

Improvement of *Eucalyptus urophylla* Wood Permeability via Urea Treatment

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To increase the loading amount of modifier in wood, a simple and universal approach was developed to improve its permeability. The generated pores in wood can be backfilled with modifiers, thereby improving the function of wood. This study aimed to improve the permeability of *Eucalyptus urophylla* wood using a urea solution. The wood was treated under different conditions, including urea concentration, treatment duration, and temperature, and the wood permeability before and after treatment was measured using water absorption as an indicator. The treatment temperature and solution concentration had considerable effects on the water absorption capacity of the treated wood. The treatment of eucalyptus wood with a 5% urea solution for 12 h, under normal pressure, resulted in the optimal effect; water absorption reached 40%, which was 78.9% higher than that of the untreated eucalyptus. Fourier-transform infrared spectroscopy, component analysis, and BET analysis were performed to examine the mechanism underlying the effect of urea treatment on eucalyptus, which is as follows: a weak alkaline solution can dissolve the internal components of wood, namely, hemicellulose, lignin, and alcohol-benzene, which leads to the destruction of the microstructure of the wood and increases the number of micropores and mesopores in the wood.

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INTRODUCTION

The porous structure of the wood is the basis of its permeability, which determines the challenges associated with its functional improvement. Wood contains various types of pores (mesopores, macroscopic pores, *etc.*). Jang and Kang (2019) identified three types of pore shapes in yellow poplar wood: through, blind, and closed pores. They also examined the correlation between the amount and improvement of gas permeability and the increase in pore size and through pore content. After heat treatment, the mass loss increases the amount of through pores in the wood. The gas permeability was greater than untreated wood, although there were no apparent cracks. Comstock (1970) and Lehringer *et al.* (2009) reported that diameter, frequency and distribution of vessels, fiber length, and type of pit affect wood permeability, as well as the deposition of extractives, which may cause partial or total occlusion and become a barrier to liquid or gas flow.

There has been an increasing interest in the permeability of wood and improvement techniques, as highly permeable wood can be handled with usable chemicals and can be dried with minor drying defects (Norimoto *et al.* 1992). The delignification treatment (Wise's method) enhances the gas permeability of wood in the fiber direction and increases

the sound adsorption efficiency of the cross-sectional surface of *Larix kaempferi* wood (Kang *et al.* 2008). Yuan (1994) reported that the gas permeability of *Eucalyptus* (*E. camaldulensis*, *E. tereticornis*, *E. viminalis*) improved remarkably after treatment with heat, and the best results were obtained after treatment at 140 °C for 5 h. The explosion of steam increases gas permeability and the drying rates of wood (Tarmian *et al.* 2020). However, due to changes in the anatomical structure of wood during heat treatment and delignification, its functioning decreases due to the emergence of defects such as internal and surface cracking, collapse, and deformation (for example, bow, spring, twist, and cup) (Rashidi *et al.* 2021).

In a tree disk with steam explosion, the increased volume of steam increases the volume of the pores and removes obstacles, such as pit aspiration or tylosis in the cell wall, which increases the permeability of the wood. The steam explosion causes multiple fine fractures, which improves the drying rate of wood and its thermal stability (relative to a control specimen) (Darus *et al.* 2020). Although heat treatment, delignification, and steam explosions can improve the permeability of wood, they can also disrupt its structure and reduce mechanical properties. Therefore, it is important to improve the permeability of wood using a simple method without damaging its structure.

Eucalyptus has fine and uniform structure, hard texture, good mechanical structure, and beautiful grain. However, due to the problems of large growth stress, poor permeability, and high extractives content (such as gum, tylosis, *etc.*) in eucalyptus, it is often used in the production of plywood, fiberboard, and particleboard (Chen *et al.* 2018). It is rarely used in furniture production and construction. Therefore, it is essential to improve the utilization value of eucalyptus by improving the performance problems such as easy cracking and poor permeability of eucalyptus. *Eucalyptus* is a broad-leaved tree. The inner factor that determines the permeability of eucalyptus is the conductive tissue-catheter and the main factor that affects the catheter is the pits on the wall of the catheter (Yuan 1994). The goal was to develop a new method that not only does not damage the main body of eucalyptus tissue, but also partially destroys the pit membrane on the vessel wall, and expands the internal penetration pathway of eucalyptus, which can improve the permeability of eucalyptus. Urea is an abundant and cheap material. Urea solution impregnation of wood has the advantages of low cost and easy operation. By saturating the wood with a urea solution, the permeability of the wood can be improved (Qin *et al.* 2020). The aim of this study was to study the improvement mechanism of eucalyptus permeability with a urea solution under different treatment conditions, including concentration, temperature and duration, to explore the basis for the subsequent preparation of functional wood.

EXPERIMENTAL

Materials

Wood samples of *Eucalyptus urophylla* at 10 years of age were obtained from a base population field trial located at Sanmenjiang Forest farm in Liuzhou Guangxi. *Eucalyptus urophylla* with an average diameter at breast height of 20 cm was selected from the plantation base, and heartwood samples were taken from 1.3 m to 3.3 m of the trunk as experimental materials. After air drying, the defects were removed, the size were 20 mm × 20 mm × 20 mm. The samples were dried at 103 ± 2 °C until a constant weight was attained, and the weight and size of the samples were recorded. Urea, CO(NH₂)₂ was purchased from

Henan Zhongyuan Chemical Co., Ltd.

