Microwave Treatment for Enhancing the Liquid Permeability of Chinese Fir

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A microwave (MW) treatment method was applied to Chinese fir wood to improve its liquid permeability. It was found that the optimum parameters for the MW treatment of Chinese fir to achieve an improved permeability without significantly affecting its mechanical properties were as follows: a MW intensity of 20 kW, moisture content (MC) ranging from 40% to 60%, and a processing time of 60 s. The microscopic structure of Chinese fir wood before and after MW treatment was examined using a scanning electron microscope (SEM), which revealed that micro-checks were formed at the intercellular layer of ray cells and longitudinal tracheids; pit membranes were destroyed; and damage to cell walls was also observed. Mercury intrusion porosimetry (MIP) test results showed that the pore diameter at pit opening range increased after MW treatment (peak value of control sample: 553.7 nm; peak value of MW-treated sample: 921.1 nm) and micropores were generated, which also contributed to the improved permeability of Chinese fir wood. Positive correlations between microstructural changes and liquid permeability were found.

Keywords: Chinese fir; MW treatment; Liquid permeability; Mechanical properties; Scanning electron microscopy; Mercury intrusion porosimetry

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INTRODUCTION

Chinese fir is a major plantation species in China. Due to its rapid growth rate and large proportion of juvenile wood, the quality of Chinese fir plantation wood is lower than that of naturally grown wood, which has resulted in much research attempting to enhance the properties of Chinese fir plantation wood (Chen 1997; Chang and Chang 2006; Shi *et al.* 2012). However, Chinese fir is a refractory species and usually requires very high pressure for impregnating the wood with chemicals or resins (Lu *et al.* 2007), and the permeability of Chinese fir has become a critical factor in achieving good modification results.

There are many factors that influence the permeability of wood, such as wood density, sapwood and heartwood, earlywood and latewood, the structure of wood rays, tracheids, resin ducts, and bordered pits. Many of these factors relate to the anatomical structure and the path of flow in wood (Flynn 1995). The opened or closed state of the pits in the tracheids has a dominant effect on the permeability of conifers (Siau 1984 1995), and there has been ample research done on pit aspiration mechanisms and how the aspirated pits affect the permeability of softwoods (*e.g.*, Liese and Bauch 1966; Comstock and Cote 1968; Bamber and Fukazawa 1985; Bao *et al.* 2001). The liquid flow paths of coniferous wood include both longitudinal and transverse flows.

The longitudinal fluid flow is considered to go through the tracheid lumen, the pit aperture, and the pit membrane pores (Bolton and Petty 1977; Keith and Chauret 1988), whereas in the transverse flow, tangential fluid flow occurs primarily through longitudinal tracheids and intertracheid bordered pits (Erickson 1970; Keith and Chauret 1988), and the ray tracheids are regarded as the main radial fluid pathway (Liese and Bauch 1967). To achieve good liquid permeability, it is important to facilitate both liquid flow paths with the help of anatomical structure changes.

Various methods have been attempted for improving the liquid permeability of lumber, and they can be classified into four categories: mechanical, physical, chemical, and biological treatments (Lehringer *et al.* 2009; Panek *et al.* 2013). Microwave (MW) treatment is one of the physical treatment methods applied in the fields of wood drying and wood modification. Parameters including MW intensity, moisture content (MC) of the treated lumbers, and processing time are prime factors influencing the efficiency of treatments. Also, the structural changes during MW treatment can lead to changes in wood properties, such as permeability, density, and strength (Seyfarth *et al.* 2003; Li *et al.* 2005; Harris *et al.* 2008; Vinden *et al.* 2011). However, a systematic investigation of how these parameters influence the properties of treated wood and the mechanisms of liquid permeability improvement of MW-treated wood is imperative.

Microstructural changes may contribute to improving the permeability of MW-treated lumbers. Scanning electron microscope (SEM) characterization provides a specialized image analysis for anatomical features at a microscopic level, and the micro-structural changes of MW-treated samples can be identified through SEM examination. Correlating the different microstructural changes to liquid flow paths may be helpful for understanding how the liquid permeability can be improved after MW treatment. Moreover, changes in microstructure could result in the variation of the porosity and distribution of pore diameter, which affect important parameters for the properties of end products, such as permeability.

Techniques for measuring the porosity of wood include MIP (Schneider 1982, 1983; Ding *et al.* 2008, Plötze and Niemz 2011) and gas adsorption isotherms or solute exclusion (Berthold and Salmen 1997), as well as thermo-porosimetry, nuclear magnetic resonance (Furo and Daicic 1999), and small-angle X-ray scattering (Jakob *et al.* 1996). The MIP method can be used to measure macro- and mesopores in the range of 1.8 nm to 58 µm (Plötze and Niemz 2011). The pore radii in wood can be classified in the range of < 0.1 µm for microvoids or cell wall capillaries, 0.1 to 5 µm for some small tracheid openings (diameter of pit margo is 0.1 to 0.7 µm), and > 5 µm for large lumens (Schneider 1979), while pit openings can occur in all of these radii classes. Therefore, the MIP method is suitable for examining the porosity and pore size distribution before and after MW treatment.

