Investigation of Low-molecular Weight Phenol Formaldehyde Distribution in Tracheid Cell Walls of Chinese Fir Wood

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Treatment with water-soluble low-molecular weight phenol-formaldehyde resin is an effective method to improve wood properties. In this paper, plantation wood of Chinese fir was modified with low-molecular weight phenol-formaldehyde resin. The absorbance by tracheid cell walls of phenol-formaldehyde resin in treated and untreated reference samples were measured with an ultraviolet micro-spectrophotometer. The UV absorbance values of earlywood tracheids and middle lamella in treated wood were significantly increased, with an average increase of 49% and 23%, respectively. Moreover, after treatment with low-molecular weight phenol-formaldehyde resin, the UV absorbance of the earlywood tracheid cell walls of Chinese fir increased to more than 47%, regardless of whether or not the cell lumens were filled with resin. After treatment with low-molecular weight phenol-formaldehyde resin, the UV absorbance of earlywood tracheid cell walls at different locations did not vary greatly. This study provides direct support for the improvement of the physical and mechanical properties of resin-modified Chinese fir in terms of penetration of the resin into the cell walls.

Keywords: Phenol-formaldehyde resin; Cell wall; Ultraviolet micro-spectrophotometer; Absorbance

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INTRODUCTION

Water-soluble phenol-formaldehyde (PF) resins use water as a solvent, which makes PF resins not only low-cost, using easily available raw materials, simple production processes, and equipment, but also non-toxic and difficult to ignite. Therefore, water-soluble PF resins have broad application prospects that follow today's environmental standards (Dong *et al*. 2009). Water-soluble low-molecular weight PF resins contain many oligomeric small molecules that can quickly enter into micron-scale cell lumens and pits, as well as nanoscale cell wall pores of wood in a vacuum under pressurized conditions (Kamke and Lee 2007; Ryu *et al*. 1993). The oligomeric small molecules then fill the cell lumen and cell walls and are self-polymerized under heat to form a complex, cross-linked structure (Laborie 2002). A small amount of resin components may also crosslink with some cell wall components by covalent bonding (Gindl 2001; Gindl *et al*. 2002; Gindl and Gupta 2002). This changes the physical or chemical structure of the wood cell walls and eventually creates significant changes in the mechanical properties, dimensional stability, flame retardancy, weathering resistance, and moldability of wood (Furuno *et al*. 2004; Liu and Wang 2004; Rowell and Banks 1985; Ryu *et al*. 1991; Wan and Kim 2008). Therefore, treatment with water-soluble, low-molecular weight PF resin offers an important way to improve wood's utilization value.

The wood cell wall is mostly composed of the polymers cellulose, hemicelluloses (xylans and glucomannans), and lignin, all of which form complex, compact structures by changing their content and arrangement. It is very difficult to detect whether or not resin diffuses into the nanoscale pores of wood cell walls. A few studies found evidence of the presence of resin in wood cell walls. As early as 1971, Smith and Cote used electron microscopy and energy-dispersive X-ray analysis to show nanoscale penetration of resin in the wood cell wall. Rapp *et al*. (1999) then used electron energy-loss spectroscopy to confirm that melamine-formaldehyde resin was present in all layers of the wood cell wall. Furuno *et al*. (2004) also observed with electron probe X-ray microanalysis that low-molecular weight PF resin could easily infiltrate the tracheid cell walls of Japanese cedar wood.

An ultraviolet (UV) micro-spectrophotometer makes it possible to monitor compositional changes in the cell walls. Using a minimum detection diameter of up to 0.5 μm, the distribution of PF resin in wood cell walls of only a few micrometers wide can be obtained on the μm scale. Due to the benzene ring structures of lignin and PF, they both have characteristic absorption peaks under UV light. Therefore, by comparing changes in the UV absorbance of treated and controlled wood cell walls, it can be determined whether PF resin diffuses into nanoscale wood cell wall pores (Gindl 2001). Using this method, Gindl *et al*. (2002; 2010) and Konnerth *et al*. (2007) found that melamine-formaldehyde resin can diffuse into the tracheid cell walls of spruce. However, the detailed distribution of PF resin in wood cell walls has not been evaluated. Therefore, this study fills an important gap in the literature.