Sample Processing

Wood samples were saturated in urea solutions with different concentrations at different temperatures. One set of samples was treated with 3%, 5%, 7%, 9%, or 10% urea solution at room temperature for 6, 12, 24, and 36 h. The number of samples per concentration was 20 (there were 5 samples for each treatment time). Another set of samples was treated with a 5% urea solution at 20, 40, and 90 °C for 6, 8, and 12 h, respectively. The number of samples at different temperatures was 15 (there were 5 samples for each treatment time). The processing conditions of these samples were determined after the last round of tests. The weight and size of the samples were recorded after removing the surface impregnating liquid, and then they were dried at 103 ± 2 °C until they reached a constant weight. The dry weight and size of the samples after immersion were recorded.

Permeability Measurement

The treated samples were immersed in water, placed under vacuum for 30 min, and soaked under atmospheric pressure for 5 h. The weight and size of the samples were then recorded, and the water absorption (WA) rate of the samples was measured to test the permeability of eucalyptus. Equation 1 was used for calculating water absorption,

$$WA (\%) = (W_2 - W_1) / W_1 \times 100 \quad (1)$$

where W_1 and W_2 are sample weights (g) before and after immersion, respectively. W_1 is the weights which the samples are oven dried at 103°C.

Determination of pH

The pH of urea solutions (3%, 5%, 7%, 9%, and 10%) was determined using a pH-meter (PHS-2F, China).

Determination of Alcohol-Benzene Extract

In China, the national standard for the determination of alcohol-benzene extract is Pulps-Determination of alcohol-benzene solubles (GB/T 10741-2008). The sample was air-dried and weighed (5 ± 0.002 g). Degreased cotton (extracted with benzene-ethanol in advance) was inserted into the drainage tube of the Soxhlet extractor and then the sample m_0 was placed into the Soxhlet extractor. The bottom bottle was dried at 105 ± 2 °C; it had a constant weight (M_0) and was connected to the Soxhlet extractor. Toluene and 95% ethanol were combined in a 1:2 volume ratio, which is equivalent to 1.5 times the volume of the Soxhlet extractor. The benzene-alcohol mixture was added to the bottom bottle, and the condenser was connected. The instrument was installed on the constant temperature water bath to start the extraction.

The boiling speed was adjusted to ensure six extraction cycles, with a total of 36 cycles (once complete, the extract was clear without fiber). Finally, the bottom bottle liquid was allowed to evaporate out, in a constant temperature water bath, and then oven-dried at 105 ± 2 °C to a constant weight (M_1). The mass difference between the first and second weighing was not greater than 0.5 mg.

The alcohol-benzene extract content was calculated using Eq. 2,

$$X = \frac{M_1 - M_0}{m_0} \times 100 \quad (2)$$

where X is the content of alcohol-benzene extract (%), $(M_1 - M_0)$ is the weight of alcohol-benzene extract (%), and m_0 is the quality of oven dry sample (g).

Weight Percentage Gain, Wet Weight Ratio, and Volume Change Rate (S)

The weight percent gain (WPG) was calculated for the treated samples as follows,

$$WPG (\%) = (W_1 - W_0) / W_0 \times 100 \quad (3)$$

where W_0 is the absolute dry weight (g) (the samples oven dried at 103°C, same below) of untreated wood, and W_1 is the absolute dry weight of urea treated wood (g).

The wet weight ratio was calculated as follows,

$$\text{wet weight ratio (\%)} = (M_1 - W_0) / W_0 \times 100 \quad (4)$$

where W_0 is the absolute dry weight (g) of untreated wood, and M_1 is the wet weight of treated wood (g).

The volume change rate(s) was calculated as follows,

$$S = (V_2 - V_1) / V_1 \times 100 \quad (5)$$

where S is the volume change rate of wood, and V_1 and V_2 are the absolute dry volumes (cm^3) of samples before and after urea treatment.

Fourier-Transform Infrared Spectroscopy

The wood samples before and after urea treatment were ground into a powder and oven-dried at 103 ± 2 °C. The samples were mixed with KBr (potassium bromide) (mg) at a sample:KBr ratio of 1:50, and then pressed into slices. The Fourier-transform infrared spectroscopy (FTIR) spectra were recorded using a Nicolet 6700 spectro-photometer (Thermo Scientific, USA).

Analysis of Sample Apertures

A pore size analyzer (ASAP 2460, Micromeritics Instrument Corp. the United States) was used, and the sample was degassed at 200 °C for 6 h at full nitrogen pore. The pore size of wood before and after treatment was measured.

