

# MOISTURE SORPTION AND ACCELERATED WEATHERING OF ACETYLATED AND METHACRYLATED ASPEN

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## ABSTRACT

Wood cell-wall modification with acetic anhydride, lumen fill with methyl methacrylate, and a combination of these two treatments were studied for their effectiveness in reducing the rate of moisture sorption and the degradative effects of accelerated weathering. Compared to that of untreated wood, the rate of moisture sorption of aspen acetylated to 18 weight-percent gain was greatly reduced as was the extent of swelling in liquid water; erosion due to accelerated weathering was reduced 50%. Methyl methacrylate treatment slightly decreased the rate of swelling in liquid water but did not reduce the extent of swelling. This lumen-fill treatment decreased erosion caused by accelerated weathering about 40%, compared to the erosion of untreated wood. A combined treatment of acetylation followed by methacrylate impregnation was the most effective in reducing the rate and extent of swelling and reducing erosion caused by accelerated weathering (85%). Chemical analysis before and after accelerated weathering showed that ultraviolet degradation caused a large loss of surface lignin and xylose (from xylans) in control specimens. Both acetylation and methacrylate treatments, or a combination of the two, reduced the loss of surface lignin with subsequent reduction in weathering. Acetylation, especially at 18 weight-percent gain, reduced the loss of xylans during accelerated weathering.

**Keywords:** Acetylation, methyl methacrylate, moisture sorption, accelerated weathering, aspen, ultraviolet degradation.

## INTRODUCTION

Wood used above ground in outdoor exposures undergoes degradation caused by ultraviolet light (UV) radiation and water (Feist and Hon 1984). The UV radiation causes photochemical degradation mainly in the lignin polymer in the cell wall. Lignin acts as an adhesive in wood to hold cellulose fibers together, and

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as the lignin is degraded and washed away by water, the wood surface becomes richer in cellulose.

Water, in combination with UV radiation, plays a major role in weathering and the surface degradation of wood. As the lignin is degraded, water leaches out degradation products and washes away loosened surface cellulose fibers, causing the rough surface usually referred to as "weathered wood." Water also causes the wood to swell, and upon drying, checks and cracks develop that expose new material to UV degradation.

Acetylation of wood greatly reduces swelling caused by moisture sorption, both for solid wood and wood composites (Rowell et al. 1986). Because the acetylation reaction takes place with hydroxyl groups in the cell-wall polymer component, we hypothesized that the reaction may help stabilize the lignin against UV degradation. However, earlier research on epoxide- and isocyanate-reacted wood (cell-wall modification) did not improve UV resistance in accelerated weathering (Rowell et al. 1981).

Filling the wood lumen with methyl methacrylate (MMA) polymerized *in situ* has been shown to increase resistance to UV radiation in accelerated weathering of southern pine (Feist and Rowell 1982; Rowell et al. 1981). This improved weathering resistance presumably resulted from the action of the MMA polymer as a water repellent to retard the rate of moisture sorption and to act as an adhesive in holding the surface wood matrix together.

The purpose of the research reported here was to determine the effect of cell-wall chemical modification of aspen wood using acetic anhydride, lumen-fill treatment with methyl methacrylate, and the combination of these two treatments in reducing the rate and extent of moisture sorption, and in reducing the photochemical degradation caused by UV radiation and water during weathering.

## EXPERIMENTAL

### *Wood specimens*

Aspen (*Populus* sp.) heartwood specimens, 1.5 by 15 by 190 mm (radial by tangential by longitudinal), were prepared from five boards. The specimens were randomized for use in different portions of the study and oven-dried for 20 h at 105 C.

### *Chemical modification*

Oven-dried specimens (10 each) were reacted with acetic anhydride at 120 C in a glass chamber using a technique described earlier (Rowell et al. 1986). One set was reacted for 30 min to obtain a 12 weight-percent gain (WPG) and a second set reacted for 2 h to obtain 18 WPG.

A second series of 10 specimens was treated at 25 C in a glass chamber with a solution of MMA monomer with 5% trimethylol propane trimethacrylate (cross-linking agent) and 0.25% azobis isobutyronitrile (catalyst) as described earlier (Rowell et al. 1982). After polymerization, a weight gain of 63% was obtained.

A third series of 10 specimens was first reacted with acetic anhydride followed by the MMA system. Specimens first acetylated to 12 WPG gave an MMA uptake of 74 WPG, and specimens acetylated to 18 WPG gave a MMA uptake of 90 WPG (Table 1).

