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BIOLOGICAL RESISTANCE OF SOUTHERN PINE AND ASPEN FLAKEBOARDS MADE FROM ACETYLATED FLAKES

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ABSTRACT

Standard soil block tests can be used for southern pine and aspen flakeboards made with phenol-formaldehyde adhesive if the boards are first leached to remove toxic residual chemicals which inhibit fungal attack. Standard fungal cellar and termite tests can be applied directly without leaching. Flakeboards made from flakes acetylated by a new simplified dip acetic anhydride procedure are resistant to attack by brown-, white-, and soft-rot fungi and tunneling bacteria at acetyl weight gains above 15%. Acetylated flakeboards at 18 to 21% acetyl weight gains are not completely resistant to attack by subterranean termites.

INTRODUCTION

A considerable amount of research has been conducted to chemically modify wood to improve such properties as dimensional stability, biological resistance, color stability, hardness, and water sorption.[2] The reaction system that has been investigated the most is acetylation, but no commercial process has yet been realized. Most of the acetylation schemes developed have required catalysts or an organic cosolvent which complicates chemical recovery and causes some wood degradation.

We developed a simple dip acetylation process that has been applied to the acetylation of wood flakes.[3] Flakeboards made from dip-acetylated flakes have been shown to have greatly improved dimensional stability both to liquid water and water vapor.[4,5,6] We have now completed biological tests on these flakeboards using fungi, bacteria, and termites.

Relative to acetylated solid wood, few studies have been done on the biological resistance of reconstituted products. In 1978, Bekere et al. found acetylated fiberboards resistant to the wood-destroying fungus Coniophora cerebella.[7] Arora et al. found pyridine catalyzed, acetic anhydride acetylated, phenol-formaldehyde particleboards resistant to "commonly occurring Indian wood-destroying fungi."[8] Using potassium acetate as catalyst, Yin and Wang vapor-phase-acetylated poplar veneers, which were made into plywood. In 5-week soil block tests, the acetylated plywood was resistant to attack by Gloeophyllum trabeum.[9] More recently, Nishimoto and Imamura made particleboards from mixtures of control and acetylated spruce chips.[▾▾] Soil block tests with Tyromyces palustris or Coriolus versicolor showed very slow decay in boards containing up to 50% acetylated chips and no decay in boards made only from acetylated chips. Boards made with 75% acetylated chips were resistant to attack by Reticulitermes speratus termites but were less resistant to attack by Coptotermes formosanus termites.[10,11]

The purpose of the present research was twofold: First, we wanted to determine if standard soil block, fungal cellar, and termite tests could be applied directly to flakeboards containing phenol-formaldehyde or if specimens must first be leached to remove any toxic adhesive components. Second, we wanted to use these test methods to determine the resistance of flakeboards made from dip-acetylated flakes to brown-, white-, and soft-rot fungi, tunneling bacteria, and subterranean termites.

EXPERIMENTAL

Reaction of Flakes and Board Production

Ovendry southern pine and aspen flakes were acetylated using the dip procedure as described earlier.[3] Flakes with acetyl weight gains of from 6 to 20% (based on the original ovendry weight) were produced.

Control and acetylated flakes were pressed into boards approximately 1.25 x 15 x 15 cm in size as previously described.[12] Each board was made with a density of approximately 640 kg/m^3 using a phenol-formaldehyde resin (6% based on ovendry control or acetylated flakes). Each flakeboard was lightly sanded and cut into 2.5 x 2.5 x 1.25 cm for soil block tests, 5 x 2.5 x 1.25 cm for fungal cellar tests, or 2.5 x 2.5 x 1.25 cm for termite tests.

Soil-Block Tests

Soil-block tests were conducted to see what effect the phenol-formaldehyde adhesive had on the brown-rot fungi. Tests were conducted as outlined in ASTM D 1413.[13] Solid blocks of southern pine and aspen (2 x 2 x 2 cm) and control flakeboards were placed in test with the brown-rot fungi *Gloeophyllum trabeum* (Pers. ex Fr.) Murr. (= *Lenzites trabea* (Pers. ex Fr.) Fr., Madison 617). Specimens were removed after 12 weeks. Extent of fungal attack was determined by weight loss.