Chinese fir (*Cunninghamia lanceolata*) is the main timber production species in south China. Because of its fast growth and short rotation period, Chinese fir has poor wood properties, including low surface hardness, mechanical properties, and dimensional stability, so its uses also are very limited. However, our results show that modification with water-soluble, low-molecular weight PF resin is an effective way to improve the properties of this species of wood. In this study, samples from a Chinese fir plantation were treated with low-molecular weight PF resin, and the absorbance of the PF resin-treated wood and untreated wood reference samples were measured with a UV micro-spectrophotometer. Then, the distribution of low-molecular weight PF resin was systematically analyzed in the middle lamellas and tracheid cell walls of earlywood. This study provides direct evidence of cell wall aspects to improve the physical and mechanical properties of modified Chinese fir.

EXPERIMENTAL

Materials

In this study, 40-year-old Chinese fir was cut from the Huangshan Gongyi Forest Farm in the Anhui province of China.

The sapwood region of mature wood with little variability was chosen at a trunk height of 1.5 m. Next, radial slices of about 100 × 12 × 1.5 mm (longitudinal × radial × tangential) were cut and numbered by sawing sequence from the location.

Industrial phenol, industrial formaldehyde (36.9%), and sodium hydroxide (analytically pure) were prepared with a molar ratio of 1:2.1:0.2 to synthesize the water-soluble low-molecular weight PF resin.

Conditions such as temperature, time, and the presence of catalysts were controlled during preparation. For the prepared PF resin, the viscosity was 36.2 cp, determined using a viscometer (Brookfield, AT85442, MA, USA), and the molecular weight generally ranged from 183 to 319 (measured with high-resolution electrostatic spray mass spectrometry) with the main structures of monomers and dimers.

Methods

PF resin treatment

Before PF resin impregnation, the moisture content of all samples was set to 12% at 20 °C and 65% humidity. Odd-numbered samples were impregnated with the low-molecular weight PF resin in a vacuum under pressurized conditions. First, PF resin with a concentration of 25% (diluted with water) was introduced into the chamber with a vacuum pressure of -0.095 MPa, which was maintained for more than 12 h. Next, the chamber was slowly pressurized to 0.2 MPa and maintained for 1 h; the pressure was then increased to 0.4 MPa and maintained for 2 h. It was then increased to 0.65 MPa and held for 4 h.

Finally, after the pressure was released, the impregnated samples were soaked in the chamber for 24 h and placed in a well-ventilated area until a moisture content of about 16% was obtained.

The samples were dried in an oven heated under a gradient of 45 °C for about 10 h (until a moisture content of 5% was obtained), 60 °C for 10 h, 80 °C for 10 h, and then 100 °C for about 0.5 h. The impregnating and curing process was designed to be mild, yet effective enough to make the PF resin penetrate sufficiently into the nanopores or micropores of the wood.

UV micro-spectrophotometer characterization

All samples were processed into small sticks with dimensions of approximately 15 × 1 × 1.5 mm (longitudinal × radial × tangential), dehydrated in a graded ethanol series, and subsequently embedded in Spurr's resin (Spurr 1969). Cross-sections 700 nm thick were cut by an ultramicrotome. Thin sections were placed flat on quartz-glass slides of high transmittance using deionized water. The area was as small as possible to ensure uniform thickness of the specimen.

The absorbance of the cell wall was determined with a UV-visible near-infrared microscope spectrophotometer (Craic QDI 2010, USA). A 40x zoom objective lens and a circular measuring spot of 1 μm in diameter were used. Wavelengths between 220 and 400 nm were set to test the absorbance spectra. For each location, 40 spectra were obtained, averaged, and plotted.