The objective of this study was to develop appropriate processing parameters (MW intensity, moisture content, and processing time) as a means of increasing the liquid permeability of Chinese fir wood without a significant decrease in mechanical properties. Microstructure examination through SEM was also carried out to correlate micro-structural changes to the permeability of MW-treated wood. Further investigation of porosity, pore size, and distribution conducted by MIP was carried out to reveal the mechanisms of permeability improvement in MW-treated Chinese fir.

EXPERIMENTAL

Materials

Samples of Chinese fir plantation wood measuring 1000 mm (length) × 80 mm (width) × 25 mm (thickness) were purchased from a lumber market in Shaoxing, Zhejiang, China. The lumbers were cut in half and divided into two groups, one half for MW treatment and the other for control samples. The moisture content (MC) of the lumbers was 20% to 80%. Both groups were also divided into plain-sawn samples and quarter-sawn samples.

Microwave Treatment

MW treatment was carried out using continuous belt MW equipment (915 MHz) (Sanle, WX20L-19). During the experiment, the effect of MW intensity on the mechanical properties and water uptake was investigated by a single factor experiment, in which MW intensity was set at 14 kW, 17 kW, and 20 kW, MC was about 40%, and MW processing time was 60 s. The optimized MW intensity was determined using the optimized mechanical properties and permeability test results.

The optimized MW intensity was then used in the full factorial experiment to further evaluate the combined effect of MC and processing time on the mechanical properties and permeability (Table 1) and to determine the optimum MC and processing time. Twenty replicates were used for each set of experiments, half of which were plain-sawed samples, the other half of which were quarter-sawed samples.

Table 1. Full Factorial Experimental Design for MW Treatment

No.	Moisture Content (%)	Processing Time(s)
1	20~40	30
2	20~40	60
3	20~40	90
4	40~60	30
5	40~60	60
6	40~60	90
7	60~80	30
8	60~80	60
9	60~80	90

Mechanical Properties

Modulus of rupture (MOR) and modulus of elasticity (MOE) were tested in accordance with the Chinese national standard for testing MOR and MOE of wood (GB/T 1936.1-2009, GB/T 1936.2-2009). The dimensions of samples were 300 mm × 20 mm × 20 mm (longitudinal × tangential × radial). The load was applied in the tangential direction of the samples, with an MC of 12%. Twenty samples were tested in each experimental condition for both MW-treated and control samples.

Water Uptake

The permeability of both MW-treated and control samples (MC of 12%) with ends sealed or unsealed was tested by the retention of distilled water in samples. Water uptake (W) was calculated according to Eq. 1. Three impregnation conditions were chosen, including 0.8 MPa with a duration of 5 min and 15 min; and -0.1 MPa with a duration of 15 min. Twenty samples were tested under each experimental condition.

$$W = \left(\frac{W_2 - W_1}{W_1} \right) \times 100\% \tag{1}$$

W_1 is the mass of MW-treated and control samples before pressure impregnation, and W_2 is the mass of these samples after pressure impregnation.

Scanning Electron Microscopy (SEM)

The microstructures of both MW-treated and control samples were examined using an SEM (KEKY-EM3200) device. A comparison of the microstructures, such as micro-checks between the intercellular layer of ray cells and tracheids, destruction of pit membranes, and damage to cell walls before and after MW treatment were carried out, and the correlation of microstructural changes with liquid permeability were also investigated.

Mercury Intrusion Porosimetry (MIP)

MIP tests were performed with an AutoPore IV 9500 (MICROMERITICS) for measuring porosity, cumulative pore volume, and other properties of MW-treated and control samples. The samples, about 0.2 g with dimensions of 10 mm × 6 mm × 6 mm (longitudinal × tangential × radial), were cut by scroll saw from both MW-treated and control materials. They were air dried to a MC of about 9% after MW treatment in order to avoid the affect of drying process on their pore characteristics. Four MW-treated and control samples were tested. Measurements were then conducted by two processes of low pressure and high pressure to increase the pressure steadily from 0 to 400 MPa on samples immersed in non-wetting mercury. Relatively low rates of pressure increase were carried out to avoid an overestimation of micropores in samples. Under increased pressure, mercury progressively intrudes into smaller voids. The pore volume can then be derived from the quantity of the intruded mercury. The pore size distribution can be determined according to Eq. 2 (Washburn 1921). Variations in porosity and pore size distribution after MW treatment were examined and related to the permeability improvement of the MW-treated samples.

$$r = -\frac{2\gamma \cos\theta}{p} \tag{2}$$

r is the pore radius, p is the pressure, γ is the surface tension of mercury (0.48 N/m), and θ is the wetting angle of mercury (141 °) (Junghans *et al.* 2005).

