EFFECTS OF MOISTURE ON THE CHEMICAL MODIFICATION OF WOOD WITH EPOXIDES AND ISOCYANATES[1]

Roger M. Rowell and *W. Dale Ellis*

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

(Received December 1982)

ABSTRACT

The effects of moisture on the reaction of epoxides and isocyanates with wood were investigated. Ponderosa pine at 0%, 5%, and 10% equilibrium moisture contents was reacted separately with either propylene oxide or butylene oxide catalyzed with triethylamine, or with butyl isocyanate catalyzed with dimethylformamide. Five successive treatments were performed while recycling the treatment solutions on specimens with 5% and 10% equilibrium moisture contents. Grinding and extracting the treated wood showed significant losses of nonbonded chemical at these original moisture levels. When antishrink efficiency was determined on propylene oxide treated wood using the double water-soak method, a high resistance to dimensional changes was observed on the first water-soak cycle. Most of this dimensional stability was lost based on the second water-soak cycle, showing that nonbonded polymer had been extracted. Somewhat higher antishrink efficiency values were obtained for butylene oxide and butyl isocyanate treatments. Gas chromatographic determination of products from the propylene and butylene oxide/triethylamine treating solutions showed little water buildup. Total accountable volatile products decreased with successive treatments on specimens originally containing 5% and 10% moisture, indicating the formation of nonvolatile polyglycols in the wood cell wall. Determination of butyl isocyanate solutions following each treatment showed that one quarter or less of the active isocyanate was lost due to reaction with the water in the wood.

Keywords: Chemical modification, moisture content, epoxides, isocyanates, ponderosa pine.

INTRODUCTION

Chemical modification of wood cell-wall polymers has been shown to be an effective way to reduce the tendency of wood to change dimensions when in contact with moisture (Rowell and Ellis 1978, 1979; Rowell and Gutzmer 1975; Rowell et al. 1976). It has also been shown to be an interesting approach to reduce biological attack by microorganisms (Rowell 1980; Rowell and Ellis 1981; Rowell and Gutzmer 1975), termites (Rowell et al. 1979), and marine organisms (Johnson and Gutzmer 1981).

Dimensional stability and resistance to biological attack depend on an adequate distribution of bonded chemicals within the wood cell-wall polymer components. Most of the research at the Forest Products Laboratory has dealt with reactions of epoxides and isocyanates with hydroxyl groups in wood cell-wall polymers.

---

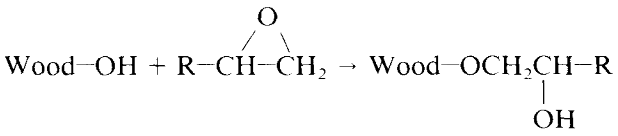
[1] Don Ballard, William Spoede, and Michael Harvath, Jr., of the Oxirane Corporation, performed the gas chromatographic analysis of epoxide treating solutions. The article was written and prepared by U.S. Government employees on official time, and it is therefore in the public domain. The use of trade, firm, or corporation names in this publication is for the information and convenience of the reader. Such use does not constitute an official endorsement or approval by the U.S. Department of Agriculture of any product or service to the exclusion of others which may be suitable.

[2] Maintained at Madison, Wisconsin, in cooperation with the University of Wisconsin.

Wood and Fiber Science, 16(2), 1984, pp. 257–267

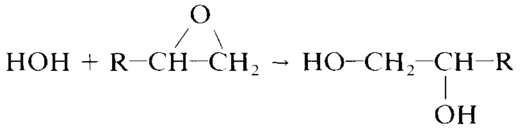
Any moisture present in wood during chemical modification with epoxides and isocyanates will cause these chemicals to react with easily accessible hydroxyl groups in water rather than with the less accessible hydroxyl group in wood cell-wall polymers. Chemical that reacts with free water in the wood ends up as a soluble adduct that is easily removed by extraction with water. For this reason, chemical modification of wood has traditionally been carried out on oven-dried material.

