DIMENSIONAL STABILITY OF ASPEN FIBERBOARD MADE FROM ACETYLATED FIBER[1]

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ABSTRACT

Aspen fiber was reacted with either ketene gas or liquid acetic anhydride to produce acetylated fiber. The fiber was formed into medium density fiberboard using phenolic resin. Boards made from acetylated fiber were smoother, more uniform in density, and slightly darker than boards made from control fiber. Acetylated boards swelled at a much lower rate and to a lesser extent in both liquid water and water vapor as compared to control boards. Boards made from ketene-reacted fiber were not as dimensionally stable as boards made from acetic-anhydride-reacted fiber. Increasing the amount of phenolic resin to produce the fiberboards increased the dimensional stability and strength of control boards but had little effect on acetylated boards. No statistical difference in moduli of elasticity or rupture was found between control and acetylated boards.

Keywords: Aspen, ketene, acetylation, fiberboards, water swelling, equilibrium moisture content, strength properties.

INTRODUCTION

For the most part, composites can be broken down into two basic types: price-driven composites, for which costs dictate the markets, and performance-driven composites, for which properties dictate the markets. A few composites might be of both types, but usually these are very different types of composites.

In general, the wood composite industry has produced mainly price-driven

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composites. Even though the wood composite industry is growing, it has lost some market share to competing materials such as steel, aluminum, plastics, and glass. Unless something is done to improve the competitive performance of wood, opportunity for growth of the wood composite industry will be limited in the future.

One property that has restricted the use of wood in high performance composites is the dimensional instability of wood in both thickness and linear swelling and shrinking with changes in moisture content. Dimensionally stable wood furnish can be produced by cell-wall chemical modification technology. Recent research at the Forest Products Laboratory has concentrated on acetylation for chemical modification of particles, chips, and flakes (Rowell et al. 1986a). Dimensionally stable wood composites have been made from these acetylated furnishes, but the ultimate goal of the research is to produce formable/shapable composites. Although wood particles, chips, and flakes can be pressed into shapes, the technology is somewhat limited.

The acetylation of wood fiber has the potential of producing a furnish that can be formed into nearly unlimited shapes that are smooth and dimensionally stable. Such technology, though higher in basic cost, can compete in performance-driven markets. A stabilized wood fiber can also be mixed with other stable materials such as metals, plastic, and glass to produce new composites in such a way that a synergism between the materials results in a composite that is better than the individual components.

We have developed a simple acetylation process using uncatalyzed acetic anhydride with no additional co-solvents (Rowell et al. 1986a, 1989). The one disadvantage of this process is that it generates by-product acetic acid during the acetylation reaction. We have also studied the use of ketene gas (which does not result in by-product acetic acid) to acetylate flakes, but we have found that the gas does not penetrate efficiently into the wood (Rowell et al. 1986b).

The purposes of this research were: (1) to determine if aspen fiber can be acetylated using ketene gas, (2) to compare moisture sorption properties of fiberboards made from fiber acetylated by ketene and acetic anhydride reactions, and (3) to determine the dimensional stability and mechanical properties of control and acetylated fiberboards.

EXPERIMENTAL

Reaction of fiber with acetic anhydride

Oven-dry aspen fiber was placed in a stainless steel mesh cylinder. The cylinder was placed inside a stainless steel reactor, the reactor closed, and the container rotated. Acetic anhydride preheated to 120 C was introduced into the reactor until the fiber was saturated with chemical. Excess anhydride was drained and added back to the holding tank. The wetted fiber was rotated and heated at 120 C for 0.5 to 3 h (depending upon the level of acetylation desired), after which a vacuum was applied to the reactor for 3 h at 120 C. Excess acetic anhydride and by-product acetic acid were collected from the bottom of this reactor. The acetylated fiber was removed from the mesh container and re-oven-dried for 12 h at 105 C. The weight percent gain (WPG) resulting from acetylation was calculated based on the weight of oven-dry unreacted fiber.

