

EFFECT OF CHEMICAL MODIFICATION AND HOT-PRESS DRYING ON POPLAR WOOD

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Urea-formaldehyde prepolymer and hot-press drying were used to improve the properties of poplar wood. The wood was impregnated with the prepolymer using a pulse-dipping machine. The impregnated timbers were compressed and dried by a multilayer hot-press drying kiln. The drying rate was more rapid during the chemical modification and hot-press drying than conventional kiln-drying. In addition, the properties of timber were also enhanced obviously. When the compression rate was 28.6%, the basic density, oven dry density and air-dried density of modified wood improved 22%, 71%, and 70%, respectively. The bending strength and compressive strength parallel to grain increased 60% and 40%. The water uptake of treated wood was significantly decreased compared with the untreated wood. The FTIR analysis successfully showed that the intensity of hydroxyl and carbonyl absorption peaks decreased significantly, which was attributed to a reaction of the NHCH_2OH of urea-formaldehyde prepolymer with the wood carboxyl ($\text{C}=\text{O}$) and hydroxyl ($-\text{OH}$) groups. The XRD results indicated that the degree of crystallinity increased from 35.09% to 36.91%. The morphologic models of chemical within wood were discovered by SEM.

Keywords: Chemical modification; Hot-press drying; Urea-formaldehyde prepolymer; Crosslinking mechanism

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INTRODUCTION

To satisfy the increasing demand for forest products, fast-growing trees such as poplar grown in managed plantations are being seriously considered for future supply needs. The wood of all poplar species has relatively low density and diffuse porous structure. The strength properties of poplar are also relatively low.

Therefore, different methods have been developed over many years to overcome the disadvantages. These methods involve chemical modification and hot-press treatment. Major research on the approach has been carried out to improve the physical properties. The physical properties could improve, but the mechanical properties of wood decrease during thermal treatment and hot-press drying at high temperature (Poncsak et al. 2006; Gunduz and Aydemir 2009; Gunduz et al. 2009).

Chemical modification of wood can be defined as a process of bonding a reactive chemical to a reactive part of a cell wall polymer, with or without catalyst, to form a covalent bond between the two (Rowell 2006). This excludes chemical impregnations (dipping or soaking non-bonding chemicals in carrier solvents), polymer inclusions, coatings, and heat treatments.

The polysaccharides (cellulose and hemicelluloses), lignin, extractives, and inorganic constituents are mainly responsible for the properties and performance of wood. Connecting studies on the chemistry of wood with observation on performance, it became clear that it was mostly the cell chemistry and properties that were responsible for the observed performances (Rowell 2006).

Rowell and coworkers (Rowell and Gutzmer 1975; Rowell et al. 1976) have studied the properties of wood chemically modified with propylene and butylenes oxides catalyzed with triethylamine. In their work, the reactions were carried out in a stainless steel reactor at 120 °C and 150 lb/in² nitrogen pressures.

Thermal modification results in formation of degradation products, which are predominantly acetic and formic acid, a small amount of phenolic compounds, other aromatic compounds, and wood extractives. The gases evolved during treatment are mainly carbon monoxide, carbon dioxide, and methanol (Tjeerdsma et al. 1998). The chemistry of the modification of the polymeric wood constituents of heat treated wood was studied by Tjeerdsma et al. (2000) using CP MAS ¹³C NMR, which showed that acetic acid is liberated from the hemicelluloses, which further catalyses carbohydrate cleavage, causing a reduction of degree of polymerization of the carbohydrates.

Gindl et al. (2007) showed that spruce wood samples could be impregnated with an aqueous solution of melamine-formaldehyde resin. After polymerization, the tangential compression strength of treated samples was 82% higher compared to the untreated reference, and radial compression strength had increased by 290%. Thus, the improvement of strength is attributed to modification of the cell wall and not to filling of tracheid lumina. Yield behavior under excessive compression load changed from plastic buckling in the reference samples to brittle fracture of cell walls in the treated samples. Even though a certain increase of brittleness has to be tolerated, it was demonstrated that melamine-formaldehyde reinforcement of cell walls distinctly improved the properties of spruce in the transverse compression.

