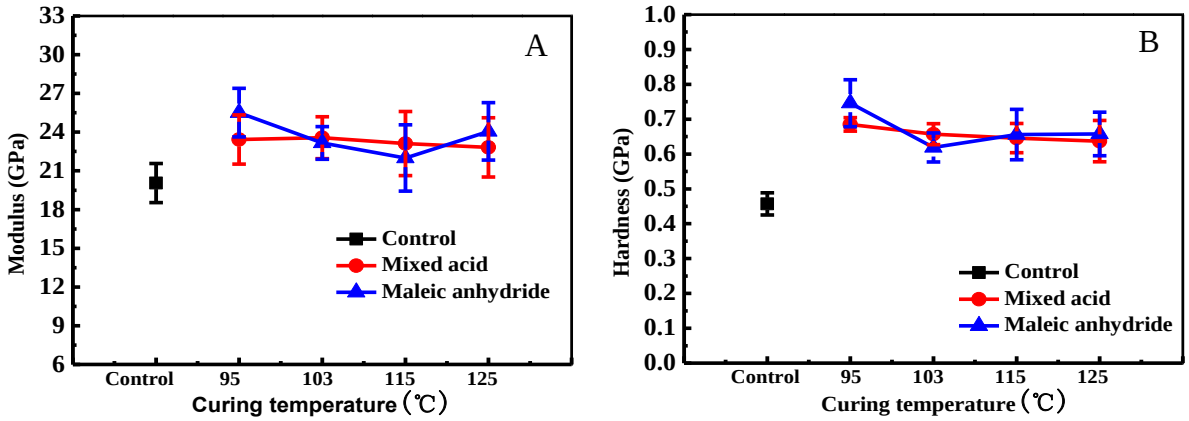

Fig. 5 (A) Indentation modulus and (B) hardness of furfurylated Masson pine wood cured under different temperature

Figure 5 shows the effect of curing temperature on the cell wall indentation modulus and hardness of wood. All the modified cell walls showed much higher modulus and hardness compared to the control cell walls. For the F1 treatment, the indentation modulus and hardness of cell walls changed slightly as curing temperature increased from 95 to 125 °C, indicating the FA in wood can be well polymerized under at 95 °C. For the F2 treatment, the indentation modulus and hardness of cell walls show obvious reduction from 95 °C to 105 °C but slightly increase can be observed with further increased temperature. Theoretically, FA will cure better at higher temperature (González *et al.* 1992), and a continuous increase of cell wall mechanical properties should be expected. However, it should be noted that the acidic degradation of cell walls caused by the acidic FA solution was positively correlated to the curing temperature, especially for the maleic anhydride that has higher acidity than the mix acid catalyst.

