

Weathering Characteristics of Modified Rubberwood (*Hevea brasiliensis*)

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ABSTRACT: Surfaces of rubberwood treated with dilute aqueous solutions of chromium trioxide, chromic nitrate, ferric chloride, and ferric nitrate and modified with acetic anhydride were weathered outdoors for periods from 1 day to 1 year. Fourier transform infrared (FTIR) spectroscopy, fluorescence spectroscopy, light microscopy (LM), and scanning electron microscopy (SEM) were used to analyze chemical and microscopic changes in treated and untreated weathered wood surfaces. Severe delignification and hemicellulose degradation occurred in untreated samples, evident from rapid decreases in IR band intensities at 1505 and 1740 cm^{-1} , respectively. Surface delignification occurred after 1 day's exposure, with severe lignin loss within 2–3 days and almost complete surface delignification after 1 week of exposure. Fluorescence spectra of weathered wood surfaces showed a rapid decrease in intensity and a large red shift in emission maxima. Scanning electron microscopy of untreated wood surfaces exposed for 125 and 360 days showed them to have ridges in the S3 cell-wall layer adjacent to the lumen, together with wall checking and pit degradation. Fungal spores and hyphae were observed in wood cell lumens. Pretreatment of wood surfaces with chromium trioxide (chromium VI compound) significantly restricted weathering deterioration and microbial colonization, whereas ferric chloride was most effective in preventing microbial colonization. Acetylation also partially prevented delignification and fungal staining. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 622–631, 2002

Key words: *Hevea brasiliensis*; weathering; FTIR; fluorescence spectroscopy; delignification; surface degradation; fungal staining; scanning electron microscopy

INTRODUCTION

Wood is a complex heterogeneous macromolecule consisting of naturally occurring polymers (cellulose, hemicelluloses, and lignin) and extractives. However, although versatile, when used above ground outdoors, it is susceptible to degradation by a combination of chemical and mechanical fac-

tors termed weathering,^{1,2} and colonization by microorganisms termed biodeterioration.

Weathering of wood results in color change, surface roughening and cracking, and damage to the microstructure. Weathering is initiated by sunlight and influenced by moisture, temperature, and atmospheric gas composition. Blue-stain fungi may also colonize weathered wood and contribute to color change. Weathering of wood is a surface phenomenon, because light does not penetrate deeply ($<200 \mu\text{m}$).¹ A number of researchers have examined the effect of weathering

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on the physical and chemical structure of wood.¹⁻⁷ Chemical analysis of weathered wood surfaces showed lignin and hemicellulose degradation and cellulose depolymerization. Microscopic studies showed characteristic ridges on the S3 wall layer, wall checking, ray/pit degrade, and middle lamella breakdown.

Although weathering does not significantly reduce wood strength, it presents a problem for surface technologists, because it influences performance of exterior wood coatings.⁸ Finishes that absorb ultraviolet (UV) light prevent photodegradation of underlying wood, but are subject to failure themselves. Photodegradation of timber surfaces underlying UV transparent finishes may also lead to early failure of coatings, because although finishes are not degraded, they can no longer adhere to wood and peel. If wood under UV transparent coatings can be protected from photodegradation, then the service life of the coatings will be extended. The development of pretreatments that do this is an important area of research.^{5,8,9}

Certain inorganic chemicals applied as dilute aqueous solutions to wood surfaces offer the following benefits⁸: they enhance photostability, improve durability of transparent and opaque polymer coatings and stains, enhance fungal resistance of wood and wood coating surfaces, improve dimensional stability of wood, and help fix water-soluble extractives. Such pretreatments may prove particularly useful in countries such as India, where the level of solar radiation is high, justifying the current research.

In the present study, rubberwood samples were exposed to natural weathering for periods of up to 1 year. Fourier transform infrared (FTIR) spectroscopy was used to study the degradation of structural wood constituents (lignin, cellulose, and hemicellulose) at the wood surface following different periods of weathering. Changes in surface color and cell structure were examined using light microscopy (LM) and scanning electron microscopy (SEM), respectively. Preliminary results from fluorescence spectroscopy of unweathered and weathered rubberwood surfaces are also presented. Wood samples treated with aqueous solutions of chromium trioxide [chromium (VI) compound], chromic nitrate [chromium (III) compound], and iron (III) compounds (ferric chloride and ferric nitrate) and acetylated with acetic anhydride were also exposed to natural weathering to assess their effectiveness as protectants. Chromium trioxide was previously shown to stabilize

wood surfaces against weathering,^{5,8,9} whereas weathering resistance of wood treated with chromic nitrate has not been tested. There were contradictory reports about the efficacy of ferric salts as antiweathering agents. Chang et al.¹⁰ showed that the application of ferric chloride to wood surfaces reduced cell wall checking by UV radiation, whereas Evans et al.⁵ reported that ferric salts were ineffective at reducing weight loss and surface deterioration in wood veneers during weathering. Rowell et al.¹¹ demonstrated the effectiveness of chemical modification at reducing weathering. However, the weathering of acetylated wood has received little attention. Owen et al.¹² showed that this type of modification protected the surface from weathering effects of light and water, although Kalnin¹³ reported that acetylation enhanced the rate of weathering.