Zhang (2006) showed that impregnation of methacrylates into sugar maple resulted in vessel and lumen filling. Brinell hardness (HB), and hardness modulus (MH) were generally enhanced through impregnation and in-situ polymerization. WPC with different monomers and their different combinations improved both Brinell hardness and hardness modulus. Modulus of elasticity was enhanced through impregnation and in-situ polymerization. Different treatments had the same impact on the modulus of elasticity.

Gao and Li (2007) pointed out that the dimension stability and mechanical property of wood treated by only acetone would be reduced, since acetone spoiled the crystallinity of celluloses and the interface between the cellulose and lignin. The dimensional stability of wood modified by only P-MDI will be well improved, because hydrophilic hydroxyl groups were blocked by isocyanate, and PU resin was subsequently deposited, while the mechanical properties were reduced relatively little. Both dimensional stability and mechanical properties of wood modified by foaming PU resin were improved, which was attributed to the combinations of some hydroxyl groups blocking, the hindrance of water movement in wood, and wood cell wall reinforcement by the foamed PU.

In the present work we have carried out chemical modification and hot-press treatment of solid wood blocks of poplar (*Populus euramevicana* cv. 'I-214') with urea-

formaldehyde prepolymer. The aim of this study was to evaluate the physical and mechanical strength, the functional groups, the crystallinity, and the SEM images of poplar modified under the pulse-dipping machine and hot-press drying kiln, with a view of developing a simple and effective means of modifying wood.

EXPERIMENTAL

Materials

The fresh poplar (*Populus euramevicana* cv. 'I-214') wood samples used during this study were obtained from Beijing, China. They had initial moisture contents that ranged from 60 to 70 % before they were impregnated.

Synthesis of Urea-formaldehyde Prepolymer

A three-necked flask was charged with urea, formaldehyde, and ammonia at a certain molar ratio (Pu et al. 2009c). The reaction mixture was stirred and heated to 30 °C for 3 hours. Then sodium hydroxide or hydrochloric acid was used to adjust the pH of the prepolymer from 7 to 8. Finally, the reaction mixture was transferred into a container and sealed.

Pulse-dipping and Hot-press Drying

The dimensions of the wood samples for the impregnation tests were 200 mm in diameter and 1000 mm in length. The fresh poplar was impregnated with carbamide (18 % w/w) and the prepolymer (15 % w/w) by the pulse-dipping machine at the pressure of 0.7 - 0.8 MPa for 30 min (Pu et al. 2009a). After the impregnation, impregnated logs were sawn into blocks about 70 mm thick (tangential) x 140mm wide (radial) x 1000 mm length (longitudinal) for hot-press drying. It takes about 120 hrs for drying, and the pressure on the timber was 0.5 MPa with compression ratio of 28.6 % (Pu et al. 2009b).

Mechanical Properties

Ten specimens of untreated and treated were analyzed with a universal mechanical testing machine (MWW-50). Tests were carried out according to GB/T 1936.1 - 91 (Method of testing in bending strength of wood, China), GB/T 1935 - 91 (Method of testing in compressive strength parallel to grain of wood, China), and GB/T 1933 - 91 (Method for determination of the density of wood, China).

Water Uptake

In order to measure the water absorption characteristics of untreated and treated wood, rectangular specimens were prepared having dimensions of 20 mm (L) x 20 mm (T) x 20 mm (R) according to GB/T 1934.1-2009 (Chinese Standards). The specimens were dried in an oven at 105 °C, cooled in a dessicator containing silica gel, and immediately weighed. The specimens were immersed in distilled water. After immersion, the excess water on the surface of the specimens was removed using a soft cloth. The weight of the specimens was then taken. The increase in the weight was calculated using the following equation,

$$\text{Water Uptake(\%)} = \frac{m - m_0}{m_0} \times 100 \quad (1)$$

where m is the final weight and m_0 is the original weight.