Determination of Wood Chemical Composition

Cellulose, hemicellulose, and lignin are the three major components of wood, and their content changes determine the performance of the wood cell wall. The main components of the wood were determined using Washing fiber analysis by Van Soest. The sample (M , g) was washed by a neutral detergent at 105 °C for 1 h and filtered using a sand-core crucible. The solid residue was first washed with distilled water (50 mL) and then with acetone (50 mL), dried at 80 °C for 12 h, and weighed (W_2). The residue was allowed to evaporate at 105 °C for 1 h with 50 ml hydrochloric acid (2 mol/L, 50 ml). After cooling, the washing and drying steps were repeated as mentioned above, and the solid residue (W_3) was weighed. Subsequently, the residue was hydrolyzed with 72% sulfuric acid (45 ml) for 3 h, followed by the addition of 45 ml distilled water, and maintained at 20°C for 12 h. The mixture was filtered, washed, and dried, and then the third weight (W_4) was obtained. Finally, the dried residue was calcined at 550 °C for 3 h in a muffle furnace. The ash product was weighed after cooling in a vacuum dryer (W_5).

The cellulose, hemicellulose, and lignin contents were calculated according to the following formulae,

$$\text{Cellulose (\%)} = (W_3 - W_4) / M \times 100 \quad (6)$$

$$\text{Hemicellulose (\%)} = (W_2 - W_3) / M \times 100 \quad (7)$$

$$\text{Lignin (\%)} = (W_4 - W_5) / M \times 100 \quad (8)$$

where M is the weight(g) of sample, W_2 is the weight(g) of solid residue after neutral detergent cleaning, W_3 is the weight(g) of solid residue after hydrochloric acid treating, W_4 is the weight (g) of solid residue after sulfuric acid treating, W_5 is the weight (g) of ash product.

Micromorphology Analysis

The surface of the wood was smoothed with a small knife, and the section of wood (longitudinal) was studied through a scanning electron microscope (Hitachi SU8010, Japan). The acceleration voltage was 10–15 KV.

Statistical Analysis

The statistical differences in the water absorption, wet weight Ratio, and WPG samples at different treatment temperatures at the same treatment time were analyzed using one-way analysis of variance.

RESULTS AND DISCUSSION

Effects of Time and Concentration on Permeability

The wood was treated with different urea concentrations (3%, 5%, 7%, 9%, and 10%) for different periods (6, 12, 24, and 36 h). The wet weight ratio and WPG of the treated wood are shown in Fig. 1. The sample treatment with urea concentration 0 % was immersed in water.

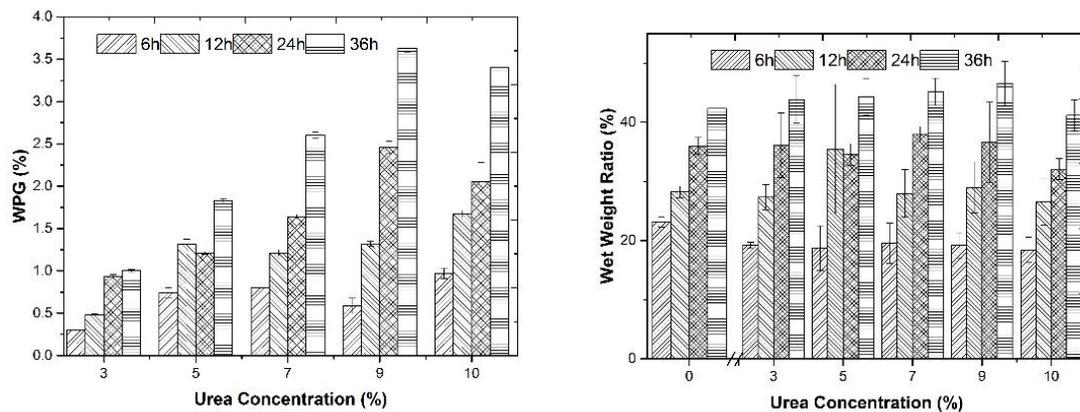


Fig. 1. Wet weight ratio and WPG (weight percent gain) of the wood treated with different urea concentrations for variable periods

Figure 1 shows that the wet weight ratio increased with an increase in immersion duration but was unaffected by the concentration of urea solution. It can be speculated that the amount of solution absorbed by eucalyptus made little difference when the solution concentration is low. For 10% urea-treated eucalyptus wood, the wet weight ratio was less than that of the sample treated with a urea solution concentration below 9%. Due to the

high concentration of the solution, the concentration difference was high, which increased pore tension and delayed the treatment of the solution on the wood. In addition, the higher the solution concentration, the less permeable the wood, as it contained more substantial substances and the solution viscosity was thick.