RESULTS AND DISCUSSION

Absorbance of Control and PF Resin-treated Tracheid Cell Walls and Middle Lamella in Earlywood

The distribution of PF resin in wood cell walls is an important indicator of impregnation, which largely affects the physical and mechanical properties of the modified wood. By comparing the change in UV absorbance of wood cell walls and middle lamellas that are untreated or treated with PF resin, one can determine whether or not the PF resin diffuses into the nanoscale pores of cell walls and middle lamellas.

As shown in Fig. 1, the differences in the UV absorption spectrum were quite obvious when a PF resin-treated cell wall, an untreated reference cell wall, and pure cured PF resin were compared.

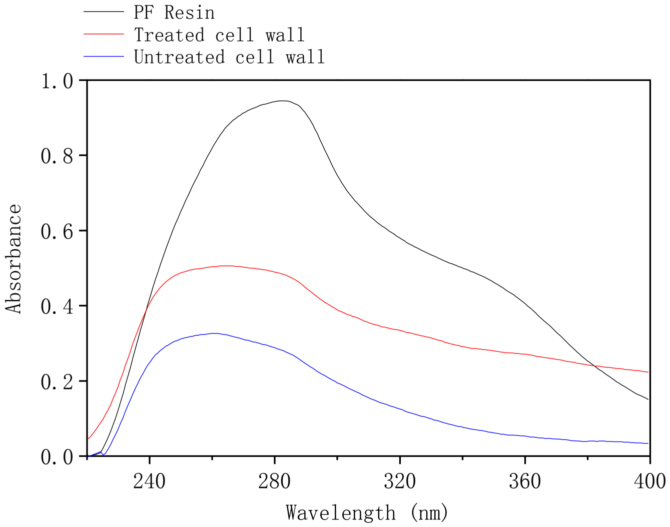

Fig. 1. UV absorbance spectra of a PF-treated cell wall, an untreated reference cell wall, and pure cured PF resin

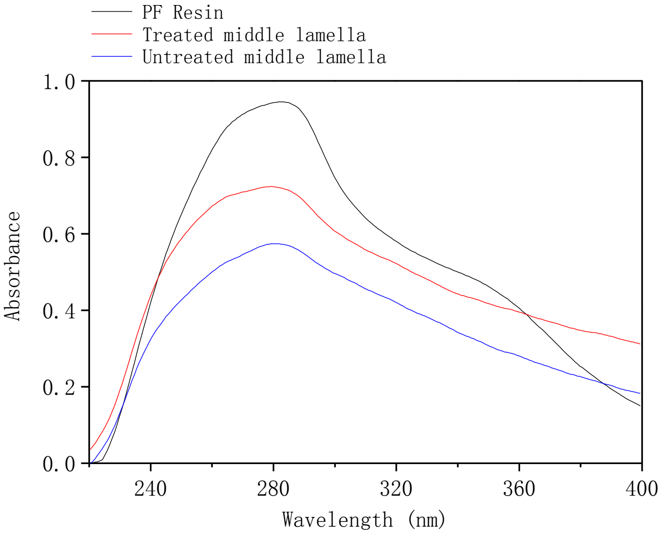

Fig. 2. UV absorbance spectra of a PF resin-treated middle lamella, an untreated reference middle lamella, and pure cured PF resin

At 280 nm on the lignin characteristic peak, the absorbance value of the pure PF resin reached a maximum of close to 1.00. The absorbance value of the untreated reference cell wall of Chinese fir tracheid was the lowest, at less than 0.35, whereas the absorbance value of the treated cell wall of the Chinese fir tracheid fell in the middle, at approximately 0.50.

The UV absorbance characteristic spectra of a PF resin-treated middle lamella, an untreated reference middle lamella, and pure cured PF resin are shown in Fig. 2. At the lignin characteristic peak of about 280 nm, the absorbance value of the middle lamella of the Chinese fir was minimal, at approximately 0.60 or less. After treatment by a low-molecular weight PF resin with a high absorbance value (close to 1.00), the absorbance value of the middle lamella of Chinese fir increased to 0.70 or higher.

