Note

Morphological Changes in Acetylated Wood Exposed to Weathering*[1]

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Abstract——Resistance of acetylated wood to degradation caused by natural weathering was investigated at different levels of acetylation. The color difference caused by sunshine exposure was minimized at an acetylation level of 20% weight gain (WG) with a rapid decline from 10% WG, even though the exposure time was prolonged. Weathering led to early disintegration and enlargement of bordered pits, extensive separation of the latewood tracheid walls in the middle lamella and checkings oriented along the microfibril angle of the S_2 layer. These characteristic patterns of cell-wall erosion due to weathering were essentially the same in both untreated and acetylated wood. However, scanning electron microscope observations revealed that more extensive microscopic and macroscopic checks leading to distortion of the cell alignment appeared in untreated wood and wood which had been treated with a low-level of acetylation. For highly acetylated wood, severe intra- and inter- cell wall erosion was limited, and the original cell alignment was retained. However, after long-term exposure to natural weathering, the surface cell-layers of acetylated wood were defibrated separately and were attached to the unexposed cellular structure beneath them. This may explain the observation that acetylated wood has more severe surface-contamination than untreated wood, in which the new cell-layers appear successively because of the severe erosion of the exposed surfaces.

Keywords: Acetylated wood, weathering, ΔE^*, photo degradation, micro check, delamination, SEM.

1. Introduction

As with other chemical modifications, acetylation involves the reaction of accessible hydroxyl groups, which are the most abundant reactants in wood. Several previous reports have examined the enhancement of biological resistance and physical properties by acetylation, such as dimension stability or mechanical strength while wet[1)].

Wood which has been exposed outdoors undergoes photochemical degradation primarily in its lignin component. Chemical modifications reportedly stabilize lignin against photolytic degradation, and may prevent wood from turning yellow. One chemical modification, acetylation, can prevent the formation of phenoxy radicals, since the phenolic hydroxyls can be blocked by esterification[1,2)].

In this study, the weathering properties of acetylated wood were evaluated, with

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emphasis on the morphological changes under exposure to sunlight or sunlight with rain.

2. Materials and Methods

Rotary veneers of spruce (*Picea jezoencis* Carr.; 3.5 mm-thick) or small blocks (2×2×1 cm length) of sugi (*Cryptomeria japonica* D. Don) sapwood were acetylated with acetic anhydride without cosolvent or catalyst.

The oven-dried specimens were first placed in a glass flask. A prevacuum was applied to the flask (15 mmHg, 30 min.), and acetic anhydride was then impregnated into the specimens under reduced pressure at 15 mmHg for 30 min. After the samples had soaked in acetic anhydride for 2 hours at atmospheric pressure, each specimen was transferred to a 500 ml round-bottomed flask containing acetic anhydride which had been heated to 120°C. The solution was kept at 120°C under reflux for between 5 minutes to 12 hours. The specimens were then rinsed in water for 24 hours. The acetylated specimens were oven-dried at 105°C for 24 hours. Acetyl content, calculated from the increase in the oven-dried weight ranged from 1.5 to 24.3 percent.

The central portions of 5×8 cm spruce rotary-veneers were marked and exposed to sunlight. The color change was measured using a color-difference meter. The color change was expressed as ΔE^*, as calculated from the values of $^*L$, $^*a$ and $^*b$ according to Hunter's diagramm.

For the scanning electron microscope (SEM) observations, transverse, radial and tangential sectional surfaces were prepared by cutting untreated and acetylated sample of sugi sapwood with a knife and microtoming the surfaces prior to exposure. The clear cut surfaces were exposed to either the sunlight only or natural outdoor weathering, at an incline 45°, facing equatorially for 1 to 12 weeks during winter. Prior to microscopic examination, the exposed specimens were rinsed and dehydrated through a graded series of ethanol, acetone and pentane. To evaluate the effect of long-term exposure on acetylated wood, sugi wood block which had been treated at 18% WG was exposed to natural weathering for one year and observed without rinsing in ethanol. These samples were mounted on specimen stubs, and then coated with gold for examination using a Hitachi S-500 scanning electron microscope.

