

Chemical Modification of Poplar Wood with Foaming Polyurethane Resins

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ABSTRACT: This study was devoted to chemically modifying poplar wood with foaming polyurethane (PU) resin, which improved both dimension stability and mechanical property of wood. The controlled tests demonstrated the poplar wood treated with only solvent acetone had decreases of both dimension stability and mechanical property, while the wood modified with solution of polymeric methylenebis(phenylisocyanate) in acetone had an excellent improvement of dimension stability but a little strength loss. Seven foaming PU resins with NCO/OH mole ratio from 12 to 2.5 were used to chemically modified wood, of which the mole ratio 3.0 gave best balance between dimension stability and mechanical property. The 24-h volumetric swelling coefficient ($VSC_{24\text{ h}}$) and 24-h water absorption coefficient ($WAC_{24\text{ h}}$) of the modified

wood reduced 34.29% and 57.60% and the modulus of rupture and modulus of elasticity improved 39.89% and 37.15%, respectively. The improvements of dimension stability were contributed to that of the hydrophilic hydroxyl groups in wood were blocked by isocyanate groups and water movement was hindered by successive cured PU deposit on the surface of vessels. The improvements of mechanical property were owed to the reinforcement of foamed PU on the cell wall and void space of wood. Four morphologic models of foamed PU within wood were discovered by SEM. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 2980–2985, 2007

Key words: modification; polyurethane; mechanical property; curing of polymers

INTRODUCTION

Wood is a biodegradable and renewable native polymeric material that is widely used in various fields for its many advantages different from other materials such as metal, cement, and synthetic polymer. However, some disadvantages of wood, such as bad dimension stability, relatively low strength, easy worm-eaten and decay, and bad fire resistance, prevent wood wider utilizations.¹ Many studies were devoted to modify these disadvantages, by which improve wood quality, enlarge their utilization, and add more value to wood. It is especially significant to fast-grown wood.

Resin impregnation treatment is one of oldest and effective methods to modify wood. The common resins used are phenol–formaldehyde resin,^{2,3} urea–formaldehyde resin,⁴ melamine–formaldehyde resin,⁵

and polyethylene glycol (PEG).⁶ Recently, some isocyanate resins were used to modify the dimension stability, decay preservation, and fire resistance of wood. Williams⁷ modified wood with monofunctional and bifunctional isocyanate monomers by which obtained the better decay resistance of wood. Engonga et al.⁸ impregnated the mixed solution of isocyanate and perfluoroalkyl alcohol into wood and well improved the dimension stability. Some scientists impregnated the mixture of isocyanate with organic compounds with element of chloride⁹ or phosphor¹⁰ to improve the fire- and/or decay resistance.

Isocyanate is a highly reactive compound that can react with most materials with active hydrogen,¹¹ which was used to prepare PU adhesive. Wood is mainly composed of cellulose, lignin, and hemicellulose all of which contain hydrophilic hydroxyl groups that lead to bad dimension stability.¹² The isocyanate will react with these hydroxyl groups, which improved dimension stability. After reacted with water, the isocyanate converted into polyurethane and released carbon dioxide, by which the isocyanate used to prepare various PU foams industrially. It was discovered that the impregnated isocyanate was distributed within void spaces of wood.^{8,13} Therefore, the study was devoted to forming the impregnated isocyanate within void spaces to improve both dimension stability and mechanical property of poplar wood.

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EXPERIMENTAL

Materials

The poplar (*P. ussuriensis*) logs were fallen from local wood farm. The fresh logs were cut into lumber with thickness of 20 mm, then enough air-dried, and finally cut into specimens with dimension 12 mm × 12 mm × 140 mm. The longest direction of specimen was perpendicular to the annual ring, and the regular specimens were selected without faults and with similar weight to ensure the equivalent density.

Polymeric methylenebis(phenylisocyanate) (P-MDI) was supplied by Yantai Wanhua polyurethane with NCO content 30.52%. PEG chemical purity was supplied by Tiantai Chemicals, Tainjin, China. The solvent acetone, catalyst triethylamine, and sodium hydroxyl were obtained from chemical market in Harbin.

