The Effect of Microwave Pretreatment on the Impregnation of Poplar Wood

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Microwave pretreatment can increase the transverse permeability of wood. The effects of impregnation on microwave-pretreated wood with low-molecular weight phenol formaldehyde resin was investigated. The results showed that the improved transverse permeability of poplar wood that had received microwave pretreatment resulted in a positive influence on the effect of the impregnation. The maximum impregnation weight gain rate was 51.08%, with the average being approximately 40%. The average density of the specimens impregnated for 1.50 h at 0.8 MPa was 584.8 kg•m^{-3}. During the course of the study, the resin present in the wood became distributed evenly in the vessel elements, wood fiber lumens, and intercellular spaces. Finally, the chromogenic reaction area accounted for 78.11% of the total area in the fluorescent staining diagram of the cross section.

Keywords: Microwave pretreatment; Permeability; PF resin; Impregnation; Poplar wood

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INTRODUCTION

As a natural polymer, wood can be classified as a polymer-based nano-composite (Qiu and Li 2003). Wood's porous capillary structure and enormous specific surface area allow it to be impregnated with nano materials or other functional materials. However, the impregnation success is affected by the permeability of the wood, which directly determines the modification results. Existing research shows that the permeability of wood is usually very low, with typical wood permeability values falling below 0.1 Darcy (Bao and Lv 1992).

To increase permeability, researchers have conducted numerous studies on the methods of improving wood permeability through the use of different techniques (Bao and Lv 1991a; 1991b; Militz 1993; Lv *et al*. 1994; Demessie *et al*. 1995; Jiang *et al*. 2006; Harris *et al*. 2008). For example, microwave pretreatment can increase the radius of the pit membrane openings by destroying the wood microstructure (such as pit, ray parenchyma cells), and the pretreatment can even form microscopic cracks inside of the wood (Mekhtiev and Torgovnikov 2004; Torgovnikov and Vinden 2009; 2010; Li *et al*. 2010). However, the effect of the improved transverse permeability of microwave pretreated wood on subsequent impregnation is not clear. Therefore, the effect of the impregnation of wood with low molecular weight phenol formaldehyde resin was studied. Furthermore, this research may provide the fundamental theorem for further study on the impregnation of wood with nano-materials or other low-molecular weight functional materials.

EXPERIMENTAL

Materials

Plantation poplar (*Populus deltoides* cv. I-69/55) was obtained from Hunan province, China. Test specimens with dimensions of 2000 mm (longitudinal) x 115 mm (tangential) x 30 mm (radial) were prepared from green poplar. Low-molecular weight phenol formaldehyde resin prepared in the laboratory possessed a dynamic viscosity of 19 MPa.s, pH of 9.8, solids content of 48.1% to 49.8%, and an average relative molecular weight of 300 to 500. Toluidine blue ($C_{15}H_{16}ClN_3S$; Biofer, Italy) was used as a fluorescent dye.

Methods

Samples with dimensions of 310 mm x 110 mm x 25 mm (L x T x R) were cut sequentially from the green poplar test specimens, where the 3-mm sections were used to determine the moisture content. The edges of the samples were sealed with epoxy resin and aluminum foil after drying at 45 °C to reach the desired moisture content of 56%. The samples were then pretreated in a microwave after the epoxy resin used to seal the edges had cured. The optimal conditions and specifications for the microwave pretreatment conditioning, determined from a previous study (Xu *et al*. 2014), was an initial moisture content of 56%, a radiation power of 19 kW, and a duration time of 89 s. After pretreatment, all the samples were air dried to a moisture content about 8% for the impregnation test.

The impregnation experiment was in the form of a central composite design (CCD), which is one kind of Response Surface Methodology (RSM). In a central composite design, each numeric factor is varied over 5 levels: plus and minus alpha (axis points), plus and minus 1 (factorial points), and the center point. The levels of each factor are shown in Table 1. The specimens were vacuum-pressure impregnated at different pressures parameters. The samples were placed into the impregnating tank first, and the tank was subsequently vacuumed to 0.095 MPa and kept to constant pressure for 15 min. The resin, diluted by water to a concentration of 25%, was sucked back to the tank. Then the samples were treated at 0.095 MPa once again. Finally, the pressure was released slowly and the specimens were taken out from the tank. The specimens were then oven-dried at 130 °C after 3 days of air-seasoning. The weight gain percentage was calculated using Eq. 1,

$$W = \frac{M_2 - M_1}{M_1} \quad (1)$$

where W is the weight gain percentage; M_1 is the weight of the oven-dried specimens before impregnation (g); and M_2 is the weight of oven-dried after impregnation (g). When conducting the calculations, five replications were tested for each treatment.