RESULTS AND DISCUSSION

Mechanical Properties and Permeability

Effect of MW intensity

The mechanical properties decreased as MW intensity increased, whereas the standard deviations increased, which was most likely caused by the different reactions of wood of various densities to the MW treatment (Table 2). However, according to the statistical analysis, the influence of MW intensity on the mechanical properties of MW-treated Chinese fir is not significant. As the MW intensity increased from 14 kW to 20 kW, the decrease in MOE varied from 2.5% to 17.3% compared to the control samples, and the largest decrease for MOR was 14.4%, when MW intensity was 20 kW. Duncan's test results also revealed that no significant differences can be observed between different levels of MW intensity when compared to control samples (Table 2). This is in agreement with the report by Liu *et al.* (2005), who treated birch wood to improve its permeability without decreasing MOE and MOR. Similar results were also reported by Torgovnikov (2009), indicating that a low degree of MW modification resulted in slight changes in wood properties that are difficult to measure, while a moderate and high degree of MW modification of the wood structure dramatically changed the physical and mechanical properties of wood. Therefore, the three levels of MW intensity used were still not severe enough to generate a significant decrease in the mechanical properties.

Table 2. Mechanical Properties and Permeability of Lumber Treated with Different MW Intensities

MW Intensity /kW	MOE /GPa	MOR /MPa	Water uptake rate/%					
			Unsealed			Sealed		
			0.8 MPa /15 min	0.8 MPa /5 min	-0.1 MPa /15 min	0.8 MPa /15 min	0.8 MPa /5 min	-0.1 MPa /15 min
14	9.83 A (1.12)	54.11 A (8.00)	160.07 A (13.30)	148.49 A (22.28)	50.04 A (19.72)	71.98 A (22.50)	44.35 BC (20.72)	15.43 A (3.60)
17	8.52 A (1.89)	42.64 A (12.90)	162.30 A (34.14)	149.15 A (18.54)	56.89 AB (29.84)	102.21 A (40.02)	56.04 B (9.22)	23.80 A (14.26)
20	8.34 A (2.71)	42.74 A (14.90)	171.11 A (45.74)	154.69 A (22.36)	82.92 B (24.45)	100.62 A (22.33)	76.96 A (22.21)	61.45 B (23.43)
Control	10.08 A (0.56)	49.94 A (8.15)	153.43 A (13.41)	140.51 A (17.05)	52.84 A (21.11)	71.86 A (12.46)	34.00 C (13.80)	15.06 A (5.29)

Note: Arithmetic means in each series are from 10 samples (n = 10). Letters following the means are Duncan's test results (α = 0.05). Numbers in parentheses are the standard deviations.

The water uptake of MW-treated samples with unsealed ends after impregnation for 15 min at a pressure of 0.8 MPa is very similar to that of the control samples (Table 2). This may be caused by the fact that the dimensions of the samples were relatively small; there is a significantly different permeability along the longitudinal and transverse directions, and the liquid flow in the transverse direction (tangential and radial directions) is much lower than that of the flow in the longitudinal direction (Tarmian and Perre 2009). Although the weak ray cells are ruptured to form pathways for easy transportation of liquids, resulting in an increase of permeability in the transverse direction during MW treatment (Torgovnikov and Vinden 2009), the increase in the permeability in the transverse direction was moderate compared to the rapid flow in the longitudinal direction when the ends of the samples were unsealed. With more moderate impregnation conditions (0.8 MPa, 5 min; -0.1 MPa, 15 min), a difference can be observed in comparison to the control samples for both sealed and unsealed ends (Table 2).

There was no significant difference in water uptake between the samples treated with an MW intensity of 14 kW and those treated with 17 kW. However, when the MW intensity reached 20 kW, the water uptake was significantly higher compared to those of the control and the 14 kW and 17 kW MW-treated samples, especially for samples with sealed ends. For instance, after treatment with an MW intensity of 20 kW, the water uptake rate increased by 126% (0.8 MPa, 5 min) and 308% (-0.1 MPa, 15 min). Because the mechanical properties did not significantly decrease compared to the control samples after treatment with an MW intensity of 20 kW, it is appropriate and reasonable to use an intensity of 20 kW for MW treatment of Chinese fir wood to enhance the permeability.

Effect of MC and processing time

MC had no significant effect on the mechanical properties (MOE and MOR) of the MW-treated lumbers (Table 3). Duncan's test results also showed similar results between levels of MC. However, the MOE decreased by 22.62% when the pressure decreased from 10.08 GPa to 7.80 GPa and the MC was between 60% and 80% (Table 3), which was a decrease significant enough to affect the practical application of the wood. The effect of MC on water uptake was different for samples with sealed ends and unsealed ends (Table 3). When the ends of the samples were sealed, a significant difference was observed at MC levels of 40% to 60% and 60% to 80% compared to control samples. As for the samples with unsealed ends, no significant difference was observed between all MC levels and control samples. The causes of the different results are similar to the effect of MW intensity on water uptake discussed above.

