

REACTION OF ISOCYANATES WITH SOUTHERN PINE WOOD TO IMPROVE DIMENSIONAL STABILITY AND DECAY RESISTANCE¹

W. Dale Ellis and Roger M. Rowell

Chemist and Research Chemist
U.S. Department of Agriculture, Forest Service
Forest Products Laboratory,² Madison, WI 53705

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ABSTRACT

Ethyl, *n*-propyl, and *n*-butyl isocyanates reacted with wood without catalyst to yield modified southern pine that was 30 to 50% more dimensionally stable than unmodified specimens and that had improved decay resistance. Phenyl and *p*-tolyl isocyanates and 1,6-diisocyanatohexane, isophorone diisocyanate, and tolylene-2,4-diisocyanate formed nonbonded polymers in wood voids and did not increase dimensional stability. In the presence of 35% dimethylformamide, however, *n*-butyl and phenyl isocyanates, 1,6-diisocyanatohexane and tolylene-2,4-diisocyanate reacted with wood, resulting in increased dimensional stability. The best dimensional stability and decay resistance of all specimens tested were shown by those modified with *n*-butyl isocyanate in the presence of 35% dimethylformamide. The dimensional stability was 70% better than that of unmodified specimens and the weight lost in the decay test was 2%, indicating a high resistance to decay.

Keywords: Isocyanates, dimensional stability, decay resistance, southern pine.

INTRODUCTION

Wood's biodegradability, flammability, changing dimensions with varying moisture contents, and degradability by ultraviolet light are all the result of chemical reactions involving degradative environmental agents. Reacting isocyanates with wood cell-wall polymers has the potential of improving some of these undesirable properties of wood by changing wood's basic chemistry. No systematic study has been conducted on the reactivity of mono- and difunctional isocyanates with wood.

This research was performed to determine the improvements in dimensional stability and decay resistance of wood through reaction with several aliphatic, aromatic, mono- and difunctional isocyanates.

In previous research methyl isocyanate reacted quickly with wood at 120 C, forming stable urethane bonds and producing no byproducts when oven-dry wood was used (Rowell and Ellis 1979). In soil-block tests, southern pine sapwood modified with methyl isocyanate was found to be resistant to attack by the brown-rot fungus *Gloeophyllum trabeum* (Pers. ex Fr.) Murr. (Madison 617) at chemical weight gains of over 20%. At this level of modification, the wood was approximately 60% dimensionally stable in a double-soak water test (Rowell and Ellis 1978). Wood volume increased as a result of reaction with methyl isocyanate and

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was proportional to the calculated volume of isocyanate added. This showed the reaction was with cell-wall components and was not polymerization in the cell lumens. Bonding of methyl isocyanate to wood was indicated by comparison of infrared spectra of unmodified and modified wood extracted with solvents to remove homopolymers and unreacted isocyanates (Rowell 1980).

Others have also reported some success in reacting isocyanates with wood. Veneers of spruce, poplar, and birch swollen in dimethylformamide (DMF) and exposed at 100 to 125 C to phenyl isocyanate vapors gave modified wood that was 77% dimensionally stable (Clermont and Bender 1957). Ethyl, allyl, butyl, *t*-butyl, and phenyl isocyanates were reacted in DMF, with white pine and Engelmann spruce. Butyl isocyanate gave the best results with weight gains of up to 50% and dimensional stabilities to 75% (Baird 1969). Beechwood, impregnated and reacted with 2,4-tolylene diisocyanate (TDI), showed a reduction in moisture sorption as a result of isocyanate bonding (Burmester and Olson 1971). The reaction of TDI with white cedar to 22% weight gain resulted in 50% dimensional stability (Wakita et al. 1977).

MATERIALS AND METHODS

Southern pine wafers, 2.5 by 2.5 by 0.7 cm (radial \times tangential \times longitudinal) were cut with three or four growth rings per cm. Specimens were cut with growth rings parallel to one edge so that specimens remained square during swelling. Before treatment, specimens were dried overnight at 105 C and weighed, and dimensions were measured.

The monofunctional isocyanates used to treat specimens were ethyl, *n*-propyl, isopropyl, *n*-butyl, *p*-tolyl, and phenyl isocyanates. The difunctional isocyanates used were 1,6-diisocyanatohexane (HDI), tolylene-2,4-diisocyanate (TDI), and isophorone diisocyanate (IPDI). Catalysts used were triethylamine (TEA), dimethylformamide (DMF), or dimethylsulfoxide (DMSO).

Duplicate specimens were submerged in 35 ml of treating solution in a 150-ml stainless steel cylinder, which was pressurized to 150 pounds per square inch with dry nitrogen and heated to 120 C for selected treatment times. Immediately after treatment, all specimens were extracted 2 h with benzene:ethanol (2:1, v:v) to remove all unreacted chemicals and soluble reaction products.