The depth and uniformity of the resin penetration inside the microwave pretreated wood were characterized by X-ray scanning, scanning electron microscopy (SEM), and fluorescence microscopy. Samples with the dimensions of 50 mm x 50 mm x 25 mm (L x T x R) were prepared from the center portion of above specimens for density scanning. The distribution of density in terms of thickness was analyzed using a DENSE-LAB Mark 3 X-ray scanner (Electronic Wood Systems, Germany) with a scanning step of 0.02 mm (Cai 2008). Samples with dimensions of 20 mm x 20 mm x 20 mm (L x T x R) were

prepared from the center portion of the density scanning pieces and then softened in water at 95 °C. Slices with a thickness of 20 μm were prepared from the softened samples for analysis by SEM and fluorescence microscopy. For SEM, slices were mounted on aluminum stubs, sputter coated, and analyzed on a Quanta 450 SEM (FEI, USA) operating at an accelerating voltage of 15 kV. For fluorescence microscopy, slices were dehydrated through an ethanol series (*i.e.*, 30%, 50%, 75%, 95%, and 100%) and dyed with one or two drops of 0.5% toluidine blue for 15 min. A fluorescence microscope (Olympus BX51, Japan) and Image-Pro Plus 6.0 software (Media Cybernetics, USA) were used to observe and analysis the fluorescence imaging, respectively. To calculate the area of the chromogenic reaction (area filled with resin), first the total pixels of the image were counted, and then the pixels of the area filled with resin (*i.e.*, fluorescence) were counted.

Design expert 8.0.6 software (Stat-Ease, USA) was used for the statistical analysis, including multiple linear regression analysis and quadratic function fitting. An F-test was used for the statistical test, and the confidence level was 95%.

Table 1. Factors and Levels for Central Composite Design

Factor	Level				
	-1.414	-1	0	1	1.414
A Impregnation Time (h)	1.29	1.5	2	2.5	2.71
B Pressure (MPa)	0.52	0.6	0.8	1.0	1.08

RESULTS AND DISCUSSION

The experiment design (CCD) and results are shown in Table 2. The effect of impregnation time and pressure on weight gain percentages of microwave pretreatment wood was studied by use of multiple regression equations, and the optimized level of each factor could be found through the analysis of the equation.

Table 2. CCD and Results

Standard order	A	B	*W* (%)
1	-1	-1	30.11
2	1	-1	34.25
3	-1	1	44.06
4	1	1	45.08
5	-1.414	0	40.77
6	1.414	0	42.62
7	0	-1.414	24.76
8	0	1.414	51.08
9	0	0	40.58
10	0	0	40.92
11	0	0	39.42
12	0	0	40.42
13	0	0	39.46

Based on the different experimental parameters and *W* in each impregnation test, the first multiple regression equation was found to be:

$$W = 0.40 + 6.541 \times 10^{-3}A + 0.093B - 7.8 \times 10^{-3}AB + 4.086 \times 10^{-3}A^2 - 0.015B^2 - 0.031A^2B + 6.359 \times 10^{-3}AB^2 \quad (2)$$

The variance analysis showed that the value of P and the multiple coefficient of determination, R^2, of this regression model were 0.0001 and 0.9888, respectively. The regression performance was obvious. However, the "lack of fit F-value" of the first equation was obvious. This indicated that the first regression model was not well suitable for presenting the real relationship between A, B, and W and calculating the optimizing parameter of A and B. In this case, a second multiple regression equation, which was rebuilt after optimizing the first regression model, was as follows:

$$W = 0.40 + 9.72 \times 10^{-3}A + 0.093B - 7.8 \times 10^{-3}AB + 4.086 \times 10^{-3}A^2 - 0.015B^2 - 0.031A^2B \quad (3)$$

The value of P in the second regression model was less than 0.0001, and the multiple correlation coefficient R^2 was 0.9873. In addition, "lack of fit F-value" of the first equation was not obvious. In the second regression model, all statistically relevant data provide an indication that there was a strong correlation in this dataset.