Separate control and acetylated flakeboard specimens were water-extracted according to the ASTM D 1413 leaching procedure for waterborne preservative.[13] All specimens were leached for

2 weeks with distilled water, changing the water every 24 hours. Ovendry weight loss was determined after leaching.

Control and acetylated flakeboard specimens, both leached and nonleached, were then placed in test with Gloeophyllum trabeum in the ASTM D 1413 test for 12 weeks and weight loss determined.

Fungal Cellar Test

Fungal cellar tests were conducted as previously described[14] to determine if the phenol-formaldehyde adhesive would have an effect on soil micro-organisms. Solid wood of southern pine and aspen and control flakeboards (5 x 2.5 x 1 cm) were incubated at approximately 25°C in moist unsterile soil. At 1-month intervals for 6 months, each specimen was removed and inspected. It was determined by microscopic examination of attacked control specimens that among the micro-organisms present in the soil were brown-, white-, and soft-rot fungi and tunneling bacteria.

Control and acetylated flakeboard specimens (5 x 2.5 x 1.25 cm) were also placed in fungal cellar tests and inspected as above. After the test was completed, sections were cut for microscopic examination.

Termite Test

Reticulitermes flavipes (Kollar) subterranean termites were collected at Janesville, Wisconsin, and maintained in a 20-gallon metal container prior to use. In a preliminary test, approximately 87% of the termites placed in containers with control blocks survived over a 4-week period, indicating that the termites would he acceptable for further experimental usage.

Termite tests were run on southern pine and aspen solid wood and flakeboards made with 6% phenol-formaldehyde to determine if the adhesive or any residual by-product acetic acid would have any toxic effect on the termites in the small containers. Termite tests were run as previously described with some minor changes.[15] An untreated paper pulp block (0.3 x 0.2 x 2.5 cm in size; about

0.5 g) was placed in a cylindrical, clear plastic container (inside dimensions, 5 cm diameter and 3.5 cm deep). The paper pulp sheet is used as a nutritive supplement. It was wetted with 1.5 ml of distilled water. Solid wood of southern pine and aspen and flake-board specimens (2.5 x 2.5 x 1 cm) were dipped into distilled water for 10 seconds prior to going into the test container. The specimens were placed on the paper pulp sheet with the 2.5- x 2.5-cm face in contact with the sheet.

To each container was added 1 g of termites (mixed caste forms). The number of termites in various caste forms (workers, nymphs, and soldiers) were counted in two out of every three replicate containers. The termite groups consisted mainly of the worker form, the form that actually attacks wood. The average number of termites in 1-g groups was 323 (89.5% workers, 9% nymphs, and 1.5% soldiers). The units, with lids, were stored in a 25°C incubator.

After 2 weeks, an additional 0.5-ml water was added to each container. After 4 weeks, the test was stopped. Specimens were brushed free of debris, ovendried at 105°C overnight, weighed, and weight loss determined. The surviving termites were weighed and final termite biomass determined.

Control and acetylated flakeboard specimens (2.5 x 2.5 x 1.25 cm) were also placed in termite tests, and weight loss and termite survival were determined as given above.

RESULTS AND DISCUSSION

Soil Block Tests

Solid pine and aspen control blocks lost, respectively, approximately 47 and 38% in weight during the 12-week test with *Gloeophyllum trabeum* (Table 1). Nonleached control flakeboards made with 6% phenol-formaldehyde adhesive lost only about 9% by weight during the same time period. Leaching the flakeboards for 2 weeks in distilled water resulted in essentially the same weight loss during the soil block test as was found for solid wood.

TABLE 1

Average Weight Loss in Soil Block Tests for Solid Blocks and Flakeboards Exposed for 12 Weeks to *Gloeophyllum trabeum*

Wood Type	Average Weight Loss (%)[a]	
	Nonleached	Leached
Southern Pine		
Solid	48.8	46.2
Flakeboards	9.2	49.4
Aspen		
Solid	37.6	39.8
Flakeboards	8.9	36.2

[a]Average of 5 specimens.