The preparation of foaming PU resin

A three-necked flask was charged with stoichiometric P-MDI, PEG, and first part of solvent acetone. The reaction mixture was stirred and heated to 40°C for 30 min, and then heated until the condenser just refluxing and held for 3 h. After that cooled to 50°C, charged second part of solvent acetone, and further stirred for 10 min. Finally, the reaction mixture was transferred into a container and sealed.

Titration of the residual isocyanate groups, NCO, was carried out according to ASTM D-2575-97: "Standard test methods for isocyanate group in urethane materials or prepolymers." Then, the prepared PU resin was diluted by acetone into concentration 20 wt %, and the 20 wt % of P-MDI/acetone solution was also prepared as controlled resin.

The impregnation and foaming of PU resin

Wood pretreatment

Totally, 20 poplar specimens without any fault were selected and labeled, and then dried at about 103°C for 5 h and weighed each specimen (W_1).

Resin impregnation

The pretreated specimens were hold under vacuum (75 kPa) for 30 min for removing air within wood. After that specimens were infused into impregnated solution under vacuum without leaking. When the specimens were immersed within solution, held for 5 min, then infused into air by atmosphere pressure, and held for another 30 min. Finally, the specimens were taken out and washed by acetone to remove the resin from the surface.

Foaming (curing) and drying

Catalyst solution was prepared in advance by solving 4 g of triethylamine and 1 g of sodium hydroxyl in 995 g of water. Then, impregnated specimens were immersed within catalyst solution for 5 min. After then, each specimen was wrapped on foil film and dried at 120°C for 90 min. Finally, the foil film and the foamed resin on surface were removed and dried at 103°C and 85 kPa vacuum for 4 h and weighed each specimen immediately (W_2).

Characterization of treated and nontreated wood

Weight percentage gain

The weight percentage gain (WPG) was determined by the difference in oven dry weight of each specimen before treatment (W_1) and after treatment (W_2) according to the following equation [$WPG = (W_2 - W_1)/W_1 \times 100$]. The average WPG of total 20 specimens was reported in the article.

Dimension stability

The dimension stability was evaluated in terms of 24-h volumetric swelling coefficient ($VSC_{24\text{ h}}$) and 24-h water absorption coefficient ($WAC_{24\text{ h}}$). The dimensions (length, width, and thickness) and weight of each specimen before soaking (l_1 , w_1 , t_1 , and W_1) and after soaking (l_2 , w_2 , t_2 , and W_3) in 20°C water for 24 h were determined by micrometer and analytic balance, respectively. The $VSC_{24\text{ h}}$ was calculated according to the following equation [$VSC_{24\text{ h}} = (l_2w_2t_2 - l_1w_1t_1)/l_1w_1t_1 \times 100$]. The $WAC_{24\text{ h}}$ was calculated according to the following equation: [$WAC_{24\text{ h}} = (W_3 - W_1)/W_1 \times 100$]. The averaged $VSC_{24\text{ h}}$ and $WAC_{24\text{ h}}$ of total 10 specimens were reported in the article.

Mechanical property

The mechanical property was evaluated in terms of modulus of rupture (MOR) and modulus of elasticity (MOE). The MOR and MOE were measured referred to Standard ISO 3122-1975. The averaged MOR and MOE of total 10 specimens were reported in the article.

Scanning electron microscope analysis

The samples cut from dry untreated and treated specimens were handsplit in the cross section and tangential surface. The SEM samples were coated with ~10–20 nm of gold before examined with QUANTA-200 SEM at 15 or 20 kV.

RESULTS AND DISCUSSION

The controlled groups

To evaluate the effects of foaming PU, P-MDI, and solvent acetone on the modified wood, the following controlled groups were selected. The Controlled I, the native poplar wood without any treatment, was compared with those treated by chemicals. The Controlled II, the poplar wood treated by acetone, was compared with the Controlled I for evaluating the effect of solvent acetone. The Controlled III, the poplar wood modified by P-MDI/acetone solution, was compared with those modified by foaming PU for verifying the purpose of foaming PU modification on wood. The averaged properties of each controlled were presented in Table I.