TABLE 1. *Aspen specimens prepared for moisture sorption and accelerated weathering (average of 10 specimens).*

Specimen type	Acetyl weight gain (percent)	Methyl methacrylate weight gain (percent)
Control	0	0
Acetylated	12 $\pm$ 0.6	0
	18 $\pm$ 0.8	0
Methacrylated	0	63 $\pm$ 2.5
	12 $\pm$ 0.6	74 $\pm$ 3.0
	18 $\pm$ 0.8	90 $\pm$ 5.0

### *Moisture sorption*

Each specimen was placed in a container fitted with a micrometer for measuring dimensional changes. Radial, tangential, and longitudinal dimensions were determined oven-dry, water was introduced into the container, and dimensions were measured every 10 min for 1 h.

### *Accelerated weathering*

The radial faces of all test specimens were exposed to a 6,500-w xenon arc light source (which closely approximates natural sunlight) in an enclosed chamber at 45 C to 50 C and 50% relative humidity (RH). Each 24-h cycle of weathering consisted of 24 h of light with 4 h of distilled water spray. Exposure time was expressed as hours of exposure to light. Weight loss and erosion were determined after 700 h of light exposure (Feist and Rowell 1982). Weight loss was determined by the difference in oven-dry weight before and after each weathering period (five replicates). The depth of weathering (erosion) was estimated from scanning electron photomicrographs.

### *Chemical analysis*

Three separate specimens were used for chemical analyses for each modification. The first was the untreated, unexposed wood. The second was the outer surface layer of approximately 0.5 mm of wood (removed by scraping with a razor) exposed in the accelerated weathering chamber (referred to as "surface specimen"). The scrapings from four replicates were combined for a single analysis because of the small amount of material available. The third specimen was the remainder of the exposed specimen after removal of 0.5-mm exposed wood surface (referred to as "remainder specimen"). All specimens were ground to pass a 40-mesh screen and oven-dried for 16 h at 105 C before chemical analysis.

Acetyl content was determined before and after accelerated weathering on surface and remainder specimens by gas chromatography following deacetylation of ground and combined samples with sodium hydroxide (Rowell et al. 1986).

Lignin determinations were made by a method similar to Technical Association of the Pulp and Paper Industry Standard T13 (TAPPI 1954). Samples were treated with 72% sulfuric acid for 1 h at 30 C, followed by 3% sulfuric acid for 4 h at reflux temperature to hydrolyze and solubilize the wood carbohydrate. The insoluble residue was measured gravimetrically as lignin. The hydrolyzate from the lignin determination was used for the reducing sugar analyses (Pettersen et al.

1984). All values shown are uncorrected for wood extractives, chemical add-on from modification, and small amount of degradation during hydrolysis.

## RESULTS AND DISCUSSION

Aspen wood was chosen for these studies because of our interest in using a species like this in determining the effects of chemical modification on wood composite properties (Rowell et al. 1986). Our earlier work on weathering resistance of modified woods involved softwoods, and no information was available on the performance of modified hardwoods (Feist and Rowell 1982; Rowell et al. 1981).

### *Chemical modification*

Aspen wood specimens were either acetylated, impregnated with MMA monomer and then polymerized *in situ*, or acetylated and treated with MMA (combined treatment). Treating aspen wood with MMA yielded 63 WPG (Table 1). Specimens that were first acetylated to 12 WPG had a higher level of MMA (74 WPG), and specimens acetylated to 18 WPG a level of 90 WPG MMA. This shows that acetylation did not reduce treatability, and in fact, facilitated it. Swelling of the wood cell wall caused by acetylation and increased MMA loading with increase in acetylation weight gain suggest that the lumen may be slightly larger after acetylation compared to that of unacetylated wood.

### *Moisture sorption*

The rate and extent of liquid water swelling were investigated (Fig. 1). Untreated aspen swelled about 16% in volume after only 10 min of immersion and about 20% after 1 h. With the small specimens used, very little additional swelling occurred after 1 h. The rate of swelling of the specimen impregnated with MMA was decreased but not to the same extent as that found for acetylated wood. Acetylation to 12 WPG greatly reduced both the rate and extent of swelling, and acetylation to 18 WPG further reduced rate and extent of swelling. Acetylation to 18 WPG followed by impregnation and polymerization of MMA resulted in the lowest rate and extent of swelling.

