Adhesive bonding of acetylated aspen flakes, Part 2. Effects of emulsifiers on phenolic resin bonding

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Acetylation of aspen flakes causes a reduction in the wettability of the flakes to a water-soluble phenolic resin. In this study, addition of emulsifiers to the phenolic resin improved wettability of the acetylated flake surface. In general, water-to-oil emulsifiers were more effective than oil-to-water emulsifiers. Internal bond strength and modulus of rupture were higher in acetylated flakeboards in which a water-to-oil emulsifier was added to the phenolic resin compared to nonacetylated control flakeboards made with phenolic resin alone. Image analysis of the failed surfaces of acetylated flakeboards after an internal bond test showed about 50% board failure in the wood and about 50% in the glueline, regardless of the emulsifier used in the phenolic resin.

Key words: acetylation; emulsifier; resin penetration; internal bond strength; flakeboard

In Part 1 of this series, it was found that acetylation made aspen flakes more hydrophobic and therefore less wettable to a water-soluble phenolic resin[1]. Electron microscopy of the flakes revealed greatly reduced resin penetration. Internal bond strength was reduced in acetylated flakeboards compared to control flakeboards made with the same phenolic resin.

Previous research showed that acetylation causes little or no strength loss in the wood itself[2-5], so any loss in strength in acetylated composites occurs in the glueline rather than in the wood. Failure in acetylated flakeboards was shown to take place almost completely in the phenolic-resin/wood interfaces; the studies concluded that failure was due to poor flake wettability and resin penetration[1,6].

Wettability of acetylated flakes should be improved by the addition of emulsifiers to the phenolic resin. For these experiments, emulsifiers were chosen from the hygrophile-lipophile balance system, commonly known as HLB[7]. In this system, each emulsifier is assigned a numerical value that expresses the balance of the size and strength of the hygrophilic and lipophilic groups of the emulsifier. All emulsifiers consist of a molecule that combines both hygrophilic and lipophilic groups. An emulsifier that is lipophilic in character is assigned a low HLB number, usually below 9, and one that is hygrophilic is assigned a high HLB number, usually above 11. Some general correlations are shown in the following tabulation:

HLB range	Use
4-6	Water-oil emulsifier
7-9	Wetting agent
8-18	Oil-water emulsifier
13-15	Detergent
10-18	Solubilizer

The purpose of this research was to: (1) evaluate wettability of flakes in response to different emulsifiers; (2) determine internal bond strength and percentage of wood glueline failure in small experimental flakeboards made with resin containing different emulsifiers; and (3) determine modulus of rupture and modulus of elasticity of larger boards made with the best emulsifier determined by the internal bond test.

Experimental details

Flake acetylation

Ovendry aspen flakes were acetylated using neat acetic anhydride at 120°C as described previously[8]. Flakes were produced with acetyl weight gains of approximately 17% (based on the original ovendry weight).

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Types of emulsifiers

Five different emulsifiers were added to the phenolic resin to determine flake wettability (Wetting test) and to determine if bonding could be improved (Internal bond test):

Emulsifier*†	HLB number
Brij 92	4.9
Span 20	8.6
Tween 20, Span 20 (50/50 mixture)	12.7
Tween 80	15.0
Tween 20	16.7

Wetting test

A simple wetting test was designed to determine the rate of resin penetration into both control and acetylated flakes. A uniformly sized droplet of resin was placed on the flake surface, and the time required to sorb the resin into the flake recorded.

Small flakeboard production and tests

Control or acetylated flakes (180 g ovendry) were sprayed with a 43.5% aqueous solution of a phenol-formaldehyde resin or with the resin plus 5% emulsifier. In either case, no catalyst or wax was added to the phenolic resin solution. The total amount of resin solids added was 6%, by weight, based on the ovendry weight of control or acetylated flakes.

After resin addition, control or acetylated flakes were hand-formed into a randomly oriented mat and pressed at an average of 4137 MPa for 10 min between platens heated to 180°C to produce boards approximately 1.25 × 15 × 15 cm in size. Each board was made with a density of approximately 640 kg m^{-3}. Five boards were made from each resin type. The outer 3 cm was cut from each side of all boards, and test specimens were cut from the remaining boards.