Radial, tangential, and longitudinal dimensions of each specimen were measured with a flatbed micrometer before and after treatment, extraction, and drying. These dimensions were used to calculate the volumetric swelling caused by reaction with the isocyanates. The total amount of chemical in the wood was calculated as weight percent gain (WPG) from the specimen weights before and after treatment, extraction, and drying. The amount of isocyanate bonded to the wood was measured as nitrogen, determined by the Kjeldahl method. All modified specimens were milled to 40 mesh and extracted with benzene:ethanol (2:1, v:v), to remove nonbonded chemical, before they were analyzed for nitrogen. Dimensional stability was determined by the water-soak method previously reported (Rowell and Ellis 1978). Two 7-day soaking cycles were used to measure dimensional stability because dimensional stability is usually lower after the second soak of specimens in which the chemical was apparently not bonded.

To determine decay resistance, standard soil-block tests were run according to

specifications in ASTM D-1413 (1973). Sextuplicate specimens for each isocyanate treatment were prepared. All blocks were extracted 2 h with benzene : ethanol (2:1, v:v) before the decay test. Isocyanate-modified specimens and unmodified controls were placed in test with the brown-rot fungus *Gloeophyllum trabeum* (Pers. ex Fr.) Murr. (Madison 617). Samples were removed from test after 12 weeks and the amount of decay measured as percent weight loss.

RESULTS AND DISCUSSION

When an isocyanate reacts with the hydroxyl groups in wood cell-wall components, permanent changes are observable. The changes most easily measured are increased nitrogen in wood, increased wood volume, increased dimensional stability, and increased decay resistance. It is with these changes that the degree of successful chemical modification is measured.

The conditions used and the results of reaction of isocyanates with specimens are shown in Table 1. All of the isocyanates react with or without a catalyst, but ethyl, *n*-propyl, *n*-butyl, and phenyl isocyanates, and TDI showed larger increases in specimen weights than did isopropyl and *p*-tolyl isocyanates, IPDI, and HDI. TEA and DMF made all the isocyanates react more quickly and to higher weight gains.

Nitrogen content

Weight gains of the modified specimens were used to calculate the apparent amount of nitrogen added to the wood. This apparent amount was compared to the amount of nitrogen found by analysis of the specimens after milling and solvent extraction. The difference provided a measure of the amount of non-bonded, extractable isocyanate.

IPDI, phenyl, and *p*-tolyl isocyanate-modified specimens lost 37 to 99% of their nitrogen (Table 2). These losses are high compared to those of specimens modified with ethyl, *n*-propyl, and *n*-butyl isocyanates, which lost 10% or less of the nitrogen by extraction, indicating that ethyl, *n*-propyl, and *n*-butyl isocyanates are bonded to the hydroxyl groups of cell-wall components. Specimens modified with HDI and TDI were inconsistent in the amount of nitrogen lost by extraction.

Volume increases

In all chemically modified wood specimens in this study, the volume of isocyanate (calculated from weight gains of specimens and densities of isocyanates) in the wood was greater than could be accounted for by the measured increase in volume of the wood. An increase in wood volume occurs only when an isocyanate reacts with the cell walls. If the increase in wood volume is less than the volume of chemical in the wood, some of that chemical must be in voids. The increase in volume of specimens modified with HDI, IPDI, TDI, phenyl and *p*-tolyl isocyanates is much less than the volume of chemical in the wood; therefore most of the chemical must be in voids and not reacted with cell walls. In contrast, specimens modified with ethyl, *n*-propyl or *n*-butyl isocyanate showed significant increases in wood volume. This increase is evidence supporting the conclusion that ethyl, *n*-propyl, and *n*-butyl isocyanate reacted with the cell walls.

TABLE I. Reaction of isocyanates^a with southern pine wood.