3. Results and Discussion

3.1 Color stability and morphological changes due to exposure to sunlight

Figure 1 shows the changes in the surface color of acetylated wood, which is expressed as the color difference ΔE^* calculated from Hunter's diagram. For acetylated wood, the value of ΔE^* decreased rapidly as acetylation levels increased, and was almost zero at 24% WG. Even after exposure to sunlight for more than one year, acetylated wood of above 20% WG retained nearly its original surface color.

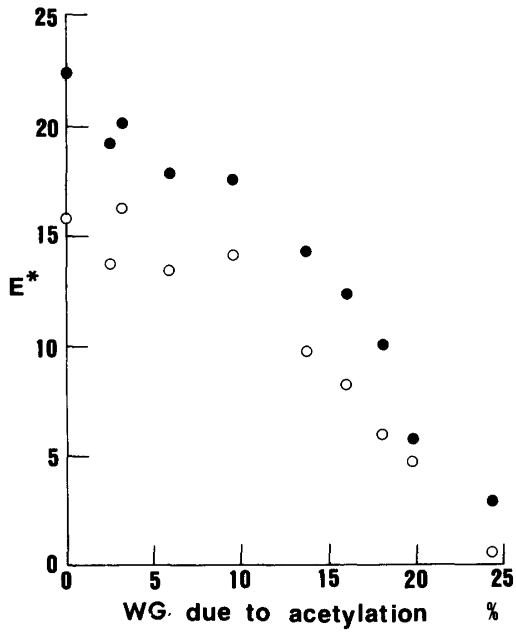

Fig. 1. Color difference (ΔE^*) of acetylated spruce wood with different levels of weight gain (WG) due to exposure to sunlight for 2 (○) and 12 (●) weeks.

For both untreated and acetylated wood, the most detectable change in the anatomical structure of the radial section appeared to take place around the pit regions of the cell walls, as described by earlier researchers[3–5]. The margo fibrils of the pit membrane are never protected by lignin, so they should be easily broken. Another typical sign of degradation was the enlargement of the apertures of bordered pits in the earlywood tracheids. The SEM observations showed that the apertures of bordered pits were enlarged to the limit of the pit chambers, and diagonal checks through the pits, which probably followed the fibril angle of the S_2 layer, were also present (Fig. 2). The area where the S_2 microfibrils should sweep above and below the pit opening was considered to be easily degraded by photo-chemical reaction, since fewer microfibrils and their uneven orientation.

The appearance of diagonal microchecks during weathering in both treated and untreated wood may be the result of local concentrations of tensile stresses at right angles to the fibril direction of the S_2 layer. As reported by other researchers[3–6], degradation of the wall substances during sunlight irradiation contracts the cell walls, resulting in microchecks along the compound middle lamella and, particularly in latewood, along the border between S_1 and S_2.

The most characteristic pattern of structural change during weathering was rapid erosion of the middle lamella, in which lignin reaches its maximum concentration. This early degradation might be due to the preferential breakdown of lignin by photo-oxidative radicals. The degradation products would then be leached away from the surface cell layers, leaving voids between adjacent tracheids.