Reaction of fiber with ketene

Air-dried aspen fiber was placed in a 5-liter, 3-neck glass reactor. p-Dioxane was added with the aid of stirring to a total concentration of 40% by weight of fiber. The mass was agitated slowly with an overhead paddle stirrer. Good interaction of the fiber and ketene was achieved only when the fiber was moistened with dioxane. Ketene gas was generated by the pyrolysis of diketene at 570 C to 600 C. The ketene was transported in a nitrogen flow to the reactor and introduced above the level of the stirred aspen fiber. Different levels of ketene reaction were obtained by reacting the fiber with the ketene gas for different times, ranging from 1 to 2.5 h. After addition of the ketene, the system was purged overnight with nitrogen, the fiber was removed, and traces of residual ketene and acetic acid or acetic anhydride were removed by drying the fiber at 50 C under nitrogen flow for an additional 12 h. The temperature rise in the aspen mass during acetylation was generally in the range of 35 C to 45 C.

Acetyl content of control and acetylated fiber from reactions with acetic anhydride and ketene was obtained by gas chromatography of acetic acid produced by deacetylation of ground and mixed samples with sodium hydroxide solution.

Fiberboard production

Control or acetylated fiber [air-dried, lab moisture content approximately 30% relative humidity (RH)] was sprayed with three levels of an aqueous solution of a phenol-formaldehyde resin, 5%, 8%, and 12% (based on the oven-dry weight of the fiber). The fiber was hand-formed into 60- by 60-cm randomly oriented mats. Control and acetylated boards were pressed to a maximum thickness of 1.25 cm for 10 min at 185 C. All boards had a target density of 640 kg/m^3 and were trimmed to a final size of approximately 55 by 55 cm.

Moisture sorption determination

Equilibrium moisture content.—Equilibrium moisture content (EMC) of control and acetylated fiber and fiberboards was determined by placing weighed, oven-dried fiber (in 200-mesh containers) or fiberboards in constant humidity rooms at 30%, 65%, and 90% RH and 27 C. After 21 days, fiber and fiberboards were reweighed, and EMC was determined. Duplicate tests were run and values averaged.

Water swelling tests.—Each fiberboard specimen (51 by 51 mm) was placed in a 10- by 10-cm container, 5 cm deep. The container was placed on a flatbed micrometer for thickness measurements. Water was added to the container and specimen thickness recorded as a function of time. Measurements were taken every 15 min for the first hour, every hour for the first 6 h, then once a day for 5 days. All water swelling tests were done in duplicate.

Water soaking tests.—Cyclic water soaking tests were run on boards (51 by 51 mm) as previously described (Rowell and Ellis 1978). Each of six cycles consisted of water soaking for 5 days followed by oven-drying at 105 C for 2 days. Thickness swelling was calculated as a percentage of the original oven-dried thickness.

Cyclic humidity tests.—Fiberboard specimens (51 by 51 mm) were placed in a humidity room at 30% RH and 27 C. Thickness was determined after 21 days. The specimens were then placed in a humidity room at 90% RH and 27 C for

TABLE 1. *Acetyl analysis and equilibrium moisture content of control and acetylated aspen fibers at various relative humidity levels.*

Fiber type	Weight percent gain	Acetyl analysis (%)	Equilibrium moisture content (%)		
			30% RH	65% RH	90% RH
Control	0	3.9	4.9	11.1	21.5
Acetylated—ketene	6.0	13.5	3.2	6.3	14.5
	17.0	17.3	1.9	4.5	10.0
Acetylated—acetic anhydride	7.3	10.1	3.2	7.8	15.0
	17.9	19.1	1.6	4.8	9.4

another 21 days; thickness was determined using a flatbed micrometer. This procedure was repeated for a total of four cycles of 30% to 90% RH. The specimens were then oven-dried, and their thickness was measured. Changes in thickness were calculated as a percentage of the original oven-dry thickness.

Strength determination

Static bending tests were conducted on board specimens (76 by 330 mm) according to ASTM Standard D1037 (ASTM 1982), using a 300-mm span. Moduli of rupture (MOR) and elasticity (MOE) were determined.