Table 3. Mechanical Properties and Permeability of MW-Treated Samples under Different MCs and Processing Times

MW Treatment	Mechanical Properties		Water uptake Rate/%					
			Unsealed			Sealed		
MC/%	MOE /GPa	MOR /MPa	0.8 MPa /15 min	0.8 MPa /5 min	-0.1 MPa /15 min	0.8 MPa /15 min	0.8 MPa /5 min	-0.1 MPa /15 min
20~40	11.24A (1.93)	45.84A (12.68)	163.78A (22.61)	157.17A (22.02)	56.59A (19.45)	81.74A (28.11)	57.94B (22.52)	26.16AC (12.31)
40~60	11.72A (2.42)	42.47A (13.09)	165.17A (18.18)	154.65A (23.55)	68.73A (28.53)	102.75BC (37.17)	66.71BC (29.71)	40.85B (18.64)
60~80	7.80A (2.04)	40.04A (11.75)	162.66A (24.95)	156.54A (23.34)	67.47A (34.32)	122.96C (33.73)	74.40C (26.92)	35.92BC (19.66)
Control	10.08A (0.56)	49.94A (8.15)	153.43A (13.41)	140.51A (17.05)	52.84A (21.11)	71.86A (12.46)	34.00A (13.80)	15.06A (5.29)
Processing Time/s	MOE /GPa	MOR /MPa	0.8MPa /15min	0.8MPa /5min	-0.1MPa /15min	0.8MPa /15min	0.8MPa /5min	-0.1MPa /15min
30	12.98A (3.34)	48.83A (10.65	160.42A (21.95)	150.23A (24.55)	52.70A (33.57)	90.46A (34.32)	50.59AB (22.53)	24.46A (8.58)
60	8.69A (2.75)	41.82AB (11.45)	164.22A (26.22)	157.52A (22.45)	67.78AB (28.96)	100.98AB (33.98)	65.32B (22.17)	37.14B (18.96)
90	9.03A (4.65)	37.34B (13.33)	166.97A (27.19)	160.61A (20.55)	72.30B (16.71)	116.01B (28.93)	83.15C (26.57)	41.33BC (20.21)
Control	10.08A (0.56)	49.94A (8.15)	153.43A (13.41)	140.51A (17.05)	52.84A (21.11)	71.86A (12.46)	34.00A (13.80)	15.06A (5.29)

Note: Arithmetic means in each series are from 10 samples (n = 10). Letters following the means are Duncan's test results (α = 0.05). Numbers in parentheses are the standard deviations.

According to the variance analyses of the mechanical properties and Duncan's test results, a significant difference for MOR compared to control samples was only observed when the processing time was 90 s (Table 3). Similarly, regarding the effect of MW processing time on water uptake, a significant difference was only observed with a processing time of 90 s and control samples with unsealed ends when the impregnation condition was -0.1 MPa/15 min. As for the samples with sealed ends, the liquid flowed only in the transverse direction. Thus, the significant influence of MW processing time on transverse permeability was confirmed because the water uptake was significantly higher than in control samples when the processing times were 60 and 90 s. For instance, under the impregnation condition of 0.8 MPa/15 min, the water uptake increased compared to the control samples by 29.12% and 37.15%, respectively, at processing times of 60 and 90 s. Similar results were also observed when the impregnation condition was 0.8 MPa/5 min and -0.1 MPa/15 min. It is thought that the enhancement of permeability after MW treatment resulted from structural changes (Torgovnikov and Vinden 2009), which will be identified in the present study through SEM examination.

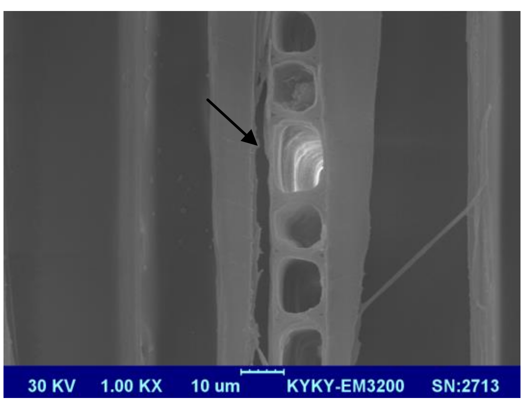
While the objective of MW modification in the present study was to improve the permeability of Chinese fir, it is also required that the mechanical properties do not decrease significantly compared to control samples. According to the above analysis, the optimum parameters of MC and MW processing time for MW modification could be 40% to 60% and 60 s, as under these conditions the liquid permeability increased signify-cantly without much decrease in the mechanical properties.