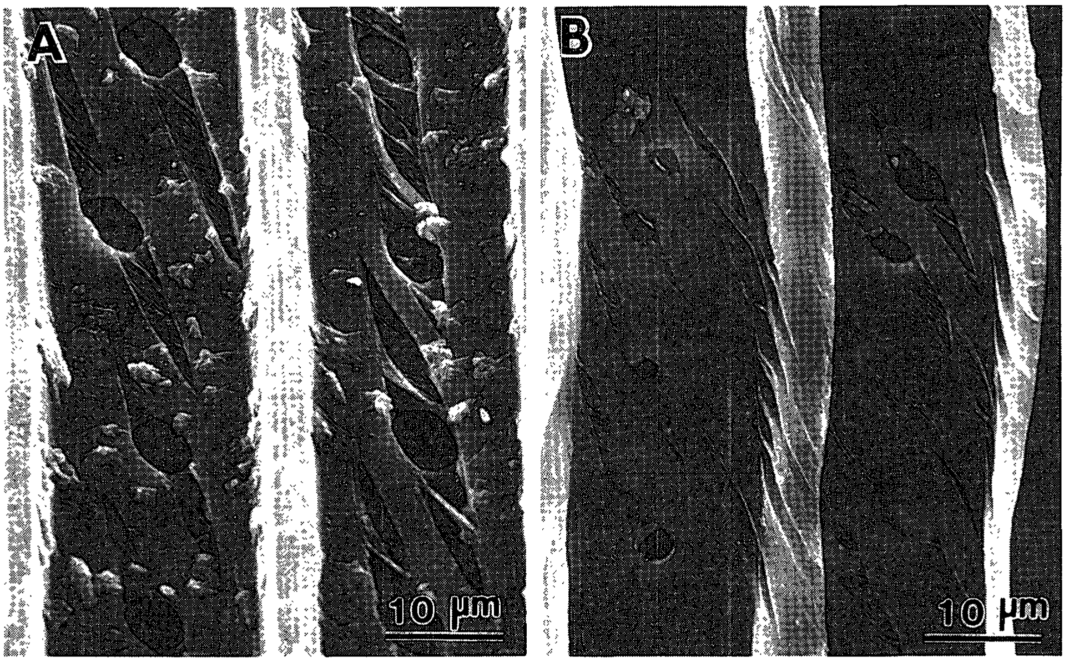

Fig. 2. Radial section of untreated sugi wood (A) and acetylated wood with 18% WG (B), showing diagonal checks through pits following the fibril angle of the S_2 layer, after exposure to sunlight irradiation for 4 weeks. More highly developed diagonal fissures were observed in untreated wood.

However, based on the SEM observations, morphological changes which would explain the photo-stability of acetylated wood were not detected.

3.2 Exposure to sunlight and rain

Although the fundamental features caused by exposure to sunlight were essentially the same in both acetylated and untreated wood, chemical modification might play an important role in controlling the natural weathering process.

Distinctly different morphological changes were recognized when cross-sections of the cell walls were exposed to natural weathering which included sunshine and rain. Wind-blown particles caused more severe damage to untreated controls when combined with the leaching effects of rain. Disintegration or fracture of the cell walls was observed sooner in untreated wood than in acetylated wood (Fig. 3). After exposure to natural weathering, a cross-section of the cell walls in untreated wood shows a roughly-eroded and rounded appearance as reported before[6]. Cellulose microfibrils may become so friable that they degrade after the decomposition of embedded lignin substances.

Figure 4 shows a comparison of untreated and acetylated wood after exposure to sunlight and rain. In both samples, the middle lamella were eroded and leached away. However, the cross-section of the cell walls appeared rounded only in untreated wood. Intra- and inter-chemical bonding was more stable in acetylated wood, as suggested by the fact that the cell walls in the treated wood remained intact for a longer period of exposure.

