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Improvements in Decay Resistance Based on Moisture Exclusion

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Moisture content has an effect on the biological decay of wood. The literature states that serious decay occurs when the moisture content of wood is above the fiber saturation point (FSP), which is the measurement of the moisture content of wood when the cell walls are saturated and the cell cavities free from water (average 30%).We can chemically modify wood hydroxyls by various treatments (i.e., acetylation, isocyanates, and epoxides) which result in the lowering of the FSP. If we modify the availability of water in the cell wall, we can reduce or eliminate biological degradation. So is biological protection as simple as removing a water molecule at the glycosidic hydrolysis site required by the degrading enzyme? Investigations are underway to chemically modify wood and fiber samples and evaluate them biologically by the soil block test, as well as by the FSP and the equilibrium moisture content (EMC). EMC is the moisture content of wood at any given relative humidity and temperature. Potential correlation between moisture exclusion and biological protection will be discussed.

Keywords: chemical modification; wood decay; wood preservation; fiber saturation point; equilibrium moisture content

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INTRODUCTION

Untreated wood that has low natural durability, such as most commercial softwood sawtimber, biologically degrades in outdoor applications. Wood preservative chemicals are impregnated into wood to combat this biological degradation. The most common wood preservatives used today are based on broad spectrum toxicity and are being examined for environmental impact [1]. Therefore, alternatives are being investigated.

In addition to the mechanism of toxicity, there are other ways of protecting wood. Suttie [2] reviews new strategies for wood protection, pointing out the main methods of preventing fungal attack on wood by: killing the fungus (toxicity); rendering the food source unusable (chemically modify); preventing the wood from becoming wet (chemically modify); or interfering with the chemicals that the wooddestroyers use to break the bonds (biochemical methods). He discusses the biochemical methods, natural timber extractives, restricting water ingress, and chemical modification. This paper will concentrate on the latter. A detailed review of treatments and procedures for chemically modifying wood was covered by Rowell in 1983 [3].

Wood is a three dimensional, polymeric composite made up primarily of lignin, hemicelluloses, and cellulose. These three polymers make up the cell wall, which is responsible for most of the physical and chemical properties of wood. Lignin, hemicelluloses, and cellulose each have accessible hydroxyls and other oxygen containing groups that attract moisture through hydrogen bonding, therefore rendering wood hygroscopic.

Wood can sorb and desorb moisture from water vapor in the atmosphere to maintain equilibrium. One way to measure this is by the equilibrium moisture content (EMC), which is the moisture content of wood at any given relative humidity and temperature. Moisture swells the cell wall and expands until the cell wall is saturated with water. This is called the fiber saturation point (FSP), which is the measurement of the moisture content of wood when the cell walls are saturated and the cell cavities free from water. Going above the FSP, water is consided "free" in the voids of wood and does not expand the wood. Each wood component sorbs moisture to a different extent: hemicelluloses > cellulose > lignin [4-6]. Some hydroxyls in the wood components are not accessible to moisture.

Chemical modification is a way to change the hydrophilic nature of the cell wall polymers of wood. The hydroxyl groups of the wood components are reacted with chemical reagents, resulting in stable, covalently-bonded group attachment. The modifications are not based on introducing biocides or toxicity and therefore should be more environmentally friendly. Chemical modification can improve water resistance, dimensional stability, and decay resistance.

This paper looks at three different ways to modify wood hydroxyls: alkyl anhydrides (acetic anhydride); epoxides (propylene oxide and butylene oxide); and isocyanates (methyl isocyanate and n-butyl isocyanate). EMC, FSP, and biological efficacy were performed on modified samples to look at the effect of water on the biological decay of wood.

MATERIALS AND METHODS

All treatments (acetylation, propylene oxide, butylene oxide, methyl isocyanate and n-butyl isocyanate) were performed on southern pine solid wood samples. Acetylation also was performed on aspen.

