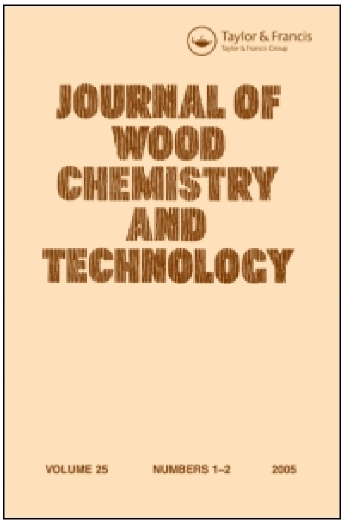

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A Simplified Procedure for the Acetylation of Hardwood and Softwood Flaxes for Flakeboard Production

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A SIMPLIFIED PROCEDURE FOR THE ACETYLATION OF HARDWOOD AND SOFTWOOD FLAKES FOR FLAKEBOARD PRODUCTION

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Keywords: Acetylation, chemical modification, flakeboard, aspen, southern pine, dimensional stabilization.

ABSTRACT

Southern pine and aspen flakes were acetylated with acetic anhydride alone without cosolvent or catalyst by a simple dip procedure. The new procedure greatly shortens reaction time and simplifies chemical recovery. Acetylation weight gains of 15% to 20% can be achieved in 1 to 3 hours with southern pine flakes and in 2 to 4 hours with aspen flakes.

Flakeboards made from acetylated southern pine or aspen flakes absorbed much less water, both in water-soaking tests and when subjected to humid air, and swelled at a lower rate and to a lower extent than did control boards.

Hygroscopicity of the resulting flakeboards decreased with increased level of wood acetylation. The equilibrium moisture content (EMC) for flakeboards made from acetylated flakes was lower at each relative humidity tested than that of control boards.

INTRODUCTION

Acetylation of both solid and reconstituted wood products has been shown to be effective in reducing swelling in water[2] through the bulking action of the acetyl group bonded to the cell wall polymers. Acetylation has been studied more than any other chemical reaction of wood. Despite such efforts, no commercial applications have yet been realized for the acetylation of wood. Two attempts, one in the United States in 1961[3] and one in U.S.S.R. in 1974,[4,5] came close to commercialization but were discontinued, presumably because they were not cost-effective.

All of the procedures to acetylate wood developed over the years have been complicated reaction schemes using either a catalyst or an organic cosolvent and have required long reaction times. Wood flour and sawdust were first acetylated in 1928 by Fuchs,[6] Horn,[7] and Suida.[8] Fuchs and Horn acetylated with acetic anhydride with sulfuric acid as catalyst. Suida used acetic anhydride-pyridine mixtures. In 1930 Friese[9] used a mixture of acetic acid-acetic anhydride catalyzed with sulfuric acid to acetylate powdered wood at room temperature.

The first acetylation of whole wood was done in 1946 by Tarkow et al. using acetic anhydride with pyridine as catalyst.[10,11] In the same year, Ridgway and Wallington used acetic anhydride with zinc chloride as catalyst.[12]

The reaction between wood and acetic anhydride is acid- or base-catalyzed, and many catalysts have been tried including potassium and sodium acetate,[13] dimethylformamide,[14,15,16] urea-ammonium sulfate,[15] magnesium perchlorate,[17,18,19] trifluoroacetic acid,[17] boron trifluoride,[14] and γ-rays.[20]

Many of these procedures use a strong mineral acid or acid salt as a catalyst. These cause hydrolysis of the carbohydrate polymers resulting in damage to the wood structure. When pyridine or dimethylformamide are used as a catalyst, carbohydrate degradation does not occur, but both of these are difficult to separate from the excess acetic anhydride and byproduct acetic acid after acetylation. The smell of pyridine or dimethylformamide can never be completely removed from the wood because they are strongly sorbed by it. All of these procedures call for reaction times of 12 to 24 hours.

In 1961, Goldstein et al. published a new procedure which eliminated the use of a catalyst.[21] They acetylated boards with a mixture of acetic anhydride and xylene. This reaction scheme called for a reaction time of 8 to 16 hours.