This study examines the effectiveness of both untested and previously tested compounds at preventing weathering of rubberwood outdoors. The efficacy of these chemicals as blue-stain inhibitors is also investigated for the first time.

EXPERIMENTAL

Air-dried rubberwood blocks (135 × 45 × 4 mm) were immersed in aqueous solutions of chromium trioxide (concentrations of 1.0 and 2.0%), chromic nitrate (concentration of 5.0%), ferric chloride (concentration of 5.0%), and ferric nitrate (concentration of 6.0%) for 1 h. Blocks were then air dried and leached with running water to remove unreacted salts and redried.

Rubberwood blocks of the same dimensions were acetylated to 10 wt % gain (WPG) by treating with 360 mL acetic anhydride in 1000 mL pyridine at 100°C for 4 h. Samples were then washed with acetone and extracted for 6 h to remove unreacted acetic anhydride and then air-dried.

Untreated and treated samples were exposed outdoors on east-facing racks at a 45° angle between March 1998 and April 1999 at Bangalore, India. Samples were initially removed at 1-day intervals (up to 15 days), after which they were removed at longer intervals.

Tangential faces of weathered blocks were analyzed by using FTIR spectroscopy. FTIR spectra were recorded by direct transmission (KBr pellet technique) by using a Nicolet Impact 400 spectrometer equipped with a deuterated triglycine sulfate (DTGS) detector. Fluorescence spectra

