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The Effect on Biological and Moisture Resistance of Epichlorohydrin Chemically Modified Wood

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ABSTRACT

Southern pine solid wood and fiber were chemically modified with epichlorohydrin to help in understanding the role of moisture in the mechanism of biological effectiveness of chemically modified wood. The solid wood had weight gains from 11% to 34%, while the fiber had weight gains from 9% to 75%. After modification, part of the specimens were water leached for 2 weeks or extracted for 2 hours with a toluene:ethanol (2:1) solution. The equilibrium moisture content (EMC) at 30%, 65%, and 90% relative humidity (RH) and 27 °C was determined on all specimens. Laboratory soil block decay testing using the brown-rot fungus *Gloeophyllum trabeum* was performed and weight loss calculated.

Results show that epichlorohydrin modified specimens did not lower the EMC significantly, yet there was biological effectiveness at 31% weight gain for the solid wood and 60% weight gain for the fiber. This indicates that the mechanism of efficacy may be due to substrate modification rather than moisture exclusion. Energy dispersive x-ray analysis (EDXA) was performed locating the chlorine throughout the wood cell wall.

Keywords: chemical modification, epichlorohydrin, equilibrium moisture content, brown-rot fungus, energy dispersive x-ray analysis, solid wood, fiber

INTRODUCTION

Chemically modifying the hydroxyls of lignocellulosic materials can improve moisture and biological resistance. Two proposed mechanisms for biological effectiveness from chemical modification are: 1.) substrate modification, and 2.) moisture exclusion. We have looked at various chemical modifications tracking the relationship of moisture and decay (Ibach and Rowell 2000; Ibach, Rowell et al. 2000). Modifications of solid wood and fiber with acetic anhydride (AA) or butylene oxide (BO) followed the moisture exclusion mechanism. Biological resistance increased with decreasing EMC, indicating

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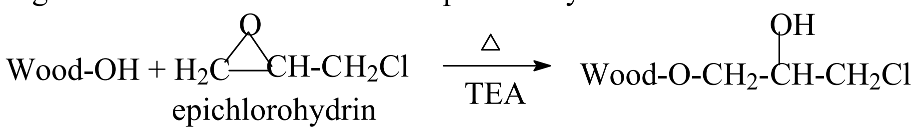
the mechanism of effectiveness is due to lowering of the cell wall moisture content. Propylene oxide (PO) did not show a correlation between the EMC and fungal resistance. The EMC was not decreased, yet showed biological resistance with the fiber specimens, indicating the mechanism of effectiveness may be due to substrate modification.

Modifications with epichlorohydrin alone or mixed with PO have been reacted with wood (Rowell and Gutzmer 1975; Rowell, Hart et al. 1979; Rowell and Ellis 1984). Epichlorohydrin modified woods resisted fungal decay and showed improved dimensional stability (Rowell, Hart et al. 1979; Enoki, Yoshioka et al. 1990; Chen 1994).

Epichlorohydrin is an excellent swelling chemical. The reaction forms the stable ether bonds with the hydroxyl groups of sugars and lignin.

Figure1. Reaction of wood with epichlorohydrin.



In reaction with lignocellulosic fibers, epichlorohydrin forms alkoxy-bonded lignocellulosic fibers containing chlorine in the alkyl side chain. This chlorine can then be monitored with energy dispersive x-ray microanalysis (EDXA.) The purpose of this study was to chemically modify solid wood and fiber with epichlorohydrin, track the chlorine throughout the decay process, and determine the role of moisture in decay.

MATERIALS AND METHODS

Both epichlorohydrin and the catalyst triethylamine were from Aldrich Chemical Company (Milwaukee, WI.)

Epichlorohydrin Modification

Southern pine specimens (2.54 cm radial x 2.54 cm tangential x 0.635 cm longitudinal) were cut and dried at 105 ^oC in a forced draft oven for 24 hours. Southern pine fiber was screened, washed, and then oven dried before treatment. The oven dried solid or fiber were weighed and then reacted in a stainless steel reactor with a mixture of epichlorohydrin and triethylamine (TEA) (95:5 (vol:vol)) at 93 ^oC or 120 ^oC and 150 psi nitrogen pressure, from 0 to 60 minutes for epichlorohydrin (Rowell and Ellis 1984). The treating solution was drained off. Specimens were air dried under a fume hood and then oven dried. Weight percent gain (WPG) was calculated.

Leaching and Extraction

Selected specimens were either water leached for 14 days (AWPA 1999) or extracted in a soxhlet extractor for 2 hours with toluene:ethanol mixture (2:1, (vol:vol)). Weight percent gain (WPG) was calculated for unleached, water leached, and solvent extracted specimens.