SEM

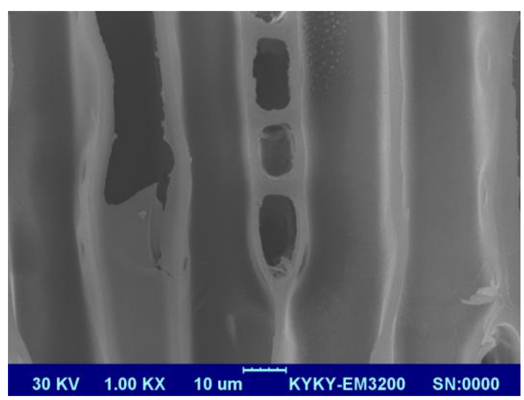
Microstructure analyses were carried out to examine the mechanisms of permeability improvement after the MW treatment. From the SEM morphologies of both MW-treated and control samples (Fig. 1), micro-checks can be observed at the intercellular layer of ray cells and longitudinal tracheids in MW-treated samples (Fig. 1a). Parts of the pit membranes in MW-treated samples were intensively damaged (Fig. 1d). Damage to cell walls was also confirmed with SEM examination (Figs. 1f and 1g). These results are also in agreement with reports by Torgovnikov and Vinden on other wood species, in which ruptures and checks in the pit membranes, tyloses in vessels, and weak ray cells were found after MW treatment (Vinden and Torgovnikov 2003; Torgovnikov and Vinden 2009).

Liquid flow in softwoods is normally in both the longitudinal and transverse directions. Previous studies indicate that longitudinal fluid flow in softwoods includes passage through the tracheid lumen, the pit aperture (and chamber), and the pit membrane pores (Bolton and Petty 1977; Keith and Chauret 1988), whereas transverse fluid flow is primarily through longitudinal tracheids and intertracheid bordered pits for tangential fluid flow (Erickson 1970; Keith and Chauret 1988), and horizontally aligned rays constitute the main pathways for flow in the radial direction. The bordered pits of the longitudinal tracheids substantially determine the permeability of a softwood species in the longitudinal direction, while the transverse permeability depends on the number and size of ray parenchyma and ray tracheids, ray parenchyma end wall pit number, and diameter (Lehringer *et al.* 2009; Ahmed and Chun 2011). After MW treatment, the ruptures generated between intercellular layers of ray parenchyma and longitudinal tracheids in the radial and longitudinal planes of Chinese fir (Fig. 1a) may form new pathways for liquid flow in the radial and longitudinal directions. Also, the improvement of the permeability in the tangential direction could also occur because it is easier for liquid to flow through voids to tracheids than through pits in ray parenchyma to tracheids. The destruction of pit membranes in tracheids (Fig. 1d) facilitated the penetration of liquids in MW-treated samples because, as most research confirms, the bordered pit is considered to be the primary structure governing the permeability of softwoods (Comstock 1967; Erickson 1970; Keith and Chauret 1988). The intertracheid liquid flow in both the longitudinal and transverse directions also depends strongly on the state of boarded pits, such as the pit aspiration and the interfibril spaces of the margo in the bordered pit (Liese and Bauch 1967). The damage to the cell walls of tracheids (Figs. 1f and 1g) also contributes to the permeability improvement because additional porosity and specific area were created, which would provide new capillaries for liquid flow, while the micro-checks in tracheid cell walls could make the transverse flow more efficient.

Microstructural changes resulted in the improvement of the liquid permeability of MW-treated Chinese fir in both the longitudinal and transverse directions. However, because the flow in the longitudinal direction is much faster than it is in the transverse direction, the improvement is relatively more significant in the transverse direction, as shown in the permeability tests where the water uptake of samples with sealed ends increased significantly while that of samples with unsealed ends did not (Table 3). Apart from the permeability improvement, a decrease in mechanical properties caused by microstructural changes was also observed. Micro-checks located at the intercellular layer of ray cells and longitudinal tracheids (Fig. 1a) and tracheid cell walls (Figs. 1f and 1g) would affect the mechanical properties of the treated samples. Similar results were reported by Torgovnikov and Vinden, *i.e.*, that the reduction of mechanical properties is caused by the fact that checks or voids occur in the radial-longitudinal planes (Torgovnikov and Vinden 2009). The destruction of pit membranes on the cell walls of tracheids (Fig. 1d) has a negligibly negative effect on the mechanical properties, as reported by Fojutowski (2004) and Panek (2013) in the investigation of fungal treatment for improving the permeability of wood.

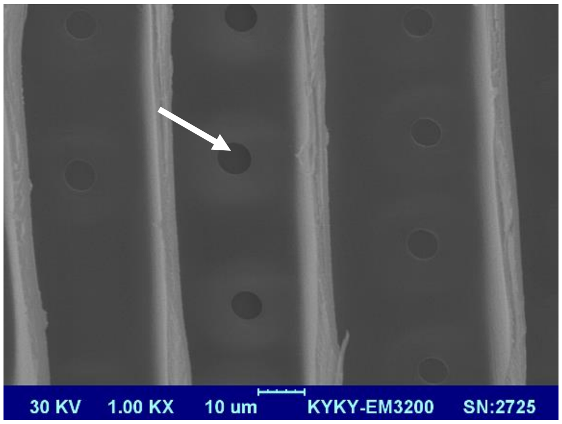


a) Microchecks located at the intercellular layer of ray cells and longitudinal tracheids in MW-treated samples (20 kW, 40% to 60%, 60 s) (×1000)