Several vapor phase acetylation procedures have also been published. Klinga and Tarkow acetylated whole hardboards with uncatalyzed acetic anhydride.[22] The board contained aluminum sulfate which may have acted as a catalyst. Arora et al. acetylated thin slices or particles of wood with acetic anhydride-pyridine vapors.[23] The authors acetylated wood flakes and particles with uncatalyzed acetic anhydride before board formation.[24,25] Youngquist et al. used the acetic anhydride/xylene treatment in a vapor system to acetylate wood flakes.[26] House *et*. *al*. acetylated wood fibers by spraying with acetic anhydride and heating.[27]

Because of the complexities of the reaction/recovery systems and the length of reaction time, none of these acetylation schemes has gone beyond laboratory scale. The purpose of the present research was to develop a simple acetylation procedure which could be used to acetylate hardwood and softwood flakes. To accomplish this, a new procedure must (1) eliminate both catalyst and organic cosolvent, (2) reduce the reaction time necessary to achieve a level of acetylation that will give a high degree of dimensional stabilization to the resulting boards, (3) shorten and simplify the chemical recovery after reaction. Flakeboards were made from flakes acetylated by the new procedure and were tested for dimensional stability in liquid water and water vapor.

EXPERIMENTAL

Wood Flakes

Southern pine and aspen flakes were used in this study. (Although different techniques were used for generating flakes, there should be no difference in a chemical reactivity between ring- and disk-cut flakes.) All flakes were retained on a 0.6-cm screen. They were ovendried for 24 hours at 105°C before use. Size of flakes (thickness x length x width (cm)): Southern pine: 0.05 x 6.4 x random; aspen: 0.06 x 3.8 x random.

Reaction of Flakes with Acetic Anhydride

The ovendried flakes (200 g) were placed in a stainless steel mesh container. The container was dipped into a tank containing acetic anhydride for 1 min, removed from the treating tank, and drained for 3 min. Dipping and draining were done at 25°C. The container with the flakes was placed in a preheated (120°C) stainless steel reactor for various lengths of time. After the reaction time was completed, a vacuum was applied to the cylinder (-0.003 MPa) for 2 hours at 120°C. A condenser on the bottom of the reactor was used to collect excess acetic anhydride and byproduct acetic acid. The flakes were then ovendried at 105°C for 12 hours. The weight percent gain (WPG) due to acetylation was calculated based on the weight of ovendried (O.D.) unreacted flakes.

Leaching and Acetyl Content of Acetylated Flakes

Weighed ovendried flakes, both acetylated and untreated, were leached under three conditions: (1) 14 days in distilled water at 24°C (changing water every 24 hrs), (2) 2 hrs in a Soxhlet extractor with refluxing water or (3) 2 hrs in a Soxhlet extractor with refluxing toluene/ethanol (1/1, v/v). After reovendrying, weight loss was determined.

Acetyl content was obtained by gas chromatography following deacetylation of ground and mixed samples with sodium hydroxide solution.

Flakeboard Preparation

Acetylated or untreated flakes (180 g, O.D.) were pressed into boards approximately 1.25 x 15 x 15 cm in size.[26] Each board was made with a density of approximately 640 kg/m^3 with a resin solids content of 6% (based on O.D. treated flakes). The adhesive used was a 43.5% aqueous solution of a phenol/formaldehyde resin. No catalyst or wax was added. The mat moisture content was 12% to 13%. Pressing lasted for 10 min at 177°C.

Each flakeboard was lightly sanded, and four pieces (5 x 5 cm) were cut out, ovendried, and weighed. The thickness was measured at the center point of each specimen, and subsequent measurements were taken at the same point.

TESTS CONDUCTED

Water Swelling Rate Tests

Each test specimen was placed in a 10- x 10-cm container, 5 cm deep. The container was on a flatbed micrometer for the thickness measurements. Water was added to the container and the thickness recorded as a function of time. Measurements were taken every 5 min for the first hour, every hour for the first 6 hours, then once a day for 5 days. All water and humidity tests were done in duplicate.

Water Soaking Tests

Cyclic water soaking tests were run as previously described.[28] Each of six cycles consisted of water soaking for 5 days followed by ovendrying at 105°C for 2 days. Thickness swelling was calculated as a percentage of the original thickness (O.D. board). After each cycle, the specimens were reweighed. The overall weight loss was determined from the original and final ovendried weights. Weight increase due to water sorption was determined after each soaking. The specimens were removed from the water, wiped of excess water, and weighed. The percent weight increase due to water sorption was based on the original weight of the ovendried board.

Humidity Tests

Ovendried specimens were placed in constant humidity rooms at 30%, 65%, and 90% relative humidity (RH) and 27°C. After 21 days the specimens were weighed to determine the equilibrium moisture content (EMC). Previous work showed that EMC for control and acetylated boards was reached at 14 days.

Separate specimens were placed in a humidity room of 30% RH and 27°C. Thickness and weight were determined after 21 days. The specimens were then placed in a humidity room at 90% RH and 27°C for another 21 days, whereafter thickness was determined. This procedure was repeated for a total of four cycles of 30% to 90% RH. The specimens were then ovendried and thickness measured. Changes in thickness were calculated as a percentage of the original thickness (o.d. board).

