FUNGAL DECAY RESISTANCE AND DIMENSIONAL STABILITY OF LOBLOLLY PINE REACTED WITH 1,6-DIISOCYANATOHEXANE

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ABSTRACT

Wood reacted with 1,6-diisocyanatohexane resisted fungal attack and had improved dimensional stability. At 25.8% chemical weight gain, the reacted wood had no weight loss by the brown-rot fungus *Gloeophyllum trabeum*; at 20.9% and 23.8% chemical weight gains, the reacted wood had antishrink efficiencies (ASEs) of 58% and 61%, respectively, with a small loss of 3% ASE after four cycles of water swelling and drying treatment. At 26.1% chemical weight gain, the reacted wood lost 5.8% bonded diisocyanate in a 12-week soil-block decay test. Evidence of cross-linking between wood and 1,6-diisocyanatohexane was provided by the characteristic carbamate infrared absorption. In the absence of water, 1,6-diisocyanatohexane reacted with wood to form cross-linking wood as the only product; in the presence of water, diisocyanate reacted preferentially with water to form mainly ureas with a small amount of biurets. These chemicals were deposited in the cell lumen of wood. Water vapor sorption of wood reacted with 1,6-diisocyanatohexane indicated that the decay resistance of this modified wood is probably due to the inability of the modified cell wall of wood to absorb sufficient water to support decay.

Keywords: Cross-linked wood, 1,6-diisocyanatohexane, fungal resistance, dimensional stability, loblolly pine, *Gloeophyllum trabeum*, *Pinus taeda*.

INTRODUCTION

Nonconventional wood protection methods based on chemical modification of wood have been investigated extensively (Rowell 1975, 1977, 1982, 1983). Two methods of wood modification are under investigation. The first method involves reaction of wood with reactive organic compounds. Organic compounds containing reactive functional groups, including isocyanates, anhydrides, and epoxides, can be reacted with the hydroxyl groups of the cellwall polymers of wood. These modified woods resist attack by fungi (Ellis and Rowell 1984; Rowell and Gutzmer 1975; Phil and Olsson 1968; Goldstein et al. 1961; Tarkow et al. 1950), termites (Rowell et al. 1979; Imamura and Nishimoto 1986), and marine organisms (Rowell 1982; Johnson and Rowell 1989). The second method involves cross-linking of wood with reactive cross-linking compounds. The hydroxyl groups of the cell-wall polymers of wood, including cellulose, hemicelluloses, and lignin, can be reacted with cross-linking compounds, including formaldehyde (Tarkow and Stamm 1953; Stevens et al. 1979).

Wood cross-linked with formaldehyde has been shown to resist fungal attack and to have improved dimensional stability (Tarkow and Stamm 1953; Stamm 1959; Stamm and Baechler 1960; Burmester 1967; Stevens et al. 1979). The advantage of cross-linking with formaldehyde is that only a low concentration of reacted formaldehyde in wood is sufficient to give good decay protection and dimensional

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stability. For example, wood reacted with formaldehyde to 2% weight gain had only a small weight loss (3%) as a result of fungal decay (Stamm and Baechler 1960). In regard to dimensional stabilization, wood reacted with formaldehyde to 3.1% and 5.4% had antishrink efficiencies (ASEs) of 47% and 60%, respectively; at 7% chemical weight gain, the ASE was greatly increased to 90% (Tarkow and Stamm 1953; Stamm 1959). However, the reaction resulting in formaldehyde-modified wood requires strong acid catalysts, including hydrochloric acid, nitric acid, and sulfuric acid, which greatly reduce the mechanical properties of wood. For example, at 60% ASE, the abrasion resistance of wood cross-linked with formaldehyde was reduced 93%, and toughness was reduced 77% (Stamm 1959).

We are searching for reactive chemicals that are able to cross-link with wood without damaging the mechanical properties of wood, that produce no byproducts in wood, and that result in good decay resistance and dimensional stability. One group of cross-linking compounds that meet these criteria is the diisocyanates. Although reaction of diisocyanates with wood has been reported (Wakita et al. 1977; Ellis and Rowell 1984), evidence of crosslinking, decay resistance, and dimensional stabilization of the modified wood has never been established. The purpose of this study was to report evidence of cross-linking between wood and 1,6-diisocyanatohexane and to investigate fungal decay resistance and dimensional stabilization of the modified wood.