These results indicated that the soil block test could give meaningful data on flakeboards containing 6% phenol-formaldehyde only if they were first leached for 2 weeks with distilled water.

The soil block tests of flakeboard made from southern pine and aspen control flakes and from acetylated flakes at various weight gains of acetyl (Table 2) show that biological protection is attained at about 10% weight gain in nonleached acetylated southern pine flakeboards, whereas leached flakeboards require about 15% weight gain to become resistant to attack. Similar results were obtained with aspen flakeboards.

Even though the weight loss caused by leaching is low (about 2%), the leachate must contain chemicals which are toxic to the fungi. Less weight loss is observed as the level of acetylation increases which may be because of the removal of soluble wood materials during the acetylation process.

Fungal Cellar Tests

Table 3 shows that both southern pine and aspen solid wood and unleached flakeboards are attacked at the same rate in the

TABLE 2

Average Weight Loss in Soil Block Tests for Flakeboards Made from Control and Dip-Acetylated Flakes Exposed for 12 Weeks to *Gloeophyllum trabeum*

Wood Species	Acetylation Weight Gain (%)	Average Weight Loss[a]		Weight[b] Loss (%)	Toxic Threshold % Weight Gain	
		Nonleached (%)	Leached (%)		Nonleached (%)	Leached (%)
Southern Pine	0.0	15.1	34.3	2.3		
	6.0	4.3	29.3	2.2		
	10.4	0.5	12.9	2.0		
	14.8	0.0	0.8	1.8		
	17.8	0.0	0.0	1.6		
					10.4	15.3
Aspen	0.0	28.5	44.1	2.8		
	7.3	3.0	22.4	2.6		
	11.5	1.2	13.9	2.6		
	13.6	0.4	2.6	2.1		
	16.3	1.2	0.6	2.0		
	17.9	1.0	0.1	2.0		
					6.8	14.8

[a]Average of 3 specimens.
[b]Due to leaching.

TABLE 3

Fungal Cellar Tests[a] on Untreated Solid Wood and Flakeboards

Wood Type	Rating[b] after:				
	2 months	3 months	4 months	5 months	6 months
Southern Pine					
Solid	1	2	3	3	4
Flakeboard	S/1	S/2	S/2	S/3	S/4
Aspen					
Solid	1	2	3	3	4
Flakeboard	S/1	S/2	S/3	S/3	S/4

[a] Brown-, white-, and soft-rot fungi and tunneling bacteria.
[b] Rating system: 0--no attack; 1--slight attack; 2--moderate attack; 3--heavy attack; 4--destroyed; S--swollen; average of 3 specimens.

fungal cellar. This showed that it was not necessary to leach the specimens going into the fungal cellar. Both solid wood and flakeboard controls are destroyed in 6 months, so the test on flakeboards was run for 6 months.

Table 4 shows the results of the 6-month fungal cellar test on control and flakeboards made from acetylated flakes. Southern pine flakeboards are resistant to attack by brown-, white-, and soft-rot fungi and tunneling bacteria above 15% weight gain of acetyl. Similar results were obtained for aspen.

In both softwood and hardwood flakeboards no biological attack occurred before swelling of the specimens. It is not known if the swelling is a result of water wetting or the initial enzymatic attack. In specimens that were degraded, tunneling bacteria were the first organisms to attack. Specimens which were heavily attacked were degraded by tunneling bacteria and brown- and soft-rot fungi.

Earlier research in fungal cellar tests on epoxide-modified wood showed that fungi were able to attack radial walls of late-

TABLE 4

Fungal Cellar Tests on Flakeboards Made from Control and Dip-Acetylated Flakes

Wood Species	Acetylation Weight Percent Gain	Rating[a] After:				
		2 Months	3 Months	4 Months	5 Months	6 Months
Southern Pine	0.0	S/1	S/2	S/2	S/3	S/4
	6.0	S/0	S/0	S/0	S/2	S/3
	10.4	0	0	S/0	S/1	S/2
	14.8	0	0	0	S/0	S/0
	17.8	0	0	0	0	S/0
	20.3	0	0	0	0	0
Aspen	0.0	S/2	S/3	S/3	S/3	S/4
	7.3	S/0	S/1	S/1	S/2	S/3
	11.5	0	0	S/0	S/1	S/2
	13.6	0	0	0	0	S/0
	16.3	0	0	0	0	0
	17.9	0	0	0	0	0

[a] See Table 3 for rating system.

wood cells even at high levels of bonded chemical.[5] This does not happen with acetylated wood, which shows that acetylation occurs more uniformly through the cell wall as compared to epoxide-modified wood.