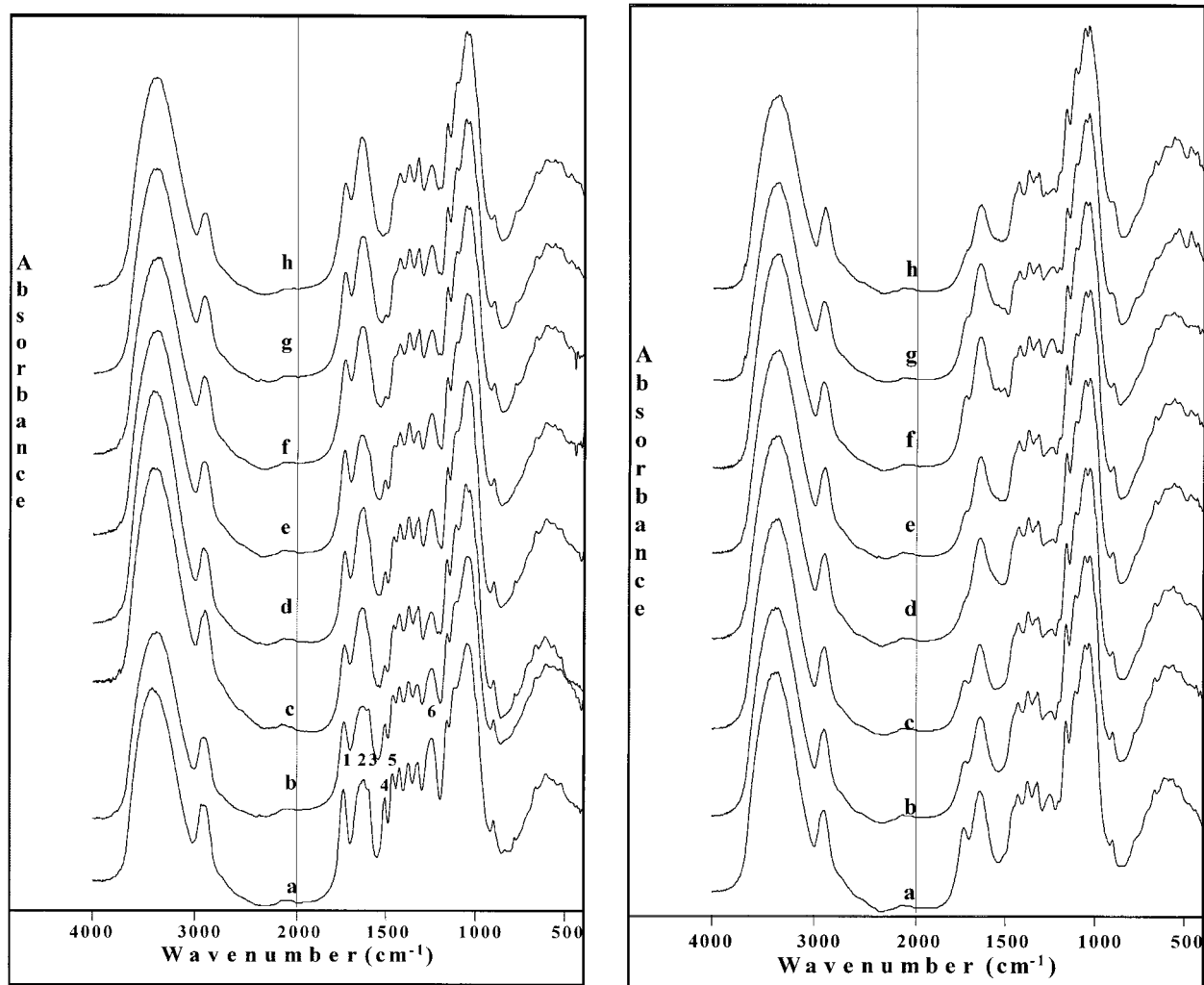


Figure 1 (A) FTIR spectra of rubberwood exposed to natural weathering for (a) 0 days; (b) 1 day; (c) 2 days; (d) 3 days; (e) 4 days; (f) 6 days; (g) 8 days; (h) 22 days. Peak numbers 1 to 6 correspond to 1740, 1660, 1600, 1505, 1465, 1245 cm^{-1} , respectively. (B) FTIR spectra of rubberwood exposed to natural weathering for (a) 34 days; (b) 50 days; (c) 72 days; (d) 98 days; (e) 125 days; (f) 150 days; (g) 222 days; (h) 360 days.

were measured directly from wood surfaces in the frontal mode by using an Edinburgh FS 900 steady-state spectrofluorometer. A 390-nm cut-off filter was placed before the emission monochromator to eliminate scattered/direct light. Sample surface appearances were also compared by using a low-power binocular microscope (Jeneval). In addition, small (3 mm^2) sections were removed from the block surfaces by using a double-sided razor blade, mounted on aluminum stabs using silver dag (Agar Scientific), gold coated (Polaron sputter coater), and examined in a Cambridge Stereoscan SEM at accelerating voltages of 10–15 kV.

RESULTS AND DISCUSSION

Weathering of Untreated Wood

The IR spectrum of untreated rubberwood shows a strong hydrogen-bonded O—H stretching absorption at around 3400 cm^{-1} and a prominent C—H stretching absorption around 2900 cm^{-1} [see curve a in Fig. 1(A)]. In the fingerprint region, between 1800 and 900 cm^{-1} , many sharp and discrete absorption bands due to various functional groups present in wood constituents are observed. The O—H (at around 3400 cm^{-1}), C—H (at around 2900 cm^{-1}), C=O (at around