In the case of epoxides, the desired addition product with a cell-wall hydroxyl group is an ether-bonded adduct.



$$\text{Wood—OH} + \text{R—}\overset{\text{O}}{\overset{/\ \backslash}{\text{CH—CH}_2}} \rightarrow \text{Wood—OCH}_2\underset{\text{OH}}{\underset{|}{\text{CH}}}\text{—R}$$

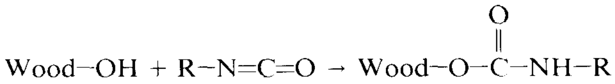
With water and an epoxide, the reaction product is a soluble glycol.



$$\text{HOH} + \text{R—}\overset{\text{O}}{\overset{/\ \backslash}{\text{CH—CH}_2}} \rightarrow \text{HO—CH}_2\text{—}\underset{\text{OH}}{\underset{|}{\text{CH}}}\text{—R}$$

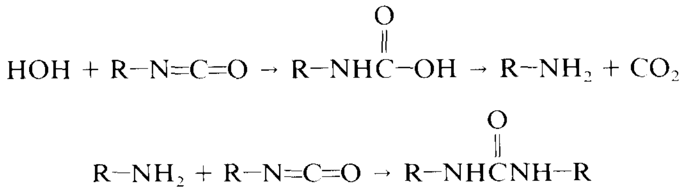
Both the ether-bonded adduct and the water-soluble glycol product give rise to new hydroxyl groups that can react further with additional epoxide. From the reaction shown, 1 mole of water consumes 1 mole of epoxide.

In the case of isocyanates, the additional product with a cell-wall hydroxyl group is an ester- (urethane) bonded adduct.



$$\text{Wood—OH} + \text{R—N=C=O} \rightarrow \text{Wood—O—}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{—NH—R}$$

With water and an isocyanate, the reaction product is a soluble urea derivative. It can be seen in this reaction scheme that for each mole of water, 2 moles of isocyanate are consumed.



$$\text{HOH} + \text{R—N=C=O} \rightarrow \text{R—NH}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{—OH} \rightarrow \text{R—NH}_2 + \text{CO}_2$$

$$\text{R—NH}_2 + \text{R—N=C=O} \rightarrow \text{R—NH}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{NH—R}$$

Since it is not possible or practical to remove all water from wood, the purpose of this research was to determine what effect reacting epoxides or isocyanates with ponderosa pine conditioned to three moisture contents (0, 5, and 10%) had on dimensional stability.

EXPERIMENTAL

Sixty-five ponderosa pine specimens, 2 by 8 by 18 centimeters (cm) (radial by tangential by longitudinal), were prepared from boards cut from the same log. Some of the specimens were oven-dried (OD), some were equilibrated at 30%

relative humidity (RH) (approximately 5% equilibrium moisture content (EMC)) at 27 C, and some were equilibrated at 65% RH (approximately 10% EMC) at 27 C. These specimens were then used to run three series of chemical modification reactions.

Series A—oven-dried.—The OD specimens were treated in a stainless steel cylinder with either (1) 1,500 milliliters (ml) of propylene oxide (PO), 95%, and triethylamine (TEA), 5%; (2) 1,500 ml of butylene oxide (BO), 95%, and TEA, 5%; or (3) 1,500 ml of butyl isocyanate (BI), 65%, and dimethylformamide (DMF), 35%. All reactions were at 120 C, 150 lb/in.^{2}. At the end of each treatment, the cylinder was drained of treating chemical, and vacuum applied for 30 min. The specimen was then removed, oven-dried at 105 C for 24 h, and the weight percent gain (WPG) was determined, based on the original untreated OD weight.

A second set of OD specimens were then treated with the first treating solution plus fresh PO or BO/TEA or BI/DMF mixture (approximately 200 ml) totaling 1,500 ml. This procedure was repeated for a total of 10 treatments on the PO/TEA and BO/TEA mixtures and 5 treatments on the BI/DMF mixture.