FTIR Characterization

FTIR spectra were measured directly from untreated and treated wood using a Tensor 27 (Bruker, Germany) device in the range of 4,000 to 600 cm^{-1} . Pellets were prepared from the mixtures of the samples and KBr (1:100 in weight). 32 scans were accumulated at a resolution of 2 cm^{-1} .

X-Ray Diffraction

Crystallinity of the samples of untreated and treated was evaluated by X-ray diffraction, using a Shimadzu diffractometer model XRD 6000. The measurement conditions were: $\text{CuK}\alpha$ radiation with graphite monochromator, 30kV voltage, and 40 mA electric current. The patterns were obtained within a 10 to 50° 2θ angular interval with 0.05° step and scan speed of 2 °/min. The degree of crystallinity was calculated as the ratio of the intensity differences in the peak positions.

Scanning Electron Microscope

A JSM 5900 model scanning electron microscope (SEM) was used to observe the untreated and treated wood. Samples to be observed under the SEM were mounted on conductive adhesive tape, sputter coated with gold, and observed in the SEM, using a voltage of 15kV.

RESULTS AND DISCUSSION

Mechanical Properties

Results for the density of the wood are summarized in Fig. 1. The treated wood exhibited higher density in comparison to the untreated wood samples. According to Fig. 1, the effect of modification was significant. The basic density of wood treated increased 22% compared with the untreated wood samples. The oven-dried density and air-dried density of treated wood were increased by 71% and 70%, respectively. The increase in density may be caused by the formation of bonding between the wood fiber and the urea-formaldehyde prepolymer. The impregnation and compression can also increase the density of wood. All of the treatment can improve the property of wood.

Mechanical properties such as bending strength and compressive strength parallel to grain are shown in Fig. 2. The treated wood exhibited significantly higher bending strength and compressive strength parallel to grain in comparison to the untreated wood samples. The bending strength and compressive strength parallel to grain increased 60% and 40% compared to the untreated wood samples.

The reason may be that the density increased. Some hemicellulose, due to its poor chemical stability is easily recombinant and subject to degradation in the hot-press drying

kiln. What's more, the carbamide and prepolymer filled in the gaps in the wood cell, which improved the mechanical properties.