RESULTS AND DISCUSSION

Because of the limited number of specimens per individual test or treatment level, statistical analysis of the data was not appropriate. The results presented here should be considered as indicative of trends that a larger, statistically valid experiment should confirm.

Reactivity

During the 1-min dipping time in acetic anhydride and 3 min draining time, southern pine flakes sorbed about 100% in weight and aspen flakes about 150%. A longer dipping time or draining time did not increase the weight gains.

Weight percent gain from acetylation as a function of reaction time for southern pine and aspen flakes is shown in Figure 1. Southern pine reacts faster than aspen. Previous research[24,25] has shown that for southern pine, a WPG above 17 is desirable and can be achieved in 1-1/2 hours. For aspen, a WPG above 15 is desirable and was achieved in about 2-1/2 hours.

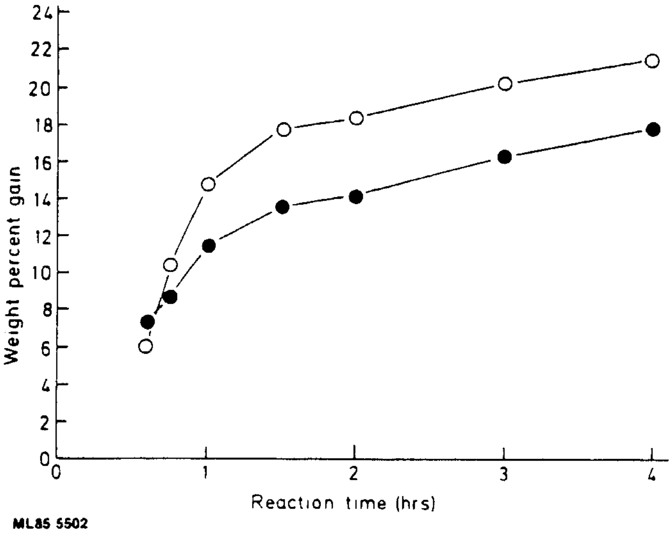


FIGURE 1 Degree of acetylation of southern pine and aspen flakes as a function of reaction time.
O Southern pine, ● Aspen. (ML85 5502)

Leaching Tests

Water leaching of unreacted and acetylated flakes at 24°C for 14 days and at reflux for 2 hours resulted in very low weight losses (Table 1). A slight loss in acetyl content resulted from water leaching. Leaching in refluxing toluene/ethanol caused considerably more loss of weight but not of acetyl content. This means that whatever is extracted from the flakes has about the same acetyl content as the remaining wood.

Liquid Water Tests

The rate of swelling of southern pine flakeboards made from acetylated flakes is shown in Figure 2. During the first 60 min, control boards swelled over 35% in thickness while the board made from flakes acetylated to 21 WPG swelled less than 4%. During

TABLE 1
Acetyl Content Before and After Leaching and Weight Loss in Various Solvents for Acetylated Southern Pine and Aspen Flakes

Species	WPG[1]	Acetyl content				Weight loss		
		Before leaching	After leaching in--			After leaching in--		
			Water 24 °C	Refluxing water 2 hr	Refluxing toluene/ethanol[2] 2 hr	Water 24 °C	Refluxing water 2 hr	Refluxing toluene/ethanol[2] 2 hr
		- - - - - - - - - - - - - - Pct - - - - - - - - - - - - - -						
Southern pine	0	1.4	1.3	1.4	1.3	1.1	1.3	2.2
	6.0	7.0	5.7	5.8	6.0	1.1	1.2	1.8
	10.4	12.0	9.8	10.7	11.7	0.3	0.6	0.9
	14.8	15.1	14.0	15.0	14.5	0.3	1.1	2.8
	17.8	17.8	16.5	17.0	16.7	0	1.1	2.7
	18.4	18.4	17.2	17.1	17.2	0	0.9	2.6
	20.3	19.4	18.3	18.4	19.5	0	0.6	2.4
	21.1	20.1	18.9	19.1	19.1	1.2	0.7	3.3
Aspen	0	3.9	3.9	3.8	3.8	0	1.2	2.6
	7.3	10.1	10.5	10.0	9.8	0.5	1.7	2.1
	8.7	12.8	13.4	12.4	13.0	0	0.2	1.3
	11.5	14.0	14.3	13.6	13.8	0.5	1.6	2.1
	13.6	15.9	16.4	16.0	16.2	0.6	0.8	2.9
	14.2	16.9	16.9	16.4	16.3	1.1	1.1	3.5
	16.3	18.4	18.3	17.4	17.5	1.5	0.4	3.3
	17.6	19.1	19.0	18.4	18.9	0	0.4	4.1

[1] Weight percent gain.