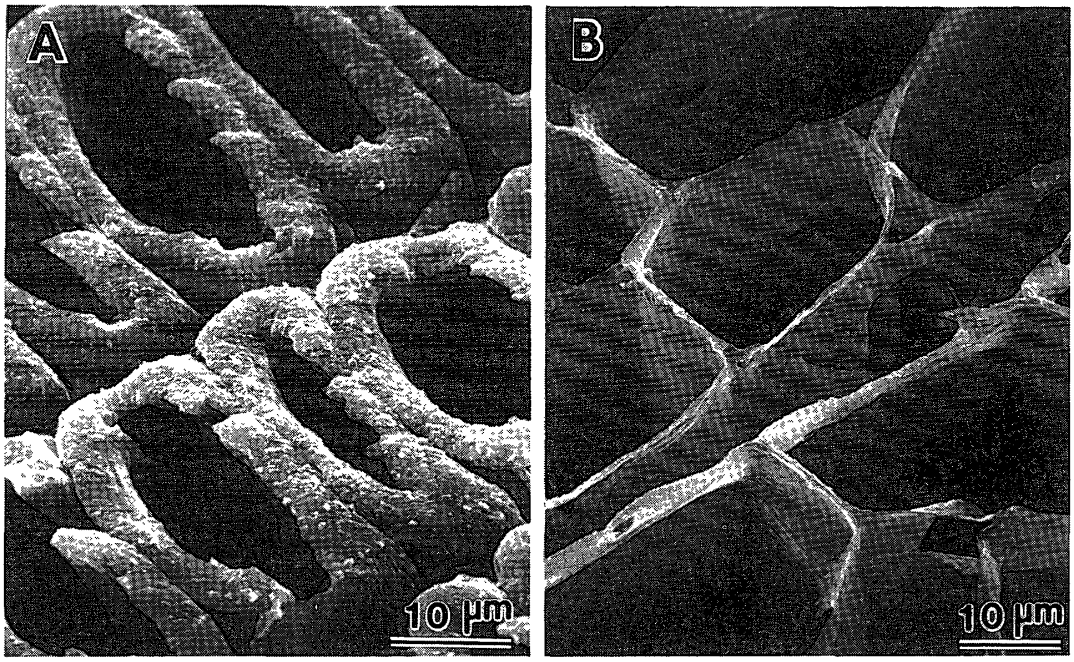

Fig. 3. Transverse latewood (A) and earlywood tracheids (B) of untreated specimens after exposure to natural weathering for 4 weeks, showing rounded appearance and cell-wall lysis.

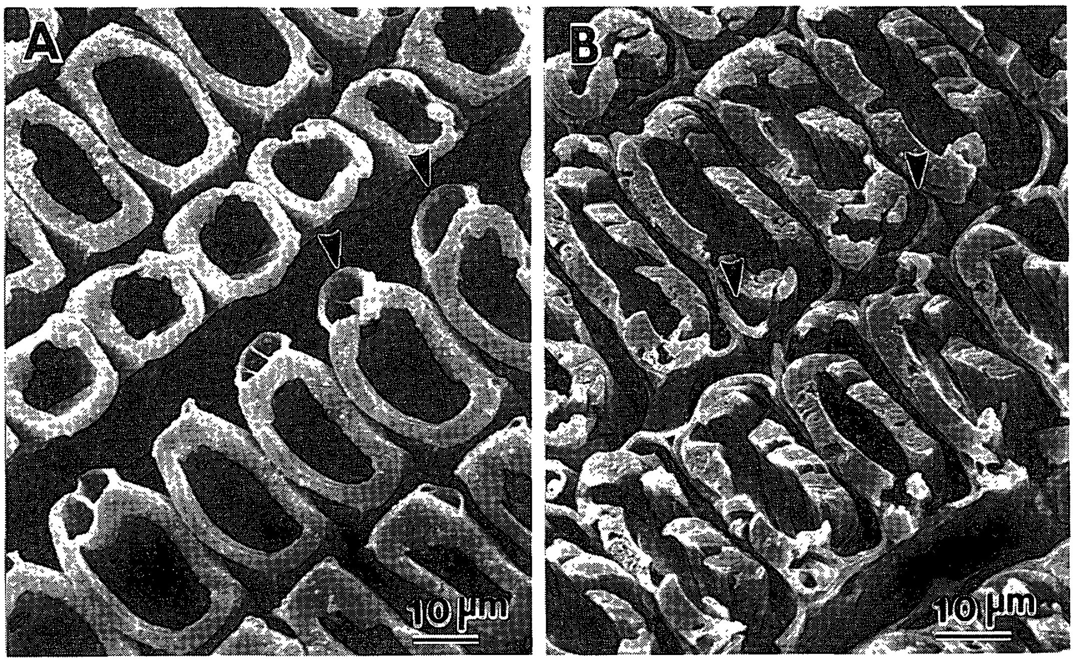

Fig. 4. Cross-sectional view of sugi latewood tracheid walls of untreated wood (A) and acetylated wood with 18% WG (B) after exposure to natural weathering for 8 weeks. Note the deep erosion of the middle lamella region and the rounded appearance of tracheids in untreated wood, and delamination of the cell wall structure at the S_1 and S_2 boundary in both specimens (arrows).