Series B—5% EMC.—The same procedure as the preceding was used, except that wood specimens were equilibrated to approximately 5% EMC before treatment. The procedure was repeated for a total of five treatments each on all three chemical mixtures.

Series C—10% EMC.—The same procedure as Series A was used, except that wood specimens were equilibrated to approximately 10% EMC before treatment. The procedure was repeated for a total of five treatments each on all three chemical mixtures.

After each of the PO/TEA and BO/TEA series was run and initial WPG determined, each specimen was oven-dried for 14 days at 105 C and weight loss determined.

Determination of dimensional stability

A 2.5-cm section was cut from the center of each specimen from the PO/TEA, BO/TEA, and BI/DMF treatments. From this section, a 2- by 2.5- by 2.5-cm (radial by tangential by longitudinal) specimen was cut and antishrink efficiency (ASE) was determined by the double water-soaking method described earlier (Rowell and Ellis 1978). One of the remaining specimen ends, 2 by 8 by 8 cm (radial by tangential by longitudinal), was conditioned at 90% RH/27 C, and after each specimen had been equilibrated for 32 days, EMC and ASE were determined. Another portion of each originally treated specimen was ground to 20 mesh, and then extracted with refluxing benzene/ethyl alcohol (2/1, vol/vol) for 2 h in order to determine the amount of treating chemical not permanently bonded to the wood.

Analysis of treating solutions

A 10-ml sample of treating solution was collected at the end of each PO/TEA and BO/TEA run and submitted for gas chromatographic analysis (GC). A Varian 3700 gas chromatograph was used with a thermal conductivity detector. A helium carrier was used with a 400-cm by 2-millimeter (mm) column packed with a 60/80-mesh Porapak QS. Starting column temperature on the GC was 75 C with a programmed temperature rise of 4 C per minute to a final temperature of 230 C.

TABLE 1. *Repeated reactions of propylene oxide/triethylamine with oven-dried and moist ponderosa pine.*[1]

Specimen	Equilibrium moisture content when treated	Weight gain	Weight loss after extraction with benzene/ethanol	Weight loss after 14 days at 105 C
	%			
1-0-PO	OD	26.0	12.2	4.1
2-0-PO	OD	38.0	13.4	5.1
3-0-PO	OD	39.0	13.1	5.2
4-0-PO	OD	38.4	13.3	5.3
5-0-PO	OD	31.9	12.7	5.1
6-0-PO	OD	32.7	14.2	5.1
7-0-PO	OD	40.4	13.8	5.4
8-0-PO	OD	33.3	14.5	5.3
9-0-PO	OD	40.3	14.9	5.3
10-0-PO	OD	32.0	15.4	4.9
1-5-PO	5.6	47.4	28.3	16.5
2-5-PO	5.7	54.1	26.5	15.5
3-5-PO	5.5	52.0	27.2	16.4
4-5-PO	5.5	53.2	29.4	16.6
5-5-PO	5.7	53.2	28.5	16.9
1-10-PO	10.8	59.0	35.6	20.2
2-10-PO	10.0	49.6	31.1	19.8
3-10-PO	10.6	61.1	33.7	20.4
4-10-PO	10.7	49.5	31.6	16.3
5-10-PO	10.0	39.3	25.1	14.0
Control	—	—	3.9	<0.2

[1] 50-minute reaction time.

The ratio of epoxide to TEA was determined, along with percent water and volatile unknowns. On the BO/TEA samples, the percentage of butylene glycol was determined. Total recovered materials were also determined.

A 10-ml sample of each treating solution was collected at the end of each BI/DMF run, and free isocyanate remaining was determined by the ASTM Standard D 2572-70 titration procedure (ASTM 1970).

RESULTS AND DISCUSSION

There is a wide variation in the properties of wood even within a single species. To minimize the effects of this variation on our results, all specimens for this study came from a single large board.

