Study on Urea-Formaldehyde Prepolymer and Hot-Press Treatment of Italian Poplar Wood

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Abstract

The purpose of this study was to modify Italian poplar (*Populus euramevicana* cv. 'I-214') wood with urea-formaldehyde prepolymer followed by hot pressing. The timbers were impregnated with urea-formaldehyde prepolymer using a pulsed-dipping machine and cured in a hot press. The results showed that the timbers could be easily compressed and cured at temperatures between 90°C and 120°C. The characteristics and quality of the modified wood were up to A grade according to Chinese Standard GB/T 6491-1999. The air-dried density of modified wood was improved by 58 percent, and the hardness in the transverse, tangential, and radial directions was increased by 67, 210, and 160 percent, respectively. The bending strength was improved by 78 percent; the bend elastic modulus was improved by 66 percent. The water absorption of treated wood decreased relative to that of the untreated timbers. Fourier transform infrared spectroscopy of the modified wood showed a significant reduction in the C=O absorbance at 1,750 cm^{-1}. The peak at 1,645 cm^{-1} was found to increase as a result of treatment with the prepolymer.

Italian poplar (*Populus euramevicana* cv. 'I-214') is a fast-growing tree species that is widely used in pulp, fiber, and chip industries and in packaging box production. However, poplar wood does have disadvantages, such as the lower mechanical properties, low density, and diffuse porous structure, which limit the use of this species in certain applications, including carpentry, furniture components, and building construction (Dwianto et al. 1998, Henrik 2009). Many methods have been used to improve the mechanical and durability-related properties of poplar, including impregnation and chemical modification (Waldemar and André 2004).

The polymeric structure of a woody cell wall mainly consists of cellulose, hemicellulose, and lignin (Devi et al. 2007). Each of these components has hydroxyl groups, which play a key role in water–wood interactions. Many reports have been published regarding compression of wood, such as surface compression in the radial direction of wood with microwave irradiation (Inoue et al. 1990, Takahisa and Kose 1998, Pradeep et al. 2008). One study reported that almost complete fixation of compressed wood can be achieved by steaming with a urea-formaldehyde (UF) prepolymer (Ito et al. 1998). However, this steaming process demands many steps and much time.

In 1997, Honda patented a process whereby wood at moisture contents below the fiber saturation point is heated under pressure to a temperature above the softening temperature of cellulose using a cyclic pressure process. A similar process of elevated temperature and cyclic pressure using dry wood was patented by Hasegawa and Tomita (1997). Another process, called the PLATO process, has also been reported. It consists of three succeeding steps in which the cell wall material is modified. In the first step (hydrothermal phase), green wood is heated under pressure at temperatures between 160°C and 190°C. In the second step (conventional wood drying process), the wood is dried to a moisture content below 10 percent. In the third step (curing reactions where reaction products are condensed into a modified polymeric complex), the wood is cured at a temperature between 170°C and 190°C at atmospheric pressure in the absence of air. The final product has a lower hygroscopicity and an improved dimensional stability in comparison with controls (Tjeerdsma et al. 1998).

Shmulsky et al. (2006) reported the effects of restraint on warp during drying when 4 by 4-inch southern yellow pine (*Pinus radiata* D. Don) lumber was initially kiln dried, pressure treated, and kiln dried again after treatment. A statistically significant reduction in average warp (e.g., crook and twist) was found for the restraint-dried material. Lumber grade mix, based on warp criteria, was higher for the restraint-dried material following both initial kiln drying and kiln drying after treatment.

It has also been reported (Ayhan and Oktay 2008) that drying 22- to 60-mm-thick pine at temperatures between 120°C and 130°C resulted in a decrease in compression, bending, and tensile strength of approximately 8 percent and a decrease in shear strength of approximately 30 percent. Wood also became darker in color.