[2] 1/1 volume ratio.

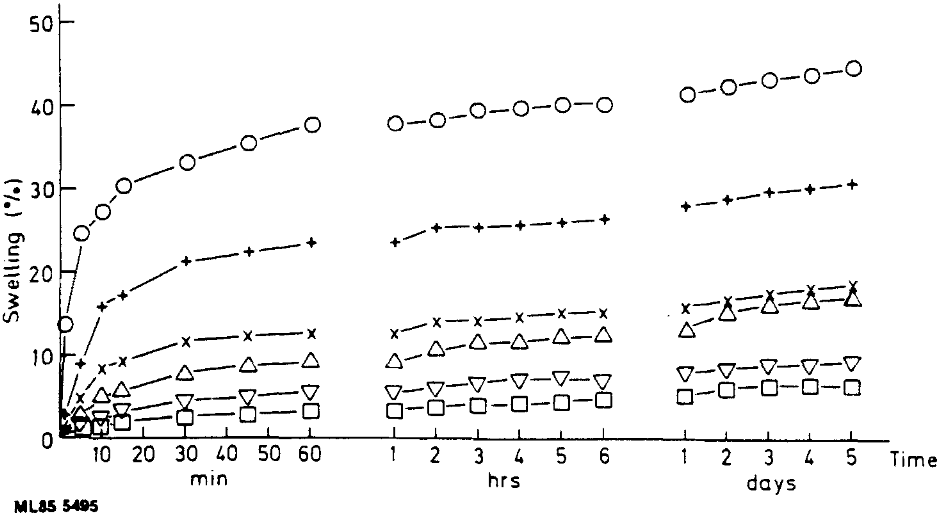


FIGURE 2 Rate of swelling in liquid water of southern pine flakeboard made from acetylated flakes.
O Control, + 6.0 WPG, X 10.4 WPG, Δ 14.8 WPG,
∇ 18.4 WPG, □ 21.1 WPG. (ML85 5495)

5 days of water soaking, the control board swelled about 45% while the 21 WPG board swelled about 6%.

Acetylation of aspen flakes resulted in a more dramatic reduction in the rate of swelling of the resulting aspen boards (Fig. 3). During the first 60 min, control boards swelled 55% in thickness while the board made from flakes acetylated to 17.9 WPG swelled less than 2%. During 5 days of water soaking, the control board swelled over 66% while the 17.9 WPG board swelled about 6%.

Thickness changes in the repeated water soaking tests for southern pine flakeboards are shown in Figure 4. The board made from flakes acetylated to 6 WPG swelled similarly to the control board. Considerable reductions in thickness swelling were observed at WPGs above 10. For all samples the increase in swelling was

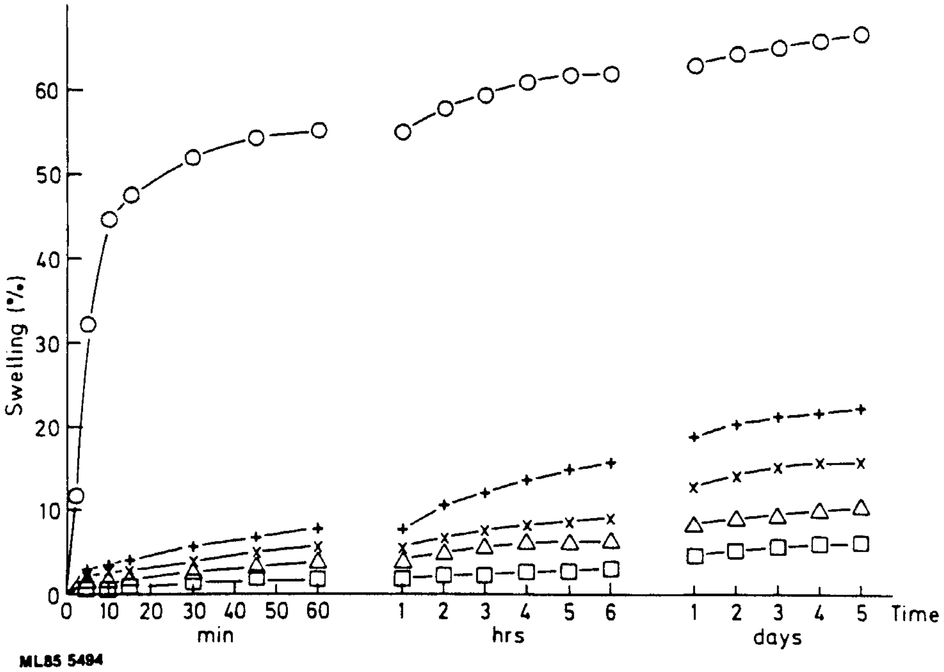


FIGURE 3 Rate of swelling in liquid water of aspen flakeboard made from acetylated flakes. O Control, + 7.3 WPG, X 11.5 WPG, Δ 14.2 WPG, □ 17.9 WPG. (ML85 5494)

greatest in the first four cycles; only a small increase in swelling occurred in the last two cycles.