Figure 1 shows that the WPG of wood gradually increased with an increase in solution concentration and saturation duration. However, the WPG value was less than 4%. The low WPG of eucalyptus was caused by the following factors. First, the microstructure of eucalyptus, especially the sieve pores on the cell wall (Fig. 2), strongly affected the flow and saturation of liquid in the wood. The vessels are hollow cells in wood, which plays a major role in transporting water and nutrients. It is one of the key factors of wood permeability. The pits on the vessel wall are the main channels for lateral flow of fluid inside the wood. Therefore, the smoothness of wood conduits and their pits is the key to the permeability of wood. However, sieve shaped pits affect the porosity of wood because the fluid cannot pass smoothly due to the sieve mesh, thus affecting the permeability of wood (Zhang *et al.* 2022). The WPG of Poplar is greater than 80% when treated with a 30% furfuryl alcohol solution, while that of eucalyptus is less than 38% (Dong *et al.* 2016). This indicates that *Eucalyptus urophylla* is a difficult to soak species and a low permeability wood. Second, urea is a weak alkaline solution; the pH values of 3%, 5%, 7%, 9%, and 10% urea solutions were 7.95, 8.06, 8.08, 8.13, and 8.11, respectively. These pH conditions can dissolve lignin and hemicellulose as well as the inclusions (pectin, wax, *etc.*) and some main components in the wood cell wall (Oka *et al.* 2013; Shi *et al.* 2014). Third, the low concentration of urea solution and less urea in the solution caused a low WPG of the pretreated wood. In the low concentration of urea solution, the quality of urea is very small, and some urea remains in the wood after treatment.

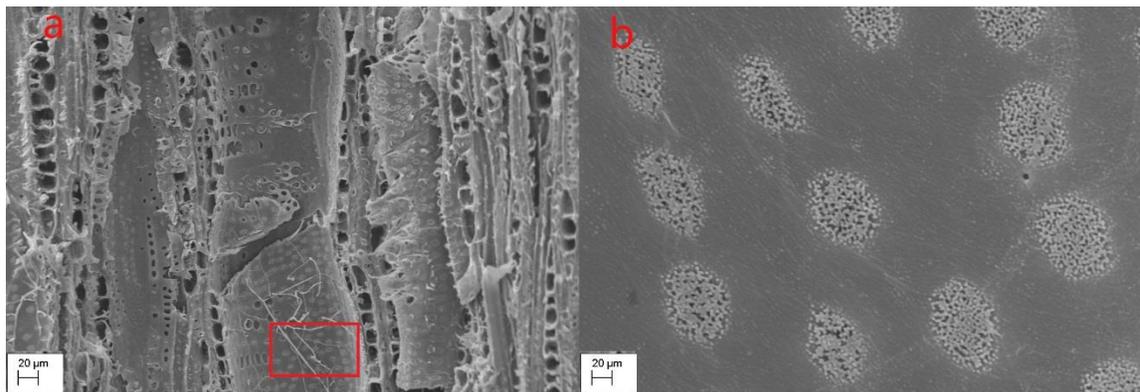


Fig. 2. SEM imaging of eucalyptus: a is the tangential direction microscopic diagram, b is the enlarged view on the vessel wall (i.e. the enlarged view inside the red frame in a)

Figure 3 shows that the volume change in eucalyptus wood treated with a low concentration urea solution for a short period decreased. The wood decreased in size, and the macro volume decreased. The eucalyptus wood treated with a high concentration urea solution (9 to 10%) showed a lower volume reduction. First, when eucalyptus was soaked in a low concentration solution, the wood cell inclusions (gum, tylosis, *etc.*) dissolved (Table 1). The hemicellulose and lignin in the wood were partially dissolved, and the wood fiber was destroyed (Fig. 4). Dissolution of extracts, hemicellulose, and lignin has a positive effect on wood permeability (Chen and Zavarin 1990). Moreover, a shorter

treatment time meant that less urea saturated the wood, which could not completely fill the gaps due to the reduction of wood content and main components. These two factors led to shrinkage of the wood. Eucalyptus wood treated with a high concentration urea solution for a long duration could fully supplement the gaps caused by the small-scale destruction of wood structure. This was due to the large amount of urea solution, which reduced the shrinkage of wood volume and maintained a high wood volume.

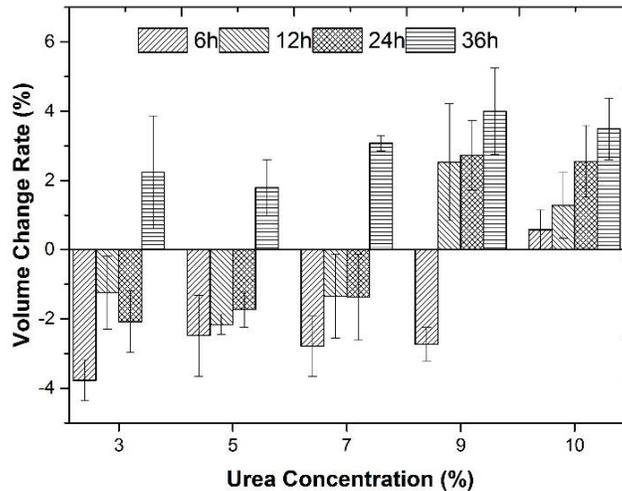


Fig. 3. Volume change rate of the wood after soaking in different urea concentrations for different periods

Table 1. Content of Alcohol-Benzene in the Sample After Treatment

Processing Conditions		Translations of Alcohol-Benzene (%)
Control		1.55
3% urea solution	room temperature and pressure, 12 h	1.2
5% urea solution		0.43
7% urea solution		1.34
90 °C	12 h, 5% urea solution under normal pressure	1.3
40 °C		0.69