Termite Tests

Table 5 shows that both solid wood and flakeboard controls show essentially the same weight loss and termite survival in the 4-week test. One gram of termites normally causes from 0.2-to 0.4-g weight loss in untreated wood during a 4-week test. Aspen specimens showed a slightly lower level of attack and termite survival as compared to southern pine.

Table 6 shows the results on control and flakeboards made from acetylated flakes. As the acetyl weight gain increases, specimen weight loss decreases. Final termite biomass remains the same except in specimens at the highest level of acetyl weight gain. At this level, there is a slightly reduced termite biomass. In the aspen flakeboards at 13.6, 16.3, and 17.6 acetyl weight gain, there were a few dead termites at the end of the 4-week test. Nevertheless, the >50% biomass survival of termites at all test levels indicates that the results were a severe test of the materials.

Even at the highest acetyl weight gain for both southern pine and aspen flakeboards, weight loss caused by termite attack was not completely stopped as it was in fungal and tunneling bacteria tests. This may be attributed to the severity of the test; however, it is known that the intestinal protozoa in termites decompose cellulose to acetic acid[16,17] and that acetic acid accounts for 85% of all acids produced from cellulose fermentation in termites.[18] Since termites can live on acetic acid, perhaps it is not surprising that acetylated wood is not completely resistant to termite attack. Wood chemically modified with epoxides was found to be more resistant to termite attack than acetylated wood.[14]

TABLE 5

Weight Loss and Termite Survival After 4 Weeks on Solid Wood and Flakeboards

Wood Species	Weight Loss[a] (g)	Final Termite Biomass[b] (g)
Southern Pine		
Solid	0.27	0.85
Flakeboard	0.25	0.83
Aspen		
Solid	0.19	0.64
Flakeboard	0.16	0.62

[a]Average of 3 specimens.
[b]Starting weight, 1 g.

TABLE 6

Weight Loss and Termite Survival After 4 Weeks on Flakeboards Made from Control and Dip-Acetylated Flakes

Wood Species	Acetylation Weight Percent Gain	Weight Loss[a] (g)	Final Termite biomass[b] (g)
Southern Pine	0	0.23	0.83
	10.4	0.09	0.67
	17.8	0.06	0.75
	21.6	0.05	0.65
Aspen	0	0.13	0.61
	8.7	0.10	0.62
	11.5	0.07	0.63
	13.6	0.08	0.60
	16.3	0.08	0.63
	17.6	0.06	0.54

[a]Average of 3 specimens.
[b]Starting weight, 1 g.

SUMMARY AND CONCLUSIONS

The standard ASTM D 1413 soil block test can be used to test flakeboards made with a phenol-formaldehyde adhesive, provided they are first leached with water. The water leaching removes residual chemicals that are otherwise toxic to fungi. Fungal cellar and termite tests can be done directly on phenol-formaldehyde-containing flakeboards without leaching.

Flakeboards made from acetylated flakes above 15% weight gain of acetyl were very resistant to attack by brown-, white-, and soft-rot fungi and tunneling bacteria. In fungal cellar tests, tunneling bacteria were the first to attack lower acetyl-substituted flakes, and no biological attack took place before swelling of the wood.

Even at the highest level of acetylation, flakeboards were not completely resistant to attack by subterranean termites. This may, in part, be caused by the termites' ability to digest acetic acid and perhaps acetate.

The mechanism of biological resistance in acetylated wood is not known; however, it is generally accepted that it is due to two factors: greatly decreased moisture sorption and substrate blocking.[19] Flakeboards made from acetylated southern pine and aspen flakes with more than 18% acetyl weight gain have an equilibrium moisture content about half that of control flakes and a fiber saturation point about 80% lower than control flakes.[illegible] There may not be enough moisture at the site for enzymes activity. A better understanding of exactly where the acetyl groups are located in the cell wall polymers could shed light on the substrate blocking theory.