Rowell and Konkol (1987) showed that chemically modifying wood could greatly improve the dimensional stability of solid wood products. The mechanism for this improvement was based on derivatizing hydroxyl groups in wood as well as bulking the lumens. The increase in volume resulting from the chemical modification was approximately equal to the theoretical volume of chemical added. Chemically modified wood swelled to near its green dimensions; therefore, little additional swelling occurred when the modified wood was wetted with water. Wood modified with anhydrides, epoxide, and isocyanate reduced swelling as much as 65 to 75 percent, with chemical weight gains of 20 to 30 percent (Sharifah et al. 2005).

Kameyama et al. (1994) impregnated wood with a thermosetting, fiber-penetrating resin and then cured the wood without compression. They reported that reaction with formaldehyde creates a bridge across two adjacent hydroxyls in the wood substrate. Forming oxymethylene (oxane) bridges between hydroxyls is termed formalization. Formalization was observed to impart a greater dimensional stability to Sitka spruce (*Picea sitchensis*) samples compared with acetylation.

Formaldehyde cross-linked wood has also been reported (Akitsu et al. 1993). That study demonstrated wood that was chemically modified to improve dimensional stability retained the vibrational properties of the unmodified wood and, thus, may have potential for use in musical instruments. UF resin with low molecular weight remains the most widely used thermosetting agent for interior applications even after stringent formaldehyde emission requirements forced UF manufacturers to modify their formulations. With impregnation, the resins can penetrate into the wood cell lumens with a 20 to 25 percent weight gain. The impregnated wood was kept in a swollen state and dried at 80°C to 93°C for 30 minutes and then heated at 155°C for 30 minutes to form a water-insoluble resin in the cell wall (Rowell and Konkol 1987). Chemical modification of wood can prevent or slow degradation processes. Although the modified wood has slower moisture sorption than unmodified wood, water affects the strength and, ultimately, promotes biological decay of the material (Wang and Morrell 2004).

The purpose of the present study was to investigate the potential of a new technique to produce completely fixed, compressively molded squares using a high-pressure, elevated-temperature chemical treatment. The drying procedure and characteristics of modified wood will be discussed.

Materials and Methods

Experimental

Materials.—Italian poplar (*P. euramevicana* cv. 'I-214') logs with an average basic density of 346 kg/m^{-3} (minimum diameter, 0.18 m) were obtained from the province of Jiangsu in eastern China. The dimensions of the wood samples for impregnation were 1,200 mm in length and 200 mm in diameter. After soaking, impregnated logs were sawn into blocks approximately 70 mm thick (tangential) by 140 mm wide (radial) by 1,000 mm long (longitudinal) for hot-press drying.

Synthesis of UF prepolymer.—A three-necked flask was charged with UF and ammonia at a molar ratio of 1:1.1. The reaction mixture was stirred and heated at 30°C for 3 hours. Subsequently, sodium hydroxide or hydrochloric acid was added to adjust the pH of the prepolymer from 7 to 8. Finally, the reaction mixture was transferred into a container and sealed.

Wood impregnation.—The freshly sawn poplar was impregnated with carbamide (18%, wt/wt) and the prepolymer (15%, wt/wt) by the pulse-impregnation machine at the pressure of 0.7 to 0.8 MPa for 30 minutes at a sawmill in Ningbo, province of Zhejing, China. The pulse-impregnation machine (Pu et al. 2009a) consisted of a fixing device, a constant-pressure device, and an infusion device, as showed in Figure 1. A sawn poplar timber was placed between the two seal plates by adjusting the height of the platform. The timber was fixed with the clamping cylinder, which connected to the trestle table. The impregnation liquid was impregnated through the fluid sealing disk by a pulsing press. The sap from the drain sealing disk was collected by the collection sump.
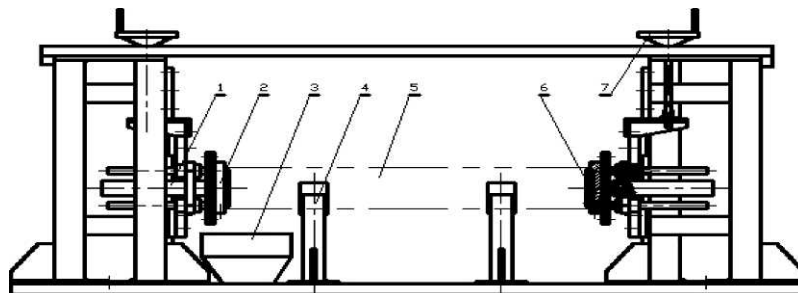