Iso-cyanate	Weight percent gain	Catalyst or solvent ^b	Reaction time (min)	Calculated chemical volume ^c (cm ³)	Increase in wood volume with treatment (cm ³)	Dimensional stability ^d	
						First soak (%)	Second soak (%)
Ethyl isocyanate							
	11	none	30	0.26	0.21	28	23
	11	none	60	0.28	0.20	31	26
	34	none	120	0.90	0.55	54	49
	36	none	180	0.92	0.58	46	45
<i>n</i> -propyl isocyanate							
	3	5% DMF	60	0.08	0.09	10	2
	3	none	60	0.09	0.11	8	6
	13	none	180	0.34	0.25	36	31
	21	none	300	0.54	0.26	36	31
	24	5% TEA	300	0.61	0.34	42	39
	35	5% DMF	120	0.89	0.28	43	36
Isopropyl isocyanate							
	3	none	60	0.07	0.06	12	3
	7	none	1,080	0.18	0.10	24	10
	12	5% TEA	240	0.32	0.20	28	18
<i>n</i> -butyl isocyanate							
	5	none	120	0.12	0.12	17	11
	7	none	420	0.18	0.13	21	17
	8	5% DMF	60	0.22	0.17	32	21
	8	5% TEA	360	0.20	0.13	17	12
	19	none	1,080	0.50	0.29	35	36
	24	5% DMF	180	0.64	0.35	44	34
	32	35% DMF	15	0.84	0.62	70	68
1,6-diisocyanatohexane							
	10	none	120	0.22	0.08	13	6
	13	none	360	0.28	0.12	16	7
	19	35% DMF	30	0.43	0.21	30	19
	22	5% DMF	120	0.49	0.05	6	4
	38	5% TEA	120	0.87	0.04	7	0
	52	5% TEA	240	1.14	0.03	8	0
Isophorone diisocyanate							
	10	5% DMF	120	0.25	0.16	0	0
	10	none	120	0.26	0.13	0	0
	17	5% TEA	120	0.42	0.05	0	0
	31	80% DMSO	60	0.70	0.19	25	0
	32	80% DMSO	120	0.80	0.30	30	0
Phenyl isocyanate							
	3	none	120	0.07	0.05	7	1
	8	none	420	0.18	0.07	15	8
	19	5% DMF	120	0.41	0.06	12	12
	25	none	1,080	0.52	0.13	29	18
	28	5% TEA	360	0.58	0.06	10	3
<i>p</i> -tolyl isocyanate							
	4	none	180	0.08	0.04	16	8
	3	none	1,440	0.06	0.01	22	12
	16	5% DMF	60	0.32	0.10	15	11
	22	5% TEA	420	0.48	0.08	10	6

TABLE 1. *Continued.*

Iso-cyanate	Weight percent gain	Catalyst or solvent ^b	Reaction time (min)	Calculated chemical volume ^c (cm ³)	Increase in wood volume with treatment (cm ³)	Dimensional stability ^d	
						First soak (%)	Second soak (%)
Tolylene-2,4-diisocyanate							
	5	none	180	0.10	0.06	4	0
	12	5% DMF	60	0.24	0.08	10	0
	13	none	330	0.24	0.06	8	0
	27	none	420	0.53	0.02	0	0
	44	35% DMF	30	0.82	0.10	19	0
	48	5% TEA	240	0.90	0.08	4	0

^a At 120 C and 150 psi.

^b Dimethylformamide (DMF), triethylamine (TEA), dimethylsulfoxide (DMSO).

^c Calculated from weight gain of specimens and densities of isocyanates.

^d Percent reduction in swelling of modified wood in liquid water compared to untreated control. Two 7-day soak periods were used.

Dimensional stability

In the water-soak test, the second soaking cycle shows the stability contributed by the chemicals that reacted with cell-wall components. Little or no dimensional stability is evident when the chemicals fill wood lumens only; therefore, isocyanates that form insoluble products in voids rather than reacting with wood can be detected by the absence of dimensional stability. Wood treated with ethyl, *n*-propyl, and *n*-butyl isocyanates had increased dimensional stability, the highest being 70% in specimens reacted with *n*-butyl isocyanate in the presence of 35% DMF. Somewhat lower dimensional stabilities were observed in ethyl and *n*-propyl isocyanate-modified specimens under the same conditions (Table 1). It was hoped that the difunctional isocyanates would act as crosslinking agents and have a greater effect on dimensional stability at the same or lower weight gains than would a monofunctional isocyanate. The difunctional isocyanates did not, however, bond well to wood cell-wall hydroxyl groups and did not increase dimensional stability any more than did monofunctional isocyanates.

Solvents

In the absence of swelling solvents, HDI, IPDI, TDI, phenyl isocyanate, and *p*-tolyl isocyanate did not show evidence of penetration or reaction in the cell walls except to a slight extent. DMF and DMSO were selected as solvents that would help these isocyanates penetrate and react with the cell walls; both solvents cause wood to swell to a greater extent than does water, and thus increase the penetration and reaction potential of the isocyanates. The reaction time necessary to achieve a given weight gain was shortened by the use of DMF with HDI, TDI, and butyl and phenyl isocyanates (Table 1). The presence of DMF with these four isocyanates caused a greater increase in wood volume than was found without DMF. The phenyl isocyanate reaction was affected more by the 35% DMF than were the other isocyanates. For example, a 30-minute reaction of phenyl isocyanate in the presence of 35% DMF gave a 98 WPG and the wood was broken into many small pieces. In comparison, a 30-minute reaction of phenyl isocyanate in the presence of 5% DMF gave a 7 WPG. The effect of DMF on the isocyanate reaction with wood is attributable to its wood-swelling ability and its ability to catalyze isocyanate reactions.

TABLE 2. Nitrogen analysis of chemically modified southern pine wood.