Based on the aforementioned second multiple regression equation, the response surface and contour plots for the relationship between impregnation time and pressure on weight gain percentage are shown in Fig. 1. From the figure it can be seen that there was no large variation in the slope of the 3D surface or the density of the contour plots when impregnation time moved from a low to high level. When the pressure was in a relatively lower level, there was an obvious upward trend in the slope of the 3D surface in Fig. 1. The density of the contour plots varied from dense to sparse, indicating that the weight gain percentage was more sensitive to changes at lower pressures (below 0.8 MPa), while it tended to small increments when the pressure was gradually increased to high level. Therefore, it can be concluded that pressure had a more significant effect on the weight gain percentage than impregnation time, which was consistent with the variance analysis.

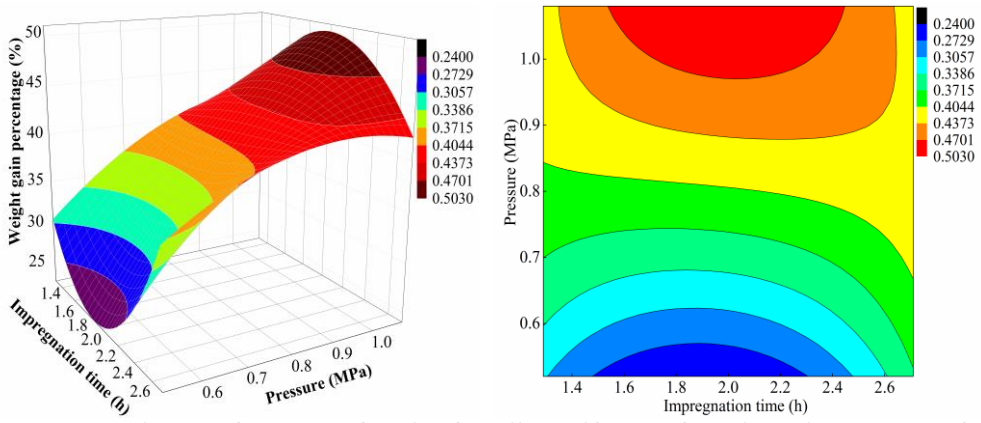

Fig. 1. Response surface and contour plots for the effect of interaction of two factors on weight gain percentage

Based on the optimization model, the theoretical maximum, represented by *W*, reached 50.29% when A = 1.99 and B = 1.08. However, the specimen tended to deform as the weight gain percentage increased, which resulted in the warping of the wide surface. When *W* was set to 40%, the calculated factors were A = 1.54 and B = 0.81. To verify the reliability of the model, a verification test was conducted based on the following: A = 1.50 and B = 0.80. The results are shown in Fig. 2. The theoretical value of *W* was determined to be 39.6% when A and B were 1.50 and 0.8, respectively. The average test value of the weight gain percentage was 39.32%, and there were no significant differences between the tested and theoretical values. Therefore, it can be concluded that this model is suitable, and the optimum impregnation time and pressure for microwave pretreated wood were 0.8 Mpa and 1.5 h, respectively.

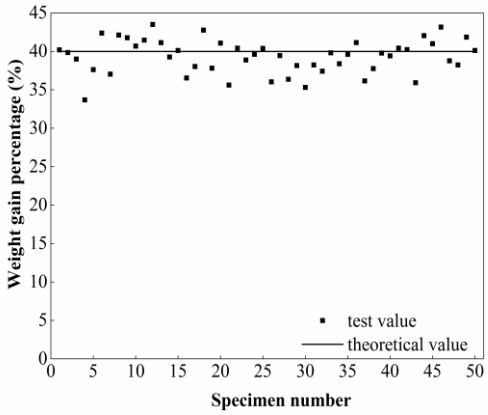

Fig. 2. Weight gain percentage for model validation

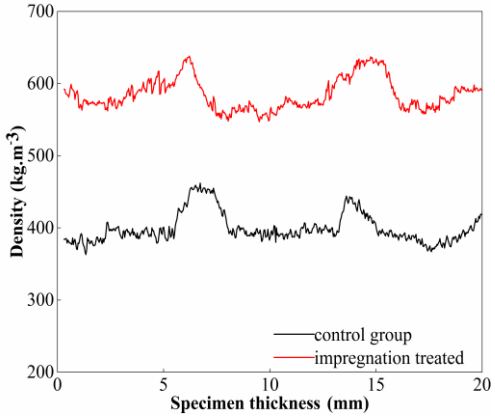

Fig. 3. Density distribution of untreated control and treated poplar by X-ray scanning