Equilibrium Moisture Content (EMC)

EMC of untreated and epichlorohydrin modified wood and fiber (1 g) specimens was determined by placing weighed, oven dried specimens in constant humidity rooms at 30%, 65%, or 90% relative humidity (RH) and 27 ^{o}C. The fiber specimens were wrapped in netting material to allow even airflow around the specimens without loss of fibers. After 14 days, specimens were reweighed until stable and the EMC was determined. Six replicates of each treatment were run and averaged.

Biological Efficacy

The ASTM D 1413 standard soil block test was performed on both solid wood and fiber specimens (ASTM 1999). Five soil bottles each of untreated controls and epichlorohydrin modified specimens of southern pine solid wood and fiber (0.5 g) specimens were exposed to the brown-rot fungus *Gloeophyllum trabeum*. Two soil bottles each with no fungus were run to monitor leaching of chemicals. The fiber weight loss of the untreated controls was monitored weekly. When 50% weight loss was reached with the unmodified fiber controls (at 10 weeks), all fiber specimens were removed. The solid wood specimens were removed from test following the standard 12 weeks. The extent of decay was determined as oven dry weight loss.

Microscopic analysis

Energy dispersive x-ray microanalysis (EDXA) was performed on selected specimens with a Tracor Northern 5500 energy dispersive spectrometer. X-ray spectra were collected for each specimen and plotted in graph form with energy from 0 to 100kV for the x axis and intensity (number of counts) in the y-axis. Cross sections were carbon coated and observed at various magnifications. Representative pictures of both earlywood and latewood were taken of the solid wood specimens.

RESULTS AND DISCUSSION

Epichlorohydrin Modification

Modification of wood with epichlorohydrin is a fast reaction and difficult to control. Ramping the warm up time to the reaction temperature of 120 °C was found to be the most successful procedure to prevent over pressurizing the system. Both ramp time (time to reach reaction temperature) and reaction time were varied to produce different weight gains.

Table 1 shows the reaction conditions and times, and the weight percentage gain (WPG) of unleached (UL), 2-week water leached (L), and 2-hour toluene:ethanol (2:1) extracted

(E) specimens. The WPG's are calculated by weight difference and not on chlorine (Cl) analysis. The water leached and extracted specimens show less WPG compared with the unleached specimens. This indicates that there may be unreacted epoxide left or soluble homopolymers formed, especially during the heating up period. The highest unleached WPG for both the solid wood (34.2% WPG) and fiber (74.5% WPG) had more loss after extraction and water leaching than the next highest weight gains for solid wood (31.1% WPG) and fiber (60.1% WPG). This is due to the shorter reaction time once 120 °C is reached (60 min. vs. 5 min. or 1 min.) Better cell wall bonding occurs with longer reaction time at 120 °C.

Equilibrium Moisture Content (EMC)

The equilibrium moisture content (EMC) as well as the weight loss from fungal and no fungal controls are presented in Table 2. As biological efficacy increases (i.e. less fungal weight loss) there is no significant lowering of the EMC. In fact, with the unleached fiber, there is a significant increase in EMC at 90% RH. A possible explanation for this increase is the formation of water-soluble glycols from unreacted epoxide with water, because there also is increasing weight losses in the no fungal controls from the soil block test.

Biological Efficacy

For the solid wood, the 31.1% WPG water leached specimens (which had 13.0% WPG after leaching) show increased biological efficacy against *G.trabeum* with only 5% weight loss after 12 weeks of exposure. The 31.1% WPG unleached and extracted (23.7% WPG after extraction) specimens showed weight losses of 10.9% UL and 6.9% E, but the no fungal controls also had weight losses of 8.2% UL and 7.3% E. This indicates that the weight losses are not completely due to the fungal attack, but loss of chemicals produced from the epichlorohydrin reactions.

A similar trend occurs for the fiber specimens. The 32.9%, 60.1%, and 74.5% WPG unleached specimens show weight losses of the no fungus controls of almost as much or more than the weight losses of the fungal exposed specimens. The extracted and leached specimens show biological efficacy with 32.3% WPG after extraction (0.1% weight loss) and 30.5% WPG after water leaching (-2.1% weight loss.)

The extraction duration for solid wood specimens should be longer. Chen performed acetone extraction of epichlorohydrin modified solid wood by soaking for 1 day and then Soxhlet extracting for 12 hours (Chen 1994). He found biological efficacy (2.3% weight loss) at 10.9% weight gain. Chen modified solid wood by refluxing in epichlorohydrin, and did not take weight gains before acetone extraction. Rowell et. al. water leached for 7 days before placing specimens in the soil block test, but unfortunately no WPG's were reported after leaching (Rowell and Ellis 1984). Our continuing research will leach or extract all epichlorohydrin specimens for a longer period of time, and identify the by-products in the leacheate as well.