Treatments:

1.) ***Acetylation***

Southern pine and aspen blocks (2 cm x 2 cm x 2 cm and 2 cm x 2 cm x 15 cm (radial x tangential x longitudinal, respectfully)) were cut and dried at 105 °C in a forced draft oven for 24 hours. Samples were weighed and then reacted in a stainless steel reactor for 1-16 hours with acetic anhydride:toluene mixture (1:1, vol.:vol.) [7]. Reaction temperature was 120 °C with 150 psi nitrogen pressure. After modification, samples were again oven dried and weighed. Weight percent gain was determined from original oven dried weight.

Percent acetyl content was determined by gas chromatography following deacetylation of ground and mixed samples with sodium hydroxide solution [8].

2.) ***Epoxides***:

Propylene oxide (PO) and butylene oxide (BO):

Southern pine blocks (2 cm x 2 cm x 2 cm) were cut and dried at 105 °C in a forced draft oven for 24 hours. Samples were weighed and then reacted in a stainless steel reactor with a mixture of propylene oxide or butylene oxide and triethylamine (95:5 (vol.:vol.)) at 120 °C and 150 psi nitrogen pressure, from 1 to 60 minutes for propylene oxide and 2 to 4 hours for butylene oxide [9]. The treating solution was drained off and the excess was vacuumed off. Samples were air dried under a fume hood, extracted in a soxhlet extractor for 2 hours with toluene:ethanol mixture (2:1, vol.:vol.), and then oven dried. Percent weight gain was calculated.

3.) Isocyanates:

Methyl isocyanate n-butyl isocyanate:

Southern pine blocks (2 cm x 2 cm x 2 cm) were cut and dried at 105 °C in a forced draft oven for 24 hours. Samples were weighed and then reacted in a stainless steel reactor with methyl isocyanate or n-butyl isocyanate and 35% dimethylformamide at 120 °C and 150 psi nitrogen pressure [10], [11]. The treating solution was drained off and the excess was vacuumed off. Samples were air dried under a fume hood, extracted in a soxhlet extractor for 2 hours with toluene:ethanol mixture (2:1, vol.:vol.), and then oven dried. Percent weight gain was calculated.

Analyses:

1.) ***Equilibrium Moisture Content (EMC):***

EMC of untreated and chemically modified wood samples was determined by placing weighed, oven dried samples in constant humidity rooms at 30%, 65%, or 90% relative humidity (RH) and 27 °C. After 14-21 days samples were reweighed until stable and the EMC was determined. Six replicates of each treatment were run and averaged.

2.) ***Fiber Saturation Point (FSP):***

FSP of acetylated aspen samples was measured using the non-solvent - water technique with slight modifications [12]. Ground wood was used which was equilibrated in a 10% dextran solution for 12 hours and then measured on a differential refractometer.

3.) ***Biological Efficacy:***

Standard soil block tests were performed according to specification outlined in ASTM D 1413 [13]. Untreated controls and chemically modified samples of southern pine and aspen wood (2 cm x 2 cm x 2 cm),

were placed in test with the brown-rot fungus *Gloeophyllum trabeum* and the white-rot fungus *Coriolus versicolor*. Samples were removed after 12 weeks and the extent of decay was determined as oven dry weight loss.

Fungal cellar testing with nonsterile soil containing brown-, white-, and soft-rot fungi and tunneling bacteria was run on acetylated southern pine wood samples [14]. Samples were exposed for 12 months. The rating system was 0 = no attack; 1 = slight attack; 2 = moderate attack; 3 = heavy attack; 4 = destroyed; S = swollen.

RESULTS AND DISCUSSION

Treatments:
Acetylation of wood;

$$\text{Wood-OH} + CH_3\text{-C(=O)-O-C(=O)-}CH_3 \rightarrow$$
$$\text{Wood-O-C(=O)-}CH_3 + CH_3\text{-C(=O)-OH}$$

is a single site reaction in which one acetyl group reacts with one hydroxyl group and no further polymerization is involved. This means that all the acetyl weight gain can be directly converted into units of hydroxyl groups blocked. In the reaction with acetic anhydride, acetylation occurs and acetic acid is split out as a by-product.