Acetylation of aspen flakes to 7 WPG gave a considerable reduction in board swelling as compared to control boards (Fig. 5). There was more swelling in aspen control boards (almost 80%) than in southern pine control boards (about 60%). To achieve maximum board stability in six cycles of water swelling, a weight gain of about 18% was needed, whereas about 21 WPG was needed for southern pine.

Increases in weight due to liquid water sorption are shown in Figures 6 and 7. Southern pine control board increased 120% in

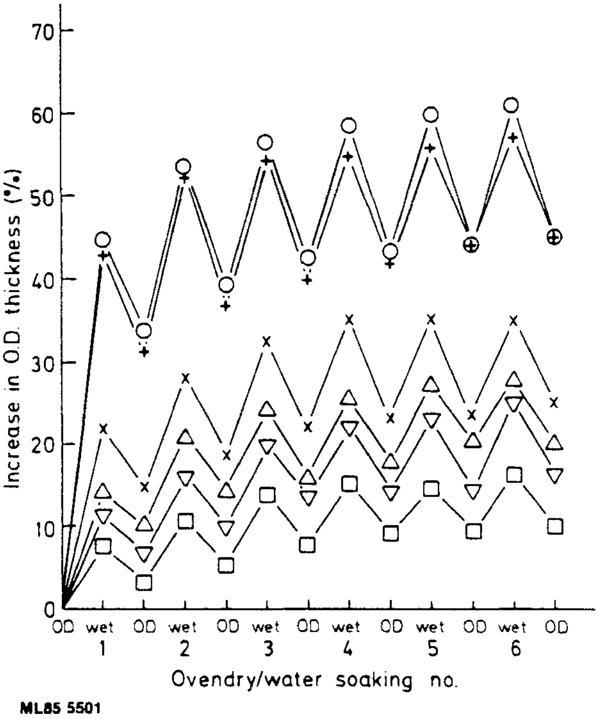


FIGURE 4 Change in thickness in repeated water swelling test of southern pine flakeboard made from acetylated flakes. O Control, + 6.0 WPG, X 10.4 WPG, Δ 14.8 WPG, ∇ 18.4 WPG, □ 21.1 WPG. (ML85 5501)

weight while the board made from flakes acetylated to 21 WPG took up less than 60% water. Aspen control boards increased over 130% in weight while the board made from flakes acetylated to 17.9 WPG took up less than 70%.

Weight losses determined after completion of the six-cycle water soaking tests are shown in Table 2. These losses, along with weight loss in a 2-week continuous water soaking test of flakeboards, also shown in Table 2, are larger than the losses that occurred with flakes (Table 1) in similar tests. This means that there was a slight loss of adhesive during the water soaking test of flakeboards.

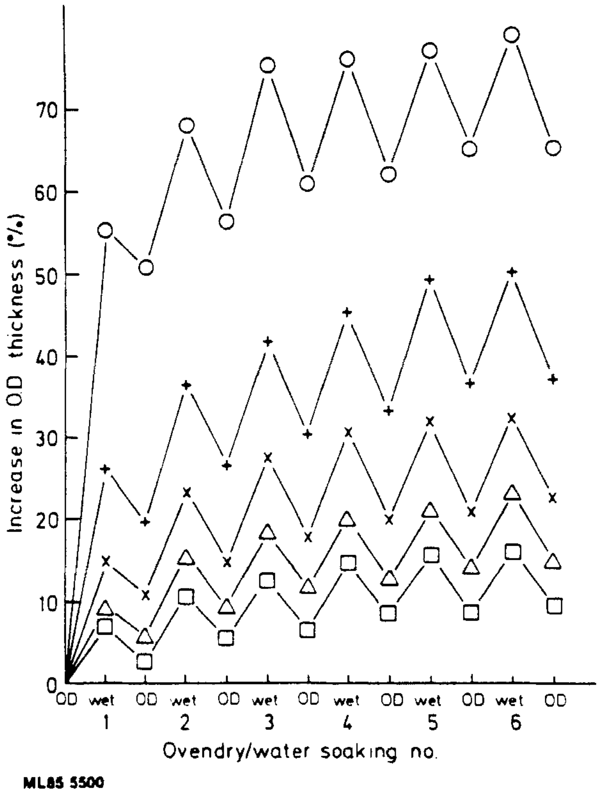


FIGURE 5 Changes in thickness in repeated water swelling test of aspen flakeboard made from acetylated flakes. O Control, + 7.3 WPG, X 11.5 WPG, Δ 14.2 WPG, □ 17.9 WPG. (ML85 5500)