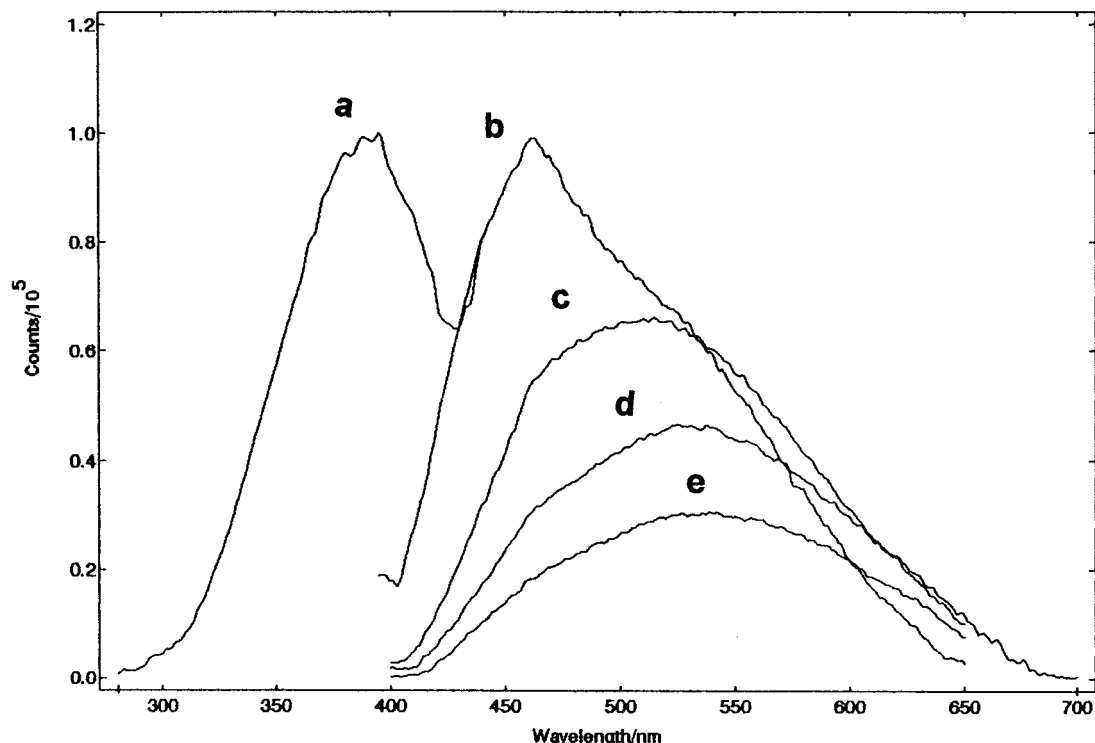


Figure 2 Fluorescence spectra of unweathered and weathered rubberwood. (a) Excitation spectrum of unweathered wood, emission wavelength = 460 nm. (b) Emission spectrum of unweathered wood, excitation wavelength = 381 nm. (c), (d), and (e) Emission spectra of wood weathered for 2, 6, and 22 days, respectively.

1740 cm^{-1}), and C=C (at around 1505 cm^{-1}) bands are pure, whereas other bands in the fingerprint region below 1460 cm^{-1} are complex, having contributions from various vibration modes in carbohydrates and lignin.¹⁴⁻¹⁷

FTIR spectra of weathered wood surfaces show severe delignification and a significant loss of hemicellulose [Fig. 1(A,B)]. This is evident from the rapid decrease in the intensities of 1505 cm^{-1} [Fig. 1(A, a, 4)] and 1600 cm^{-1} [Fig. 1(A, a, 3)] bands (which correspond to aromatic C=C stretching vibration in lignin), and the band at 1740 cm^{-1} [Fig. 1(A, a, 1), which corresponds to unconjugated C=O vibration in xylan]. Delignification was seen after just 1 day's exposure, with almost complete delignification following 6–8 days' weathering, evident from a decrease in the intensity of bands at 1505 and 1600 cm^{-1} , which are almost completely absent following 8 days' exposure. A similar rate of delignification and hemicellulose breakdown was observed in radiata pine (*Pinus radiata*) exposed to natural weathering.⁶

The intensities of bands at 1465 cm^{-1} [Fig. 1(A, a, 5), which arises due to CH₂ deformation in

lignin and xylan] and 1245 cm^{-1} [Fig. 1(A, a, 6), due to C—O stretching vibration in lignin and carbohydrates] decreased over time and were absent at around 70 days' exposure, whereas the band intensity at 1660 cm^{-1} [Fig. 1(A, a, 2)] increases relative to 1375 cm^{-1} between 2 and 22 days' exposure [Fig. 1(A, c–h)]. However, after longer exposure, no changes were observed [Fig. 1(B)]. The band at 1660 cm^{-1} is characteristic of carbonyl stretching vibration of conjugated esters and carboxylic acids, although some of the absorption peak results from the H—O—H bending vibration of water present in the sample.

Figure 2 shows fluorescence spectra for unweathered and weathered rubberwood surfaces. Unweathered wood has a major emission peak at around 460 nm with a shoulder at around 520 nm and an excitation maximum at around 380 nm. Weathering results in a rapid decrease in the intensity of the emission peak at 460 nm and a significant red shift in the emission maximum. A red shift of ~ 100 nm was observed after about 22 days' weathering. This is the first time fluorescence spectroscopy was used to study weathering of wood surfaces.