The $VSC_{24\text{ h}}$ and $WAC_{24\text{ h}}$ of wood treated by only acetone were 34.90% and 43.86% more than that of wood without any chemical treatments, respectively, and the 9.65% MOR and 23.36% MOE were reduced. These indicated solvent acetone could spoil the crystallinity of celluloses and the structure of cellulose-lignin-hemicellulose composite by reducing the hydrogen bonding between celluloses or destroying the interface of cellulose and lignin. The primary function of lignin in wood is crosslinking and stiffening agent.¹² Therefore, the wood treated by acetone was the looser, which resulted in water that could be easily moved within wood and more absorbed by wood and wood lost some strength.

The dimension stability of wood modified by P-MDI was well improved with 50.72% $VSC_{24\text{ h}}$ and 56.83% $WAC_{24\text{ h}}$ reduced because the hydrophilic hydroxyl groups were blocked by isocyanate and converted into hydrophobic carbamate. In addition, the P-MDI-entered wood cured on the surface of wood void space and formed successive PU deposit, as shown in SEM photos in Figure 1, which could further prevent water moving or entering. In the cross section of wood, the thickness of cell wall in P-MDI-treated wood [Fig. 1(C)] was thicker than that in acetone-treated one [Fig. 1(A)] because of the PU deposit, and some small void spaces were crammed with deposit. In the tangential surface of wood, the vessel of acetone-treated wood seemed to be smooth and clean, as shown in Figure 1(B), while that of P-MDI-treated wood was filled with dry mudlike deposit and the

surface had many crystallized polyurea. These SEM photos also indicated that only P-MDI could not and did not foam in void spaces of wood.

The P-MDI could react with the hydroxyl groups in wood, which resulted in some crosslinks between wood fibers within the P-MDI-treated wood. Besides, the successive PU deposit on the vessel surface could reinforce the vessel to some degree. Therefore, the MOR and MOE of P-MDI-treated wood were 31.70% and 27.95%, respectively, more than those of acetone-treated wood. When compared with the nontreated one, the MOR and MOE of P-MDI-treated wood were reduced to 6.78% and 19.32%, respectively, because of the crystallinity of cellulose spoiled by the solvent acetone. It was interesting that all MOR specimens of P-MDI-treated wood were ruptured brittly during mechanical testing.

Poplar modified by foaming PU resins

The controlled results indicated that wood modified by only P-MDI would improve the dimension stability and do a little harm to strength. As a result, the study devoted to forming impregnated PU in void space of wood by which improved both the dimension stability and mechanical property.

The different formulations of foaming PU resin will give different modified effects. To balance the dimension stability and mechanical property best, total seven PU resins with different NCO/OH mole ratio were prepared. The properties of seven PU resins and their modifications on poplar wood were shown in Table II.

Under the same treating condition, the weight percentage gains of each batch were ranged between 20.60% and 23.94% though the NCO/OH ratio varied from 12 to 2.5. The average weight percentage gain of all specimens was 21.68%. The VSCs ranged between 7.05% and 13.79% did not correlate with the NCO/OH ratio. Both all $VSC_{24\text{ h}}$ and $WAC_{24\text{ h}}$, higher than that modified with only P-MDI for some isocyanate groups, were reacted with water to foam. However, all $WAC_{24\text{ h}}$ and four out of seven $VSC_{24\text{ h}}$ of woods modified with foaming PU were better than that of Controlled II (wood treated with acetone).