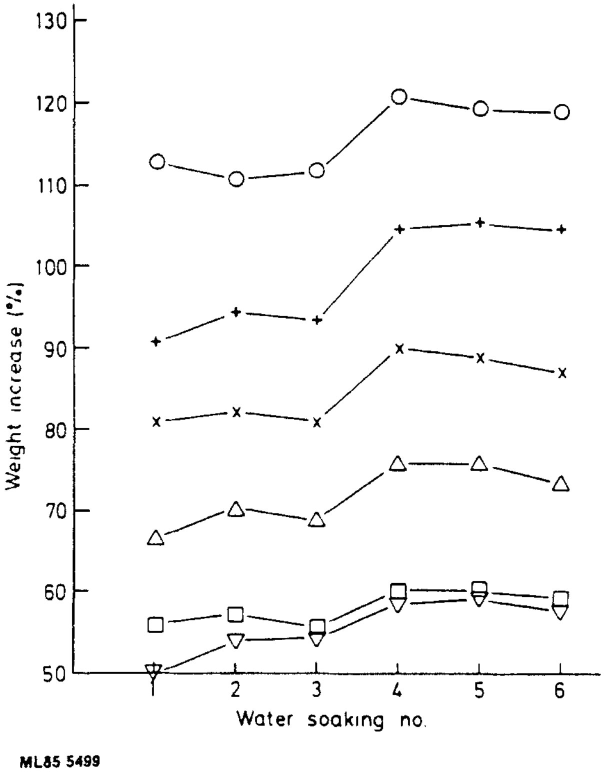
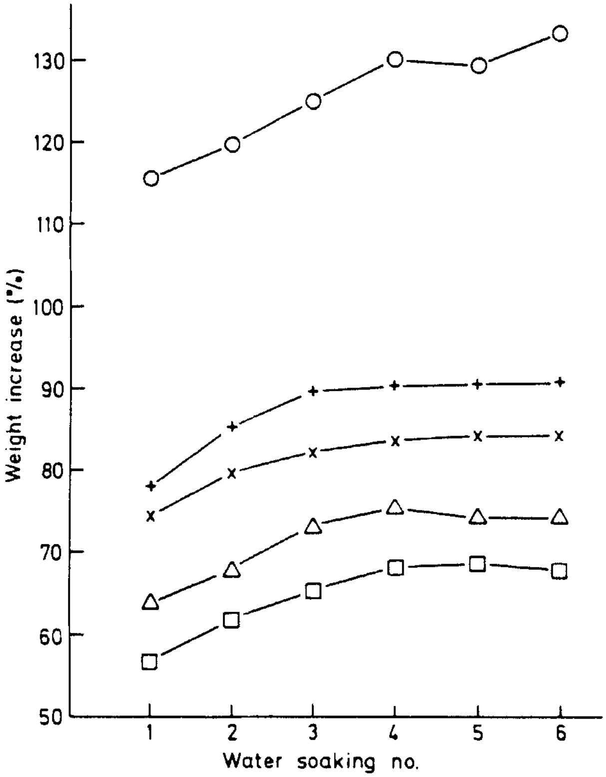


FIGURE 6 Weight increase due to liquid water sorption of southern pine flakeboard made from acetylated flakes. O Control, + 6.0 WPG, X 10.4 WPG, Δ 14.8 WPG, ∇ 18.4 WPG, □ 21.1 WPG. (ML85 5499)



ML85 5498

FIGURE 7 Weight increase due to liquid water sorption of aspen flakeboard made from acetylated flakes. O Control, + 7.3 WPG, X 11.5 WPG, Δ 14.2 WPG, □ 17.9 WPG. (ML85 5498)

TABLE 2

Weight Losses from Water Soaking of Flakeboards Made From Acetylated Flakes

		Weight loss after--	
Specimen	WPG[1]	2-week continuous water soaking (25°C)	Six-cycle water soaking/ovendried tests
		%	%
Southern pine	0	2.3	3.7
	6.0	2.2	2.5
	10.4	2.0	2.8
	14.8	1.8	2.1
	18.4	1.6	2.1
	21.1	1.6	2.0
Aspen	0	2.8	3.2
	7.3	2.6	2.8
	11.5	2.4	2.6
	14.2	2.0	2.3
	17.9	2.0	2.4

[1] Weight percent gain.