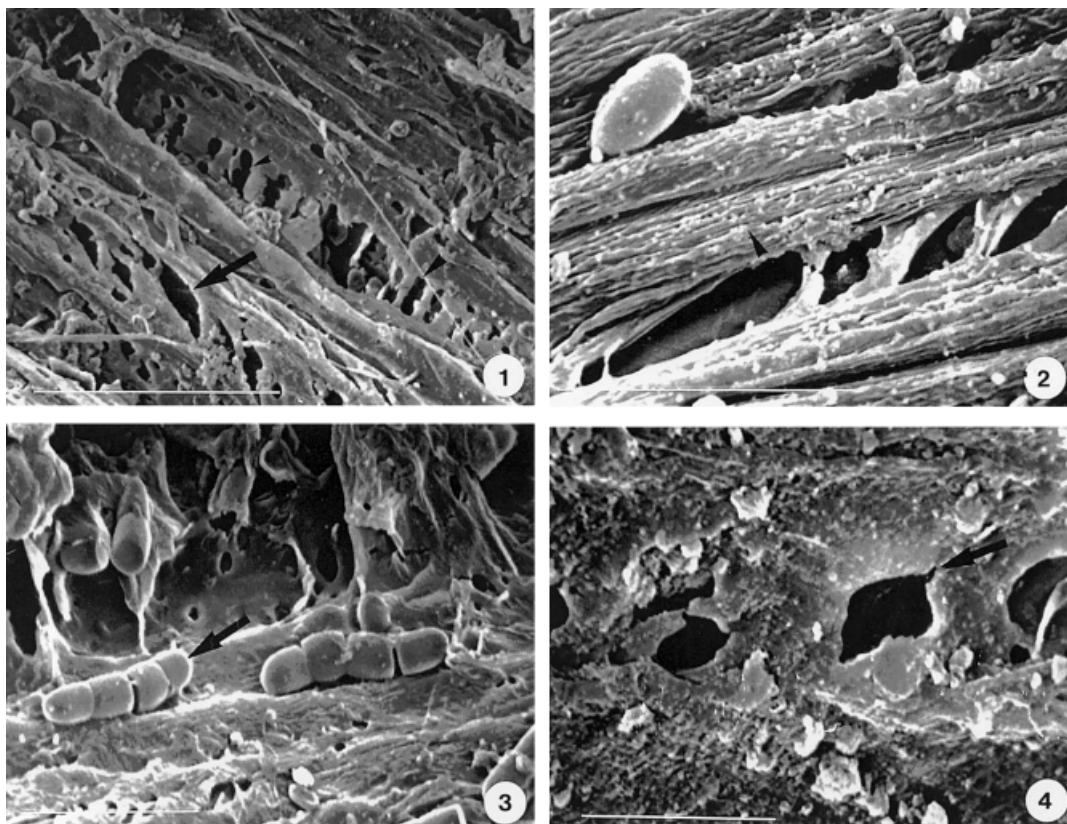


Figure 3 SEM micrographs of untreated rubberwood weathered for (1) 125 days, large arrow, checks; small arrow, pit degrade (scale bar = 50 μm); (2) 360 days, arrow, ridging of S3 layer (scale bar = 20 μm); (3) 125 days, arrow, fungal spores (scale bar = 20 μm); (4) 360 days, arrow, pit checking (scale bar = 10 μm).

SEM examination of weathered surfaces showed checks in the wood cell wall and degradation of pits in untreated rubberwood exposed for 125 days [Fig. 3 (1)] and 360 days [Fig. 3 (4)]. In addition, ridges on the S3 layer adjacent to cell lumens were observed in wood exposed for 360 days [Fig. 3 (2)]. Stain hyphae and spores were also observed colonizing wood cell lumens [Fig. 3 (1,3)]. Examination of weathered wood surfaces using LM showed no discernible discoloration following 1 day's exposure [Fig. 4 (1)]. After 125 days, staining of vessels and rays was apparent and the wood was colored silvery gray [Fig. 4 (6)]. After 360 days' exposure, the surface was softened, with black fruiting bodies visible on wood cell surfaces and in the vessel lumens [Fig. 4 (7)].

Weathering of Wood Treated with Chromium and Iron Compounds

The stabilization effect of chromium trioxide against weathering of rubberwood surfaces is

shown in Figure 5. This treatment results in a reduction of the intensity of the lignin bands at 1505 cm^{-1} (aromatic C=C vibration) and 1245 cm^{-1} (C—O vibration) when compared to the untreated controls. The spectrum for the chromium trioxide modified surface remained almost unchanged after 6 months of natural weathering and the rate of change was very much reduced following longer exposures than untreated controls.

Figure 6 shows FTIR spectra of unweathered and weathered wood samples pretreated with ferric chloride. The spectrum for unweathered wood shows a slight reduction in the intensity of bands at 1505 and 1245 cm^{-1} and an increased intensity at 1660 cm^{-1} relative to untreated wood [Fig. 6(b)], indicating some degree of reaction, although much less than for chromium trioxide. From Figure 6, it can be observed that ferric chloride reduces delignification only partially when compared to untreated samples exposed for the same duration.