RESULTS AND DISCUSSION

Reactivity

The acetylation of aspen fiber took place faster with liquid acetic anhydride than with ketene. Acetylated samples from both anhydride and ketene reactions showed the characteristic infrared (IR) absorption at 1,750 cm^{-1} for the presence of carbonyl groups in the bonded acetate.

Table 1 shows that the analytically determined acetyl content at low levels of acetylation with ketene was higher than the acetyl content from anhydride reactions. This may have been due to a small mass loss caused by extraction of the fiber in the liquid anhydride, which was not possible in the dioxane-wetted ketene reactions.

Because the ketene reaction was done on 100-g lots of fiber, it was very time-consuming to acquire large amounts of ketene-reacted fiber. For this reason, only a limited number of fiberboards could be made from ketene-reacted fiber. This limited a total comparison of test data from control boards with both acetic-anhydride- and ketene-reacted boards.

Fiberboard production

Control and acetic-anhydride-reacted fibers were sprayed with three levels of phenol-formaldehyde resin, 5%, 8%, and 12%. Ketene-reacted fiber was sprayed with 8% resin. All boards were pressed to metal stops that were 1.25 cm thick. About 10% more pressure was required to close the press to the stops for the acetylated fiber compared to the pressure used for the control fiber. This may have been due to the lower moisture content of the acetylated fiber and the slightly higher density. Both types of acetylated fiber produced boards that were slightly darker than the control boards.

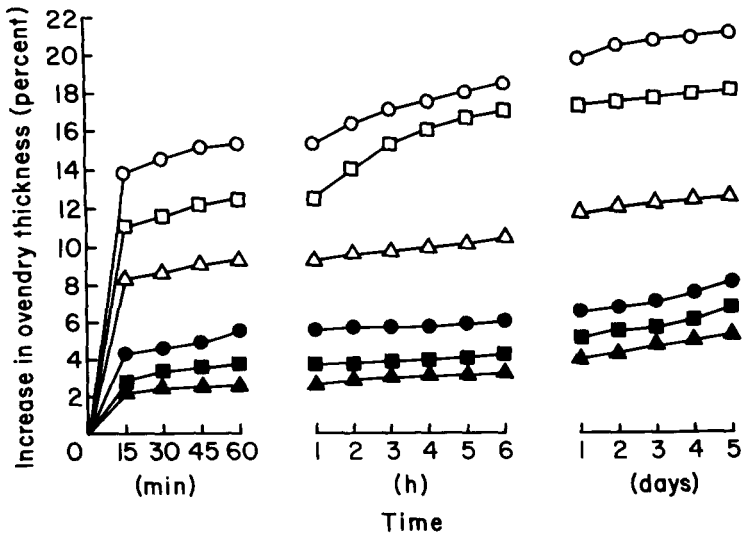

FIG. 1. Increase in thickness swelling of control and acetylated aspen fiberboards made with different levels of phenolic resin. Open symbols, control boards; closed symbols, acetylated boards. Circles, 5% resin; squares, 8% resin; triangles, 12% resin. (ML90 5430)

Boards made from acetylated fiber had higher surface consolidation and a much smoother surface than control boards and did not require sanding. Density measurements on control and acetylated boards showed that the acetylated boards had more uniform density throughout the thickness compared to that of the control boards.

Moisture sorption determination

Equilibrium moisture content.—Table 1 shows the EMC of control and acetylated fibers made from both acetic anhydride and ketene reactions. There is very little difference in EMC between the two types of acetylated fiber. Similar results are shown in Table 2 for EMC of fiberboards made from control and acetylated fibers. Boards made from acetic-anhydride-reacted fiber showed slightly lower EMC values than did ketene-reacted boards.