As shown in Table 1, at the lignin characteristic peak of about 280 nm, the average value of absorbance of pure PF resin was up to 0.9665, while the average value of absorbance of the cell wall from the Chinese fir tracheid was only 0.3185. The average value of absorbance of the middle lamella of a Chinese fir was rather high, at approximately 0.5797. After treatment by low-molecular weight PF resin, the average absorbance of cell walls and middle lamella from Chinese fir tracheids showed increases of 49% and 23%, respectively.

Table 1. UV Absorbance at 280 nm of PF Resin-treated Cell Walls and Middle Lamella, Untreated Reference Cell Walls and Middle Lamella, and Pure Cured PF Resin

	Cell wall		Middle lamella		PF
	Untreated samples	PF treated samples	Untreated samples	PF treated samples	
Ave.	0.3185	0.4751	0.5797	0.7125	0.9665
S.D.	0.0241	0.0390	0.0299	0.0134	0.0343

After treatment with low-molecular weight PF resin of high absorbance, the absorbance of tracheid cell walls and of middle lamellas increased significantly, indicating that the low-molecular weight PF resin was able to diffuse into the nanopores of the S2 layer of earlywood tracheids of the cell walls and middle lamella of Chinese fir. This eventually caused a significant increase in the absorbance of the cell walls and middle lamellas. There are many micropores and nanopores in wood cell walls and middle lamellas, even under dry conditions. In the densest crystalline region in the S2 layer of the secondary wall, researchers have found approximately 15- to 20-nm interspaces between the fibril units in the transverse section using a transmission electron microscope (TEM) and an atomic force microscope (AFM) (Ding and Himmel 2006). The low-molecular weight PF resin used in the tests had an average molecular size of less than 10 nm under the multiple beneficial effects of moisture, vacuum and pressure, and NaOH (an added catalyst during glue preparation) contributing to the swelling of the wood. Under these conditions, the PF resin was fully capable of diffusing into the nanopores of the S2 layer in tracheid cell walls and middle lamellas. Many researchers have directly confirmed through experiments that small-molecule resins can diffuse into the nanopores of tracheid cell walls (Furuno *et al*. 2004; Laborie 2002; Rapp *et al*. 1999; Smith and Cote 1971). The findings reported by Gindl *et al.* (Gindl *et al*. 2002; Gindl and Gupta 2002), *i.e.*, improved mechanical properties and absorbance of cell walls after modification with melamine formaldehyde resin, also directly support this conclusion.

Absorbance of Cell Walls with and without Resin Filling in Tracheid Lumens of Earlywood after Treatment with PF Resin

As shown in Fig. 3, after treatment by low-molecular weight PF resin, at the lignin characteristic peak of about 280 nm, the average values of absorbances of cell walls with and without PF resin filling in the lumen increased by 47.95% and 50.41% (compared to untreated cell walls), respectively. Both differences were small, which indicated that the low-molecular weight PF resin was more evenly diffused into the S2 layer of cell walls of earlywood tracheids, and therefore, the treatment effect was improved.

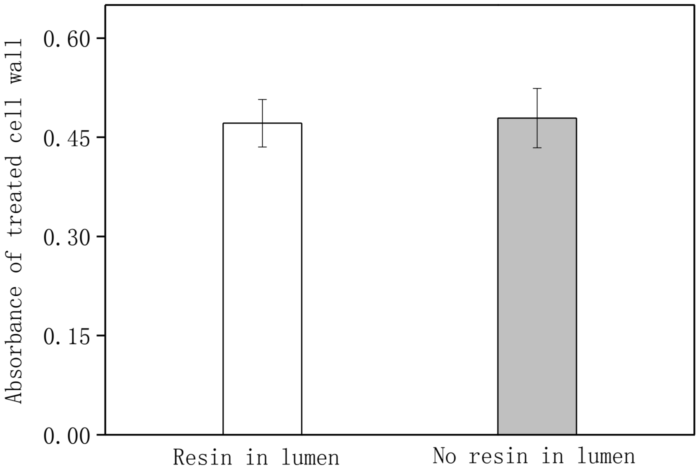

Fig. 3. Cell wall absorbance and standard deviation with and without resin filling in tracheid lumens of earlywood after PF resin treatment