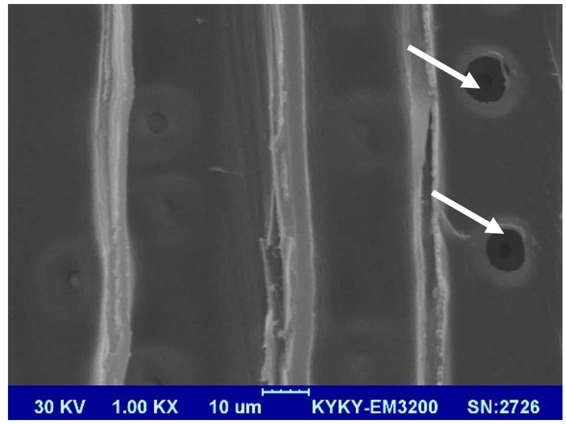


b) Intercellular ray cells and longitudinal tracheids without checks in control samples (×1000)

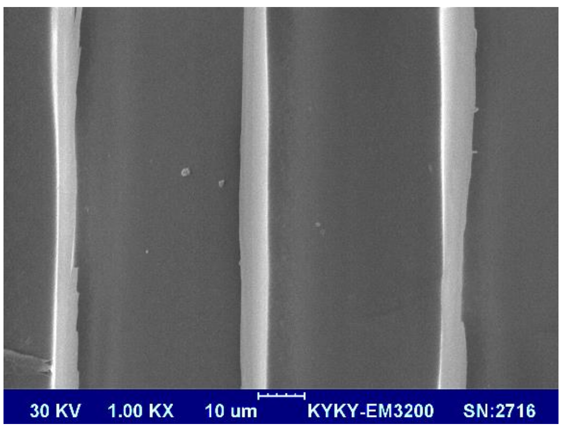
Fig. 1. SEM images of MW-treated and control samples



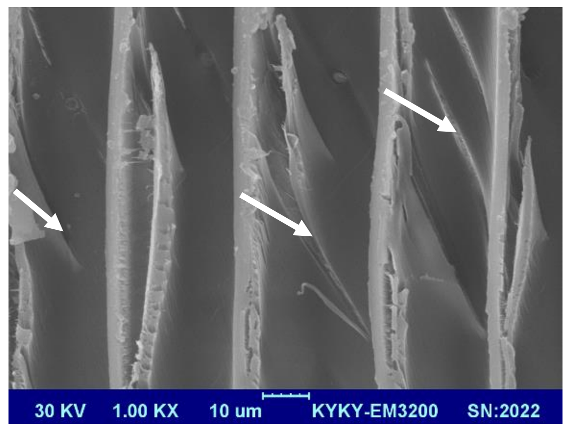
c) Pit membranes in control samples (×1000)



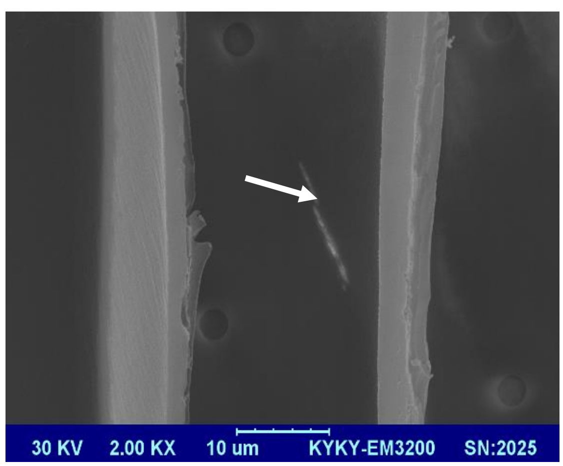
d) Pit membranes in MW-treated samples (×1000)



e) Cell wall of tracheids in control samples (×1000)



f) Checks in cell wall of tracheids in MW-treated samples (×1000)



g) Microchecks in cell wall of MW-treated samples (×2000)

Fig. 1. (cont.) SEM images of MW-treated and control samples

Mercury Intrusion Porosimetry

Microstructural changes in MW-treated lumbers created additional porosity and altered the pore size distribution, which are important parameters influencing permeability. Table 4 shows the results of the MIP measurements for samples before and after MW treatment. Total intrusion volume, total pore area, and porosity all increased after MW treatment. Parameters such as the median pore diameter (volume), median pore diameter (area), and average pore diameter (4V/A) also varied, even though the bulk density of control and MW-treated samples taken for the MIP test was almost the same (0.241 and 0.246 g/cm^3, respectively).

Table 4. MIP Test Results Before and After MW Treatment

	Total Intrusion Volume/ mL/g	Total Pore Area/ m^2/g	Median Pore Diameter (Volume)/ nm	Median Pore Diameter (Area)/ nm	Average Pore Diameter (4V/A)/ nm	Bulk Density at 0.56 psia/ g/cm^3	Porosity/ %
MW-treated	3.60	34.05	1336.5	20.0	422.5	0.241	86.65
Control	3.28	22.37	780.4	436.5	585.6	0.246	80.50

Figures 2 and 3 show the cumulative pore volume and percentage of intrusion volume over the range of pore diameters between 3 nm and 300 μm. Figure 2 indicates that the primary increase in cumulative pore volume after MW treatment occurs in the pore diameter range from 8039.7 nm to 36320.8 nm, and a similar phenomenon is observed in Fig. 3 for the increase of percentage of intrusion volume.