The permeability of eucalyptus before and after treatment is shown in Fig. 5, where the WA of untreated eucalyptus was 23% after 6 h of immersion in water. After urea solution treatment, the WA of eucalyptus was higher than that of untreated wood but the volume was different. Although the WPG of wood increased with an increase in treatment time, the WA was not affected substantially, except for the wood treated for 12 h. The highest WA was observed for the wood treated with a 5% urea solution for 12 h. The water absorption rate reached 41%, which was 78.26% higher than that of the untreated wood. This finding indicated that the 5% urea solution had a large influence on improving the liquid permeability of *Eucalyptus urophylla* under normal temperature and pressure. First, 5% urea solution had less urea, which was not deposited in the wood cell cavity and did not occupy the internal space of wood, thus having little effect on the WA of wood. Some of the high concentrations of urea solution substances became deposited in the cell cavity (Fig. 4, as shown at the arrow), thereby blocking the cell wall pits and hindering water absorption into the wood. Second, the change in wood volume indicated that the treatment of wood with low concentrations of urea caused a reduction in the wood size. The wood

that was re-soaked in water had a greater absorption surface area. Third, the dissolution of extracts (Table 1) in wood also improved the water absorption of wood. The reason is that the extractives mostly were present on the inner wall of the cell and the pit mouth, which hinders the permeability of the wood. Therefore, the WA of wood was considerably higher than that obtained with a high concentration urea solution.

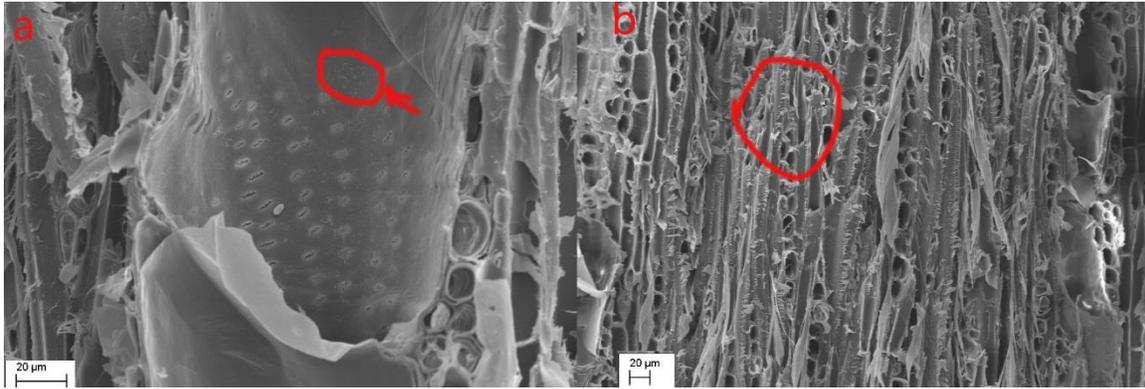


Fig. 4. Microstructure of the urea-treated wood: a is the microscopic images of the urea-treated wood, which shows that the holes on the pipe wall are cracked. b is the chordal microscopic images of urea-treated wood, in which the wood fiber is torn.

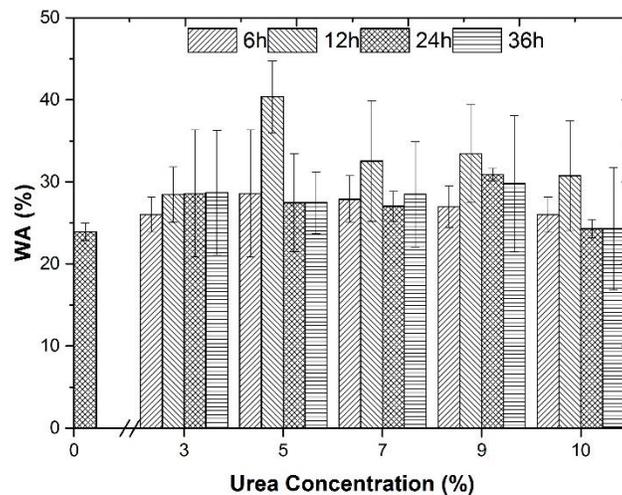


Fig. 5. WA of wood after treatment

Effect of Reaction Temperature on the Permeability of Eucalyptus Wood

The effects of different temperatures (20, 40, 90 °C) and durations (6, 8, 12 h) of urea treatment on wood permeability are shown in Table 2 (under the same concentration). At the same temperature, the wet weight ratio of wood increased with treatment time, indicating that duration had an important effect on the absorption of liquid by the wood. Concurrently, the wet weight ratio of wood increased with an increase in solution temperature. The higher the temperature, the higher the fluidity of the liquid (Li *et al.* 2011), and therefore, the lower the viscous resistance to flow of the liquid to wood pits, which led to an increase in the wet weight ratio of wood. However, the wet weight ratio of the wood treated at 40 °C for 12 h was lower than that of the wood treated at 20 °C. The reason may be that the urea solution dissolved the components of the wood and leached, resulting in a reduced wet weight ratio. The WPG was similar to the wet weight ratio.