Internal bond test

An internal bond test (ASTM Standard D 1037) was carried out on 51 × 51 mm specimens cut from flakeboards[9].

Determination of failed area

After failure in the internal bond test, each failed surface was scanned with an image analyser. A Quantimet 970 image analysis system was used, which allowed a double detection pause to set up the scanner and shading corrector. At the first detection pause, detect levels were set for wood failure (light areas); at the second pause, detect levels were set for resin failure (dark areas). The machine automatically performed the analysis at both detect levels.

Each specimen was imaged on a macroviewer using incident illumination. The system computer maintained constant illumination voltage and scanner sensitivity to avoid variations in thresholding during the detection process. The analog image was digitized using a two-dimensional image processor. The machine determined the percentage of wood failure and resin failure in each test specimen.

Large flakeboard production and static bending test

Control or acetylated flakes sprayed with either phenolic resin alone or with phenolic resin containing Brij 92 emulsifier (5% or 10% by weight) were hand-formed into 597 × 686 mm randomly-oriented mats. A fully automatic, programmable, particleboard press system with data collection capability was used. The press was accurately controlled through an electrical servoactivated pump actuated by pressure- and position-monitoring transducers. Position was reproducible to within 0.51 mm under a no-load condition and to within 0.127 mm under pressure. Line pressure was controlled to within 68.95 kPa of the targeted values at pressures below 3.45 MPa and to within 206.84 kPa at pressures above 3.45 MPa. The press was time-base programmed to operate to specific press openings or pressures, or alternated between these two modes of control.

Control boards were pressed to a maximum pressure of 4.14 MPa for 8 min at 194°C. Acetylated boards were pressed to a maximum pressure of 4.48 MPa for 8 min at 194°C. All boards had an approximate density of 640 kg m^{-3} and were trimmed to a final size of approximately 56 × 66 cm.

Flakeboards (7.6 × 33 cm) were tested for static bending over a 30.5 mm span according to ASTM Standard D 1037[9]. Modulus of rupture and modulus of elasticity were determined.

Results and discussion

Because of the limited number of specimens per individual test or treatment level, no statistical analysis of the data was possible. The results presented here should be considered as indicative of trends, and a larger, statistically valid experiment should be done to confirm these results.

In the simple qualitative wetting test, a droplet of 43.5% aqueous phenol-formaldehyde resin was sorbed into a control flake immediately. The same droplet on an acetylated flake was still in its original form after 30 min. When the droplet contained the resin plus 5% Brij 92 (HLB No. 4.9), the droplet was sorbed as quickly into an acetylated flake as into a control flake. The time to sorb the modified resin solution into the acetylated flake increased as the HLB number increased; time to sorb Brij 92 < Span 20 < Tween 20 + Span 20 < Tween 80 < Tween 20. Wetting of the acetylated flakes decreased as the HLB number of the emulsifier increased.

Table 1 shows the density and internal bond strength of all small boards tested. The density of the control boards was slightly higher than that of other boards. The internal bond strength of acetylated boards without emulsifier was about 20% lower than the strength of control boards. The internal bond strength of acetylated boards with Brij 92 was higher than that of control boards. With the exception of boards containing Tween 80, internal bond strength decreased as the HLB number increased.

After the internal bond test, each failed surface was scanned with an image analysis system that determined the percentage of wood failure (light areas) and resin

*Use of trade names does not imply endorsement by the US Department of Agriculture of any product.
† Emulsifiers mentioned are all produced by ICI Americas, Inc., Wilmington, DE, USA and specific names such as Brij 92 and Tween 20 are registered trademarks of this corporation.