Figure 1.—The impregnation machine. 1 = clamping cylinder; 2 = drain sealing disk; 3 = collection sump; 4 = platform; 5 = log; 6 = fluid sealing disk; 7 = hand wheel.
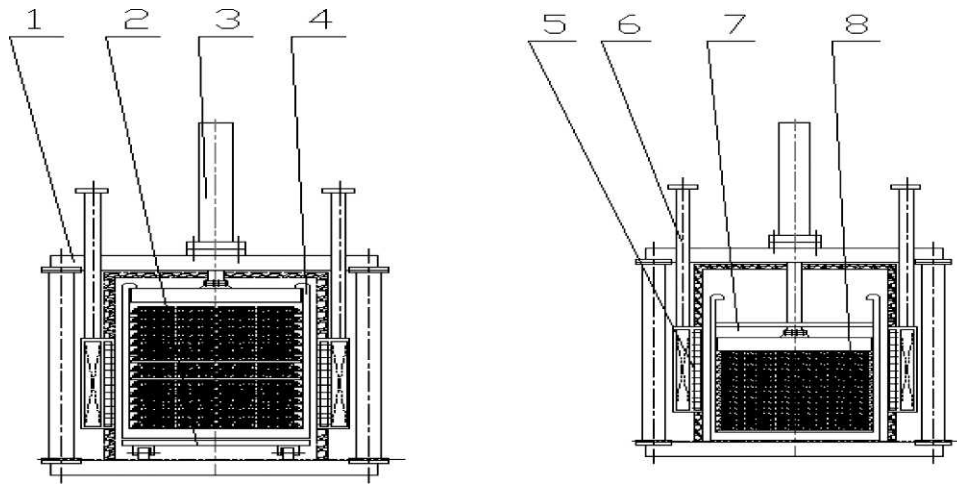
Figure 2.—The hot-press drying kiln. 1 = support frame; 2 = kiln car; 3 = pressurized cylinder; 4 = box of wood; 5 = valve; 6 = heating platens; 7 = compression plate; 8 = dummy plate.

The hot-press drying kiln.—The wood was dried in an air convection hot-press drying kiln (Pu et al. 2009b) with a thermocompressor, compression plate, and wooden box, as shown in Figure 2. The impregnated logs were sawed into planks for drying. Ten layers of timbers were placed in the wooden box. The planks were compressed by the compression plate, which was connected to a pressurized cylinder, as the wood dried. The kiln measured 1.2 m long by 1.0 m wide. The maximum pressure of the thermocompressor reached 20 MPa. The wood was subjected to this hot-press drying in a manner similar to previously described methods (Pu et al. 2009c).

Characterization methods

The drying schedule.—Figure 3 presents the results for the hot-press drying with an upper limit temperature of 120°C using a rising-temperature schedule. The temperature quickly increased to 90°C as the relative humidity gradually decreased; the temperature of the wood was kept at 120°C. The wood resident time in kiln was 120 hours, with a target moisture content of 12 percent (ovendry basis).

Figure 4 displays changes in moisture content during drying. In the drying process, the moisture content of poplar timbers decreased from 70 to 10 percent after 120 hours at a drying rate of 0.5 percent per h. Humidity conditioning was regulated after the falling drying rate period to eliminate residual stress and to obtain better drying quality. Moreover, steaming may repair minor splitting of the wood. Subsequently, the temperature of wood decreased to 44°C after cooling for 2 hours with a temperature of 37°C. When the temperature of the timber dropped below 40°C, the kiln door was opened, and the pressure was released.