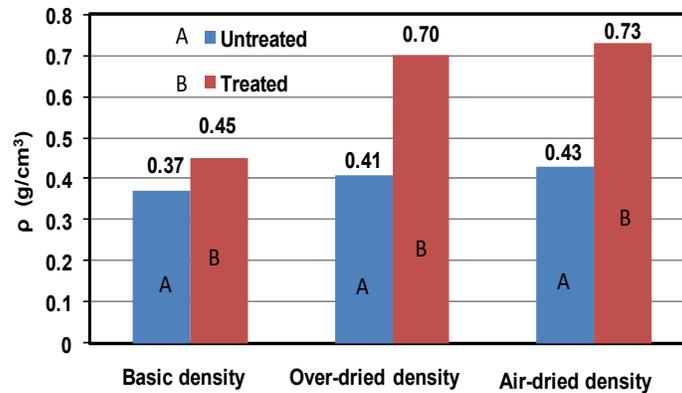


Fig. 1. Density of untreated and treated wood

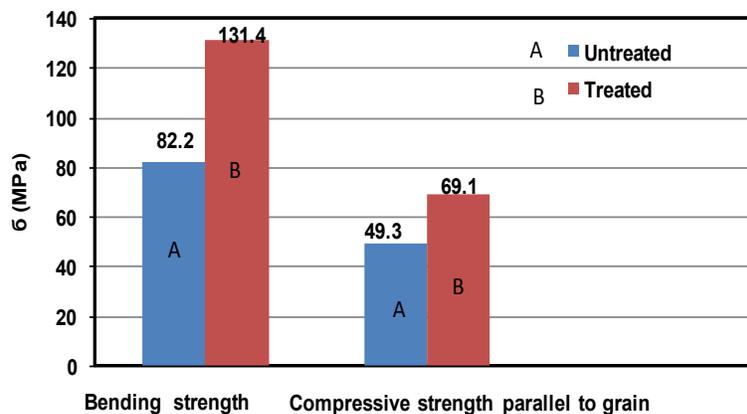


Fig. 2. Mechanical properties of untreated and treated wood

Water Uptake

Water absorption properties of untreated and treated wood are shown in Fig. 3. The figure shows the results for cold water immersion during 54 hrs. As shown, the water uptake of treated wood was significantly decreased compared with untreated samples. Both treated and untreated wood absorb water quickly within 24 hrs. The water uptake of treated wood was nearly stable after 24 hrs, while the untreated wood was still increasing rapidly.

Treated wood had lower water content compared to the untreated samples. In a wood cell, the hydroxyl groups in the wood promote increased water absorption. However, the chemical modification reduced the hydroxyl groups and reduced the water absorption due to the crosslinking reaction between urea-formaldehyde prepolymer and the wood (Rahman et al. 2010).

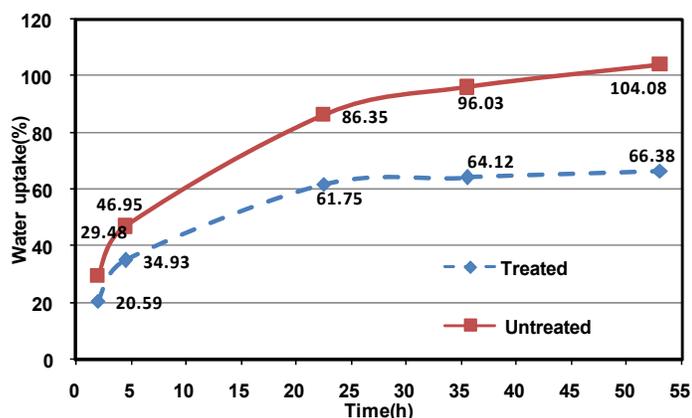


Fig. 3. Water uptake for untreated and treated wood

FTIR Analysis

FTIR spectroscopy was used to characterize chemical changes in the modified wood (Fig. 4). Significant changes in the FTIR spectra were observed after the modification. FTIR spectra of treated wood showed a significant reduction in the -OH absorbance at 3350 cm^{-1} . The decreasing in the intensity of bands at 1457 cm^{-1} (CH_2 scissoring) is indicative of a decrease in methylene groups as a result of modification. They indicate a crosslinking reaction between the urea-formaldehyde prepolymer and the hydroxyl groups of the cellulose surface (Pandey et al. 2010; Rahman et al. 2010). The decrease in the intensity at 1741 cm^{-1} is attributable to a reduction of absorption associated with carbonyl ($\text{C}=\text{O}$) stretching vibrations, indicating that xylan in the hemicelluloses degradation occurred and carbonyl or reaction involving the prepolymer occurred. The absorption peak at 1665 cm^{-1} corresponds to amide ($\text{N}-\text{C}=\text{O}$), which is from the carbamide. This is due to the bond between the function groups of $-\text{NHCH}_2\text{OH}$ of the urea-formaldehyde prepolymer and the wood carboxyl $\text{C}=\text{O}$. The reduction in the $\text{C}-\text{O}-\text{C}$ absorbance at 1244 cm^{-1} , which is attributable to the hydroxyl stretching vibration absorption peak, indicated degradation of the lignin.