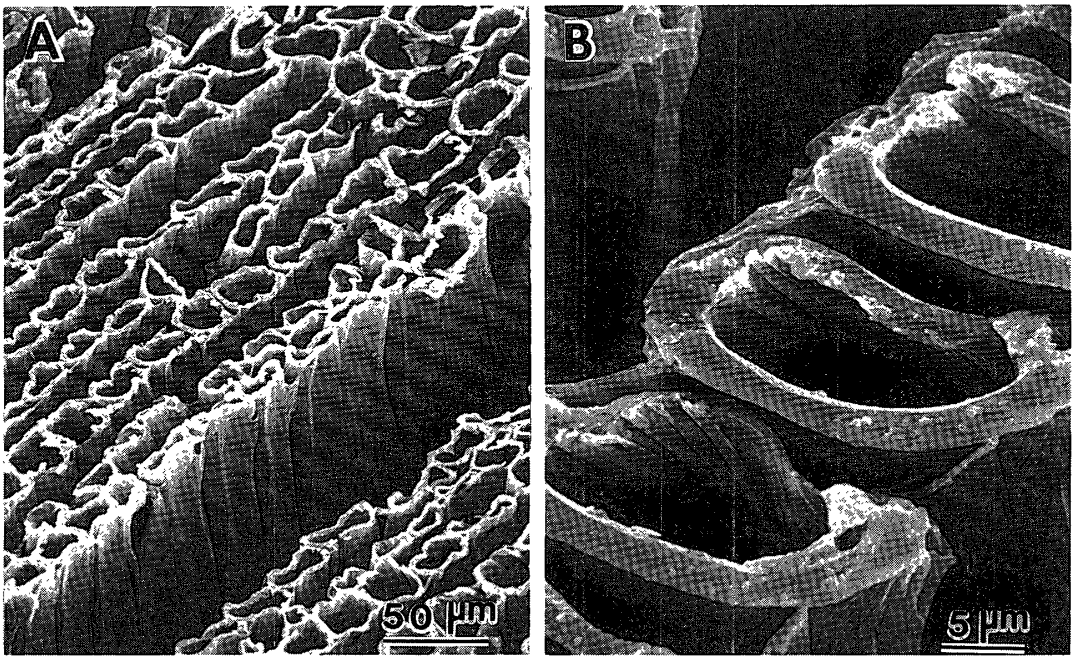

Fig. 5. Cross-section of acetylated sugi wood (10% WG) showing separation of rows of tracheids along radial checks, after exposure to natural weathering for 12 weeks (A). Enlarged view of typical latewood tracheids is shown in photograph B.

At 10% WG in acetylated wood, the cross-section of the cell walls appeared only slightly rounded. However, cell alignment was still disordered in the radial file, as was often observed in untreated wood (Fig. 5). During natural weathering, the leaching effects and the swelling-shrinkage stresses due to water-uptake apparently facilitate enlargement of microchecks in the cell alignment. These checks include the formation of longitudinal checks between adjacent walls of neighbouring elements that apparently occur in, or close to, the middle lamella. These checks, which occurred in untreated wood after just a short time, generally enlarged as the exposure time progressed, and became macro checks which could be easily detected even with the naked eye.

The photographs in Fig. 6 show the surface appearance of untreated wood and acetylated wood at 18% WG. In untreated wood, checks developed across the cell walls, which showed a high degree of degradation in the earlywood tracheids. The cell walls were collapsed, thus leading to total degradation originating at the top surfaces of the specimens. However, in acetylated wood, degradation of the cell walls was limited, and the original alignment was maintained for a long period after exposure to natural weathering.

3.3 Long term exposure to natural weathering

After exposure to natural weathering, acetylated wood generally had a darker surface than untreated wood, even though it maintained its original surface color when exposed to sunlight only.

In untreated wood, the exposed surfaces were degraded and new layers of wood were progressively exposed at the top surface of the sample. For acetylated wood, in which intra-