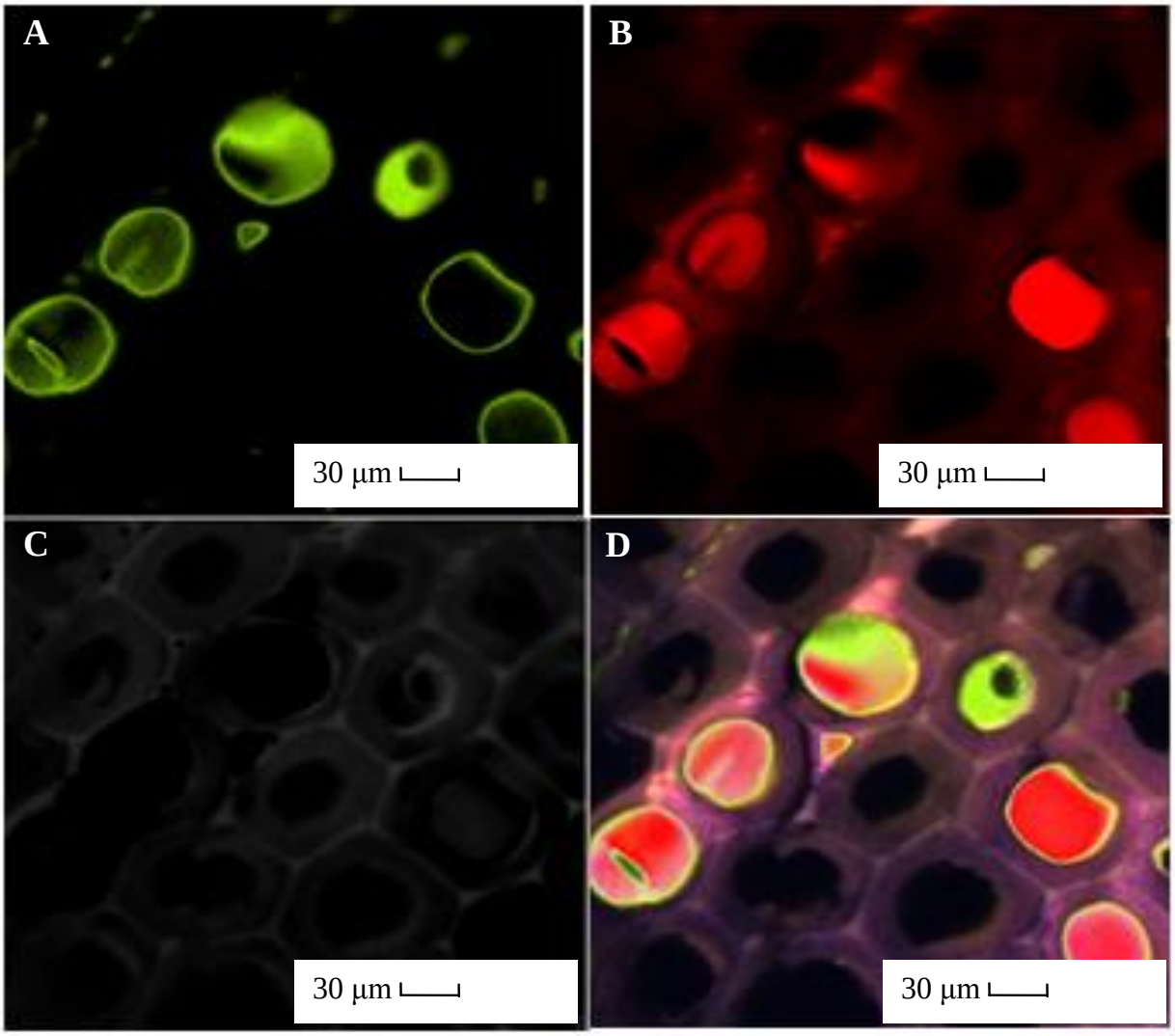

Fig. 6 Confocal laser scanning microscopy images of wood furfurylated with 70% F2 solution. A) resin I with better polymerization degree was visualized in the first channel (650–700 nm), and B) resin II with lower polymerization degree in the second channel (700–750 nm). C) The anatomical structure of wood. D) A reconstructed image obtained from all the channels.

Figure 6 shows the multi-channel CLSM images of furfurylated wood initiated with maleic anhydride (F2). It can be observed that the resin directly adhered to the inner cell wall surface was better polymerized than those distributed in both the central zone of cell lumen and cell walls. Thygesen *et al.* (2010) suggested that cell wall polymers constituted a restricted environment for FA polymerization and results in shorter conjugation lengths in the FA resin.

Mechanical Properties of Wood Cell Walls in Relation to Curing Time

Determining the appropriate curing time is very important for assessing the cost of production. The effects of curing time on the indentation modulus and hardness of wood cell walls are shown in Fig. 7. All the samples were furfurylated with 50% FA under 103 °C. The curing time was set at 3, 5, 8, and 11 h, respectively.

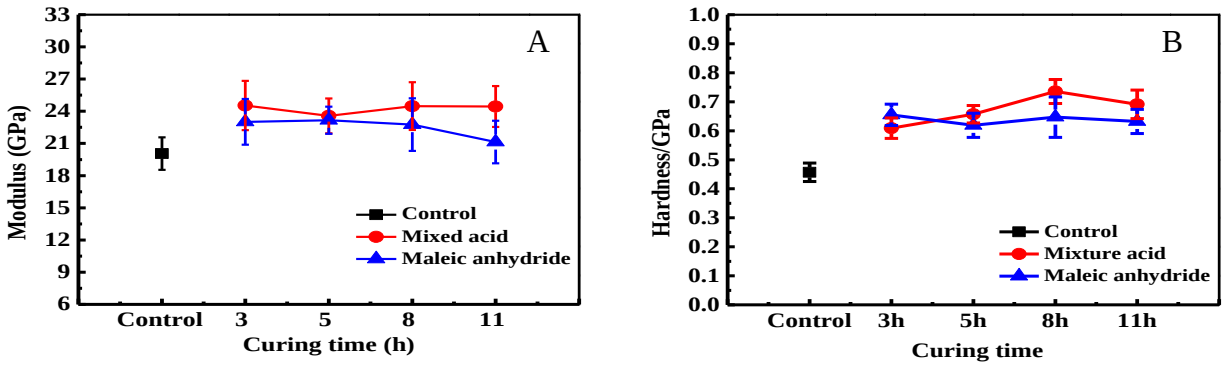

Fig. 7. (A) Indentation modulus and (B) hardness of furfurylated Masson pine wood at different curing times.

The indentation modulus of wood cell wall treated by F1 changed little as the curing time increased from 3 to 11 h while its hardness improved significantly as the curing time was increased from 3 to 8 h. This result indicates 8 h curing time might be a better choice when using the mixed organic acid as a catalyst. For the wood treated with F2, both indentation modulus and hardness of cell walls showed little improvement with increased curing time. This can again be explained by the stronger acid sites of maleic anhydride that allow for FA to sufficiently polymerize in a shorter period of time. This conclusion is also supported by the WPG shown in Tab.2 (Groups B, G, H and I). It can clearly observe that the WPG of samples treated with F1 exhibited a significant increase when the curing time was increased from 5 to 8 h. In contrast, the WPG of samples treated with F2 peaked at 3 h and showed little variation with increased curing time.

CONCLUSIONS

1. The results of CLSM observation showed that FA can easily infiltrate both into cell lumina and walls of wood during furfurylation. FA resin existing in cell lumina and walls showed different extent of polymerization due to the steric hindrance of the latter.
2. Both the indentation modulus and hardness of furfurylated wood cells were greatly improved, which confirmed the existence of FA resin in wood cell walls.
3. Maleic anhydride has stronger acid sites than the mixed organic acid, resulting in higher resin WPG. Additionally, maleic anhydride favors the polymerization of FA at shorter time and lower temperature, but tends to cause more serious degradation of cell wall at higher temperature and longer curing time.

4. Based on the results of this study, we propose the following starting parameters for furfurylation of Masson pine wood with F1 and F2: 50% FA, 95 °C and 8 h for F1; 50% FA, 95 °C and 3 h for F2. These parameters may be used as the starting point for the development of a more practical wood furfurylation process.

ACKNOWLEDGMENTS

We would like to thank the Special Research Funds for Forestry Public Welfare of China (201404510) and Beijing City Board of Education Key Lab Co-built Project for their financial support.

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Article submitted: September 11, 2015; Peer review completed: December 18, 2016; Revised version received and accepted: February 20, 2016; Published: February 29, 2016.
DOI: 10.15376/biores.11.2.3614-3625