Equilibrium moisture contents of approximately 5% and 10% were selected to determine the effects of low levels of moisture in wood on epoxide and isocyanate reactions because these represent the approximate moisture contents found in kiln-dried lumber. Equilibrium moisture content was determined at 30% or 65% RH (Tables 1–3) after equilibration.

In the industrial application of epoxides to dry wood material (such as particleboard production), reaction chemicals would be reused as many times as possible before recovery was completed. For this reason, 10 runs are reported for propylene and butylene oxides on OD wood, but for all other treatments and EMC levels 5 runs were reported.

TABLE 2. *Repeated reactions of butylene oxide/triethylamine with oven-dried and moist ponderosa pine.*[1]

Specimen	Equilibrium moisture content when treated	Weight gain	Weight loss after extraction with benzene/ethanol	Weight loss after 14 days at 105 C
	%			
1-0-BO	OD	33.6	12.6	5.1
2-0-BO	OD	26.3	13.7	4.2
3-0-BO	OD	33.1	13.1	5.0
4-0-BO	OD	23.4	15.4	4.1
5-0-BO	OD	29.7	15.2	5.9
6-0-BO	OD	38.0	18.4	6.7
7-0-BO	OD	21.2	16.4	3.0
8-0-BO	OD	32.7	16.2	4.1
9-0-BO	OD	29.6	15.8	5.0
10-0-BO	OD	36.4	17.3	5.4
1-5-BO	4.9	50.7	34.8	14.6
2-5-BO	5.1	52.6	33.1	15.7
3-5-BO	5.5	71.8	38.1	18.5
4-5-BO	5.4	65.8	36.5	17.7
5-5-BO	5.5	70.8	38.1	20.0
1-10-BO	10.5	69.7	39.7	24.4
2-10-BO	10.4	77.8	43.6	25.7
3-10-BO	9.8	77.3	43.7	25.9
4-10-BO	10.3	91.1	47.2	27.8
5-10-BO	10.0	68.3	39.4	24.3
Control	—	—	3.9	<0.2

[1] 3.5-hour reaction time.

TABLE 3. *Repeated reactions of butyl isocyanate/dimethylformamide with oven-dried and moist ponderosa pine.*

Specimen	Equilibrium moisture content when treated	Reaction time	Weight gain	Weight loss after extraction with benzene/ethanol
	%	*min*	%	%
1-0-BI	OD	45	34.7	5.5
2-0-BI	OD	45	36.0	6.1
3-0-BI	OD	45	43.6	7.1
4-0-BI	OD	45	44.1	6.6
5-0-BI	OD	45	56.4	11.9
1-5-BI	5.0	35	38.3	18.4
2-5-BI	5.5	30	45.8	19.2
3-5-BI	5.5	30	45.3	21.3
4-5-BI	5.7	20	51.3	21.7
5-5-BI	5.2	20	55.8	21.9
1-10-BI	10.1	10	62.6	24.1
2-10-BI	10.0	10	59.4	37.4
3-10-BI	10.6	10	41.4	24.1
4-10-BI	10.1	10	40.3	24.0
5-10-BI	10.8	10	28.0	18.2
Control	—	—	—	3.9

TABLE 4. *Dimensional stability of propylene oxide/triethylamine-modified ponderosa pine.*