Table 3 shows the EMC and thickness swelling at 30%, 65%, and 90% RH of control and acetic-anhydride-reacted fibers sprayed with three levels of phenolic resin. Control boards showed a significant reduction in thickness swelling with

TABLE 2. *Equilibrium moisture content of control and acetylated aspen fiberboards made at various relative humidity levels.*[a]

Board type	Equilibrium moisture content (%)		
	30% RH	65% RH	90% RH
Control	3.3	7.3	20.3
Acetylated—ketene 17.0 WPG[b]	2.4	5.1	13.0
Acetylated—acetic anhydride 17.9 WPG	1.5	3.8	11.8

[a] Phenolic resin content of 8%.
[b] Weight percent gain.

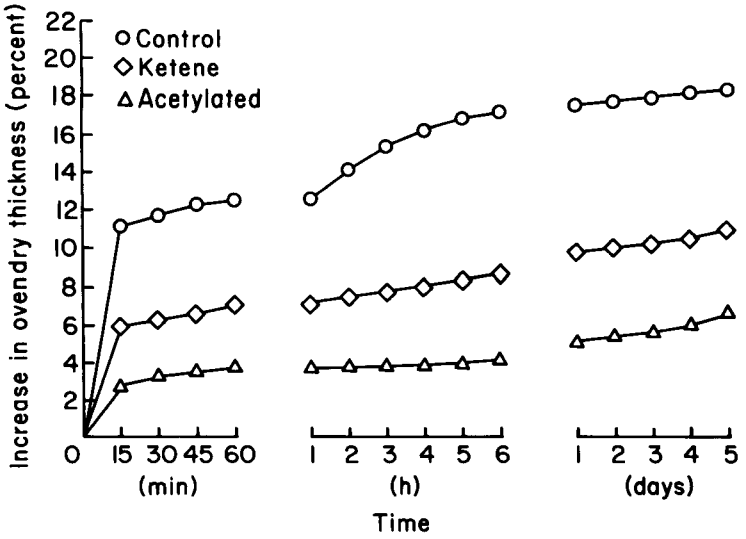

FIG. 2. Increase in thickness swelling of aspen fiberboards made from control or acetylated fiber (8% phenolic resin). (ML90 5431)

increase in resin content; the percentage of resin had less effect on the swelling of acetylated boards.

In all EMC tests, acetylated fiber and boards made from acetylated fiber had about half the EMC of control fiber and boards at the same RH.

Water swelling tests.—Figure 1 shows the rate of swelling of control and acetic-anhydride-reacted fiberboards using three levels of phenolic resin. Even at the highest level of resin, control boards swelled faster and to a greater extent than did acetylated boards at the lowest level of resin. After 5 days of water swelling, control boards at 5% resin swelled about 21% in thickness, whereas control boards at 12% resin swelled about 13%. Acetylated boards at 5% resin swelled 8% in thickness during the same time, and acetylated boards at 12% resin swelled about 5%. The higher level of resin greatly helped the control boards resist thickness swelling but only slightly improved the acetylated boards.

TABLE 3. *Equilibrium moisture content and thickness swelling of control and acetylated aspen fiberboards made at various relative humidity levels.*

Board type	Phenolic resin (%)	Moisture sorption (%)[a]					
		30% RH		65% RH		90% RH	
		EMC	TS	EMC	TS	EMC	TS
Control	5	3.3	0.7	7.2	3.0	19.6	12.6
	8	3.3	1.0	7.2	3.1	19.8	11.2
	12	3.5	0.8	7.2	2.5	20.2	9.7
Acetylated[b]	5	1.6	0.2	3.7	1.8	7.9	3.2
	8	1.6	0.2	3.9	1.7	9.3	3.1
	12	1.7	0.1	4.2	1.7	10.7	2.9

[a] EMC is equilibrium moisture content, TS is thickness swelling.
[b] Acetylated boards were reacted with acetic anhydride.