The generalized reaction of epoxides with hydroxyl groups is:

$$\text{Wood-OH} + \text{R-CH(-O-)}CH_2 \rightarrow \text{Wood-O-}CH_2\text{CH(OH)-R}$$

With epoxides, a new hydroxyl group develops from the reaction, which provides an initiation step fordeveloping a short chain polymer.

The generalized reaction of isocyanates with wood hydroxyls is:

$$\text{Wood-OH} + \text{R-N=C=O} \rightarrow \text{Wood-O-C(=O)-NHR}$$

Methyl isocyanate reacts quickly with wood and forms stable urethane bonds. n-Butyl isocyanate reacts best with 35% dimethylformamide present.

Analyses

1. ***EMC*:**

The EMC at 30%, 65%, or 90% RH and 27 °C of various percent weight gains of acetylated southern pine and aspen woods are found in Table I. Graphically, Figure I shows over 50% reduction in the EMC of the highest level of acetylated wood (21.1 % weight gain) at 90% RH, compared to the untreated control, for both pine and aspen.

The EMC at 90% RH and 27 °C of various percent weight gains of propylene oxide, butylene oxide, and n-butyl isocyanate are found in Table 11. Figure I shows the effectiveness of n-butyl isocyanate and to a lesser extent, butylene oxide, to lower the EMC of southern pine wood. The propylene oxide did not make a significant contribution in lowering the EMC of pine wood.

2. ***FSP*:**

The FSP of acetylated southern pine and aspen are presented in Table I. From the data, one can see the effectiveness of acetylation on lowering the FSP by at least 75% at 21.1 percent weight gain of southern pine and by at least 65% at 17.6 percent weight gain for aspen.

3. ***Biological Efficacy*:**

The results of the soil block test are found in Table I and Table II. The results are presented graphically in Figure II. Both the brown-rotter, *G. trabeum* and the white-rotter *C. versicolor* were used in the evaluation of the acetylated pine samples. The white-rotter showed little weight loss, which is to be expected with the softwoods. The brown-rot untreated control had a weight loss of 68%. At 14.8% acetylation weight gain the samples lost only 0.8 %.

The average weight losses of acetylated aspen exposed to *G. trabeum* for 12 weeks are presented in Figure II. The untreated control lost 44.1%, while at 13.0% acetylation, the samples only had 2.6% weight loss.

The propylene oxide treated samples (Figure 11) were not effective in arresting decay by the brown-rotter *G. trabeum*, but they did show less decay than the untreated controls. At 50% PO weight gain there was a weight loss of 25.2%

The butylene oxide treated southern pine samples (Figure II) showed biological effectiveness against *G. trabeum* at 23.0% weight gain with only 3.8% weight loss.

The methyl isocyanate treated samples at 17.7% weight gain (Figure II) were effective against *G. trabeum* with only 3.4% weight loss. The untreated control had 48.8% weight loss.

The n-butyl isocyanate treated samples also were effective in arresting decay by *G. trabeum* at 18.0% weight gain with less than 2% weight loss, compared with the untreated control of 39.0% weight loss (Figure II).

The fungal cellar data for acetylated pine is presented in Table III. The samples had no swelling or decay at 19.1% acetylation weight gain after 12 months in test.

TABLE I Percent weight gain, acetyl, EMC at 30%, 65%, or 90% RH, FSP, and soil block testing of acetylated southern pine and aspen wood.

			EMC at 27 °C:			Weight Loss (%)		FSP
Wood	WPG	%Acetyl	30%RH	65%RH	90%RH	Brown-rot	White-rot	(%)
Pine	0.0	1.4	5.6	12.1	22.6	68.0	7.0	45
	6.0	7.0	4.1	9.2	17.5			24
	6.3		4.5	10.2	19.5	29.3		
	13.8		2.7	6.8	13.2			
	14.8	15.1	2.6	6.0	11.6	0.8		15
	17.0					<2	<2	
	18.2		2.1	5.1	9.9	0.0		
	21.1	20.1	1.7	4.3	8.1			10
Aspen	0.0	3.9	4.9	11.1	21.5	44.1		46
	7.3	10.1	3.2	7.8	15.0	22.4		
	8.7		3.1	7.7	14.9			29
	13.0		2.0	5.9	11.8	2.6		20
	14.2	16.9	2.3	5.9	11.4			
	17.6	19.1	1.6	4.8	9.4	0.1		15

TABLE II: Percent weight gain, EMC at 90%, and weight loss of southern pine chemically modified wood samples.