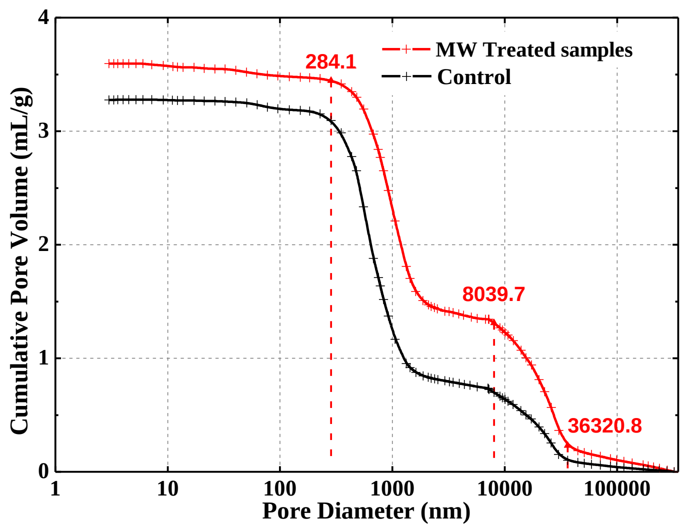


Fig. 2. Cumulative pore volume *versus* pore diameter of MW-treated and control samples

As reported by Schneider after investigating the pore size distribution of 30 different wood species with MIP, the pore radii in wood were classified in the range of < 0.1 μm for microvoids or cell wall capillaries, 0.1 to 5 μm for some small tracheid openings (diameter of margo capillaries is 0.1 to 0.7 μm), and > 5 μm for large lumens (Schneider 1979). Thus, pores with diameters ranging from 8039.7 nm to 36320.8 nm are mainly from the tracheid lumens, or checks caused by MW treatment, which still needs confirmation. Because microstructural changes such as damage to pit membranes could accelerate the flow of liquid through tracheids, it is reasonable to assume that the increase in cumulative pore volume or intrusion volume results from increases in the liquid permeability of tracheid lumens. The checks caused by MW treatment may also contribute to the increase in cumulative pore volume. As the pore diameter decreased to below 284.1 nm, the cumulative pore volume remained almost unchanged, which indicates that pores with diameters below 284.1 nm made no significant contribution to the pore volume.

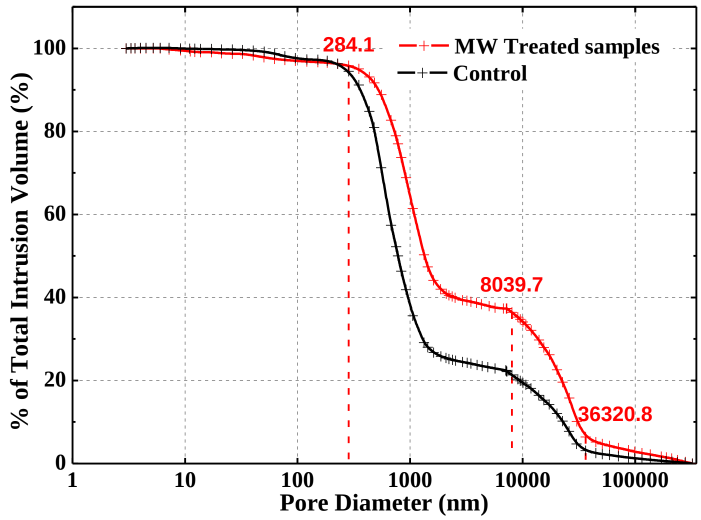


Fig. 3. Percentage of intrusion volume *versus* pore diameter of MW-treated and control samples

The main difference observed in Figs. 2 and 3 between MW treatment and control samples occurs in the pore diameter range from 8039.7 nm to 36320.8 nm. However, the pore diameter distribution is also different. Figure 4 refers to the pore volumes calculated using the log of the differential pore diameters; different pore diameter distributions between MW-treated and control samples can be observed. It is apparent that the diameter distribution of macropores includes tracheid lumen as well as some smaller tracheid openings that remain almost unchanged (peak value of control sample: 25908.4 nm; peak value of MW-treated sample: 25918.2 nm). This means hardly any damage was caused by enlarging the diameter of the tracheid lumen, and no checks with a diameter larger than the lumen diameter were produced. As for the pores of pit openings that occur in the mesopore (500~80 nm) as well as in the macropore range (> 0.5 µm), the pore diameter turned out to be larger after MW treatment (peak value of control sample: 553.7 nm; peak value of MW-treated sample: 921.1 nm) (Fig. 4). This phenomenon was also confirmed in SEM examinations (Fig. 1d); the pit membranes can be destroyed to make the pores of pit openings larger and facilitate the intercellular liquid flow. The intensity variation of the curve can be explained by the permeability improvement in the tracheid lumen diameter range, which results from larger pit openings. Because the bordered pit is the prime factor affecting the liquid flow through tracheids, larger pit openings after MW treatment caused the intrusion volume to increase dramatically in the tracheid lumen diameter range, which is reflected in the higher intensity in the tracheid lumen diameter range (Fig. 4). Moreover, the intensity of the curve in the pit opening diameter range somewhat weakened because most of the intrusion volume had already been occupied in the tracheid lumen diameter range.