MATERIALS AND METHODS

Chemical modification of wood

The wood blocks used for fungal decay tests and water swelling tests were reacted under different conditions. For decay tests, wood blocks (1.9 by 1.9 by 1.9 cm) were reacted with 1,6-diisocyanatohexane in 1:1 or 1.8:1 molar ratio of diisocyanate to anhydrous glucose pyranose equivalent of wood at 65 C for 1 to 24 h. The level of chemical weight gain in wood was controlled by chemical concentration, temperature, and reaction time. The blocks were dried at 60 C for 1 day before and after reaction. For swelling tests, wood blocks (1.9 by 1.9 by 0.64 cm) were reacted with 1,6-diisocyanatohexane in 1:1 molar ratio of diisocyanate to anhydrous glucose pyranose equivalent of wood at solvent reflux temperature for 4 to 33 h. The blocks were dried at 105 C for 24 h before and after reaction.

Reaction of moist wood blocks (1.9 by 1.9 by 0.64 cm) with 1,6-diisocyanatohexane was carried out for 1 or 4 days at room temperature in a desiccator saturated with water vapor.

Infrared spectra of dry wood reacted with 1,6-diisocyanatohexane or air-dried wood impregnated with 1,6-diisocyanatohexane and then exposed to moisture were recorded on an infrared instrument using KBr pellets. Nitrogen content of the modified and unmodified wood was analyzed by Galbraith Laboratories, Inc.²

Decay test

Twenty-four loblolly pine (Pinus taeda L.) sapwood blocks (87.65 g, calculated as anhydrous glucose pyranose equivalent, 476 mmol) (1.9 by 1.9 by 1.9 cm in radial, tangential, and longitudinal directions) after drying at 60 C for 1 day were placed in a desiccator under vacuum at 2 to 3.33 kPa (15 to 25 mmHg) for 1 h and then impregnated with pyridine [400 ml, dried over a 0.4-nm (4-Å) molecular sieve for more than 1 day]. The blocks were soaked in pyridine overnight (17 h), and then 1,6-diisocyanatohexane (25.7 ml, 263 mmol) was added to the solution. The blocks were soaked 0.5 h with occasional shaking. The blocks were then reacted at 65 C for 24 h. During reaction, six blocks were withdrawn after 1, 3, 6, and 24 h of reaction. The six blocks from each treatment were soaked in acetone [300 ml, dried over a 0.4-nm (4-Å) molecular sieve for more than 1 day] for 1 day and then extracted with acetone in a Soxhlet extractor for 16 h. The

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blocks were air-dried for 1 day and then ovendried at 60 C for 1 day. Weight gain of chemical in wood was based on oven-dry weight at 60 C before and after reaction. The average weight gain of chemical in wood was 1.7%, 4.9%, 7.4%, and 13.8% for 1-, 3-, 6-, and 24-h reactions, respectively. Five blocks from each treatment were conditioned at 27 C and 30% relative humidity (RH) for 3 weeks prior to the soil-block fungal decay tests.

Blocks with average weight gain of chemical of 25.8% were obtained by reacting 18 wood blocks (64.14 g, calculated as anhydrous glucose pyranose equivalent, 349 mmol) with 1,6diisocyanatohexane (56.4 ml, 349 mmol) in pyridine [200 ml, dried over a 0.4-nm (4-Å) molecular sieve for more than 1 day] at 90 C for 17 h. The procedures to purify and to condition the blocks were the same as those used for the lower weight gain. Five blocks were used in the decay tests.

Decay tests were performed for 12 weeks according to the American Society for Testing and Materials (ASTM) standard (ASTM 1990) using the brown-rot fungus *Gloeophyllum trabeum* (Pers. ex Fr.) Murr. (Madison 617). Five blocks were used for each fungal decay test. The extent of fungal attack was determined by weight loss of the blocks.