The density distributions relative to the thickness of both the impregnated and untreated poplar are shown in Fig. 3. From the figure it can be seen that the impregnated samples had a higher density. The average density, which was calculated from the data of mass and volume of untreated (control) poplar, was 399.2 kg•m^{-3}, while the density of impregnated poplar was 584.8 kg•m^{-3}. The samples for scanning electron microscopy and fluorescence microscopy were cut from the center of the density specimens in order to further observe the penetration and distribution of resin in the wood. The SEM micrographs show cross-sections of the control (Fig. 4a) and impregnated wood without and with microwave pretreatment (Fig. 4b, 4c), the wood fiber in a cross-section of control and impregnated wood (Fig. 4d, 4e), and a radial section of impregnated poplar (Fig. 4f). As can be seen in the figures, the resin penetrated into the vessel elements, wood fiber lumens, and intercellular spaces of wood after microwave pretreatment, with the most extreme penetration occurring in the vessel elements.

Treatment with toluidine blue can inhibit autofluorescence of the wood material and motivates the resin's fluorescence (Kamke and Lee 2007). Therefore, the penetration and distribution of the resin inside of the wood was characterized by the fluorescent color reaction between toluidine blue and the resin. The control is shown in Fig. 4a, while the impregnated poplar characterized by the monochromatic color is shown in Fig. 5. The area of the chromogenic reaction in Fig. 5a was analyzed quantitatively by means of Image-Pro Plus 6.0 software, and in total accounted for 78.11% of the total area. From Fig. 5, it can be seen that the resin was distributed evenly in the central location of the

wood, indicating that wood subjected to microwave pretreatment would possess good permeability. The uneven luminance of the fluorescence and the lack of color in the reaction of some parts of the wood fiber may be caused by the quenching effect of fluorescent dye as well as the wood's own variability.