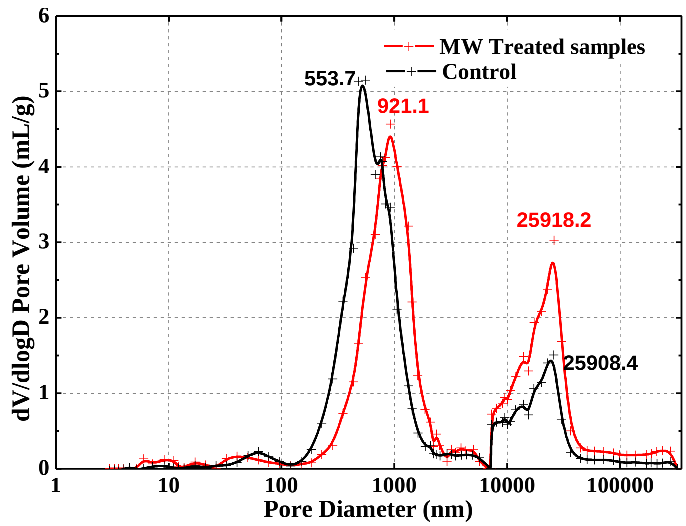


Fig. 4. Log differential intrusion *versus* pore diameter of MW-treated and control samples

Figure 5 shows the cumulative pore area changes before and after MW treatment. It is evident that pores with diameters below 1000 nm contributed to 90% of the total pore area for both MW-treated and control samples. Because the pore diameter is inversely proportional to the specific area, the cumulative pore area is smaller for MW-treated samples because the pore diameter increased in the pit opening diameter range after MW treatment. However, there was a dramatic increase when the pore diameter was below 13.7 nm (Fig. 5). It can be inferred that there are more micropores found after MW treatment and that these micropores contribute to an increase in the pore area; however, they did not contribute much to the pore volume (Fig. 2). These pores could be located at the interfibril spaces of the margo in the bordered pit. Since liquid permeability is determined by the interfibril spaces of the margo in the bordered pit, the micropores could be an important parameter in improving the liquid permeability of MW-treated Chinese fir.

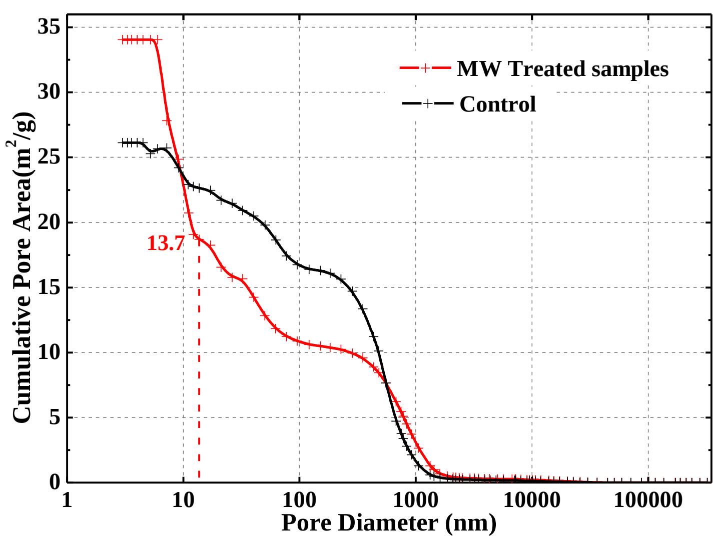


Fig. 5. Cumulative pore area *versus* pore diameter of MW-treated and control samples

CONCLUSIONS

1. The optimized microwave (MW) treatment parameters were a MW intensity of 20 kW, MC range of 40 to 60%, and processing time of 60 s. With these parameters, the liquid permeability of MW-treated Chinese fir increased significantly without a significant decrease in mechanical properties.
2. Micro-checks were found at the intercellular layer of ray cells and longitudinal tracheids after MW treatment and pit membranes were destroyed, while damage to cell walls was also observed. These microstructural changes were prime factors accounting for the permeability improvement of MW-treated Chinese fir.
3. The mercury intrusion porosimetry (MIP) test revealed a positive correlation between microstructural changes and liquid permeability. Corresponding to the destruction of pit membranes, the pore diameter became larger in the pit opening diameter range (peak value of control sample: 553.7 nm; peak value of MW-treated sample: 921.1 nm), and liquid flow was much easier through tracheids, which was reflected in the increase in cumulative pore volume in the pore diameter range of the tracheid lumen (8040 nm to 36321 nm). The cumulative pore area changes indicated that micropores were generated after MW treatment, which may also contribute to the permeability improvement.

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