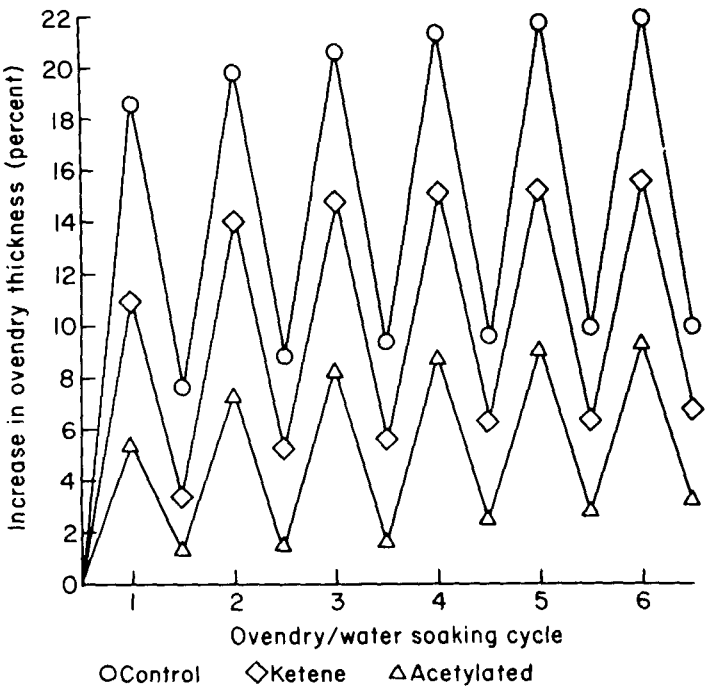

FIG. 3. Results of cyclic water soaking/oven-drying test. Change in thickness of aspen fiberboard made from control or acetylated fiber with 8% phenolic resin. Minimal values are associated with oven-drying phase of cycle and peak values with water soaking phase. (ML90 5432)

Figure 2 compares the rate of swelling of control boards with that of boards made from acetic-anhydride- and ketene-reacted fiber at 8% resin content. In this test, the control board swelled about 18% in thickness in 5 days, the ketene-reacted board about 11%, and the acetic-anhydride-reacted board about 7%.

Water soaking tests.—Thickness changes in the cyclic water soaking/oven-drying test are shown in Fig. 3. Irreversible swelling (caused by release of residual compressive stresses imparted during board pressing) was greatest in control boards, lower in ketene-reacted fiberboards, and lowest in acetic-anhydride-reacted boards. Reversible swelling (normal wood cell-wall swelling) was much greater in control boards (about 12%) compared to ketene-reacted boards (about 9%) and acetic-anhydride-reacted boards (about 7%).

All boards showed an increase in permanent thickness swelling; permanent swelling was about 10% in control boards compared to about 6% in ketene-reacted boards and about 3% in acetic-anhydride-reacted boards. Permanent swelling was probably caused by adhesive failures resulting from the test conditions.

Cyclic humidity tests.—Thickness change in cyclic 30% to 90% RH tests is shown in Fig. 4. The results are similar to those from the cyclic water soaking/oven-drying test; control boards swelled to a much greater extent (about 13%) compared to ketene-reacted boards (about 8%) and acetic-anhydride-reacted boards (about 4%). Control boards had about 6% permanent swelling compared to 2% and 0.5% permanent swelling in ketene- and acetic-anhydride-reacted boards, respectively.