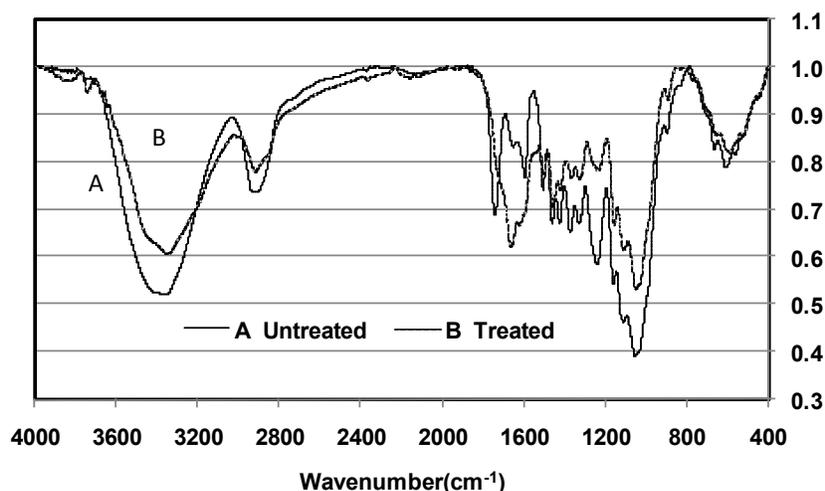


Fig. 4. FTIR spectrum of untreated and treated wood

In summary, the spectral results showed that the structure of wood lignin, cellulose, and hemicelluloses had been changed by the chemical modification with urea-formaldehyde prepolymer. Chemical reactions occurred between the wood components and prepolymer involved in crosslinking during the treatment. The reaction played a key role in enhancing the mechanical properties and improving the density of the wood.

XRD Diffraction

Figure 5 presents the results of X-ray diffraction tests for untreated and treated samples. The spectrum corresponding to the untreated and treated wood shows diffraction peaks at the following 2θ angles: 17° , 22.5° , and 35° , which correspond to the cellulose crystallographic planes I_{101} , I_{002} , and I_{040} , respectively (Mulinari et al. 2010). The numerical values for X-axis (2θ axis) of untreated wood are 16.4° , 22.0° , and 34.6° . The numerical values for X-axis (2θ axis) of untreated wood are 16.8° , 22.4° , and 35.2° . The position of these peaks changed a little, which indicated that the structure of cellulose did not change in comparison with the untreated wood. According to the experimentation, untreated and treated wood showed 35.09 % and 36.91 % crystallinity, respectively. These values can be attributed to modification of the wood by the urea-formaldehyde prepolymer. The reason may be that the prepolymer has been injected into the lumen of wood cell. The crosslinking reaction occurred between the groups of prepolymer and the surface hydroxyl (OH) groups of wood. A quasi-crystalline form was generated in the X-ray diffraction, but actually it may not represent an increase in the crystallinity of cellulose (Wu et al. 2004).

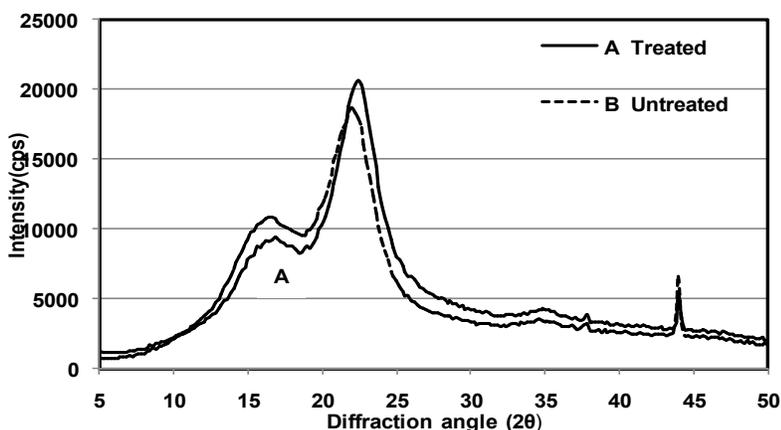


Fig. 5. XRD curves of untreated and treated wood

Scanning Electron Microscopy

Scanning electron micrographs (SEM) of untreated and treated wood are shown in Fig. 6. The SEM micrographs showed that the untreated wood surfaces were covered with an uneven layer with a number of void/hole spaces, while the treated wood surfaces were smooth (see Fig. 6 (a) and (b)). The smooth surface may be caused by the good penetration of the monomer mixture to the cell wall and vessels of the wood (Rahman 2010). Figure 6 (c) and (d) showed the transaction of untreated and treated wood. The cell wall and vessels were filled with impregnated chemicals and has been deformed by the compression during the hot-press process.