Figure 4 also displays the pressure curve in hot-press drying. In this study, wood timber was compressed from 0.07 to 0.05 m (28.6% compression). Thus, the treated and compressed wood increased not only in density but also in hardness and other mechanical properties. With these improved properties, the scope of the application for wood will be expanded. The pressure was applied while the temperature of the timber reached 90°C through conduction. The pressure was increased along with the drying process. The pressure was kept at 0.5 MPa until the end of drying.

The mechanical properties.—The densities of wood materials were determined according to Chinese Standard GB/T 1933-91 (Standardization Administration of the People's Republic of China [SAC] 1991a). For determining the air-dry density, test samples with a dimension of 0.02
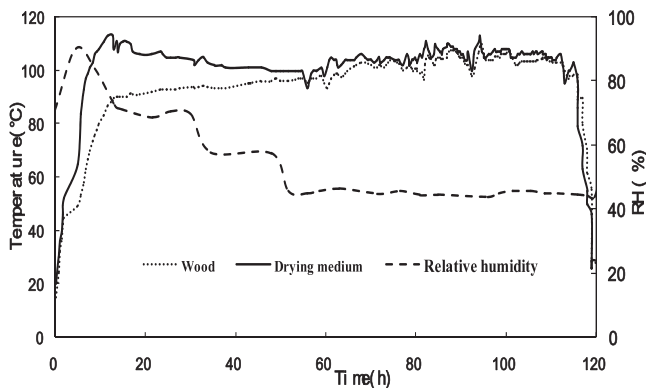

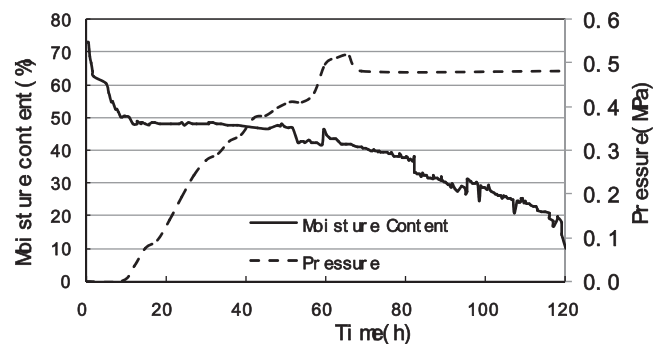Figure 3.—Curves of the temperature of hot-press drying. RH = relative humidity.

Figure 4.—Curves of pressure and moisture content of hot-press drying.

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(longitudinal) by 0.02 (radial) by 0.02 (tangential) m were prepared and kept at 20°C ± 2°C and a relative humidity of 65 ± 5 percent until they reached a stable weight. The weights were measured with an analytic balance to ±0.001 g. Afterward, the dimensions were measured with a digital micrometer to the nearest ±0.01 mm. The air-dried densities (ρ_{12}) of the samples, which had a constant moisture content of 12 percent, were calculated using the following formula:

$$\rho_{12} = \frac{M_{12}}{V_{12}} \qquad (1)$$

where ρ_{12} is the air-dried density (kg/m^3), M_{12} is the air-dry weight (kg), and V_{12} is the volume (m^3) at air-dry condition.

The samples were kept under water until they reached a stable dimension. Their dimensions were measured with a digital micrometer to the nearest ±0.01 mm and were kept at a temperature of 103°C ± 2°C in the drying oven until they reached a stable weight for the assessment of basic density. Afterward, the fully dried samples were cooled in desiccators containing $CaCl_2$ and then weighed with the analytic scale. The basic density (ρ_y) was calculated using the following equation:

$$\rho_y = \frac{M_0}{V_{max}} \qquad (2)$$

where ρ_y is the basic density (kg/m^3), M_0 is the fully dried sample weight (kg), and V_{max} is the full saturation volume (m^3) of the wood material.