The mechanical property analysis indicated that all wood modified with foaming PU had better MOR and MOE than that of P-MDI-modified one or acetone-treated one. In general, the MOR was increased at first and then decreased with NCO/OH ratio reducing. The PU resins with higher NCO/OH ratio, more than 4.5, were bad foamed for the resin had smaller molecular weight, which brought about bad sustainment against the PU bubbles during foaming. However, PU resins with too lower NCO/OH ratio could not well form as well because the resin had too less free isocyanate groups, and

TABLE I
The Averaged Properties of the Controlled

ID	WPG (%)	$VSC_{24\text{ h}}$ (%)	$WAC_{24\text{ h}}$ (%)	MOR (MPa)	MOE (MPa)
Controlled I	–	11.75	56.57	93.20	6368
Controlled II	–	12.16	81.38	84.21	4880
Controlled III	22.55	5.79	24.42	86.88	6245

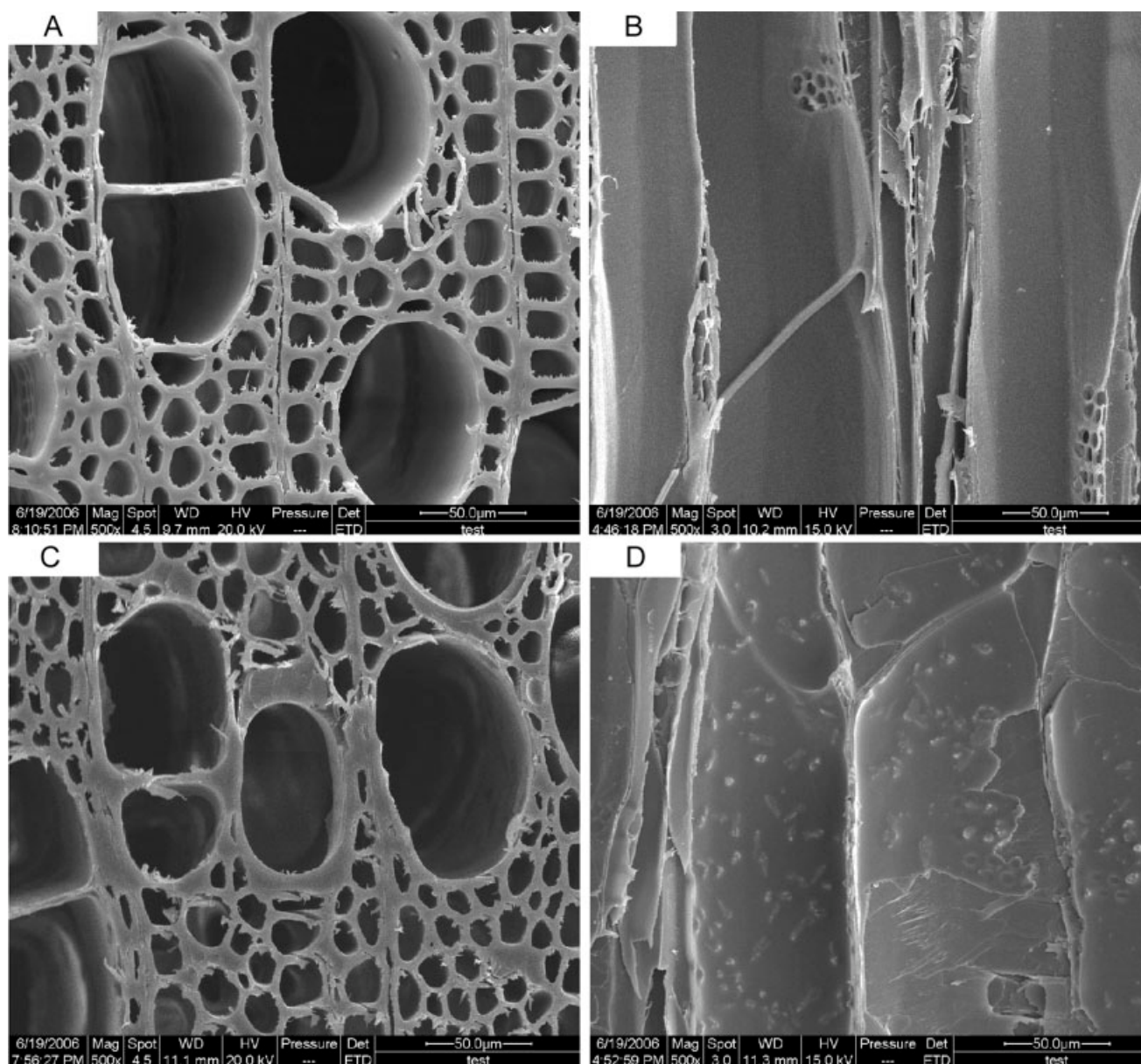


Figure 1 The SEM photos of acetone-treated and P-MDI-treated wood. A: Acetone-treated wood in the cross section; B: Acetone-treated wood in the tangential surface; C: P-MDI-treated wood in the cross section; D: P-MDI-treated wood in the tangential surface.