Humidity Tests

Table 3 shows that for both species, at each RH tested the EMC decreased as the weight gain due to acetylation increased. The EMC for southern pine was reduced about 50% at the highest WPG, while for aspen the EMC was reduced about 30% at the highest WPG tested.

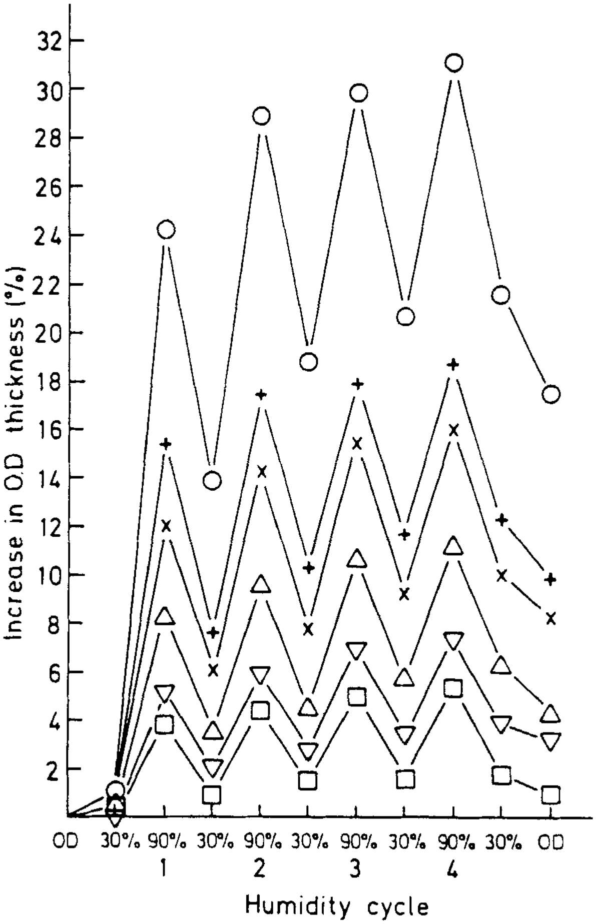
Figures 8 and 9 show the thickness change at 30% and 90% RH of boards made from nonacetylated and acetylated flakes. For both species the extent of swelling decreased as WPG was increased.

In both the repeated water soaking and humidity tests, irreversible swelling was evident in the early cycles. This was much more so in control boards. Irreversible and reversible swelling were considerably reduced in boards made from acetylated flakes. There was always some increase in permanent swelling, however, even during later cycles, and this was more prominent for control boards

TABLE 3
Equilibrium Moisture Content (EMC) of Acetylated Southern Pine and Aspen Flakes and Flakeboards Made From Acetylated Flakes at Various Relative Humidities (RH)

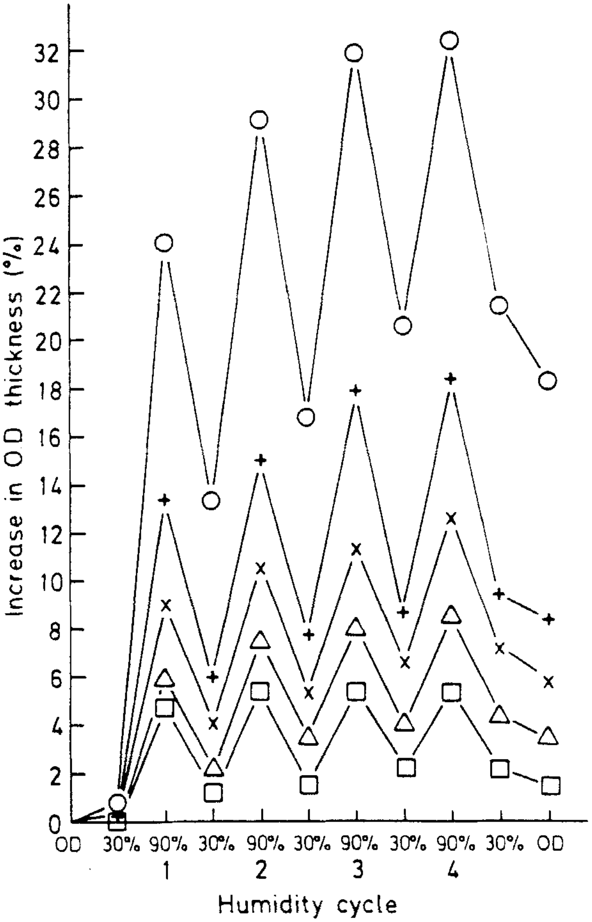
		EMC at--							
		30% RH		65% RH		80% RH		90% RH	
Sample	WPG[1]	Flakes	Board	Flakes	Board	Flakes	Board	Flakes	Board
Southern pine	0	5.8	4.5	12.0	10.3	16.2	14.5	21.7	20.1
	6.0	4.1	3.3	9.2	7.9	12.8	11.8	17.5	16.7
	10.4	3.3	2.7	7.5	6.9	10.3	10.3	14.4	14.9
	14.8	2.6	1.6	6.0	5.7	8.8	8.7	11.6	12.9
	18.4	2.3	2.3	5.0	5.3	7.1	8.9	9.2	12.7
	21.6	1.7	2.1	4.3	5.1	6.1	9.0	8.1	11.5
Aspen	0	4.9	3.8	11.1	8.6	15.3	13.2	21.5	19.0
	7.3	3.2	2.8	7.8	7.3	10.7	11.0	15.0	16.1
	11.5	2.7	2.2	6.9	6.5	9.2	10.1	12.9	15.8
	14.2	2.3	2.1	5.9	6.2	7.9	9.4	11.4	14.4
	17.9	1.6	1.8	4.8	5.5	6.7	9.2	9.4	13.6