Microscopic analysis

From EDXA, the X-ray distribution maps for both decayed solid wood and fiber, leached and unleached, show even distribution of Cl throughout the cell wall. Figure 2 is the X-ray spectrum showing the relative amount of chlorine in an epichlorohydrin modified (60.1% WPG), unleached southern pine fiber specimen. Figure 3 is the X-ray spectrum showing the relative amount of chlorine in an epichlorohydrin modified (60.1% WPG), water leached southern pine fiber specimen. The X-ray analysis spectra show the same relative amount of Cl in the leached and unleached decayed specimens, indicating no loss of modification of the cell wall even after fungal exposure.

Moisture Exclusion

One example of a chemical modification system that seems to work by lowering the EMC of wood is acetylation (Ibach, Rowell et al. 2000). The WPG, as well as the percentage acetyl content, are presented in Table 3. Unlike the epichlorohydrin, there is negligible weight loss and acetyl loss after 2 weeks of water leaching with both the solid wood and fiber.

Table 3 also contains the EMC and weight loss from biological decay (*G.trabeum*) of acetylated solid wood and fiber and unmodified controls. The AA modified solid wood shows moderate effectiveness at 19% weight gain for the unleached (5.0% weight loss) and leached (8.2% weight loss) specimens. At the same time the EMC is significantly lowered from 20.2% to 8.6% for the unleached and from 22.1% to 9.2% for the leached specimens. The AA modified fiber was effective in arresting decay at 13% weight gain for the unleached (1.4% weight loss) and leached (2.7% weight loss) specimens. The EMC was also lowered from 12.4% to 6.4% for the unleached and from 12.2% to 6.6% for the leached specimens. These results indicate that the mechanism of effectiveness is by lowering the cell wall moisture content below the level required for microorganism attack.

SUMMARY AND CONCLUSION

Southern pine solid wood and fiber were chemically modified with epichlorohydrin to various WPG's to assist in understanding the mechanism of effectiveness of chemically modifying wood. Biological efficacy was achieved, but did not correlate with the lowering of the EMC, unlike acetylation. This indicates that the epichlorohydrin mechanism of efficacy may be due to substrate modification rather than moisture exclusion. The UL specimens had significant increases in the EMC indicating possible formation of glycols from the by-products of the epichlorohydrin reaction. Also, the unleached, no fungal controls had significant weight losses. Research continues on epichlorohydrin modified wood looking at different leaching/extraction protocol, identification of products in the leacheate, and varying the reaction time once 120 °C is reached. Determining the effectiveness of controlling the moisture content as a means of providing biological protection is ongoing.

ACKNOWLEDGEMENTS

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Table 1. Weight percent gain of epichlorohydrin modified solid wood and fiber before and after water leaching and toluene:ethanol (2:1) extraction.

Epichlorohydrin					
	Time to reach reaction temp.	**Reaction Time** (min)	**Unleached** (WPG)	**Tol:Eth (2:1) Extracted** (WPG)	**Water Leached** (WPG)
Solid Block	To 120 °C:	Control	0.0	0.0	-1.0
5 % TEA	31 min	0	11.4	7.5	3.2
150 psi	40 min	0	12.1	7.9	2.7
	45 min	60	31.1	23.7	13.0
	60 min	5	34.2	20.1	6.3
Fiber		Control	0.0	-2.6	-2.4
5 % TEA	To 93 °C: 10 min	0	9.0	3.4	1.2
150 psi	To 121 °C: 15 min	0	32.9	15.3	8.1
	To 120 °C: 46 min	60	60.1	32.3	30.5
	To 120 °C: 45 min	1	74.5	22.8	15.9

Table 2. EMC and soil block weight loss after exposure to *G.trabeum* and no fungus controls of epichlorohydrin modified southern pine solid wood and fiber.*