Modification chemical	Wood	Weight Gain (%)	EMC at 90%RH	Weight Loss (%) Brown-rot
Propylene	Pine	0.0	22.6	62.9
oxide		20.0		40.0
		24.0	20.2	35.5
		37.0	20.5	28.7
		50.0	19.1	25.2
Butylene	Pine	7.0		18.8
oxide		14.0		12.4
		23.0	14.5	3.8
Methyl	Pine	0.0	22.0	48.8
Isocyanate		5.5		15.8
		10.0		9.2
		17.7		3.4
		23.5		2.3
		47.2		<2
n-Butyl	Pine	0.0		39.0
isocyanate		18.0		<2
		36.0	7.8	<2

TABLE III Fungal cellar ratings of acetylated southern pine wood exposed for 12 months.*

WPG	Rating	Time (Months)
0	S/1	1
7.3	S/0	2
7.3	S/1	3
11.5	S/0	4
11.5	S/1	5
17.9	S/0	6
17.9	S/1	12
19.1	0/0	12

*Rating system: 0=no attack; 1 =slight attack; 2=moderate attack; 3–heavy attack; 4=destroyed; S=swollen

FIGURE I EMC of chemically modified wood at 90% relative humidity and 27 °C.

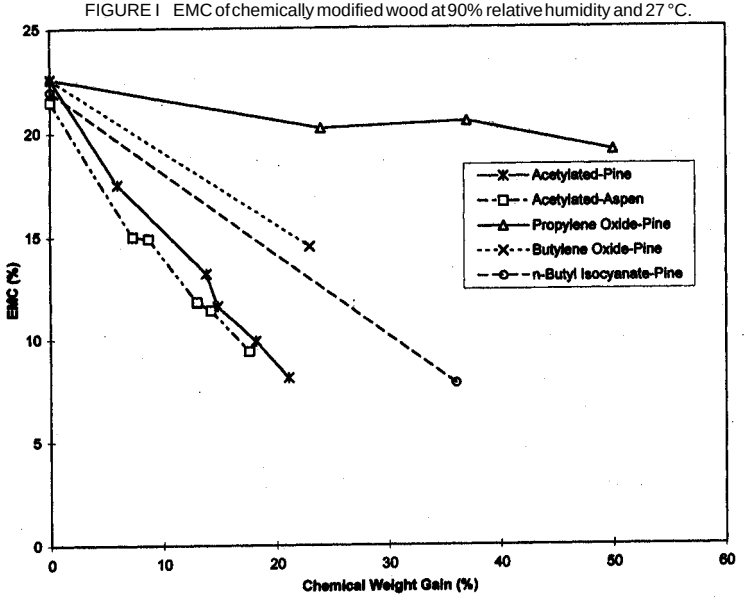
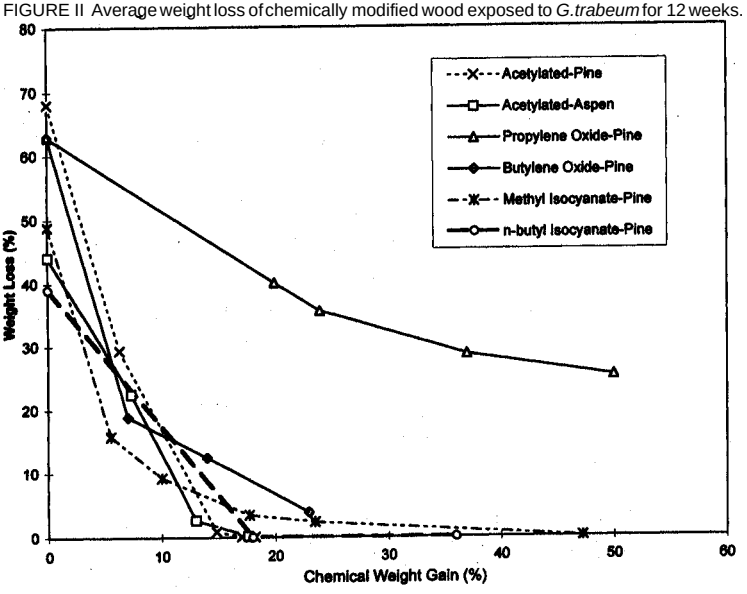


FIGURE II Average weight loss of chemically modified wood exposed to *G.trabeum* for 12 weeks.