The carbohydrate polymers are the most susceptible to biological attack with the hemicelluloses the most accessible and hygroscopic of the cell wall polymers. If the first step in fungal degradation of wood is attacking the hemicelluloses, acetylation of this fraction may be the key to biological protection by chemical modification.

Flakeboard stakes made from various levels of acetylated southern pine and aspen flakes using phenol-formaldehyde or isocyanate adhesive are presently in field tests in Mississippi to determine the durability of the product as well as the stability of bonded acetyl groups with periodic acetyl analysis. The Mississippi stakes will be tested in the presence of various types of brown-, white-, and soft-rot fungi, soil bacteria, and subterranean termites. Acetylated flakeboards are also in test in the ocean to determine their resistance to marine organisms.

Acetylated flakes at various levels of bonded acetyl groups are also under test in laboratory-simulated high humidity where acetyl stability will also be determined. It is important to find out if acetyl is lost over time due to hydrolysis. If this occurs, then it is only a matter of time before the acetyl concentration will be below the threshold level, and the board will start to fail. If acetyl is hydrolyzed, it will probably be in the most accessible regions of the cell wall polymers which are the most susceptible to biological attack.

Whereas it is probably not realistic to assume acetylated wood can replace broad-spectra toxic preservatives for inground and marine applications, it is important to determine the limits of its biological resistance. This information will lead to a better understanding of the mechanics of biological resistance through chemical modification and perhaps to the development of a nontoxic leach-resistant procedure that is durable for aboveground applications if not inground applications.

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REFERENCES

1. Maintained at Madison, WI, in cooperation with the University of Wisconsin.

2. R. M. Rowell, In The Chemistry of Solid Wood, Chap. 4, R. M. Rowell (ed.), Advances in Chemistry Series No. 207, American Chemical Society, Washington, D. C., 1984.

3. R. M. Rowell, A.-M. Tillman, and R. Simonson, J. Wood Chem. Technol. (in press).

4. R. M. Rowell, A.-M. Tillman, and Z. Liu, Wood Sci. Technol., 20, 83 (1986).

5. J. A. Youngquist, A. Krzyskik, and R. M. Rowell, Holz als Roh-und Werkstoff (in press).

6. R. M. Rowell, A.-M. Tillman, and R. Simonson, Wood Modification, M. Lawniczak (ed.), Polish Academy of Sci., 5,358 (1986).

7. M. Bekere, K. Shvalbe, and I. Ozolinya, Latv. Lauksaimn. Akad. Raksti, 163, 31 (1978).

8. M. Arora, M. S. Rajawat, and R. C. Gupta, Holzforsch. Holzverwert., 33(1), 8 (1981).

9. S. C. Yin and W. H. Wang, Scientia Silvae Sinicae, 19(2), 168 (1983).

10. K. Nishimoto and Y. Imamura, Mokuzai Kogyo, 40, 414 (1985)

11. Y. Imamura and K. Nishimoto, Japan J. Wood Res., 72, 37-44 (1986).

12. J. A. Youngquist, A. Krzysik, and,R. M. Rowell, Wood and Fiber Sci., 18(1), 90 (1986).

13. American Society for Testing and Materials, ASTM D 1413 (1973).

14. T. Nilsson and R. M. Rowell, Int. J. Wood Preserv., 2(3), 119 (1982).

15. G. C. Chen, G. R. Esenther, and R. M. Rowell, Forest Prod. J., 36(5), 18-20 (1986).

16. R. E. Hungate, Ann. Entomol. Soc. Am., 36, 730 (1943).

17. R. E. Hungate, Biochem. Physiol. Protozoa, 2, 159 (1955).

18. R. E. Hungate, Ecology, 20, 230 (1939).

19. R. M. Rowell, Chemical Aspects of Wood Technology, Swedish Forest Products Laboratory, STFI Series A, 772, 32 (1982).

20. R. M. Rowell, J. A. Youngquist, and H. Montrey, Forest Prod. J. (in press).