Swelling test

Fifteen loblolly pine sapwood blocks (17.78 g, calculated as anhydrous glucose pyranose equivalent, 97 mmol) (1.9 by 1.9 by 0.64 cm in radial, tangential, and longitudinal directions, cut from the same board and with the same ratio of earlywood and latewood) were dried at 105 C for 1 day. The blocks were placed in a desiccator under vacuum at 2.27 kPa (17 mmHg) for 30 min and then impregnated with pyridine [100 ml, dried over a 0.4nm (4-Å) molecular sieve for more than 1 day]. The blocks were soaked overnight (17 h); 1,6diisocyanatohexane (15.63 ml, 97 mmol) was added. The blocks were soaked 0.5 h with occasional shaking. The blocks were then reacted at reflux temperature for 33 h. During the reaction, three blocks were withdrawn after 4, 8,

and 12 h of reaction, and the remaining six blocks were withdrawn after 33 h. Three blocks from each treatment were soaked in acetone [100 ml, dried over a 0.4-nm (4-Å) molecular sieve for more than 1 day] for 1 day and then extracted with acetone in a Soxhlet extractor for 8 h. The blocks were air-dried for 1 day and then dried in an oven at 105 C for 1 day. The average weight gain of chemical in wood was 17.3%, 19.9%, and 23.8% for 4-, 8-, 12-, and 33-h reactions, respectively.

Reaction of wood with 1,6-diisocyanatohexane in the presence of water

Two air-dried loblolly pine sapwood blocks (1.32 g; 1.9 by 1.9 by 0.64 cm in radial, tangential, and longitudinal directions) were placed in a desiccator under vacuum at 2.27 kPa (17 mmHg) for 5 min and then impregnated with pyridine [25 ml, dried over a 0.4-nm (4-Å) molecular sieve for more than 1 day]; 1,6-diisocyanatohexane (10.1 ml) was added and the blocks were soaked for 2 h. The blocks were withdrawn and weighed. The blocks were then placed in a desiccator saturated with water vapor for 1 or 4 days. The blocks were air-dried at room temperature under a hood for 1 week prior to infrared analysis.

Determination of water sorption

Water sorption of wood (1.9-cm cubes) reacted with 1,6-diisocyanatohexane was determined by weight gain after exposure to water vapor at 98% relative humidity and 20 C for 4 weeks. Saturated atmospheres were developed in a desiccator containing a saturated copper(II) sulfate pentahydrate solution.

Measurement of dimensional stability

Dimensional stability of wood reacted with 1,6-diisocyanatohexane (1.9 by 1.9 by 0.64 cm in radial, tangential, and longitudinal directions, from the same board with the same ratio of earlywood and latewood) was determined by measuring the dimensions of the modified wood in the radial, tangential, and longitudinal directions using a flatbed micrometer. Mea-

surements were made after soaking the blocks in water for 1 day and after drying at 105 C for 1 day using the water-soak method (Rowell and Ellis 1979), except that vacuum was not applied. The water soaking and drying treatment was repeated four times. Antishrink efficiency was expressed as a percentage of the reduction in volumetric shrinkage of the modified wood relative to that of the unmodified wood (Tarkow and Stamm 1953).

RESULTS AND DISCUSSION

Evidence of cross-linking

Cross-linking between wood and 1,6-diisocyanatohexane was evidenced by the characteristic infrared absorptions of the modified wood. The infrared spectrum for unmodified wood in the region of 1,730 cm⁻¹ showed a weak carbonyl stretching vibration compared with a strong absorption near 1,650 cm⁻¹ (Fig. 1A). The absorption at 1,730 cm⁻¹ is attributed to carbonyl stretching vibration of acetyl and carboxylic acid of hemicelluloses, and absorption near 1,650 cm⁻¹ is attributed to H-O-H deformation vibration (1,635 cm⁻¹) of adsorbed water and carbonyl stretching vibration (1,670 cm⁻¹) of lignin (Marchessault 1960; Marchessault and Liang 1962).

The infrared spectrum of wood reacted with 1,6-diisocyanatohexane showed a strong carbamate absorption $(1,730 \text{ cm}^{-1})$ but no urea $(1,635 \text{ cm}^{-1})$ or isocyanate $(2,235 \text{ cm}^{-1})$ absorption (Fig. 1C). The only carbamate bond appearing in the modified wood indicated that cross-linking between wood and 1,6-diisocyanatohexane took place. The infrared absorption at 1,730 cm⁻¹ in modified wood has been attributed to carbonyl stretching vibration of carbamate (Conley 1970; Socrates 1980). The intensity of this absorption became very strong when the weight gain of chemical in the modified wood increased from 6.2% to 26.1% (Fig. 1B, C). Other characteristic carbamate absorptions in modified wood are N-H deformation (1,550 cm⁻¹) and C-N stretching vibration (1,230 cm⁻¹) (Conley 1970; Socrates 1980). The absorptions at 2,935 and 2,865 cm⁻¹, attributed to asymmetric and symmet-