the molecular weight may be too large to well impregnate into wood. The resin with low free isocyanate groups would lead to bad dimension stability

of modified wood for much fewer isocyanate groups could block the hydrophilic hydroxyl groups in wood, which confirmed by A7 modified wood

TABLE II
The Modified Effects of Seven PU Resins

ID	NCO/OH mole ratio	NCO content (%)	WPG (%)	VSC _{24 h} (%)	WAC _{24 h} (%)	MOR (MPa)	MOE (MPa)
PU A1	12	17.32	21.14	7.05	37.39	94.97	5112
PU A2	8	15.27	20.60	12.43	55.69	93.48	5391
PU A3	6	13.93	23.94	11.37	54.96	94.81	4865
PU A4	4.5	12.06	20.95	10.69	47.94	105.48	6317
PU A5	3.5	10.47	20.89	12.75	49.94	120.13	7725
PU A6	3	9.36	21.39	7.99	34.50	117.80	6693
PU A7	2.5	7.83	22.87	13.79	54.10	100.31	5531

whose $VSC_{24\text{ h}}$ was higher than that of the Controlled II.

Among seven foaming PU resins, resin A6 with NCO/OH ratio 3.0 embodied best balances of dimension stability and mechanical property. When compared with the Controlled II, the $VSC_{24\text{ h}}$ and $WAC_{24\text{ h}}$ reduced 34.29% and 57.60%, respectively, and the MOR and MOE improved 39.89% and 37.15%, respectively. The resin A5 with NCO/OH

ratio 3.5 gave best improvement of mechanical property with 42.66% MOR and 58.30% MOE more than that of Controlled II.

The SEM analysis indicated the PU resin impregnated wood was foamed indeed, as shown in Figure 2(A,B). The foamed PU adhered to the vessel wall and finally made the wall become thicker than those modified by P-MDI, which gave better sustentation when suffered from stress and manifested