Specimen	Water soak		90% relative humidity/27 C	
	ASE$_1$[1]	ASE$_2$[2]	ASE$_1$[3]	Equilibrium moisture content
	%			
1-0-PO	52.8	11.1	3.8	20.2
2-0-PO	67.7	34.3	96.6	20.5
3-0-PO	57.0	22.0	—	—
4-0-PO	64.0	34.3	—	—
5-0-PO	61.0	25.1	—	—
6-0-PO	62.7	29.8	26.4	20.4
7-0-PO	68.8	42.0	—	—
8-0-PO	60.8	12.6	32.1	20.2
9-0-PO	59.3	20.3	77.4	19.1
10-0-PO	58.2	13.8	17.0	20.4
1-5-PO	88.1	29.3	0.0	21.6
2-5-PO	76.4	18.5	77.4	28.1
3-5-PO	83.4	24.4	—	—
4-5-PO	84.5	33.4	—	—
5-5-PO	79.6	23.7	64.2	28.1
1-10-PO	85.6	16.5	79.2	34.5
2-10-PO	88.1	0.0	77.4	32.3
3-10-PO	87.0	24.1	83.0	34.3
4-10-PO	80.6	27.1	71.7	31.5
5-10-PO	72.3	0.0	64.2	28.0
Control	—	—	—	19.4

[1] Value derived from oven-dry to wet—first cycle.
[2] Value derived from reoven-dry to wet—second cycle.
[3] Value derived from oven-dry to 90% relative humidity.

It can be seen that the WPG for PO/TEA (Table 1) and for BO/TEA (Table 2) OD ranges between 26 and 40 during the 10 separate treatments. Oven-drying these specimens for 14 days at 105 C caused about a 5% weight loss. This weight loss represents the nonbonded materials that could be removed by heating alone. Extraction with benzene/ethanol removed additional nonbonded materials. Weight losses from nontreated control specimens were less than 0.2% in the 14-day OD test and less than 4% after benzene/ethanol extraction. For the OD BI/DMF system, the WPG ranged between 35 and 56. Extraction with benzene/ethanol resulted in weight losses ranging between 5.5 and 11.9%. Low molecular weight oligomers at PO and BO are volatile enough to be removed with heat, whereas BI oligomers, being less volatile, are not, so the 14-day heating experiment was not done on the BI-modified specimens.

Treatment of wood at 5% EMC with PO/TEA resulted in WPG between 47 and 54 (Table 1), BO/TEA between 50 and 72 WPG (Table 2), and BI/DMF between 38 and 56 WPG (Table 3). High WPGs were evident on the first treatment and increased generally in subsequent treatments. The extraction levels with benzene/ethanol are higher than those obtained with OD specimens, and for the PO/TEA and BO/TEA, there is a greater loss after 14 days at 105 C than was observed in the treated OD specimens.

A similar pattern was observed in those specimens treated at 10% EMC, except that the extracted materials with benzene/ethanol are higher than specimens

TABLE 5. *Dimensional stability of butylene oxide/triethylamine-modified ponderosa pine.*

			90% relative humidity/27 C	
	Water soak			Equilibrium moisture content
Specimen	ASE$_1$[1]	ASE$_2$[2]	ASE$_1$[3]	
	%			
1-0-BO	69.2	58.7	60.4	12.9
2-0-BO	68.1	56.5	—	—
3-0-BO	68.1	59.1	—	—
4-0-BO	39.9	25.5	0.0	14.5
5-0-BO	57.2	42.9	—	—
6-0-BO	75.4	65.2	—	—
7-0-BO	58.2	52.8	37.7	14.3
8-0-BO	75.5	58.1	—	—
9-0-BO	70.2	59.8	41.5	14.7
10-0-BO	75.4	68.8	—	—
1-5-BO	91.8	49.7	66.0	14.4
2-5-BO	91.9	46.6	94.0	14.3
3-5-BO	100.0	62.0	77.4	14.4
4-5-BO	100.0	66.2	—	—
5-5-BO	96.4	57.5	73.6	14.8
1-10-BO	98.8	50.0	—	—
2-10-BO	97.6	53.5	—	—
3-10-BO	93.0	43.7	58.5	16.5
4-10-BO	100.0	57.9	88.7	17.7
5-10-BO	90.8	35.2	67.9	16.4
Control	—	—	—	19.4

[1] Value derived from oven-dry to wet—first cycle.

[2] Value derived from reoven-dry to wet—second cycle.