The MMA-impregnated specimens reached the same extent of swelling as control specimens after only 1 h in liquid water (Fig. 1). Thus, the effect of MMA on reducing UV degradation is probably not caused by any water repellency from the treatment. The MMA polymer seems to be acting as additional cell matrix adhesive that holds degraded wood fibers together; the fibers would be released if lignin alone were the adhesive. In addition, the MMA may change the path of energy flow to minimize detrimental energy for wood degradation (at the expense of MMA degradation).

### *Accelerated weathering*

Table 2 shows weight loss, statistical data, erosion rate, and depth of weathering penetration after 700 h of accelerated weathering. Control specimens eroded at about 0.12  $\mu\text{m}/\text{h}$  or about 0.02%/h. The effects of weathering have been shown to penetrate about 200  $\mu\text{m}$  into the wood surface (Feist and Hon 1984). Acetylation to 18 WPG reduced erosion by 50%. Impregnation with MMA alone reduced erosion by 40%, whereas acetylation to 12 or 18 WPG followed by MMA im-

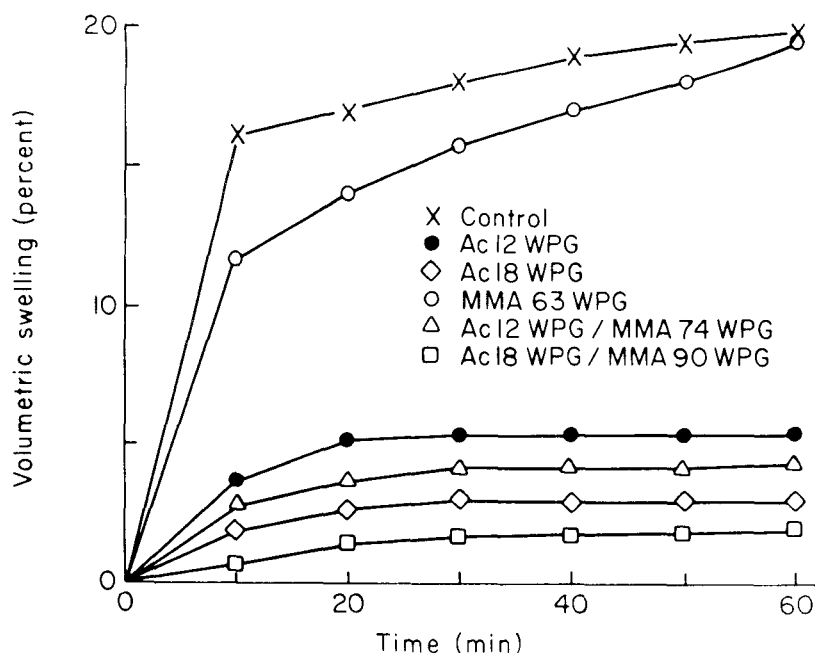


FIG. 1. Rate of volumetric swelling of modified aspen wood in liquid water (average of five specimens). Ac, acetylation; MMA, methyl methacrylate; WPG, weight percent gain. (ML89 5754).

pregnation reduced erosion 74 and 85%, respectively; the result of the combined treatment was essentially the sum of the two separate treatments. Almost no surface degradation could be seen or measured with the combined treatment.

Weight loss was determined as a function of accelerated weathering time (Fig. 2). Statistical analysis of wood weight loss data indicated a linear relationship, and a least-squares fit gave the erosion rate or slope in percentage per hour. Acetylation at 12 WPG and MMA treatment at 63 WPG reduced erosion to nearly the same extent compared to that of the untreated control. A further reduction in weight loss occurred with acetylation at 18 WPG. The lowest weight losses were observed for combined treatment specimens. Weight loss is a more sensitive measure of degradation by weathering than erosion, which is the generally used method.

#### Chemical analysis

Table 3 shows the acetyl content of the outer 0.5-mm wood surface before and after accelerated weathering (surface specimen) and of the remaining specimen after the surface had been removed (remainder specimen). The acetyl content was decreased from 22 to 73% of that before weathering, with an average reduction of 48%. Thus, acetylation was partially successful in controlling weathering. This is in contrast to earlier findings on wood chemically modified with butylene oxide, butyl isocyanate, or methyl isocyanate (Rowell et al. 1982), where the modified southern pine wood weathered the same or slightly faster than the untreated wood. Several workers have shown that acetylated or methylated lignocellulosic materials were deacetylated or demethylated when exposed to UV radiation (Callow and

TABLE 2. Weight loss and erosion of modified aspen after 700 hours of weathering.