Iso-cyanate	Catalyst or solvent ^a	Weight percent gain	Nitrogen calculated ^b (%)	Nitrogen analyzed ^c (%)	Nitrogen lost (%)
None (control)	none	0	0.03	0.03	0
Ethyl isocyanate	none	34	5.1	4.9	3.9
	none	62	7.5	7.4	1.3
<i>n</i> -propyl isocyanate	5% TEA	24	3.2	3.0	6.2
	5% DMF	35	4.3	3.8	11.6
<i>n</i> -butyl isocyanate	none	20	2.4	2.3	4.2
	35% DMF	32	3.5	3.3	5.7
1,6-diisocyanatohexane	none	14	2.2	0.6	72.7
	5% TEA	38	4.7	5.4	0
	5% TEA	52	5.8	6.2	0
Isophorone diisocyanate	none	10	1.3	0.2	84.6
	5% TEA	17	1.9	1.2	36.8
	80% DMSO	32	3.5	1.8	48.6
Phenyl isocyanate	none	25	2.3	1.2	47.8
	5% TEA	28	2.6	0.6	76.8
<i>p</i> -tolyl isocyanate	none	4	0.4	0.1	75.0
	5% DMF	16	1.6	0.1	93.8
	5% TEA	22	2.0	0.7	65.0
Tolylenc-2,4-diisocyanate	5% DMF	12	1.9	0.2	89.5
	none	27	3.5	3.4	2.9
	35% DMF	44	5.2	4.7	9.6

^a Dimethylformamide (DMF), triethylamine (TEA), dimethylsulfoxide (DMSO).

^b Calculated from weight gain caused by modification.

^c Wood milled to 40 mesh and extracted with benzene:ethanol (2:1, v:v) before analysis.

Decay resistance

Ethyl, *n*-propyl, and *n*-butyl isocyanate-modified specimens were subjected to a standard soil-block decay test. These isocyanates were selected because all reacted with the wood cell-wall components. Unmodified samples lost 39% of their weight during the 12-week decay test. In comparison, the weight lost by *n*-butyl and *n*-propyl isocyanate-modified wood was 2% and 4%, respectively, at isocyanate weight gains above 18% (Table 3). Ethyl isocyanate-modified wood at 7 WPG lost 23% of its weight by decay while at 26 WPG the loss was only 3%. In the soil-block decay test, IPDI-modified wood was not very decay resistant, losing 11% of its weight during the 12-week test even at weight gains as high as 38%.

TABLE 3. Soil block decay test of southern pine wood chemically modified with isocyanates and inoculated with *Gloeophyllum trabeum*.

Isocyanate	Catalyst or solvent ^a	Weight percent gain	Weight loss (%)
None (control)	none	0	39
Ethyl isocyanate	none	7	23
	none	15	6
	none	26	3
<i>n</i> -propyl isocyanate	5% TEA	10	4
	5% DMF	11	7
	5% DMF	19	4
	5% TEA	26	4
<i>n</i> -butyl isocyanate	35% DMF	18	2
	35% DMF	36	2
Isophorone diisocyanate	90% DMSO	25	11
	80% DMSO	28	10
	80% DMSO	38	11

^a Dimethylformamide (DMF), triethylamine (TEA), dimethylsulfoxide (DMSO).

This poor performance in the decay test by IPDI-modified specimens was expected because the IPDI did not react with the wood but filled lumens with reaction products. The IPDI did not react well with wood in part because of the hygroscopicity of DMSO. The moisture present in the solvent reacted with the isocyanate, preventing reaction with the wood. There are indications that moisture, whether present in the wood or the solvent, will interfere with the reaction of isocyanates with wood. Research on the effects of moisture on the reaction of isocyanates is now in progress.

CONCLUSIONS

Phenyl and *p*-tolyl isocyanates, 1,6-diisocyanatohexane, isophorone diisocyanate, and tolylene-2,4-diisocyanate formed mostly nonbonded polymers in the wood voids when 5% or less catalyst was present. These nonbonded lumen-filling polymers did not increase dimensional stability or decay resistance.

Ethyl, *n*-propyl and *n*-butyl isocyanates reacted with wood with no solvent or catalyst present gave modified wood that had 30 to 50% better dimensional stability than unmodified wood and high resistance to decay. Four percent or less weight was lost in a standard soil-block decay test.

Phenyl isocyanate, 1,6-diisocyanatohexane, tolylene-2,4-diisocyanate and *n*-butyl isocyanate in the presence of 35% dimethylformamide reacted with wood increased the specimens' weight, volume, and dimensional stability. The catalyzed *n*-butyl isocyanate modified wood at 30 to 35% weight gains was 70% more dimensionally stable than unmodified wood and had high resistance to decay. Two percent of specimen weight was lost in a standard soil-block decay test.

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