The tests for bending strength were carried out with the Universal Testing Equipment according to Chinese Standard GB/T 1936.1-91 (SAC 1991b). The test sample had a dimension of 0.02 (longitudinal) by 0.02 (radial) by 0.03 (tangential) m, and the span length was 0.24 m with sensitivity of 0.01 mm. All of the test samples were set to fail within 2 minutes (from start to end). The bending strength was calculated using the following formula:

$$\partial_{bw} = \frac{3,000 P_{max} l}{2bh^2} \qquad (3)$$

where ∂_{bw} is the bending strength (GPa), P is the maximum

load (N), l is the span (m), b is the cross-sectional width of the test sample (m), and h is the cross-sectional thickness of the test sample (m).

The bending tests for modulus of elasticity (MOE) were carried out with the Universal Testing Equipment according to Chinese Standard GB/T 1936.2-91 (SAC 1991c). The dimensions of test specimens were 0.02 (longitudinal) by 0.02 (radial) by 0.03 (tangential) m. The capacity of the Universal Testing Equipment was 400 N. Deformations on the test samples were measured in the middle of the specimen within a zone of fivefold the width of the sample by comparator. The deformations caused by incrementally increasing the force were assessed with a sensitivity of 0.01 mm. In the elastic deformation zone, the MOE was calculated using the following formula:

$$E_w = \frac{23,000 P l^3}{108 b h^3 f} \qquad (4)$$

where E_w is the MOE (GPa), P is the difference between the arithmetic average of the upper and the lower limits of applied force in the elastic deformation zone (N), f is the net elastic deflection difference between the measured elastic deflection in the upper and the lower loading limits (m), l is the span (m), b is the cross-sectional width of the test sample (m), and h is the cross-sectional thickness of the test sample (m).

The tests for hardness of wood were carried out with the Universal Testing Equipment according to Chinese Standard GB/T 1941-91 (SAC 1991d). The test specimens with a dimension of 0.07 (longitudinal) by 0.05 (radial) by 0.05 (tangential) m were conducted with speed of 3 to 6 mm/min. The hardness of wood was calculated using the following formula:

$$H_w = KP \qquad (5)$$

where H_w is the hardness of wood, P is the maximum load (N), and K is coefficient of indentation depth.

Results and Discussion

The drying characteristics and drying quality of hot-press drying were evaluated according to Chinese Standard GB/T 6491-1999 (SAC 1999) and are shown in Table 1. Table 2 shows the physical and mechanical properties of uncompressed timber versus compressed wood (compression of 28.6%). Ten specimens were measured for the density of wood. Fifteen specimens were measured for hardness, bending strength, and the bend elastic modulus. The mechanical properties of the compressed wood were significantly improved. The air-dried density of modified wood was improved by 58 percent, and the hardness of the transverse, tangential, and

Table 1.—*Drying characteristics and drying quality.*[a]

Characteristic/quality	Value
MC (%)	6.50
SD (%)	0.92
MC SD in thickness (%)	0.17
Residual stress (%)	1.38
Level of quality (grade)	A

[a] MC = moisture content.

Table 2.—*Physical and mechanical properties of untreated and treated wood.*[a]

Specimens	Bending strength (MPa)	MOE in static bending (GPa)	Hardness (kN)			Basic density (kg/m^3)	Air-dried density (kg/m^3)
			Transverse section	Tangential direction	Radial direction		
Untreated	48.7 (4.28)	7.55 (1.32)	2.33 (0.29)	1.74 (0.75)	1.55 (0.49)	286 (12.52)	346 (14.29)
Treated	86.6 (6.27)	12.56 (3.84)	3.89 (0.31)	5.38 (1.28)	4.02 (1.06)	386 (15.28)	547 (15.72)