Table 1. Internal bond strength of small control and acetylated flakeboards with emulsifier in the phenolic resin

Flake	Emulsifier[a]	HLB number	Specific gravity[b]	Internal bond (kPa)[b]
Control	None	—	0.771 (0.691-0.819)	773 (267-991)
Acetylated	None	—	0.664 (0.605-0.715)	591 (373-731)
	Brij 92	4.9	0.702 (0.672-0.758)	830 (668-1090)
	Span 20	8.6	0.695 (0.654-0.721)	597 (246-808)
	Tween 20, Span 20[c]	12.7	0.660 (0.569-0.734)	583 (330-780)
	Tween 80	15.0	0.666 (0.569-0.734)	724 (380-970)
	Tween 20	16.7	0.672 (0.617-0.721)	527 (267-752)

[a]5% emulsifier added to phenolic resin
[b]Numbers in parentheses show range in 5 boards (12 specimens) tested
[c]50-50 mixture

Table 2. Results of image analysis of surfaces broken after internal bond test of small flakeboards

Flake	Emulsifier[a]	HLB number	Wood failure[b, c] (%)	Resin failure[b, d] (%)
Control	None	—	88.7 (80.0-97.0)	11.3 (5.0-30.0)
Acetylated	None	—	65.0 (58.0-71.4)	42.7 (31.3-50.5)
	Brij 92	4.9	57.7 (45.7-67.3)	39.8 (23.7-47.9)
	Span 20	8.6	58.9 (40.7-66.1)	37.3 (16.7-59.7)
	Tween 20, Span 20[e]	12.7	50.3 (38.6-61.2)	45.7 (33.1-62.5)
	Tween 80	15.0	56.6 (40.7-78.1)	35.8 (16.1-57.0)
	Tween 20	16.7	52.6 (42.9-65.9)	45.9 (23.1-58.0)

[a]5% emulsifier added to phenolic resin
[b]Numbers in parentheses show range in 5 boards (12 specimens) tested
[c]Light surface
[d]Dark surface
[e]50-50 mixture

Table 3. Moduli of rupture and elasticity of large acetylated flakeboards using different levels of Brij 92 emulsifier in the phenolic resin

Brij 92 (%)	Modulus of rupture[a] (MPa)	Modulus of elasticity[a] (MPa)
0	28 (24-34)	5.019 (4.816-5.399)
5	25 (21-32)	5.104 (4.865-5.758)
10	24 (18-27)	5.230 (4.935-5.666)

[a]Numbers in parentheses show range in 12 specimens cut from 4 boards tested

failure (dark areas) (Table 2). Because the cured phenol resin was very dark reddish brown, it was easily distinguished from the light aspen wood. Obviously there were areas where the analysis could not detect if the surface was light or dark because the percentage of wood failure plus the percentage of resin failure in Table 2 do not always total 100%. About 90% of the failure in control boards occurred in the wood and about 10% in the resin (Table 2). In acetylated boards without emulsifier, slightly more wood failure occurred than resin failure (65% compared to 43%). Adding emulsifier to the phenolic resin resulted in very little change in the percentage of wood to resin failure compared to acetylated boards without emulsifiers. Span 20 was slightly more effective than Brij 92 in reducing the percentage of resin failure but not significantly better than Tween 20. There was a wide variation in the data, and no conclusion was drawn from these results.

Because Brij 92 had increased the internal bond strength of the small experimental boards, it was decided to increase the board size and test two different levels of Brij 92. The results of these experiments showed an increase in modulus of elasticity from 0 to 10% and a decrease in modulus of rupture with increased levels of Brij 92 (Table 3). The boards had become slightly more elastic, but the force required to break them had decreased slightly.

Conclusions

Results from this study indicate that a 5% to 10% addition of a water-to-oil emulsifier with a low hygrophile-lipophile balance system (HLB) number does improve wetting of acetylated flakes to water-soluble phenolic resins. It is questionable, however, if the increase in strength properties is large enough to merit the increased cost of the added emulsifier.

It may be that acetylation not only negatively affects wettability of the wood but also interferes with the polymerization reaction so that the phenolic resin is not fully cured.

Future research is directed at studying isocyanate resins with acetylated flakes with and without steam injection.

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