Compared to the longitudinal and radial directions, the permeability of the tangential direction has been found to be inferior (Miao and Zhang 2009). Due to the small tangential size of the processed samples, at only 1.5 mm, in conditions of lengthy vacuum, pressurization, and immersion treatment, low-molecular weight PF resin can more uniformly diffuse into the cell wall S2 layer of earlywood tracheids. With increased curing temperature, the water in the PF resin solution gradually evaporates in the form of steam, while the low-molecular weight PF resin can form continuous, crosslinked polymer networks in wood (Laborie 2002). It may also form covalent bond crosslinking with the cell walls through a chemical reaction (Gindl *et al*. 2002; Konnerth *et al*. 2007). In short, because wood is a biological material with a complex pore structure, after the steam evaporates, the PF resin in cell lumens can be firmly absorbed in the inner cell wall or is partially aggregated and cured in some cell lumens due to surface free energy. However, the PF resin within the cell wall is absorbed into the complex micropores and nanopores of cell walls. Therefore, after treatment with low-molecular weight PF resin, regardless of whether the cell lumens are filled with resin, the increase in absorbance of the earlywood tracheids cell walls are similar.

Absorbance at Different Positions in the Same Earlywood Tracheid Cell Walls Treated with PF Resin

As shown in Table 2, before treatment with low-molecular weight PF resin in the same tracheid, the mean UV absorbance values of the corner and radial/tangential locations were 0.3915 and 0.3228, respectively. After treatment with low-molecular weight PF resin, the mean absorbance values were 0.4800 and 0.4668, respectively. This showed that they were largely improved, with an almost identical increase. The results also show that low-molecular weight PF resin was able to penetrate and diffuse evenly into the corner and radial/tangential locations of the same tracheid cell wall.

Because wood is a biological material, variability among tracheids is large. Under the limitations of the testing conditions, it is impossible to guarantee that the properties of control and treated tracheids are exactly the same. The absorbance of the corner location was slightly higher than that of the radial/tangential locations, and after treatment with low-molecular weight PF resin, the absorbance of the three locations was approximately the same. The structure, chemical composition, and mechanical properties in the different positions of the cell wall S2 layer in softwood tracheids, such as the orientation of the microfibril, the lignin content, and the elastic modulus, are quite similar (Fromm *et al*. 2003; Huang *et al*. 2012), Thus, the void structures in different positions of the cell wall S2 layer are also very similar. This enables the low-molecular weight PF resin to diffuse into them in a relatively uniform manner.

Table 2. UV Absorbance at 280 nm of Untreated and PF Resin-treated Cell Walls in the Same Tracheid

	Untreated Cell wall		Treated Cell wall	
	Radial/Tangential	Cell corner	Radial/Tangential	Cell corner
Ave.	0.3228	0.3915	0.4668	0.4800
SD	0.0210	0.0346	0.0386	0.0424

CONCLUSIONS

1. This study found that treatment by water-soluble, low-molecular weight PF resin largely increased the UV absorbance of earlywood tracheids and middle lamellas, with an average increase of up to 49% and 23%, respectively. This indicates that low-molecular weight PF resin can largely diffuse into the nanopores of the S2 layer of earlywood tracheids cell walls and middle lamellas of Chinese fir.
2. After treatment with low-molecular weight PF resin, regardless of whether or not the cell lumens are filled with resin, the average absorbance of earlywood tracheid cell walls of Chinese fir increased similarly, at 48% and 50%, respectively. These results demonstrate that low-molecular weight PF resin can be evenly distributed in the cell walls of different earlywood tracheids.
3. For the same tracheid cell walls, the absorbance at different positions showed little difference, which indicated that low-molecular weight PF resin had a relatively uniform distribution. These findings provide direct evidence of cell wall aspects to improve the properties of Chinese fir modified by PF resin.

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