[3] Value derived from oven-dry to 90% relative humidity.

treated at both OD and 5% EMC, and there was a greater loss of volatile material on oven-drying at 105 C for 14 days.

The PO/TEA treatment gave high initial dimensional stability when specimens were treated OD (Table 4). On the second soak cycle, the ASE value was significantly lower. This also occurred on specimens conditioned to 5% and 10% EMC and indicates that cell-wall penetration by the chemical had taken place but with little or no bonding to the wood cell-wall components. Similar results were obtained with BO/TEA treating system (Table 5), except that there was less difference between the first and second soak cycle ASE tests, and the ASE values were somewhat higher than PO/TEA. The BI/DMF-modified specimens had high initial ASE values and retained values on the second soak cycle (Table 6), indicating that bonding of chemicals with wood cell-wall components was high for this system when treated OD. Results at 5% and 10% EMC are similar to the PO and BO systems.

At 90% RH, PO/TEA- (Table 4) and BO/TEA-modified (Table 5) specimens have erratic ASE values ranging from 0% to 97% at all levels of initial moisture content. Not all PO and BO specimens were equilibrated at 90% RH, but of those that were, there was no clear pattern of consistency that could be used to predict the moisture vapor ASE value. Part of the explanation of this inconsistency may be due to overtreatment of some specimens, which causes cell-wall rupture. It has been shown that if this takes place, it has a dramatic effect on ASE (Rowell

TABLE 6. *Dimensional stability of butyl isocyanate/dimethylformamide-modified ponderosa pine.*

Specimen	Water soak		90% relative humidity/27 C	
	ASE$_1$[1]	ASE$_2$[2]	ASE$_1$[3]	Equilibrium moisture content
	%			
1-0-BI	71.4	73.8	67.7	8.1
2-0-BI	76.4	75.1	60.9	7.8
3-0-BI	69.3	70.4	58.1	7.0
4-0-BI	72.5	75.0	62.8	7.1
5-0-BI	79.4	80.6	70.8	5.9
1-5-BI	66.0	48.5	87.6	10.2
2-5-BI	85.6	77.0	79.1	9.2
3-5-BI	80.8	70.8	75.7	9.5
4-5-BI	83.3	73.4	90.9	9.4
5-5-BI	69.1	47.8	77.7	9.0
1-10-BI	67.0	45.4	88.1	10.2
2-10-BI	72.7	44.8	92.6	10.2
3-10-BI	72.4	61.2	92.4	12.0
4-10-BI	63.3	32.6	80.9	11.6
5-10-BI	72.2	60.7	93.8	12.6
Control	—	—	—	19.4

[1] Value derived from oven-dry to wet—first cycle.
[2] Value derived from reoven-dry to wet—second cycle.
[3] Value derived from oven-dry to 90% relative humidity.

TABLE 7. *Gas chromatographic analysis of propylene oxide/triethylamine solutions used to modify ponderosa pine.*

Sample no.	PO/TEA ratio	Water	Volatile unknown	Total
			%	
1-0-PO	21.4	0.03	0.04	92.0
2-0-PO	21.5	0.04	0.06	92.7
3-0-PO	20.5	0.05	0.22	93.4
4-0-PO	19.8	0.22	1.62	97.5
5-0-PO	19.6	0.09	0.18	96.0
6-0-PO	18.9	0.04	0.13	92.1
7-0-PO	19.6	0.17	0.14	90.6
8-0-PO	19.0	0.08	0.13	91.1
9-0-PO	18.1	0.06	0.31	91.4
10-0-PO	16.7	0.15	0.23	84.4
1-5-PO	17.5	0.09	0.07	88.7
2-5-PO	19.3	0.18	0.16	82.6
3-5-PO	19.2	0.11	0.06	77.8
4-5-PO	20.1	0.12	0.06	76.7
5-5-PO	20.6	0.08	0.03	68.4
1-10-PO	23.4	0.23	0.85	90.1
2-10-PO	23.9	0.08	0.07	78.1
3-10-PO	24.1	0.08	0.05	71.2
4-10-PO	21.2	0.17	0.11	60.3
5-10-PO	23.7	0.34	0.54	50.5
Starting solution	19	<0.01	<0.02	99+