Epichlorohydrin						
			EMC		**Fungal**	**No Fungal**
	WPG		**(RH)**		**Wt. Loss**	**Wt. Loss**
Solid Wood	**(UL)**	**30 %**	**65 %**	**90 %**	**(%)**	**(%)**
UL C	0	5.71	10.60	16.32	64.6	0.0
UL	11	4.10	8.23	14.75	28.0	4.2
UL	12	4.14	8.85	16.20	35.8	6.2
UL	31	2.85	6.88	15.22	10.9	8.2
UL	34	3.38	10.28	15.61	21.0	15.8
L C	0	5.66	10.61	16.85	61.4	0.1
L	11	5.45	10.30	16.34	38.4	0.2
L	12	5.26	10.18	16.47	33.5	0.1
L	31	4.63	9.27	14.98	5.0	0.0
L	34	5.19	10.13	16.90	32.5	-0.3
E C	0	5.07	9.47	15.14	65.9	1.3
E	11	4.46	8.67	14.58	36.3	2.9
E	12	4.38	8.80	15.04	41.0	3.2
E	31	3.45	7.27	13.87	6.9	7.3
E	34	4.09	9.19	19.86	27.9	9.1
Fiber						
UL C	0	4.36	7.96	13.88	52.9	0.5
UL	9	3.53	8.24	17.03	32.2	2.4
UL	33	4.20	11.81	29.93	18.4	16.1
UL	60	2.84	8.91	23.51	9.8	15.7
UL	75	5.64	16.58	44.21	32.1	31.3
L C	0	4.02	8.12	14.03	52.7	0.6
L	9	4.21	8.59	14.92	25.0	0.2
L	33	4.32	8.85	16.08	8.2	0.1
L	60	3.78	8.61	16.17	-2.1	2.4
L	75	4.49	9.28	17.26	2.8	0.5
E	C	3.64	7.15	12.27	54.6	-0.3
E	9	3.68	7.25	12.98	39.0	1.3
E	33	4.07	7.53	14.55	13.1	1.4
E	60	3.25	7.33	14.81	0.1	1.2
E	75	3.39	7.31	15.30	4.5	1.7

*C = control, UL = unleached, L = water leached, E = toluene:ethanol (2:1) extracted

Table 3. EMC and weight loss (*G.trabeum*) of acetylated southern pine solid wood and fiber.*

Acetic Anhydride						
		Acetyl		***EMC*** **(RH)**		**Fungal Wt. Loss**
Solid Wood	**WPG**	**(%)**	**30%**	**65%**	**90%**	**(%)**
UL C	0	1.5	4.2	9.4	20.2	65.8
UL	5.1	7.3	2.9	7.0	16.5	58.8
UL	11.9	12.1	2.4	5.2	13.0	44.9
UL	14.4	15.0	1.8	4.6	11.4	35.6
UL	18.8	19.5	1.1	3.7	8.6	5.0
L C	-1.6	1.1	5.0	11.0	22.1	64.4
L	5.1	6.5	4.0	8.9	18.2	52.0
L	11.8	12.6	2.7	6.2	14.1	33.6
L	14.3	14.6	2.4	5.5	12.2	31.1
L	18.7	19.6	1.7	4.3	9.2	8.2
Fiber						
UL C	0	1.0	2.9	7.9	12.4	51.7
UL	4.5	7.5	2.2	6.2	10.1	26.5
UL	8.8	11.9	1.6	5.2	8.5	5.9
UL	13.4	15.3	1.0	3.8	6.4	1.4
UL	14.8	16.3	0.9	3.5	5.9	0.7
L C	-3.9	1.0	2.7	7.7	12.2	55.3
L	4.1	6.4	2.1	6.4	10.4	34.3
L	8.6	12.0	1.5	5.1	8.5	13.6
L	12.8	15.5	1.0	3.9	6.6	2.7
L	14.3	17.0	1.0	3.6	6.1	0.4

*C = control, UL = unleached, L = water leached

Figure 2. X-ray spectrum of 4-mm^2 specimen of epichlorohydrin modified (60.1 WPG), unleached southern pine fiber showing presence of chlorine.