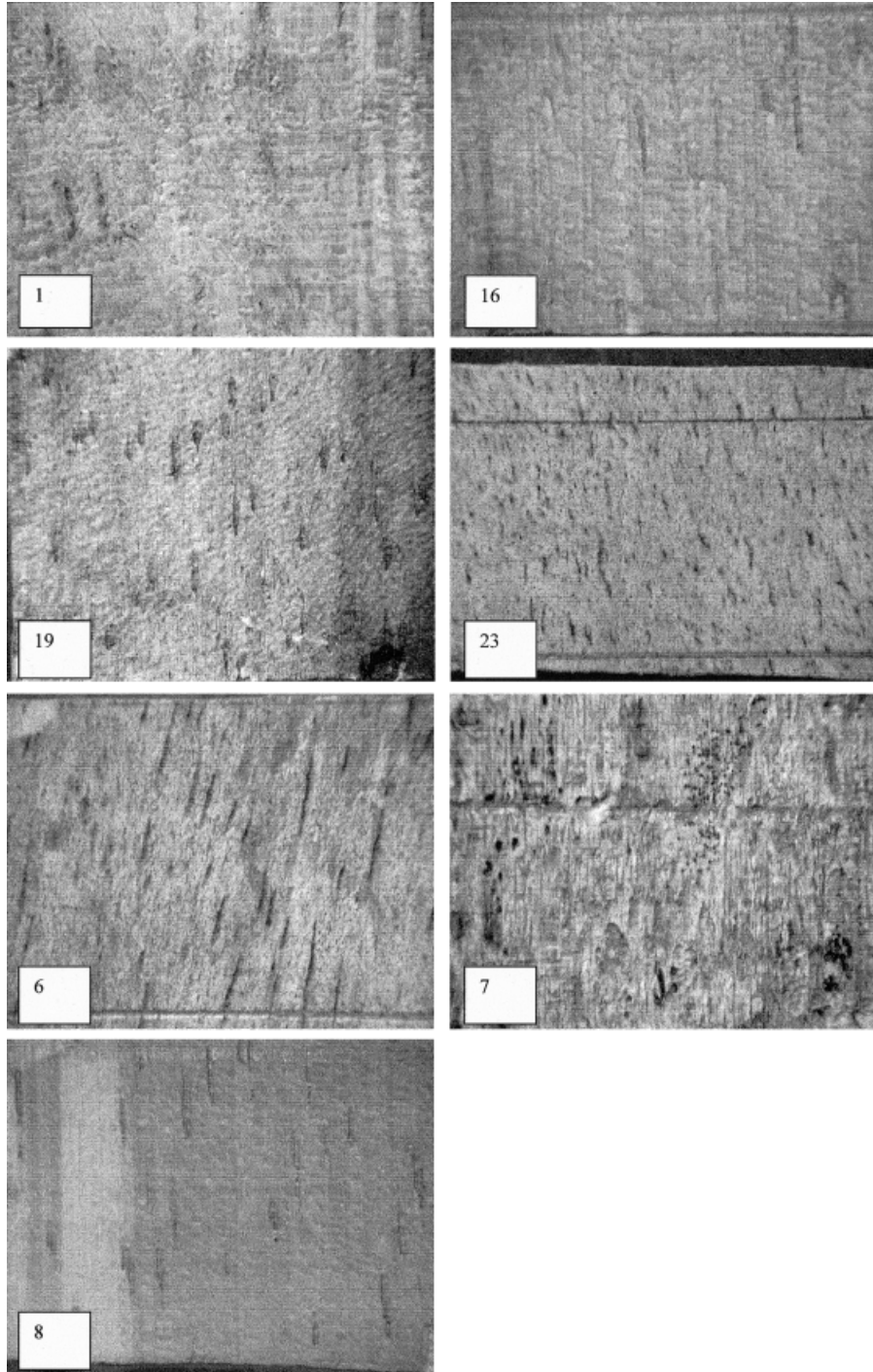


Figure 4 Light micrograph ($\times 10$) of rubberwood (1) weathered for 1 day; (6) staining of vessels and rays after 125 days weathering; (7) weathered for 360 days; (8) unweathered wood treated with chromium trioxide; (16) treated with ferric chloride and weathered for 125 days; (19) treated with chromium trioxide and weathered for 125 days; (23) acetylated wood weathered for 125 days.