The chemical can be immersed in the wood fiber and other vertical cells under the pulse-dipping pressure. The chemical particles became distributed as rod-like structures or discontinuously in the wood cell. The SEM analysis indicated that the prepolymer was impregnated into cell wall and cell cavities of wood.

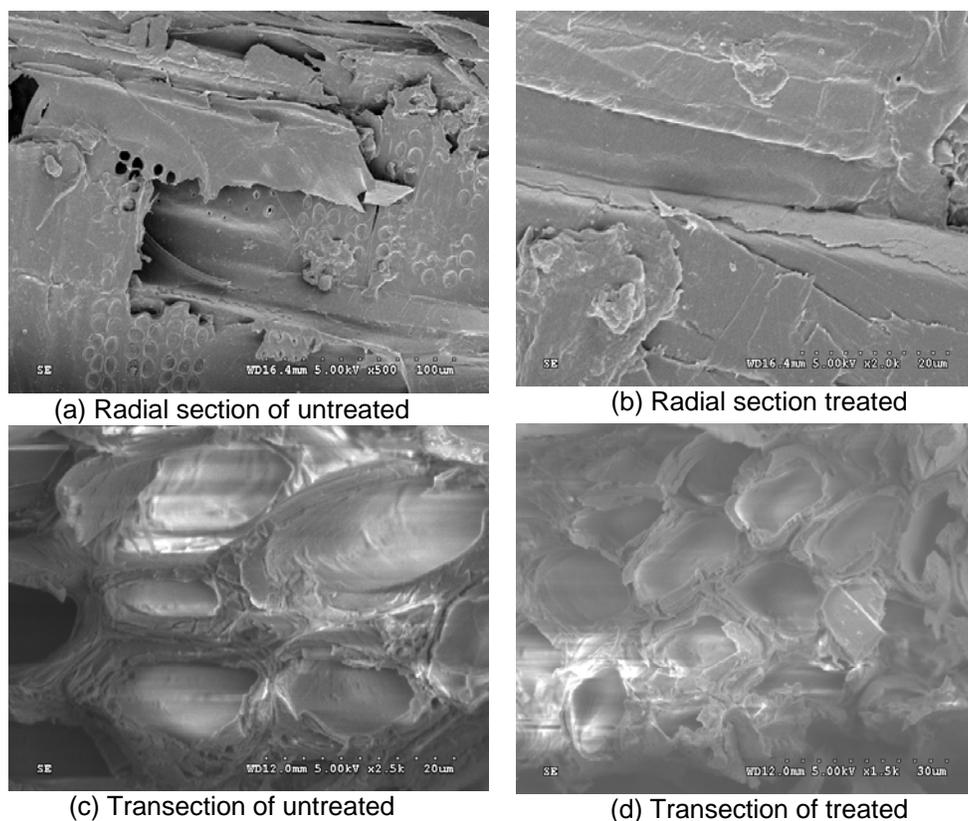


Fig. 6. SEM micrographs of untreated and treated wood

CONCLUSIONS

1. The properties of poplar wood can be improved by chemical modification and hot-press drying treatment. This approach can expand the range of utilization for fast-growing wood species such as poplar wood.

2. The basic density, oven dry density, and air-dried density of modified wood were improved by 22%, 71%, and 70%, respectively as a result of the chemical treatment. The bending strength and compressive strength parallel to grain were increased 60% and 40%.

3. FTIR test results confirmed that crosslinking reactions occurred during the process. The water uptake of treated wood was significantly decreased compared with the untreated wood. The degree of crystallinity increased from 35.09% to 36.91%.

4. The chemical treatment was not totally effective for improving the adhesion between the wood and prepolymer. Evidence of improved adhesion could be observed in SEM micrographs.

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