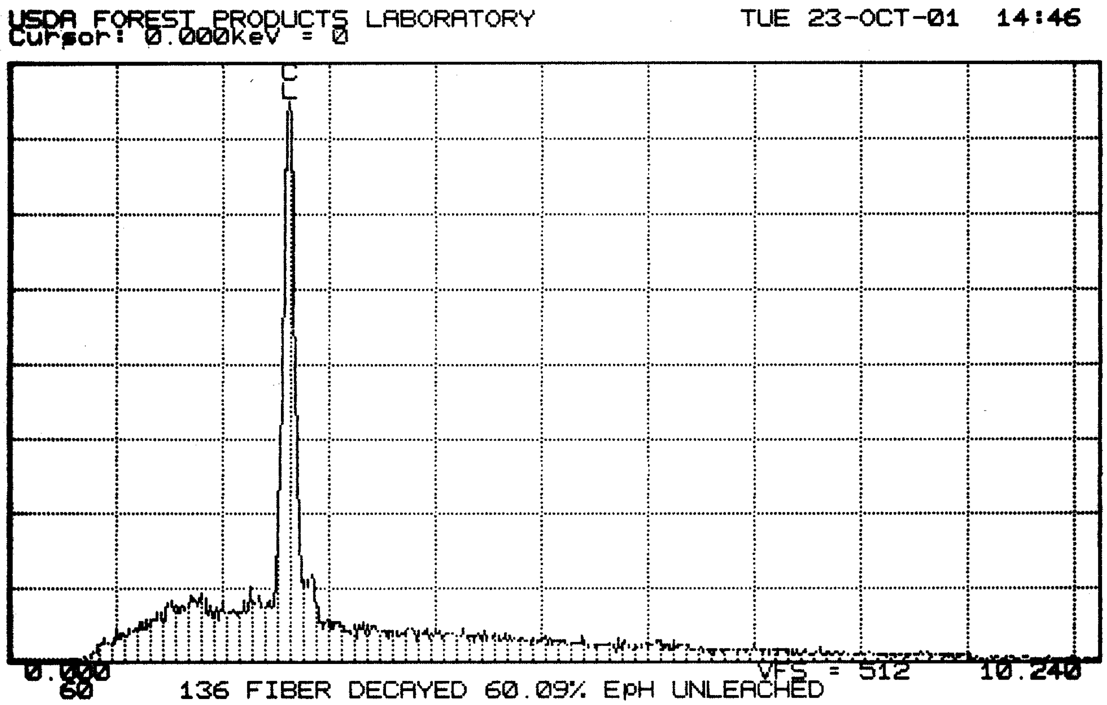
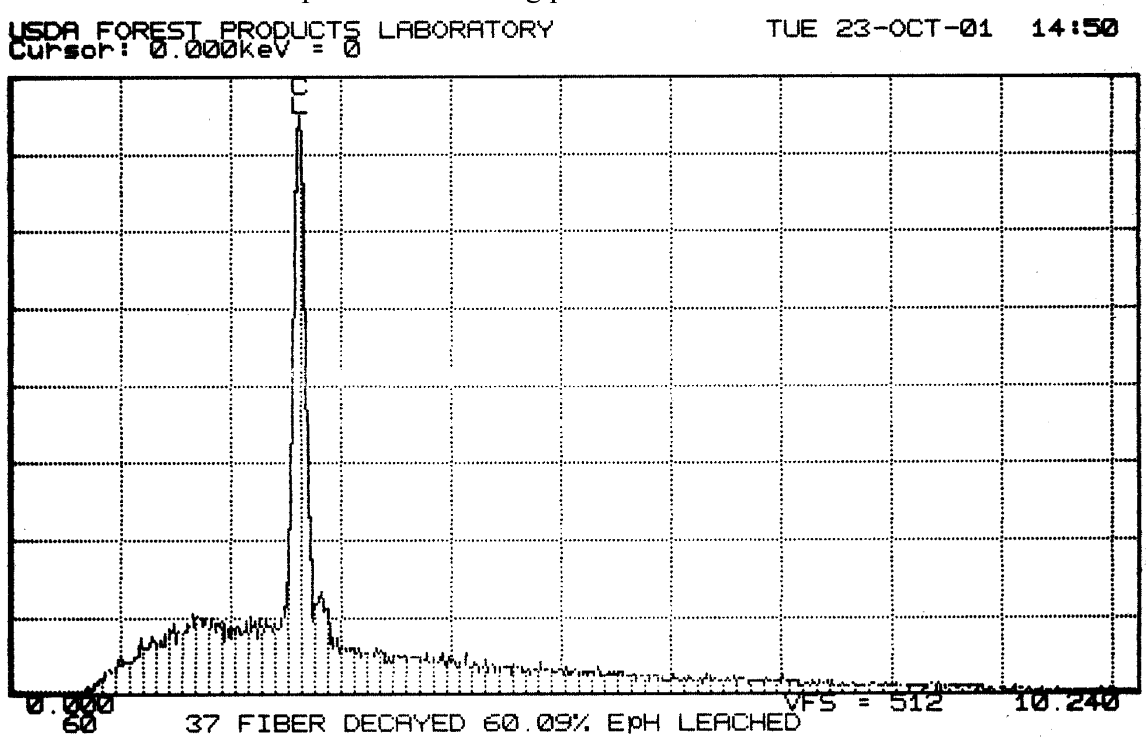


Figure 3. X-ray spectrum of 4-mm^2 specimen of epichlorohydrin modified (60.1 WPG), water leached southern pine fiber showing presence of chlorine.



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