FTIR spectra of unweathered and weathered wood samples treated with ferric nitrate are shown in Figure 7. Unweathered samples treated

with ferric nitrate again show a slight reduction in the intensity of bands at 1740 and 1505 cm^{-1} compared to untreated wood, suggesting some re-

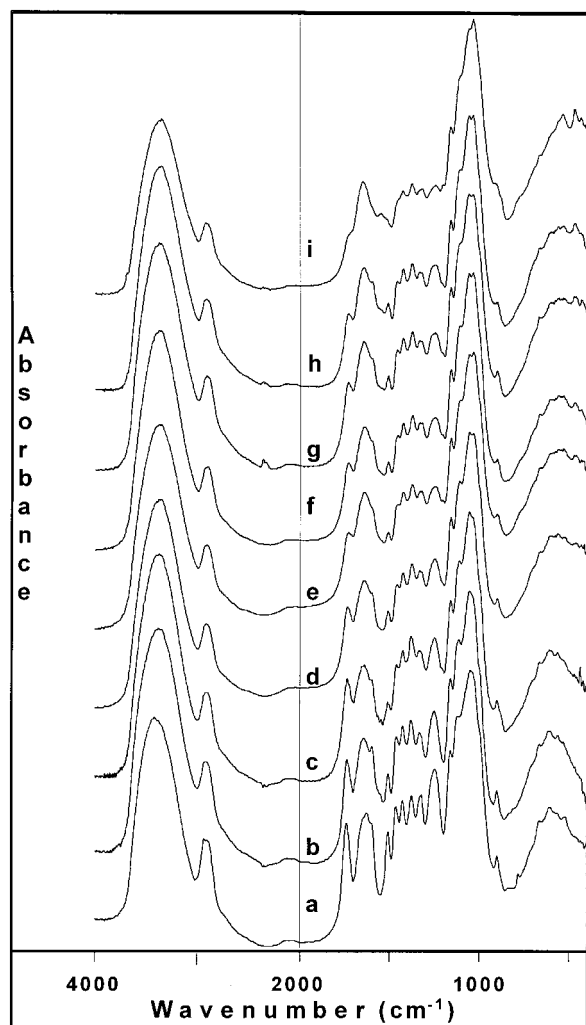


Figure 5 FTIR spectra of rubberwood treated with CrO_3 (conc. 2.0%) and weathered for (b) 0 days; (c) 34 days; (d) 72 days; (e) 98 days; (f) 125 days; (g) 175 days; (h) 222 days; (i) 365 days. Curve (a) corresponds to the untreated and unweathered wood.

action with hemicellulose and lignin. Treatment with ferric nitrate also results in an increased intensity and broad spectrum around 1370 cm^{-1} because of the presence of the nitrate ion. It can be seen from Figure 7 that ferric nitrate is not very effective in preventing delignification.

Pretreatment with chromic nitrate resulted in a slight reduction in intensity of bands at 1740 , 1505 , 1465 , and 1245 cm^{-1} , implying wood polymers reacted less with chromic nitrate than with chromium trioxide. The degree of weathering protection was also much less than that provided by chromium trioxide in wood exposed for the same period. In fact, chromic nitrate also had little effect in preventing delignification.

When the effectiveness of pretreatments against colonization by stain fungi was assessed, severe fungal staining was observed within 1 months' exposure of untreated samples. Far less fungal staining was observed on wood samples treated by chromium trioxide and ferric chloride after this period, the latter being most effective. Ferric nitrate also restricted stain, although the degree of protection was less than that of chromium trioxide and ferric chloride. Chromic ni-