TABLE 8. *Gas chromatographic analysis of butylene oxide/triethylamine solution used to modify ponderosa pine.*

Sample no.	BO/TEA ratio	Butylene glycol	Water	Volatile unknown	Total
		%			
1-0-BO	22.1	0.03	0.03	0.34	93.6
2-0-BO	19.1	0.07	0.03	0.31	94.6
3-0-BO	17.9	0.07	0.23	0.60	94.1
4-0-BO	15.8	0.07	0.12	0.39	93.3
5-0-BO	15.0	0.09	0.13	0.36	91.9
6-0-BO	14.0	0.13	0.34	0.37	90.8
7-0-BO	15.2	0.10	0.09	0.48	84.9
8-0-BO	15.5	0.12	0.18	0.45	89.7
9-0-BO	16.4	0.11	0.12	0.29	90.3
10-0-BO	16.3	0.12	0.18	0.33	90.1
1-5-BO	21.0	0.02	0.26	0.22	95.6
2-5-BO	21.3	0.04	0.97	0.17	92.0
3-5-BO	22.1	0.06	0.07	0.23	85.4
4-5-BO	21.3	0.07	0.45	0.43	81.7
5-5-BO	22.5	0.07	0.63	0.34	78.5
1-10-BO	21.6	0.01	0.11	0.38	89.9
2-10-BO	22.3	0.04	0.10	0.38	80.8
3-10-BO	22.7	0.04	0.09	0.26	73.8
4-10-BO	21.3	0.02	0.09	0.27	67.1
5-10-BO	24.4	0.04	0.05	0.33	58.7
Starting solution	19.0	<0.01	<0.01	<0.02	99+

et al. 1976). The BI/DMF-modified specimens are higher and relatively more constant than PO/TEA or BO/TEA, ranging from 58 to 94% (Table 6). It is interesting to note that a control specimen at 90% RH had an EMC of 19.4%, while PO/TEA-modified specimens had an EMC ranging from 20 to 34%. The BO/TEA-modified specimens showed a lower EMC than the control (14 to 17%), and BI/DMF-modified specimens showed a significantly lower EMC than the control (6 to 12%).

Little difference in specimen properties was observed on repeated use of the treating solution. The effects of moisture content are seen in the first sample treated, and subsequent treatments do not compound the effects of accumulated moisture.

Gas chromatographic examination of the treating solutions (Tables 7 and 8) showed no buildup of water in reusing the solutions up to five times on moist specimens. With the BO solutions there was an increasing amount of butylene glycol as the treating solution was reused, showing that some of the BO was hydrolyzed to the glycol. There was not a great deal of variation in the amount of unknown volatile material from both PO/TEA and BO/TEA treating solutions.

The most significant difference between OD, 5% and 10% EMC specimens on PO/TEA and BO/TEA solutions was observed in the total recovered accountable materials (Tables 7 and 8). Over 90% of each treating solution could be accounted for as unreacted epoxide, TEA, or a low molecular weight volatile glycol when OD specimens were reacted. As the moisture content in the wood increased, the

TABLE 9. *Determination of isocyanate activity in butyl isocyanate solution used to modify ponderosa pine.*

Specimen	Isocyanate activity remaining
	%
1-0-BI	62.30
2-0-BI	60.96
3-0-BI	60.33
4-0-BI	58.63
5-0-BI	58.14
1-5-BI	59.90
2-5-BI	56.98
3-5-BI	54.48
4-5-BI	52.18
5-5-BI	49.18
1-10-BI	59.42
2-10-BI	55.44
3-10-BI	52.62
4-10-BI	49.61
5-10-BI	46.02
65% BI/35% DMF	63.08
100% BI	100.03

total accountable material decreased significantly with continuous solution use. This would indicate that higher molecular weight materials were formed which were not volatile enough to pass through the gas chromatograph. These epoxy polymers were not bonded to the wood cell-wall components.