The treatment of wood with a urea solution resulted in the combination of amino groups in the solution and hydroxyl groups in the wood cell wall. The higher the reaction temperature, the faster the molecular movement and the higher the collision frequency between molecules, thus speeding up the reaction rate. In the initial stage, the number of hydroxyl groups that can be replaced (the soluble content) was higher (Cai 2015); hence, the reaction rate was fast (at a certain temperature). After most of the reactions were completed, the reaction rate gradually decreased; hence, the wet weight ratio of the wood treated for 12 h was less than that of the wood treated for 8 h.

Table 2. Properties of the Wood Treated at Different Temperatures and Different Immersion Periods

Impregnation Time (h)	Solution Temperature (°C)	Wet Weight Ratio (%)	WPG (%)	WA (%)
6	20	18.70(3.80) ^a	0.74(0.60) ^b	28.59(7.76) ^b
	40	25.35(0.98) ^a	0.87(0.03) ^b	22.08(2.86) ^b
	90	39.39(2.31) ^a	1.61(0.29) ^b	25.77(1.45) ^b
8	20	-	-	-
	40	28.01(2.35) ^a	1.03(0.13) ^b	26.06(7.95) ^b
	90	48.25(8.34) ^a	2.66(0.65) ^b	27.50(7.47) ^b
12	20	34.56(1.82) ^a	1.21(0.16) ^b	40.37(14.37) ^b
	40	30.98(1.51) ^a	0.80(0.14) ^b	25.74(1.77) ^b
	90	46.12(2.74) ^a	8.35(3.27) ^b	22.92(3.12) ^b

Note: The values in brackets are standard deviations. The letter a next to the mean indicates that the samples at different treatment temperatures at the same treatment time are significant at the 5 % significance level. The mark with the letter b is not significant.

Table 2 shows that the temperature of the urea solution had little effect on the permeability of eucalyptus wood. The increase in solution temperature could improve the WPG of wood but had little effect on the WA. The urea was saturated into the wood, which hindered the absorption of water. At 20 °C, the urea solution dissolved the wood inclusions at a treatment time of 12 h. This formed a liquid flow channel and increased the permeability of wood.

Effect of Urea Solution on the Chemical Constituents of Eucalyptus

The Fourier-transform infrared spectroscopy of eucalyptus treated with different urea concentrations is shown in Fig. 6 (all samples treated at 20 °C). After treatment with different urea solutions, the basic chemical composition of wood changed slightly. The O-H stretching vibration near 3,334 cm⁻¹ and the band vibration near 2,918 cm⁻¹ (asymmetric and symmetric methyl and methylene stretching vibrations in wood components) of the wood treated with 3%, 5% and 10% urea solutions decreased slightly (Kubovsky *et al.* 2020). Additionally, the spectral peak was transferred to a lower wavelength, with associated broadening of the band. This may be caused by the oxidation and hydrolysis of acetyl groups in hemicellulose or the crosslinking of free hydroxyl groups. Alternatively, it may be caused by the change in structure and relative composition, including the cellulose crystallinity (Spiridon *et al.* 2011). This result indicated that the vibration intensity as well as the number of hydroxyl groups of the wood decreased after treatment.

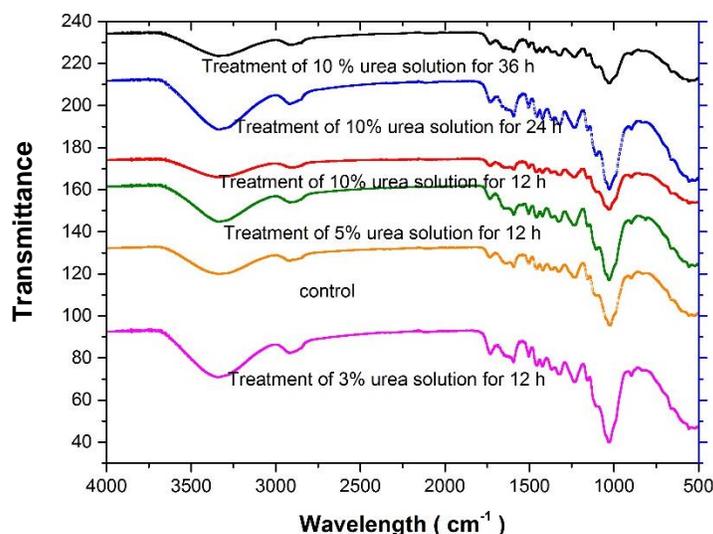


Fig. 6. FTIR spectrum of wood under different treatment conditions

In the fingerprint identification region of $1,800\text{--}800\text{ cm}^{-1}$, the FTIR spectra of the treated wood exhibited slight changes. The FTIR spectra included bands between $1,750$ and $1,700\text{ cm}^{-1}$, reflecting changes in the functional groups of lignin and hemicellulose (carbonyl, ester, *etc.*) (Esteves *et al.* 2013). The results showed that vibration weakened at $1,732\text{ cm}^{-1}$ (Fig. 6). This change may be due to the cleavage of the acetyl group of hemicellulose under the action of urea and the deacetylation reaction with a free hydroxyl group to form acetic acid. The dissolution of hemicellulose increased with an increase in urea concentration (Sun and Li 2010). Coupling of the carbonyl group with other double bonds (such as aromatics and alkenes) and the increase in the carbonyl or carboxyl group were because of the urea solution reaction (Esteves *et al.* 2013). Degradation of lignin and hemicellulose occurs in wood under alkaline conditions (Xu *et al.* 2020).