Specimen	Weight loss (%/h)	Analysis of weight loss data			Erosion <sup>a</sup> (μm/h)	Reduction in erosion <sup>b</sup> (%)	Depth of penetration of weathering <sup>c</sup> (μm)
		Y Intercept	R <sup>2</sup> (%)	Standard deviation (±%)			
Control	0.019	0.02	99.7	0.23	0.121	—	190–210
Ac 12 WPG	0.013	−1.16	99.5	0.19	0.081	33	170–190
Ac 18 WPG	0.010	−1.17	98.8	0.22	0.059	51	85–105
MMA 63 WPG	0.012	0.55	99.6	0.15	0.072	40	150–170
Ac 12 WPG/MMA 74 WPG	0.005	−0.65	99.4	0.08	0.031	74	50–65
Ac 18 WPG/MMA 90 WPG	0.003	−0.55	98.0	0.09	0.018	85	<10

AC, acetylation; MMA, methyl methacrylate; WPG, weight percent gain.

<sup>a</sup> Average of five specimens. Calculated from weight loss data.<sup>b</sup> Compared to control.<sup>c</sup> Measured in cross section from scanning electron micrographs.

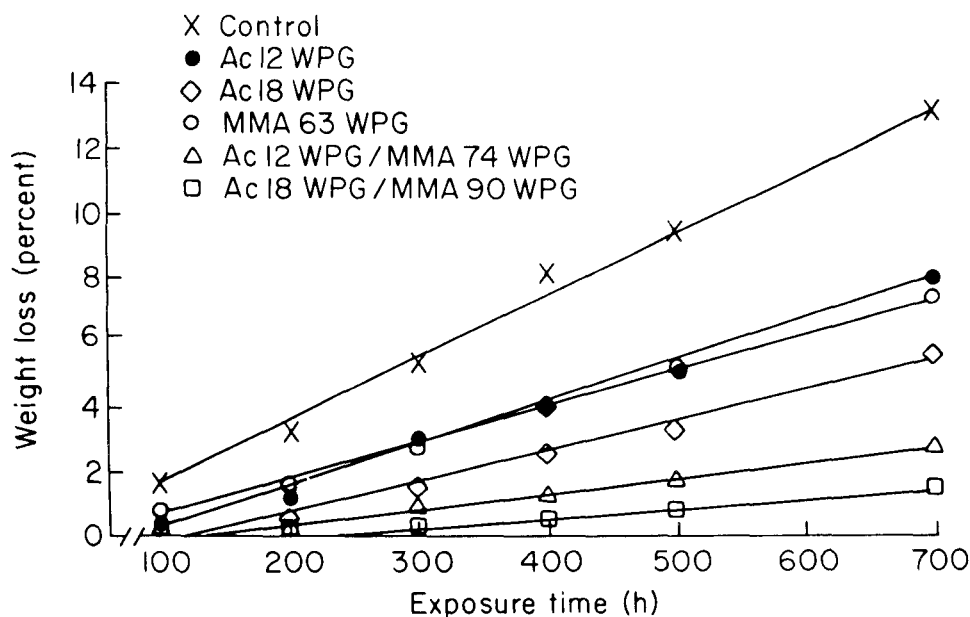


FIG. 2. Weight loss of modified aspen wood in accelerated weathering (average of five specimens). Ac, acetylation; MMA, methyl methacrylate; WPG, weight percent gain. (ML89 5753).

Speakman 1949; Forman 1940; Leary 1968). Removal of the acetyl group on the lignin hydroxyls could allow the photochemical degradation reactions to take place.

The UV radiation did not remove all the blocking acetyl groups (Table 3). Some stabilizing effect to photochemical degradation remained as well as decreased swelling. The stabilizing effect may be a result of acetylation of the hydroxyls on the hemicellulose xylans. The loss of acetyl was confined to the outer 0.5-mm wood surface; the remaining wood had the same acetyl content before and after accelerated weathering.

After accelerated weathering and photochemical degradation, the surface of untreated wood (control) was higher in glucose (cellulose), lower in xylose (xylans) and mannose (glucomannans), and lower in lignin content (Table 4). Wood just below this surface (remainder specimen) was essentially unchanged in chemical

TABLE 3. Acetyl analysis before and after 700 hours of accelerated weathering of modified aspen.<sup>a</sup>

Specimens	Before weathering (percent)		After weathering (percent)	
	Surface <sup>b</sup>	Remainder <sup>c</sup>	Surface	Remainder
Control	4.5	4.5	1.9	3.9
Ac 12 WPG	13.0	14.0	8.1	14.6
Ac 18 WPG	17.5	18.5	12.8	18.3
MMA 63 WPG	2.8	2.8	0.5	2.6
Ac 12 WPG/MMA 74 WPG	9.0	9.0	3.6	8.3
Ac 18 WPG/MMA 90 WPG	10.0	10.0	5.1	10.2

Ac, acetylation; MMA, methyl methacrylate; WPG, weight percent gain.