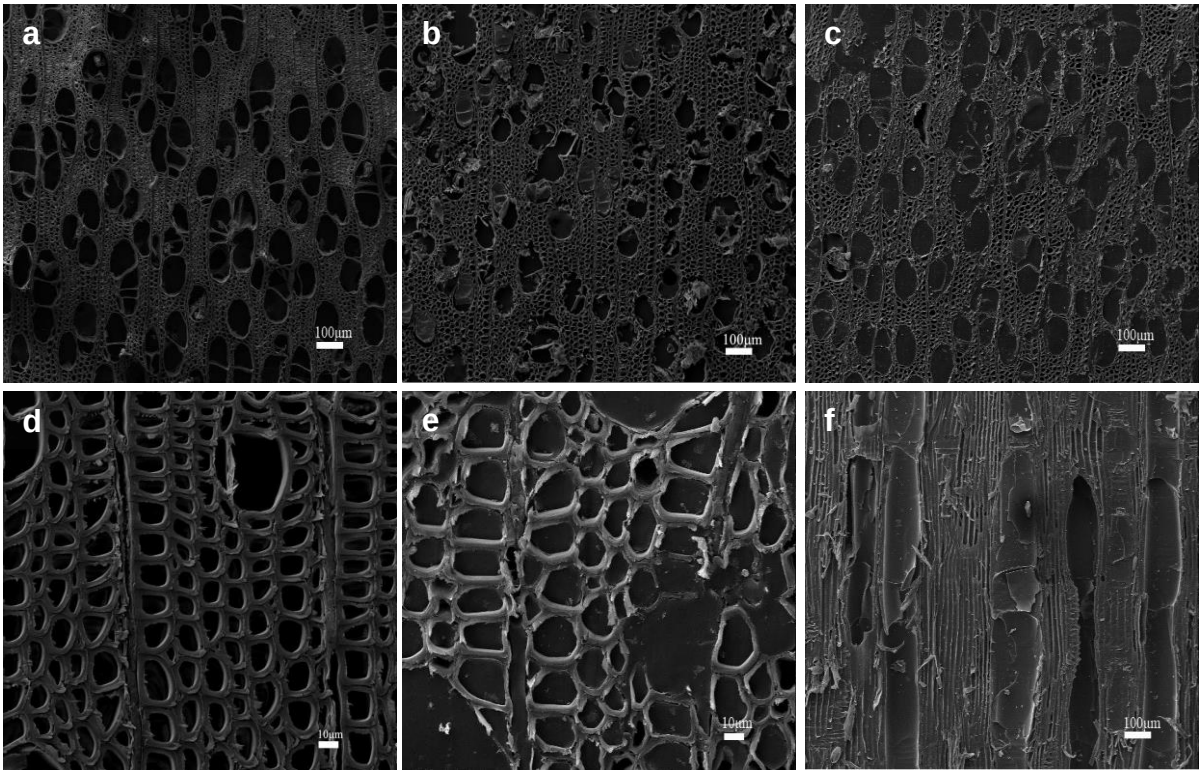

Fig. 4. SEM micrographs of control and RF resin impregnated wood. (a**)** Cross-section of control wood; (b) Cross-section of impregnated wood without microwave pretreatment; (c) Cross-section of impregnated wood with microwave pretreatment; (d**)** Cross-section of wood fiber in control wood; (e) Cross-section of wood fiber in impregnated wood; (f) Radial section of impregnated wood

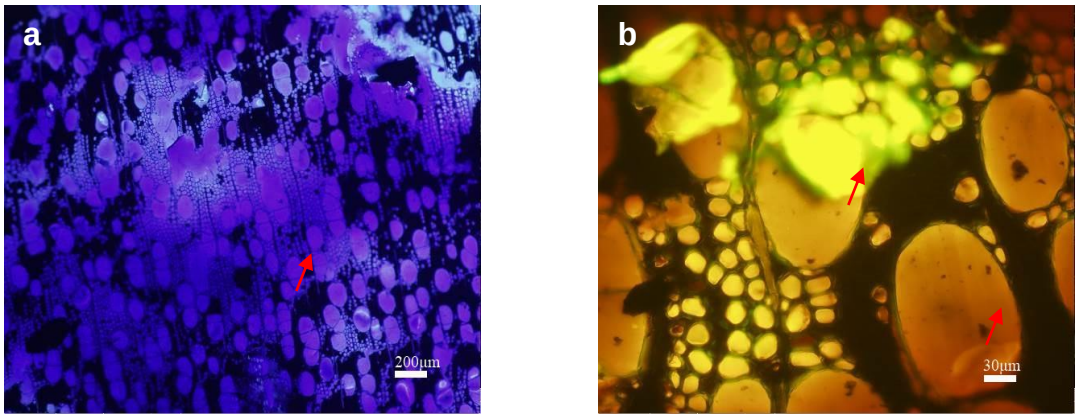

Fig. 5. Fluorescent micrographs of impregnated wood

CONCLUSIONS

1. Appropriate microwave pretreatment, resulting in the rupturing of wood cell pore membranes and ray cells, greatly improved the permeability in the radial and longitudinal directions, which created favorable conditions for the impregnation of resin and fabrication of wood-based composite materials.
2. The average density of microwave-pretreated specimens impregnated for 1.5 h at 0.8 MPa was 584.8 $kg \cdot m^{-3}$. Compared with untreated poplar (399.2 $kg \cdot m^{-3}$), the average density increased by 46.49%. The area of the chromogenic reaction accounted for 78.11% of the total area in the fluorescent staining diagram of the cross section. The resin was distributed evenly in the vessel elements, wood fiber's lumens, and intercellular spaces.
3. Due to its appropriate density, the wood-based composites prepared by this study can be widely used for interior and exterior decoration and high-grade furniture fabrication. The effect of microwave pretreatment on the impregnation of poplar with phenol formaldehyde resin could be a guideline for preparation of high value-added wood-based nanocomposites or other functional materials.

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