The stretching of the C=C aromatic skeleton bond vibration of the benzene ring in lignin was near $1,590\text{ cm}^{-1}$. The strength of wood treated with 3% and 10% urea solutions for 24 h was slightly reduced, at approximately $1,590\text{ cm}^{-1}$, indicating that the lignin in the treated wood was dissolved (Xu *et al.* 2020). When the treatment duration was short, the lignin was softened, carbohydrates (especially glucomannan) were lost, and pectin was dissolved.

The $1,460\text{ cm}^{-1}$ band represents asymmetric CH deformation in lignin, and the $1,420\text{ cm}^{-1}$ band represents the aromatic skeleton vibration in lignin, CH deformation, and carbohydrates. These FTIR band intensities of wood treated with a 10% urea solution for 12 h and 36 h decreased, which was caused by lignin degradation (František *et al.* 2016). The bands at $1,267\text{ cm}^{-1}$ (C-O extension of guaiacol) and $1,219\text{ cm}^{-1}$ (C-O extension of syringyl) increased slightly in the wood treated with 3%, 5% and 10% urea concentrations for 12 h, 12 h and 24 h, respectively. In summary, the urea solution caused hemicellulose and lignin in the wood to dissolve partially, and the chemical structure of the wood changed.

Table 3 shows the changes in the chemical composition of wood after urea treatment. The contents of benzene-alcohol reduced, cellulose, and lignin components increased, and hemicellulose component decreased, indicating that hemicellulose of the wood was degraded upon urea treatment, resulting in a reduction in its content. After the

wood fiber was treated with a low concentration alkali solution, the pectin on the fiber surface was removed. When the concentration of alkali solution was in the range 2 to 8%, the pectin in the fiber gradually dissolved completely and the hemicellulose partially dissolved. However, when the concentration was 8 to 12%, it was not sufficient to dissolve the lignin (Qin *et al.* 2010). This indicates that a high concentration urea solution does not improve wood permeability, and with the overall mass generally unchanged. The increase of lignin quality may be caused by the addition of other components to lignin quality during the test. In addition, the reduction of extracts will also increase the permeability of wood. Zeni *et al.* (2013) reported that fungi consume wood extracts, increasing the vertical gas permeability of wood. Therefore, the extraction of wood extract is also a factor in the increase of wood permeability (Table1).

Table 3. Wood Composition Before and After Urea Treatment

Treated Wood	Cellulose (%)	Hemicellulose (%)	Lignin (%)
control	47.56	28.75	20.13
5 % treatment for 36 h at 20 °C	49.12	24.47	23.03

Effects of Urea Pretreatment on the Specific Surface Area and Pore Size of Eucalyptus Wood

The pores in wood are the channels for gas and liquid permeation and, additionally, the key to the treatment modification of wood. To analyze whether the pore size and volume of eucalyptus wood changed after urea treatment, the specific surface areas of the treated eucalyptus wood were measured.

The specific surface area and pore structure of the samples are shown in Fig. 7 and 8. The cumulative pore volume of the untreated wood increased rapidly in a pore size range of 0 to 20 nm, which indicated that there were many pores in this range. The cumulative pore volume in the diameter of 21 to 60 nm increased slowly, indicating that the pore volume was less in this range (He *et al.* 2017; Wang 2020). The cumulative pore volume in the range of >60 nm remained unchanged. This indicated that there were few large-aperture pores, which was confirmed by the infiltration difficulty. After the wood was treated with a 5% urea solution for 12 h at 20 °C, the cumulative pore volume of the wood rapidly increased in the pore size range of 0 to 15 nm and slowly increased in the pore size range of 16 to 80 nm. When the pore size was >80 nm, the cumulative pore volume curve flattened. This indicated that when comparing treated and untreated wood, the treated wood had more pores within the size range of 16 to 80 nm, indicating that the mesoporous content in the wood increased. After urea treatment, the pore size of wood increased due to the partial dissolution of hemicellulose and the removal of inclusions. A high cumulative pore volume can also be the result of a high content of micropores with poorer accessibility (Zauer *et al.* 2014).

The increase in the pore volume of the untreated wood indicated resulted in growth peaks in the ranges of 0 to 5 nm and 15 to 20 nm (Fig. 8). The increase in pore volume decreased and then flattened in the 20 to 60 nm range. When the pore volume >60 nm, the increase in pore volume was close to 0, which indicated that the main pores in eucalyptus wood were micropores and mesopores and that it contained a smaller number of macropores.