FtG. 1. Infrared spectra of wood cross-linked with 1,6diisocyanatohexane. A. Control; B. 6.2% diisocyanatebonded wood; C. 26.1% diisocyanate-bonded wood.

ric C-H stretching vibrations of methylene group, and at 1,465 cm⁻¹, attributed to C-H bending vibration of methylene group (Conley 1970; Socrates 1980), are characteristic of methylene of the hexamethylene diisocarbamoyl group in the modified wood.

The infrared spectrum of wood reacted with 1,6-diisocyanatohexane in the presence of water for 1 day showed mainly ureas $(1,635 \text{ cm}^{-1})$ with a small amount of biurets $(1,695 \text{ cm}^{-1})$ but no diisocyanate (2.235 cm^{-1}) (Fig. 2B). These chemicals were deposited in the cell lumen of wood and did not involve bonding with wood. A small amount of diisocyanate was cross-linked with wood $(1,730 \text{ cm}^{-1})$ (Fig. 2B, C). The diisocyanate in wood in the presence of water at room temperature reacts preferentially with water to form a linear urea (Hartman 1977) and a cyclic urea (Eaton and Pramod 1990). The ureas further react with diisocyanate to form biurets (Hartman 1977). The weak absorption at 1,635 cm⁻¹ can be attributed to carbonyl stretching vibration of urea (Conley 1970; Socrates 1980). The intensity of this absorption was very strong (Fig. 2B, C). The weak absorption at 1,695 cm^{-1} can be attributed to carbonyl stretching vibration of biuret (Fig. 2B) (Conley 1970; Socrates 1980).



FIG. 2. Infrared spectra of control wood (A) and wood reacted with 1,6-diisocyanatohexane in the presence of moisture for 1 day (B) and 4 days (C).

In the absence of water, 1,6-diisocyanatohexane generally reacted by cross-linking with the wood; in the presence of water, diisocyanate reacted preferentially with water to form mainly ureas with a small amount of biurets. These chemicals were deposited in the wood cell lumens. A small amount of diisocyanate reacted with wood was also found.

Loss of wood and chemical during decay test

Decay resistance of chemically modified wood has been postulated to occur by reducing the ability of the modified cell wall to absorb water to the level that enzymatic degradation of wood cannot take place or by changing the configuration of the cell-wall polymers of wood so that decay enzymes cannot metabolize the modified wood substrates (Stamm and Baechler 1960). Decreased water absorption can be achieved by increasing the hydrophobic nature of wood through chemical modification. Modification of wood with anhydrides, isocyanates, or epoxides reduces the ability of the modified cell wall to absorb water, increasing decay resistance of the modified wood (Stamm and Baechler 1960).

Decay tests showed that wood reacted with 1,6-diisocyanatohexane to 25.8% weight gain (153 mmol/100 g wood) had no weight loss by *Gloeophyllum trabeum* in a 12-week soil-block

 TABLE 1.
 Effect of Gloeophyllum trabeum on wood crosslinked with 1,6-diisocyanatohexane in a 12-week soil-block decay test.

Cross-linking compound	Waisht sain	Weight loss by decay ^a (%)	
	of chemical in wood [*] (%)	Mean	Standard error
1,6-diisocyanatohexane	1.7	46	6.2
	4.9	33	4.5
	7.4	30	2.9
	13.8	13	1.7
	25.8 (153) ^b	0	0
Solvent only (pyridine)	_	41	7.9
Control	_	50	6.5

^a Mean of five replicates.
 ^b Value in parentheses is mmol/100 g wood.

