Decay of chemically modified pine and eucalyptus flakeboards exposed to white- and brown-rot fungi

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Flakes of two planted wood species, *Pinus taeda* L. and *Eucalyptus grandis* Hill ex-Maiden, were acetylated with acetic anhydride without co-solvents or catalyst for 4 h at 120°C. Acetylated and nonacetylated (control) boards were produced with 8 and 12% of phenol-formaldehyde resin solids (based on the oven-dry weight of particles). These boards were tested for decay according to ASTM D 2017-71. Two wood-attacking fungi were selected: A brown-rot fungus *Gloeophyllum trabeum* (Pers. ex Fr.) Murr., and a white-rot fungus *Pycnoporus sanguineus* (Pers. ex Fr.) Murr. Most of the pine and eucalyptus control flakeboards were classified as "resistant" against the tested fungi, the only exception being the pine control flakeboard bonded with 8% of resin solids, which was classified as "moderately resistant" against the fungus *Gloeophyllum trabeum.* Acetylated pine and eucalyptus flakeboards were both classified as "highly resistant" to the wood-destroying basidiomycetes tested. Besides improving dimensional stability, the acetylation treatment inhibited the attack from both fungi tested.

*Partículas tipo "flakes" de madeira, de duas espécies exóticas cultivadas, **Pinus taeda** L. e **Eucalyptus grandis** Hill ex Maiden, foram acetilados com anidrido acético sem co-solvente ou catalisador. Chapas acetiladas e não-acetiladas (controles) foram produzidas com 8 e 12% de sólidos de resina fenólica (baseados no peso seco das partículas). A degradação biológica das chapas foram testadas segundo a norma ASTM D 2017-71. Dois fungos destruidores da madeira foram selecionados: **Gloeophyllum trabeum** (Pers. ex Fr.) Murr., um fungo da podridão parda e **Pycnoporus sanguineus** (Pers. ex Fr.) Murr., um fungo da podridão branca. As chapas controles de pinus e eucalipto foram classificadas como "resistentes" aos fungos testados, com exceção da chapa controle de pinus colada com 8% de sólidos de resina que foi classificada como "moderadamente resistente" ao fungo **Gloeophyllum trabeum**. Chapas acetiladas de pinus e eucalipto foram ambas classificadas como "altamente resistentes" aos basidiomicetos destruidores da madeira. Consequentemente, o tratamento de acetilação inibiu o ataque de ambos os fungos testados, além de melhorar a estabilidade dimensional das chapas.*

Dimensional instability and susceptibility of wood to biological attack have removed wood products from many potential markets.

In a previous paper (1), dimensional stability of acetylated pine and eucalyptus flakeboards were greatly improved by acetylation. Water sorption and strength properties of these flakeboards are reported as being good.

For biological resistance, however, the data indicate that not only is the amount of bonded acetate in the cell-wall polymers important, but also the types of cell-wall polymers that have been modified.

The reactivity of isolated cell-wall components from pine wood with acetic anhydride and the distribution of acetyl groups in cell-wall polymers of acetylated whole pine wood at different levels of bonded acetyl weight gains have already been determined (2).

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Lignin, holocellulose, cellulose and hemicelluloses were isolated from pine wood and made to react with acetic anhydride. No acetylation took place when cellulose reacted with acetic anhydride during 4 h. The most reactive isolated cell-wall component was lignin, whose theoretical maximum is 26%. An acetyl content of almost 10% was achieved within 15 min of reaction with a maximum acetyl content of about 18% after 4 h. Isolated pine hemicelluloses were the next most reactive components. A maximum acetyl content of 30% was achieved after 3 h. Briefly, the order of reactivity was found to be lignin > hemicelluloses >> holocellulose (2).

The distribution of acetyl groups in acetylated whole wood, holocellulose and lignin cell-wall components was described and determined by removing the lignin from wood with sodium chlorite. The sodium chlorite isolation procedure did not hydrolyze the acetyl groups (2).

The decay resistance of chemically modified wood has been postulated to occur rather by reducing the ability of the cell-wall to absorb water to the level that enzymatic degradation of wood cannot take place than by changing the configuration of the cell-wall polymers of wood so that decay enzymes cannot metabolize the modified wood substrates (3).

During the past decade, research investigating particleboard and board material durability has determined that wood species, particle geometry, manufacturing condition, surface properties, board structure and density as well as type and amount of adhesive are all involved in the susceptibility of particleboard to fungi (4).