CONCLUSION

Chemical modification of southern pine wood by acetylation, propylene oxide, butylene oxide, methyl isocyanate and n-butyl isocyanate were performed and analyzed for equilibrium moisture content (at 30%, 65%, or 90% and 27 °C), fiber saturation point (non-solvent water technique), and biologically (soil block test and fungal cellar).

Acetylation of southern pine wood samples showed biological efficacy against *G.trabeum* at 14.8% weight gain or 15.1% acetyl content, as well as lowering both the EMC at 90% RH from 22.6% to 11.6%, and the FSP from 45% to 15% at this level of treatment. Yet in the fungal cellar test, protection from swelling or decay after 12 months came at a 19.1% weight gain level. The aspen acetylated wood showed biological efficacy against G.trabeum in the soil block test at 13.0% weight gain, with a lowering of the EMC from 21.5% to 11.8% at 90% RH and the FSP from 46% to 20%.

Propylene oxide treated southern pine was not effective in the soil block test with G.trabeum, nor did it significantly lower the EMC at 90% RH even at the highest weight gain of 50%.

Butylene oxide treated southern pine was biologically effective in the soil block test at 23.0% weight gain and it lowered the EMC at 90% RH from 22.6% to 14.5%.

Methyl isocyanate treated southern pine was biologically effective at 17.7% weight gain and n-butyl isocyanate was effective at 18.0% weight gain, and at 36.0% weight gain lowered the EMC to 7.8% at 90% RH.

This is an ongoing study looking at the relationship of lowering the FSP and EMC to provide more data on determining the effectiveness of controlling the moisture content as a means of providing biological protection to wood used in adverse environments.

References

[1] S. Lebow, USDA Forest Service Forest Products Laboratory, Madison, WI, General Technical Report **FPL-GTR-93** (1996).

[2] E. Suttie, *Chemistry and Industry* **18,** 720–724 (1997).

[3] R. M. Rowell, *For. Prod. Abstracts* **6,** 363–382 (1983).

[4] G. N. Christensen and K. E. Kelsey, *Hols als Roh-und Werkstoff* **17**, 178–203 (1959).

[5] R. M. Rowell, *Wood Sci.* **15,** 172–182 (1982).

[6] R. M. Rowell and J. S. Rowell, "Moisture Sorption Properties of Acetylated Lignocellulosic Fibers," presented at Cellulose and wood --Chemistry and technology: Proceedings of the 10th cellulose conference, Syracuse, NY (1988).
[7] I. S. Goldstein, E. B. Jeroski, A. E. Lund, J. F. Nielson, and J. M. Weater, *For. Prod. J.* **11,** 363–370 (1961).
[8] W. E. Moore and D. B. Johnson, "Procedures for the chemical analysis of wood and wood products," USDA Forest Service Forest Products Laboratory, Madison Unnumbered report (1967).
[9] R. M. Rowell and D. I. Gutzmer, *Wood Sci.* **7,** 240–246 (1975).
[10] R. M. Rowell, *Wood Sci.* **13,** 102–110 (1980).
[11] W. D. Ellis and R. M. Rowell, *Wood and Fiber Sci.* **16,** 349–356, (1984).
[12] W. C. Feist and H. Tarkow, *For. Prod. J.* **17,** 65–68, (1967).
[13] ASTM, *American Society for Testing and Materials* **Des. D 1413,** (1976).
[14] T. Nilsson and R. M. Rowell, *The International Journal of Wood Preservation* **2,** 119–121 (1982).