[1] Weight percent gain.



ML85 5497

FIGURE 8 Changes in thickness at 30% and 90% RH of southern pine flakeboard made from acetylated flakes (27°C).
O Control, + 6.0 WPG, X 10.4 WPG, Δ 14.8 WPG,
∇ 18.4 WPG, □ 21.1 WPG. (ML85 5497)



ML85 5496

FIGURE 9 Changes in thickness at 30% and 90% RH of aspen flakeboard made from acetylated flakes (27°C). O Control, + 7.3 WPG, X 11.5 WPG, Δ 14.2 WPG, □ 17.9 WPG. (ML85 5496) and boards made from acetylated flakes with low WPGs. This was probably caused by adhesive and wood failures resulting from the harsh test conditions.

SUMMARY AND CONCLUSIONS

We set out to develop a rapid acetylation method for wood flakes which eliminated both catalyst and organic cosolvent. The procedure described had these qualities and also greatly simplified the handling of flakes before and during acetylation. The small size of the flake permitted quick sorption of acetic anhydride and a short drainage time removed most of the excess.

Eliminating the organic cosolvent increased the rate of acetylation. Since the organic cosolvent does not swell the wood cell wall or aid in the acetylation, it is only a diluent effectively, decreasing the available acetic anhydride. As compared to earlier results from acetylation with refluxing acetic anhydride/xylene,[24,25] the reaction time has been decreased to one-third for southern pine and one-fifth for aspen (i.e. to achieve 15 WPG in refluxing acetic anhydride/xylene, 3 hours reaction time was needed for southern pine and 12 hours for aspen, whereas only 1 and 2.5 hours, respectively, were needed with the dip procedure).

Chemicals, after reaction, were quickly removed by a short vacuum cycle because of the small size of the wood being acetylated. The recovery of removed chemicals is greatly simplified by the absence of catalyst and organic cosolvent in the mixture.

Flakeboards made from flakes acetylated by the new dip procedure performed nearly identically in dimensional stabilization tests with boards made from flakes acetylated by refluxing acetic anhydride/xylene and were superior to boards made from flakes acetylated with vaporous acetic anhydride alone.[24,25,29]

Southern pine and aspen flakeboards made from flakes acetylated by the new dip procedure sorbed much less water, both in liquid water soaking tests and in humid air, and swelled at a lower rate and to a lower extent than did control boards.

The EMC of flakeboards made from flakes acetylated by the dip procedure was greatly reduced at each RH tested as compared to control boards. Hygroscopicity of the resulting flakeboards decreased with increased level of flake acetylation.

FUTURE RESEARCH

Research on the mass balance of the new acetylating procedure is continuing, the ultimate goal being to develop a system for acetylating flakes quickly, with a simplified clean-up procedure and reuse of the chemicals. Also under investigation is a procedure in which only the amount of acetic anhydride needed to achieve the desired acetyl content is added to the flakes. This can be done by spraying acetic anhydride onto the flakes or dipping for a shorter period of time. Studies are currently underway to analyze the economics of the new system. Improvements in biological protection properties are also under investigation as well as mechanical properties of flakeboards made from dip-acetylated flakes.

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