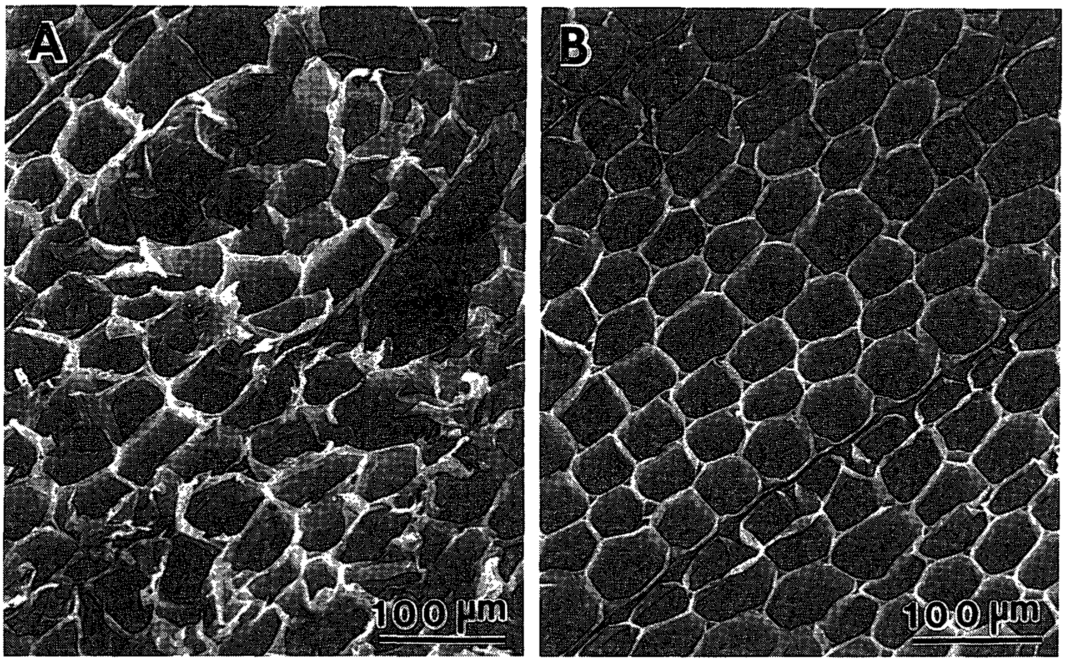

Fig. 6. Severe disindegration of earlywood tracheids in untreated sugi wood (A), and maintenance of original cell-alignment and less eroded cell-walls structure in acetylated wood with 18% WG (B), after exposure to natural weathering for 8 weeks.

and inter-cellular contraction might be limited, the exposed tracheids were macerated separately, without a severe degradation in cell wall structure, and remained for a longer period by being

Fig. 7. Surfaces of untreated (A) and acetylated wood (B) after one year of weathering tests under outdoor conditions.

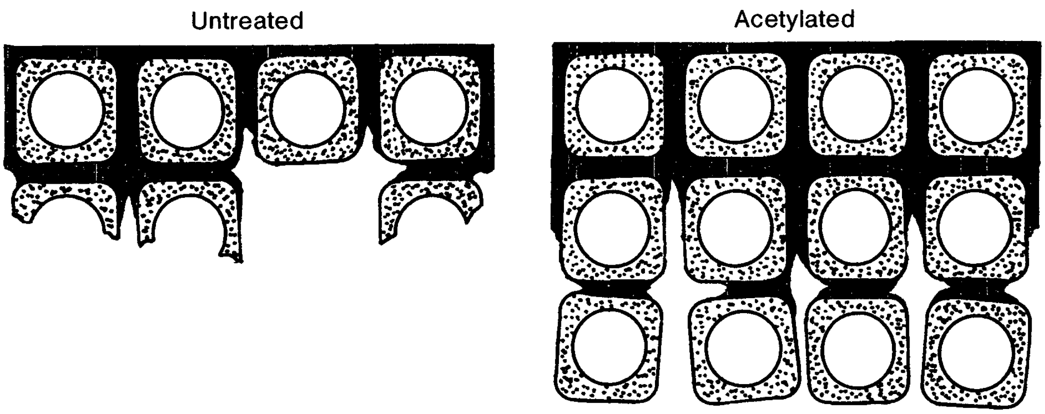

Fig. 8. Diagrammatic cross-sectional view of cell-wall lysis of untreated wood and macerated cell structure for acetylated wood caused by natural weathering.

attached to the sound elements beneath them (Fig. 7).

Airborne particulates, such as dust, chemical pollution, small sand and microscopic spore may have been caught or sandwiched between roughly aligned tracheids which were macerated to form most of the void structure (Fig. 8). This would explain why acetylated wood obtained a grey to dark-grey appearance, when compared to the lighter colored surfaces of untreated controls, after long-term exposure to natural weathering.

4. Conclusions

The erosion rate of earlywood and latewood, and wood substance loss during weathering are significantly reduced in wood which has been chemically modified by acetylation. Blocking accessible hydroxyl groups of lignin and holocellulose by using acetyl units reduces water uptake and retards subsequent leaching of wood degradation products. Acetylated wood may suffer minor internal stresses caused by swelling and shrinkage due to moisture gradients between the surface and the interior.

The weathering properties of acetylated wood may also be affected by the method of treatment. Nevertheless, acetylated wood behaved differently than untreated controls when exposed to sunlight or sunlight and rain.

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