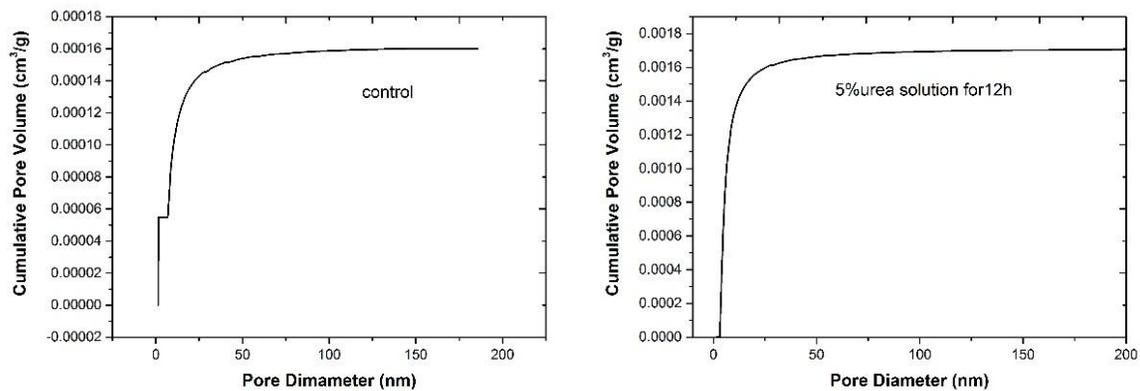


Fig. 7. Relationship between wood pore width and cumulative pore volume

After treatment with the 5% urea solution for 12 h at 20 °C, the increase in pore volume of the treated wood was mainly in the pore size range of 3 to 13 nm. It can be inferred that the increase in the internal specific surface area of the treated wood was mainly due to the increase in the number of micropores and mesopores in this range. According to Wang (2020), the micropore volume contributes the most to specific surface area; therefore, the permeability of wood increases due to an increase in the number of micropores.

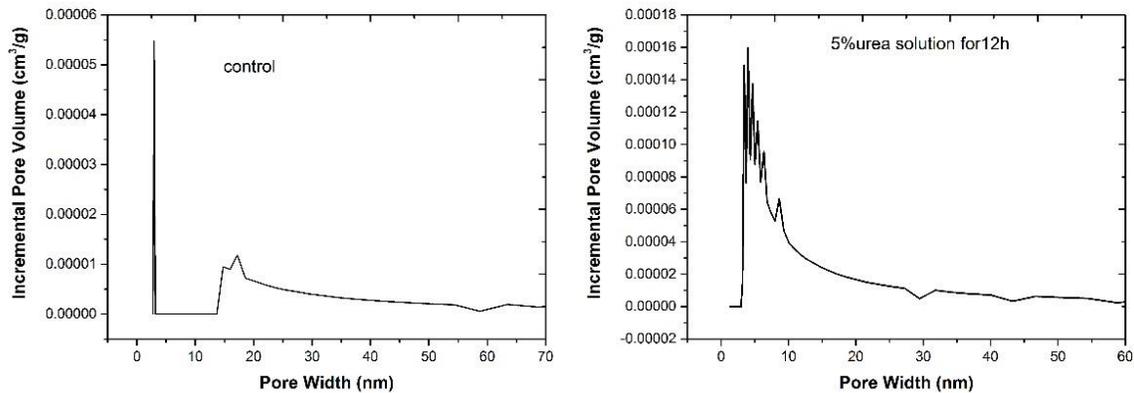


Fig. 8. Relationship between wood pore width and incremental pore volume

Mechanism of Improvement of Eucalyptus Wood Permeability via Urea Treatment

Treating eucalyptus wood with a weak alkaline urea solution has two main advantages. First, the urea solution has good swelling properties (Xu *et al.* 2020); hence, it can cause the wood fiber cell wall to swell, expand the distance between microfibrils, and destroy the bonding between fibers. Second, weak alkaline solutions can dissolve wood internal inclusions, hemicellulose and lignin, disrupt the wood fiber structure, increase the number of micropores and mesopores, and reduce the distance between microfibrils, thereby affecting the elastic modulus and stiffness of the wood. Concurrently, hemicellulose and lignin were partially removed by the urea solution, and miniscule gaps appeared on the cell walls, which improved its permeability. In summary, urea solution improves the permeability and water absorption of wood, and its effect is similar to that of a surfactant.

CONCLUSIONS

1. The effect of urea concentration on the permeability modification of wood was clear. Optimal conditions for the permeability modification effect included treatment with a 5% urea solution at 20 °C, under atmospheric pressure, for 12 h. The water absorption (WA) of the treated eucalyptus wood was 41%, which was 78.3% higher than that of the untreated wood. At the same urea concentration, higher temperatures improved the treatment effect.
2. The mechanism of urea solution to improve the permeability of wood was attributed to the weak alkaline urea that dissolves the internal contents of wood, destroys the components of hemicellulose and lignin on the wood cell walls, and partially degrades hemicellulose and lignin. This results in the formation of pores on the wood cell wall, thereby increasing the liquid infiltration.
3. Although urea treatment can improve the permeability of eucalyptus, it changed microstructure and composition of treatment wood.

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Conflicts of Interest

There are no conflicts of interest to declare.

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