<sup>a</sup> Material from four specimens combined for single analysis.

<sup>b</sup> Outer 0.5-mm wood surface of exposed specimen.

<sup>c</sup> Remainder of exposed specimen after removal of 0.5-mm exposed wood surface.

TABLE 4. Chemical analysis of modified aspen after 700 hours of accelerated weathering.<sup>a</sup>

Specimen	Klason lignin (percent)	Soluble lignin (percent)	Sugar (percent)		
			Glucose	Xylose	Mannose
Control					
(Before weathering)					
Surface	19.8	2.9	50.9	24.5	3.3
Remainder	20.5	2.7	49.8	23.3	4.2
(After weathering)					
Surface	1.9	1.6	82.2	10.1	1.6
Remainder	17.9	1.6	52.8	22.9	4.0
Ac 12 WPG					
Surface	5.5	3.6	73.5	15.0	1.0
Remainder	17.7	3.6	52.3	22.8	3.6
Ac 18 WPG					
Surface	5.5	3.8	66.6	20.2	1.9
Remainder	18.1	3.8	49.4	21.1	2.7
MMA 63 WPG					
Surface	109.0 <sup>b</sup>	0.8	46.8	4.7	0.7
Remainder	68.5 <sup>b</sup>	0.8	58.7	25.3	5.2
Ac 12 WPG/MMA 74 WPG					
Surface	125.9 <sup>b</sup>	2.7	42.3	6.0	1.2
Remainder	93.0 <sup>b</sup>	2.7	50.5	21.6	2.5
Ac 18 WPG/MMA 90 WPG					
Surface	138.8 <sup>b</sup>	3.6	46.9	15.5	2.7
Remainder	118.8 <sup>b</sup>	3.6	50.0	21.3	2.9

Ac, acetylation; MMA, methyl methacrylate; WPG, weight percent gain.

<sup>a</sup> Material from four specimens combined for single analysis. Values calculated on the basis of 100-g oven-dried, untreated wood.

<sup>b</sup> Spurious values for lignin created because of insolubility of MMA polymer in sulfuric acid used to determine lignin.

content. This shows the preferential degradation of lignin and hemicellulose (xylans and mannans), leaving behind the more UV-light-resistant cellulose (glucose). Thus, the hemicellulose component of aspen wood is not totally resistant to photochemical degradation. All previous work on wood weathering had suggested that the hemicellulose component of all woods is resistant to weathering (Feist and Hon 1984; Kalnins 1966). Earlier work on the accelerated weathering of southern pine (Feist and Rowell 1982) indicated only a small and inconsistent change in the hemicellulose content on the exposed wood surface.

The acetylated wood had chemical changes in lignin and cellulose similar to that of untreated wood but less change in the reduction of xylans or mannans. This suggests that the observed reduction in weathering (reduced erosion and weight loss) of acetylated wood may be a result of acetylation of both lignin and hemicelluloses. The free radical process (Feist and Hon 1984) may be disrupted during weathering when these components are acetylated and the weathering process is then retarded.

Aspen specimens impregnated with MMA showed a very high level of klason lignin whether acetylated or not. This is because the highly cross-linked MMA was not dissolved in the 72% sulfuric acid. Analysis of the chemical data from



these treated samples is more difficult, but even here, we observed a reduction in xylan content on the wood surface, suggesting the important role of the hemicelluloses in the weathering of the treated wood. When the wood was both acetylated and MMA impregnated, xylan losses were less when compared on a percentage basis to the material remaining under the weathered wood surface (Table 4).

#### CONCLUSIONS

The results of this study show that acetylation of aspen wood helps protect wood from photochemical degradation during accelerated weathering. Impregnation with methyl methacrylate monomer followed by polymerization also reduces the effects of weathering. The combination of acetylation and impregnation with methyl methacrylate greatly reduces the degradation caused by UV radiation and water. Improvements in weathering after this combined treatment were the sum of the single treatments. Acetylation protects the lignin component in wood to a small extent and the hemicellulose component (xylan) to a larger extent.

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