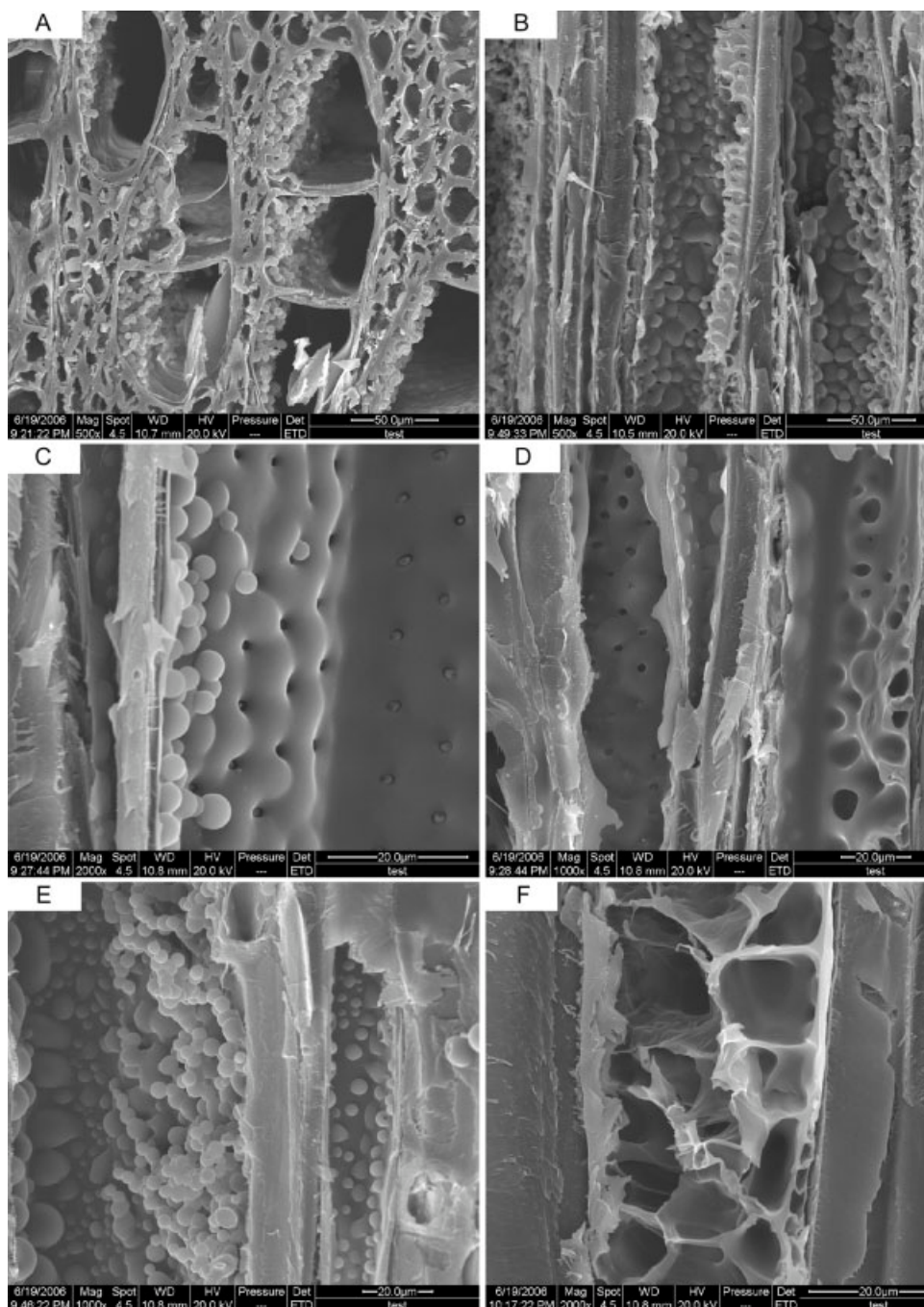


Figure 2 The SEM photos of foaming PU-modified wood and their four morphologic models. A: Foamed PU within wood in the cross section; B: Foamed PU within wood in the tangential surface; C: PU foamed within wood (Model I); D: PU foamed within wood (Model II); E: PU foamed within wood (Model III); F: PU foamed within wood (Model IV).

better MOR apparently. The PU foam in wood generally presented four morphologic models, as shown in Figure 2(C–F). Due to the difference of foaming degree of PU resin, which resulted from the catalyst, (the mixture of triethylamine and NaOH) was introduced after PU resin impregnated and therefore was distributed unevenly within the wood. The Models I and IV embodied that the PU foamed worst and best within wood, respectively. The PU foam as Model IV was preferably thought to be in favor of the improvement of mechanical property for the foam was full of void space and could sustain the vessel. However, the detailed effects of each foaming model on the dimension stability and mechanical property need more devotions, and how to control the foaming model shall be well studied as well.

CONCLUSIONS

The dimension stability and mechanical property of wood treated by only acetone would be reduced for acetone spoiled the crystallinity of celluloses and the interface of cellulose and lignin. The dimension stability of wood modified by only P-MDI will be well improved for hydrophilic hydroxyl groups was blocked by isocyanate and PU resin formed successive deposit, while the mechanical property was reduced a little.

Both dimension stability and mechanical property of wood modified by foaming PU resin were

improved since combinations of some hydroxyl groups blocking, hindrance of water movement in wood, and wood cell wall reinforced by the foamed PU. The modification was affected by NCO/OH mole ratio of PU resin. The PU resin with NCO/OH mole ratio 3.0 gave best balance between dimension stability and mechanical property, while the PU resin with mole ratio 3.5 manifested best mechanical property. Four morphologic models of foamed PU within wood were discovered by SEM.

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