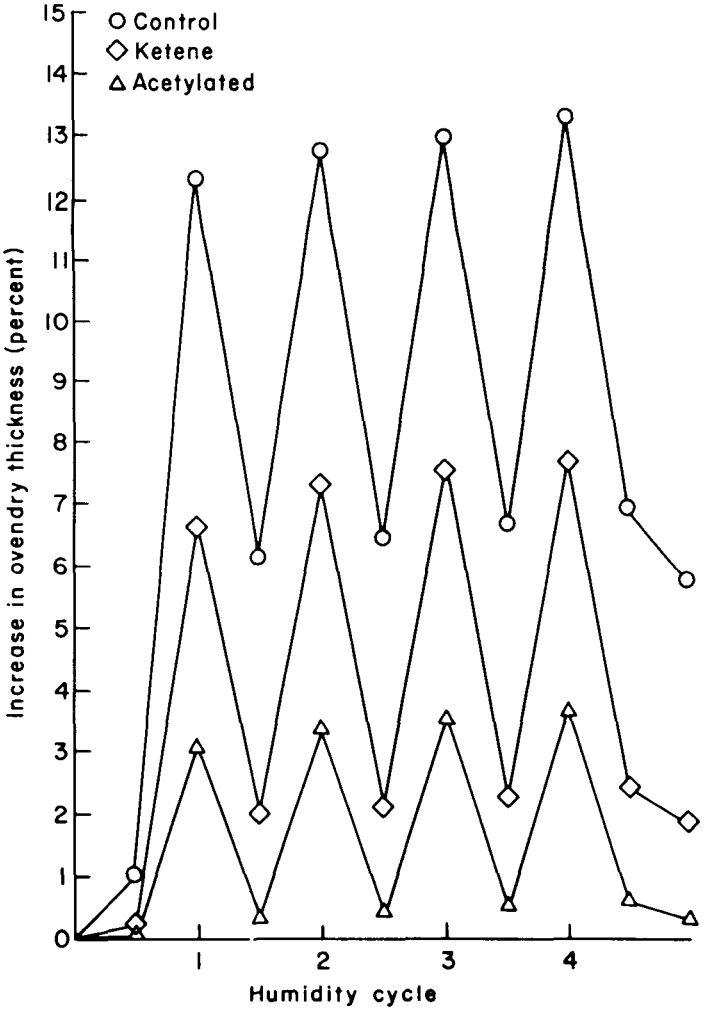

FIG. 4. Results of cyclic humidity test. Change in thickness of aspen fiberboard made from control or acetylated fiber with 8% phenolic resin. Minimal values are associated with 30% relative humidity and peak values with 90% relative humidity. Initial and final values are oven-dry values. (ML90 5433)

Strength determination

Table 4 shows the MOE and MOR of control and acetic-anhydride-reacted boards at 5%, 8%, and 12% resin. Each mean value is an average of 12 test specimens. The range of values determined was large in all boards in both tests. This probably means that there was not a consistent spread of resin on the fiber. The range may also be due to variations in density between the boards.

Increasing the amount of resin did improve the strength of control boards but had little effect on acetylated boards.

In general, MOE and MOR values were higher in acetylated boards than in control boards, but the difference was not statistically significant. The higher values may be explained by the stiffer fiber in the acetylated boards, which resulted from the lower EMC.

TABLE 4. *Strength properties of control and acetylated aspen fiberboards.*

Board type	Phenolic resin (%)	Modulus of rupture (MPa)		Modulus of elasticity (MPa)	
		Mean	Range	Mean	Range
Control	5	15.1	12.4–18.3	1,476	1,145–1,710
	8	17.2	11.4–22.4	1,454	1,014–1,924
	12	18.6	14.9–22.9	1,751	1,345–2,544
Acetylated[a]	5	15.3	13.7–18.7	1,613	1,227–2,000
	8	19.8	14.8–23.5	2,041	1,710–2,268
	12	17.9	13.9–25.9	1,772	1,379–2,503

[a] Acetylated boards were reacted with acetic anhydride.

CONCLUSIONS

Fiberboards made from acetylated aspen fiber, either by acetic anhydride or ketene reactions, were smoother, more uniform in density, higher in surface consolidation, and slightly darker than fiberboards made from control aspen fiber. Acetylated fiberboards did not require any sanding to obtain a very smooth surface. Fiberboards made from ketene-reacted fiber were not as dimensionally stable as fiberboards made from acetic-anhydride-reacted fiber at the same level of acetylation. The reason for this is not known.

The rate and extent of swelling in liquid water and water vapor were much greater in control boards than in acetylated boards. Increasing the amount of phenolic resin improved the stability of control boards but did not have a significant effect on acetylated boards.

At the 8% phenolic resin level, there was no statistical difference in moduli of rupture and elasticity between control and acetylated boards.

Future research will be directed at combining stabilized acetylated fiber with other fibers and veneers made from glass, metals, synthetic fibers, and other biomass fibers, and with acetylated wood veneers. We will also be studying the formation of flexible fiber mats by nonwoven needling and thermoplastic fiber melt matrix technologies to produce complex shaped composites.

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