[a] Values are means (standard deviations). MOE = modulus of elasticity.
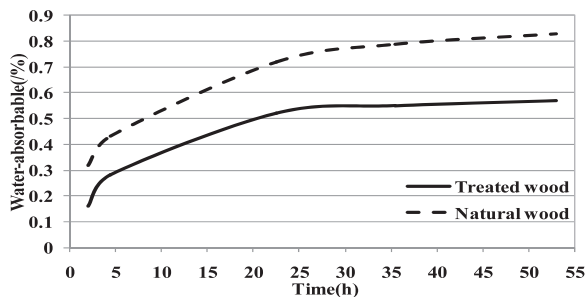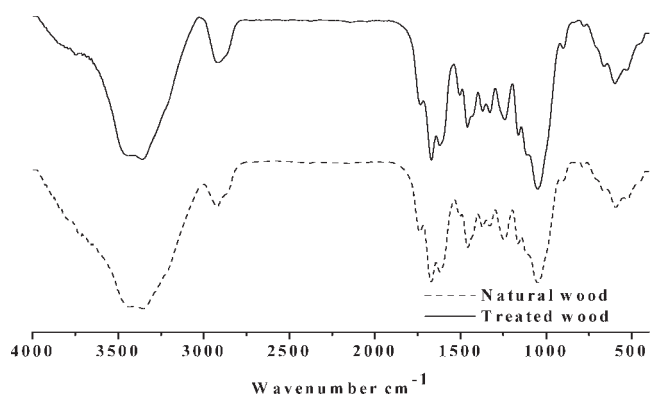
Figure 5.—Water absorption of wood.

Figure 6.—Fourier transform infrared spectroscopy curves of wood.

radial direction was increased by 67, 210, and 160 percent, respectively. The bending strength was improved by 78 percent, and the bend elastic modulus was improved by 66 percent. The significant transformation between modified and untreated wood was probably due to the reinforcement and stabilization of matrix hemicelluloses and to the softening of lignin by the chemical modifier at the higher temperatures.

Figure 5 shows that the water absorption rate of treated wood was slightly lower than that of the untreated timber after immersion in water for 48 hours at atmospheric pressure. The UF prepolymer can react with accessible hydroxyl groups in wood. Our hypothesis is that modified timber absorbs less water than untreated timber, because prepolymer and wood components potentially react to form a cross-linking structure, which in turn improves the dimensional stability of treated wood.

Fourier transform infrared (FTIR) spectroscopy was used to characterize chemical changes of the natural and modified wood, and the spectra are shown in Figure 6. The FTIR spectrum of the modified wood showed a significant reduction in the C=O absorbance at 1,750 cm^{-1}, while the absorption at 1,645 cm^{-1} was markedly enhanced. This absorption band is ascribed to the bond formation between the functional -NHCH$_2$OH groups in UV prepolymer and the wood carboxyl C=O groups, and the -NH group causes a strong shift to higher wave numbers. The increases in the intensity of bands at 1,370 cm^{-1} (CH$_3$ bending) and 1,645 cm^{-1} (CH$_2$ bending) are indicative of an increase in isopropyl and methylene groups as a result of modification (Wu et al. 2010).

The color and luster of the compressed wood are shown in Figure 7. The changes to the color and luster of the timber surface were probably due to the thermal effect during hot-press drying and the dye that mixed with the chemical modifier.

Conclusions

The development of modified wood based on UF prepolymer treatment and hot-press drying processes was examined in this study. The timbers met A grade according to the Chinese standards. The air-dried density of modified wood was improved by 58 percent, and the hardness of the transverse, tangential, and radial direction was increased by 67, 210, and 160 percent, respectively. The bending strength was improved by 78 percent; the bend elastic modulus was improved by 66 percent. It was also found that the water absorption rate of treated wood was slightly lower than that of the untreated timber. FTIR spectra revealed potential bond formation between wood and UF prepolymer.

Acknowledgments

Figure 7.—(Left) Treated specimen and (right) comparison between treated and untreated specimens.

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