decay test (Table 1). The decay resistance of this modified wood was less effective than that of formaldehyde-modified wood. The formaldehyde cross-linked wood required only 67 mmol of chemical per 100 g of wood (2% weight gain of chemical) (Stamm and Baechler 1960), while diisocyanate-reacted wood required 153 mmol or 2.3 times more chemical (25.8% weight gain of chemical) (Table 1). This difference in decay resistance is probably due to the lower reactivity of 1,6-diisocyanatohexane to cellulose. Wood cross-linked with formaldehyde requires only a small amount of formaldehyde to achieve high dimensional stability and decay resistance. This decay resistance has been attributed to lack of water in the modified cell wall (Stevens et al. 1979) rather than a change in configuration of the wood polymers (Stamm and Baechler 1960). Wood reacted with 1,6-diisocyanatohexane required the high chemical loading of 25.8% (153 mmol/100 g wood) to be effective against decay. This higher loading may indicate that the modified cell wall, which is unable to absorb sufficient water, plays a more important role in decay efficacy than does a change in configuration of cell-wall polymers. Results of water sorption of the diisocyanate-reacted wood further support this explanation.

Water sorption showed that wood reacted with 1,6-diisocyanatohexane to 26.4% and 16% weight gains had equilibrium moisture contents (EMC) of 16.4% and 21.4%, respectively, **TABLE 2.** Effect of cross-linking with 1,6-diisocyanatohexane on water sorption of blocks exposed for 4 weeks at 98% relative humidity and 20 C.

	Weight gain of chemical in wood ^a (%)	Water sorption at equilibrium moisture content ^b (%)
Cross-linking with	3.0°	28.2
1,6-diisocyanatohexane	16.0	21.4
	26.4	16.4
Control	_	29.2

* Mean of three replicates.

^b Water sorption based on oven-dry weight at 105 C for 1 day.

S Two replicates

while the unmodified wood had an EMC of 29.2% (Table 2). An EMC of about 20% in the cell wall of wood is necessary to support fungal decay (Hunt and Garratt 1953). Therefore, the decay resistance of diisocyanate-modified wood probably reflects the lack of water in the cell wall to support decay.

The permanence of the carbamate bond of the modified wood in the presence of decay was determined by analyzing nitrogen content of the decayed and undecayed blocks. Wood reacted with 1,6-diisocyanatohexane lost 5.8% nitrogen in the 12-week soil-block decay test (Table 3). The increase in the hydrophobic nature of the modified wood, which limited water availability in the cell wall of the wood to be used for enzymatic hydrolysis, may have contributed to a small loss of bonded diisocyanate in the decay tests. This small loss of bonded diisocyanate in the modified wood in the decay tests may be attributed to the combined hy
 TABLE 4. Effect of cross-linking with 1,6-diisocyanatohexane on dimensional stability of wood.^a

Weight gain		Dimensional	stability ^b (%)	
in wood (%)	ASE1	ASE2	ASE3	ASE4
17.3	44	49	52	50
19.9	53	55	55	47
20.9	58	57	57	55
23.8	61	64	58	58

* Mean of three replicates.

^b ASE is antishrink efficiency. ASE1 determined from first oven-dry volume to water swollen volume; ASE2 determined from water-swollen volume to second oven-dry volume; ASE3 determined from second oven-dry volume to second water-swollen volume; ASE4 determined from second water-swollen volume to third oven-dry volume.

drolytic, oxidative, and free radical reactions produced by fungal degradation of wood.

Dimensional stabilization

Wood blocks reacted with 1,6-diisocyanatohexane showed improved dimensional stability. The carbamate bond between the wood and the cross-linking compound was more stable than the carbamate bond of methyl-isocyanate-modified wood (Ellis and Rowell 1984) when exposed to the multicycle water swelling and drying treatments. For example, water swelling tests showed that wood reacted with 1,6-diisocyanatohexane to weight gains of 20.9% and 23.8% had ASEs of 58% and 61%, respectively, in the first water swelling and drying treatment. After the fourth water swelling and drying treatment, the ASEs were 55% and 58%, respectively, at the same weight gains (Table 4). This corresponded to a loss of only 3% ASE after four cycles of water swelling and

 TABLE 3. Percentage of nitrogen in wood blocks cross-linked with 1,6-diisocyanatohexane before and after a 12-week soil-block decay test.

	Nitrogen in wood ^a (%)				
	Weight gain	Based on weight of	Actual a	amount ^b	 Nitropen loss from
Treatment	in wood (%)	chemical in wood	Nondecay blocks	Decayed blocks	decayed wood (%)
Wood cross-linking with	26.16	4.20	_	3.27	5.8
1,6-diisocyanatohexane	26.24	4.32	3.57	-	
Solvent (pyridine)	_	_	0.028		_
Control	_	_	0.013	-	_

* Correction for nitrogen (0.03%) in reacted wood as a result of solvent (pyridine).