Increased utilization of particleboard for structural purposes in home construction and mobile homes for siding, garage door panels, and pallet decking, dictates the need to better understand the deleterious effects of moisture and, consequently, microorganisms on particleboard in such external or high-risk internal uses (4).

The greater surface area and porosity of wood composites compared to solid wood and the use of woods with low decay resistance for composites may contribute to their greater susceptibility to biological attack (5).

The mechanisms of wood decay by white- and brown-rot fungi have received increased attention in recent years as a result of environmental concern over the use of broad-spectrum and highly toxic wood preservatives.

Protection from biodegradation is mainly required in the holocellulose fraction, this being the main food source for microorganisms and attack resulting in great strength loss in wood due to hydrolysis and depolimerization (6).

The mechanism of biological resistance in acetylated wood is not known, however, it is thought to be due to two factors: Greatly decreased moisture sorption or lack of water in the modified cell-wall and substrate blocking (7). The fiber saturation point of flakeboards made from acetylated pine and eucalyptus flakes is lower than that of control flakes, thus there may not be enough moisture at the site for enzymes to hydrolyze the target linkages.

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 of wood to make it unsuitable for fungal digestion or growth (7).

Chemical modification of lignin might also block decay because wood-destroying organisms utilize wood after altering lignin which protects the carbohydrates. In addition, chemical modification of wood might interfere with the recognition of wood by the fungus as an appropriate substrate. Modification of lignin should make the alteration more difficult, or possibly yield fragments harmful to the invading organisms (8).

Hardwoods or softwoods are commonly attacked by both brown- and white-rot fungi, when in ground contact, finding conditions that favor fungal growth such as food material, suitable temperature, air supply, and moisture. From past observation the presence of brown-rot in softwoods used aboveground has been known. Overall, white-rot predominates in hardwood. It is known that hardwood in use aboveground is particularly prone to attack by white-rot fungi (9).

The present study was carried out to evaluate the resistance of acetylated flakeboard against two kinds of fungi, brown-rot fungus *Gloeophyllum trabeum* and a white-rot fungus *Pycnoporus sanguineus*.

Flakes of two planted wood species, *Pinus taeda* L., 18-year-old and *Eucalyptus grandis* Hill ex-Maiden, 11 -year-old were cut from logs.

Pine and eucalyptus flakes were acetylated with acetic anhydride without co-solvents or catalyst for 4 h at 120°C using a procedure described by Rowe11 (10).

The degree of acetylation can be reported as either weight percent gain (WPG) or actual analytically determined acetyl content. In this research the acetyl content was determined analytically using a gas chromatographic method after saponification of the bonded acetyl with sodium hydroxide followed by acidification, according to the procedure described by Moore and Johnson (11).

The average sizes of pine and eucalyptus flakes, obtained in a high speed disk-cut flaker, were respectively: 4 by 2 by 0.025 cm and 3.8 by 1.3 by 0.045 cm.

Acetylated and nonacetylated flakes were used to produce boards with 8 and 12% of commercial phenol-formaldehyde adhesives, based on the oven-dry weight of particles.

Control and acetylated mats were formed and pressed for 8 min at 190°C with pressure ranging from 50.2 to 77.2 kgf/cm^2. All panels were trimmed to a final size of 32.5 by 32.5 cm. The target specific gravity was 0.7.

These boards were tested according to ASTM D 2017-71 (12) for decay by the two representative wood-attacking fungi, brown-rot fungus *Gloeophyllum trabeum* (Pers. ex Fr.) Murr., and white-rot fungus *Pycnoporus sanguineus* (Pers. ex Fr.) Murr.

The treatments tested were: Wood species, level of acetylation, and resin level. The experimental design was an incomplete randomized design with a 2^3 factorial arrangement of treatments and five replications. The two different fungi were analyzed by separate analysis of variance.

The percentage of weight losses in the test blocks provided a measure of the relative decay susceptibility or, inversely,

of decay resistance of the sampled material. The blocks were classified after testing using the ranges described in Table 1.

Acetylation substantially reduced the water absorption of all pine and eucalyptus flakeboards. Thickness swelling of acetylated pine flakeboard was reduced 94% on the average compared to control boards. Thickness swelling of acetylated eucalyptus flakeboard was 77% less than that of the control boards. Another property that was extremely enhanced by the acetylation process was moisture absorption at 30,65 and 95% relative humidity (1).

The acetyl content was 1.3% and 20.2% for control and acetylated pine particles, respectively. For eucalyptus it was 2.6% and 18.7% for control and acetylated particles, respectively. Therefore, the acetyl gain of the particles was 18.9 and 16.1% for pine and eucalyptus, respectively.