The starting ratio of PO/TEA or BO/TEA of 95/5 was 19. After one treatment of the wood, the ratio was up to 21 to 22 for both PO and BO and then it decreased with subsequent treatments to 15 to 16 (Tables 7 and 8). This means that the epoxide was removed and TEA was increasing as new 95/5 mix was added to make up the volume for the next treatment. When moisture was present in the wood, the ratio of epoxide/TEA increased somewhat. This means that TEA was also being destroyed by the presence of water.

The number of reactive isocyanate groups left after solution use in the BI/DMF system is shown in Table 9. Pure BI shows 100% activity, and a treatment solution of 65% BI and 35% DMF had 63% activity. Some activity was lost during reuse of the treating solution on OD, 5% and 10% EMC specimens but still remained high even after five treatments with specimens containing 10% EMC.

CONCLUSIONS

Reactions of simple epoxides and isocyanates with wood were sensitive to even low levels of moisture. The propylene oxide/triethylamine reaction system seemed to be the most affected by moisture, as shown by both high weight losses by extraction of nonbonded chemical and by losses in antishrink efficiency. The butylene oxide/triethylamine-modified moist wood retained about 50% of the antishrink efficiency in a double water-soaking test even though large amounts of nonbonded chemicals were removed upon extraction. Butyl isocyanate-modified moist wood also retained about 50% antishrink efficiency in the double water-soaking test with significant losses of nonbonded chemical.

The high antishrink efficiency found at 90% RH on wood conditioned at 10% EMC showed that reaction between water in the wood and the chemicals took place in the cell wall.

As evidenced by gas chromatographic data, a high percentage of nonbonded, nonvolatile products were formed in specimens that were initially conditioned to 10% EMC. Simple propylene glycol or butylene glycol are volatile, so glycols of higher molecules were formed.

Because cell-wall bonded chemical modification procedures are sensitive to moisture, the greatest single application of this type of technology would occur in the manufacture of reconstituted products where standard operating procedures call for dry wood materials, spray chemical addition for maximum distribution, small sample size for good penetration, and high temperature and pressure in product formation. These are exactly the procedures required for successful chemical modification.

REFERENCES

American Society for Testing and Materials. 1970. Isocyanate groups in urethane materials or prepolymers. ASTM D 2572. ASTM, Philadelphia, PA.

Johnson, B. R., and D. I. Gutzmer. 1981. Marine exposure of preservative-treated small wood panels. U.S. Department of Agriculture, For. Serv. Res. Pap. FPL 399. For. Prod. Lab., Madison, WI. 14 pp.

Rowell, R. M. 1980. Distribution of reacted chemicals in southern pine modified with methyl isocyanate. Wood Sci. 13(2):102–110.

———, and W. D. Ellis. 1978. Determination of dimensional stabilization of wood using the water-soak method. Wood Fiber 10(2):104–111.

———, and ———. 1979. Chemical modification of wood: Reaction of methyl isocyanate with southern pine. Wood Sci. 12(1):52–58.

———, and ———. 1981. Bonding of isocyanates to wood. Pages 263–284 *in* K. N. Edwards, ed. Urethane chemistry and applications. Am. Chem. Soc. Symposium Series 172, Chap. 19.

———, and D. I. Gutzmer. 1975. Chemical modification of wood: Reactions of alkylene oxides with southern yellow pine. Wood Sci. 7(3):240–246.

———, ———, I. B. Sachs, and R. E. Kinney. 1976. Effects of alkylene oxide treatments on dimensional stability of wood. Wood Sci. 9(1):51–54.

———, S. V. Hart, and G. R. Esenther. 1979. Resistance of alkylene-oxide modified southern pine to attack by subterranean termites. Wood Sci. 11(4):271–274.