^b Chemically analyzed.

12-week soil-block decay test.

 TABLE 5.
 Effect of reaction time of wood cross-linked with

 1,6-diisocyanatohexane on weight gain of chemical.

Reaction time ^a (h)	Weight gain of chemical in wood ^b (%)
4	17.3
8	19.9
12	20.9
33	23.8

" Reflux temperature using pyridine as a solvent.

^b Mean of three replicates.

drying treatments. Previous studies with wood blocks reacted with methyl isocyanate showed ASE loss of 7% to 33% from the initial ASEs of between 60% to 77% (Ellis and Rowell 1984).

Improved dimensional stability of wood reacted with 1,6-diisocyanatohexane was comparable to that of wood reacted with methyl isocyanate but was less than that of wood crosslinked with formaldehyde. Wood blocks crosslinked with formaldehyde to only 7% (233 mmol/100 g wood) weight gain had a very high ASE of 90% (Tarkow and Stamm 1953), whereas wood reacted with 1,6-diisocyanatohexane to 24% (143 mmol/100 g wood) weight gain achieved an ASE of 61%. The high dimensional stability of formaldehyde-crosslinked wood can probably be attributed to the higher reactivity of formaldehyde to cellulose in wood, whereas the low dimensional stability of wood reacted with 1,6-diisocyanatohexane probably reflects a decreased reaction of diisocyanate to cellulose in wood. Because diisocyanate is a larger molecule and less polar than formaldehyde, it probably was unable to react with cellulose in wood as readily as formaldehyde. The results of reaction of wood with 1,6-diisocyanatohexane further illustrate this explanation.

Attempts to increase weight gain of reacted diisocyanate in wood by extending reflux time from 12 to 33 h resulted in only a 3% weight gain over the initial treatment, although an excess of 74 mmol of unreacted diisocyanate remained from the initial 97 mmol after the 33-h treatment (Table 5). The above reaction was essentially completed after 12 h. The inability to increase weight gain of the crosslinking compound in wood in this reaction was probably due to decreased accessibility of cellulose to diisocyanate, particularly in the crystalline region of cellulose. Therefore, 1,6-diisocyanatohexane in wood may react preferentially with lignin, hemicelluloses, and to a lesser extent with cellulose. A similar explanation was given to wood modified with methyl isocyanate, which showed that 60% of the lignin hydroxyls and 12% of holocellulose hydroxyls were reacted with methyl isocyanate (Ellis and Rowell 1984).

The dimensional stability of wood reacted with 1,6-diisocyanatohexane resembled that of wood reacted with methyl isocyanate in the initial swelling test. However, the diisocyanate-reacted wood was more stable than the methyl-isocyanate-modified wood in the multicycle swelling tests. This difference in dimensional stability can probably be attributed to the ability of diisocyanate to cross-link with lignin, hemicelluloses, and to some extent with cellulose in wood. Methyl isocyanate only bulked the wood cell wall. The dimensional stability of wood reacted with diisocyanate also had a lower ASE than wood cross-linked with formaldehyde. Cross-linking cellulose, if achievable to a significant extent, may markedly improve dimensional stability.

CONCLUSION

The reaction of wood blocks with 1,6-diisocyanatohexane to 25.8% weight gain prevented attack by a brown-rot fungus, Gloeophyllum trabeum, in a 12-week soil-block decay test. At weight gains of 20.9% and 23.8%, the reacted wood had antishrink efficiencies (ASEs) of 58% and 61%, respectively, with only a small loss of 3% ASE after four cycles of water swelling and drying treatments. Water vapor sorption of wood reacted with 1,6-diisocyanatohexane indicated that the decay resistance of this modified wood is probably due to the inability of the modified cell wall of wood to absorb sufficient water to support decay. Evidence of cross-linking between wood and 1,6diisocyanatohexane was provided by the characteristic carbamate infrared absorption of the modified wood. The data of this study suggested that cross-linking between wood and 1,6-diisocyanatohexane may take place in lignin, hemicelluloses, and to a lesser extent in cellulose. Cross-linking of cellulose in wood, if achievable to a significant extent, may markedly improve dimensional stability.

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