Acetylated and control flakeboards were exposed to two kinds of fungi. The results, in weight loss, are presented in Table 2. Control and acetylated flakeboard samples unexposed to any fungus species, did not change weight, all acetylated samples exposed to fungi showing the same behavior to fungal decay.

According to ASTM Standard D 2017-71, control pine flakeboard at 8% resin level (Table 2) showed "moderated" decay resistance against *Gloeophyllum trabeum*. This flakeboard should perform well on use with commonly encountered fungi even considering loss of 27.7% in the accelerated laboratory test. The indicated class for all other control flakeboard-fungus combinations were "resistant" to decay with these specified fungi. The boards with lower resin content were more attacked. Fungal mycelia fully covered the surfaces of all control-fungi combinations within 2 weeks of the test.

Table 2 shows that both pine and eucalyptus boards made from acetylated flakes were "highly resistant" to attack by both *Gloeophyllum trabeum* and *Pycnoporus sanguineus.* The extent of mycelium development in acetylated flakeboards showed no colonization on the surfaces, and there was no weight loss. Acetylated blocks showed no visual evidence of decay, such as softening or delamination. When the mycelium was removed from the test blocks, some replicates were slightly contaminated with green mold. In another project (13), these green molds were identified as *Aspergillus* sp. and mainly the soft-rot fungus *Trichoderma viride.*

With the exception of the interaction acetylation x resin (pine, *Pycnoporus sanguineus)* the statistical analysis indicated significant differences in all other treatment combinations for both fungus species. Therefore, on changing the resin level from 8 to 12%, the attack resistance was significantly improved. The same is valid for acetylation.

Comparing the two fungi for pine, there were three different groups, according to the REGWF-F test. *Gloeophyllum trabeum* and *Pycnoporus sanguineus* had a different behavior. Each fungus had its preference. The former attacked more pine flakeboards while *Pycnoporus sanguineus* attacked more eucalyptus. This confirms that the brown-rot fungus attacks more softwoods than the white-rot fungus.

Chemical modification of wood through acetylation inhibits fungal growth and attack.

Flakeboards made from acetylated pine and eucalyptus flakes using commercial phenol-formaldehyde resin are "highly resistant" to attack by brown- and white-rot fungi in pure culture tests designed to simulate aboveground exposure.

Fungal growth was inhibited in part due to the toxic phenolic component. Acetylation added to phenol-formaldehyde bonding were the main factors of high resistance against the activities of fungi due to high pH and abundance of noncondensed phenols.

The high mean chemical loading of 18.9 and 16.1% for pine and eucalyptus respectively may indicate that the modified cell-wall, which is unable to absorb sufficient water, plays an important role in decay efficacy. The mechanism of effectiveness is probably the result of substrate modification and enzyme blocking rather than toxicity.

It can also be concluded that the acetylation treatment is inversely correlated with the degree of decay. Statistically, the resin level makes a difference regarding control flakeboards, but not regarding the acetylated ones, because of the great efficacy of the acetylation process only.

The two fungi showed different ways of attack and each had its preference. Brown-rot fungi attacked more pine flakeboard while white-rot fungi attacked more eucalyptus flakeboard.

Future improvements in this research should include the evaluation of the impact test and/or bending creep test regarding decay resistance. ■

Table 1 - Decay resistance expressed as either weight loss or residual weight according to ASTM D 2017-71.

Average weight loss (%)	*Average residual weight (%)*	*Indicated class resistance to a specific test fungus*
0 to 10	90 to 100	highly resistant
11 to 24	76 to 89	resistant
25 to 44	56 to 75	moderately resistant
45 or above	55 or less	slightly resistant or nonresistant

Table 2 - Average weight loss in a 12-week accelerated decay test of pine and eucalyptus flakeboards made from control and acetylated flakes, exposed to *Gloeophyllum trabeum* (Pers. ex Fr.) Murr. and *Pycnoporus sanguineus* (Pers. ex Fr.) Murr.

Type of flakeboard	*Resin level (%)*	*Weight loss*[a]	
		***Gloeophyllum trabeum* (%)**	***Pycnoporus sanguineus* (%)**
Control pine	8	27.7 (7.8)[b]	13.5 (4.0)
Acetylated	8	0	0
Control pine	12	20.6 (5.2)	11.0 (2.9)
Acetylated pine	12	0	0
Control eucalyptus	8	10.9 (4.1)	14.8 (4.3)
Acetylated eucalyptus	8	0	0

[a] Average of 20 specimens.
[b] Standard deviation, [%].
The data for eucalyptus with 12% resin level not included.

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