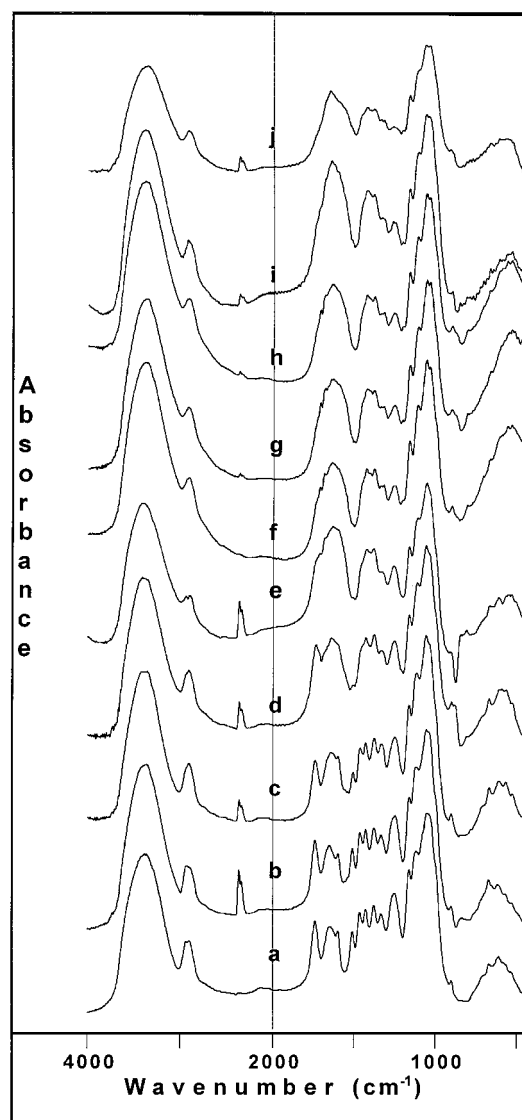


Figure 6 FTIR spectra of rubberwood treated with ferric chloride (conc. 5.0%) and weathered for (b) 0 days; (c) 14 days; (d) 34 days; (e) 42 days; (f) 72 days; (g) 98 days; (h) 125 days; (i) 175 days; (j) 322 days. Curve (a) corresponds to the untreated and unweathered wood.

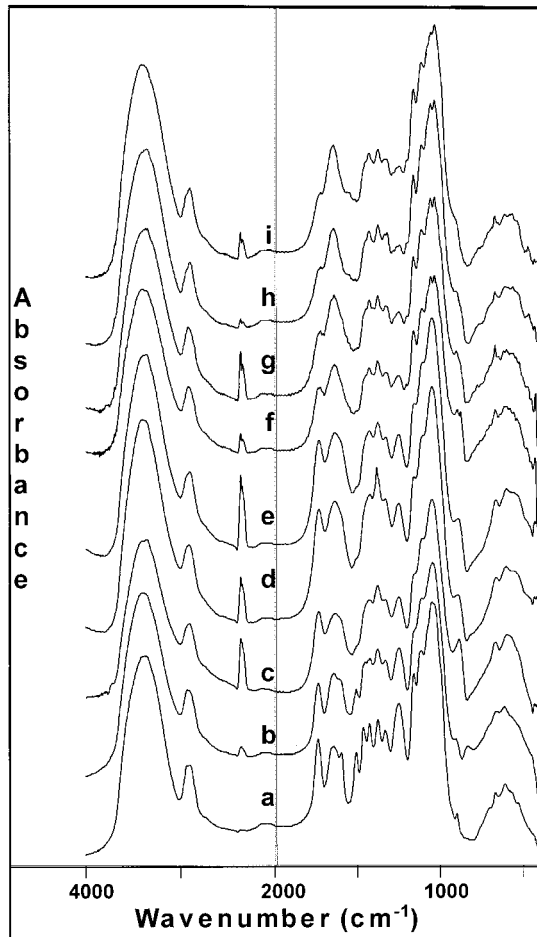


Figure 7 FTIR spectra of rubberwood treated with ferric nitrate (conc. 6.0%) and weathered for (b) 0 days; (c) 14 days; (d) 34 days; (e) 42 days; (f) 72 days; (g) 98 days; (h) 125 days; (i) 222 days. Curve (a) corresponds to the untreated and unweathered wood.

trate was least effective in restricting staining fungi.

SEM examination of wood block surfaces treated with ferric chloride, ferric nitrate, chromium trioxide, and chromic nitrate showed far less cell-wall degradation (checking, pit degradation, and S3 ridging) than untreated controls exposed for the same periods (though figures for these have not been included). Also, in contrast to untreated wood samples, there was little surface discoloration following weathering [other than that caused by pretreatment of blocks [Fig. 4 (16) and (19)]] when examined by using light microscopy.

Results show hexavalent chromium trioxide to be most effective at providing weathering resistance. Ferric chloride also provided some resis-

tance, although the extent of protection was less than for chromium trioxide. The least effective pretreatments were ferric nitrate and chromic nitrate. Much of the lignin polymer at the wood surface is chemically modified when treated with aqueous chromium trioxide.¹⁸ Modification is characterized by a reduction in the intensity of the C=C band at 1505 cm^{-1} and C—O band at 1245 cm^{-1} . Attempts were made to elucidate the way in which chromium (VI) photostabilizes wood.^{19–22} Formation of a photostable and water-insoluble hexavalent and trivalent chromium complexes,¹⁹ and a covalent-bonded wood chromate ester,^{18–20} were suggested. Mechanisms for the interaction of chromium compounds [Cr(VI) and Cr(III)] with lignin, cellulose, and hemicellulose were examined (Pizzi^{19,21,22}). Pizzi²¹ showed Cr formed a covalently bonded compound with lignin, confirmed through solid-state $^{13}\text{C-NMR}$ of solid wood. In carbohydrates, Cr(III) is weakly adsorbed, whereas Cr(VI) as CrO_4^{2-} formed transition complexes with cellobiose in cellulose and disaccharides found in hemicellulose.²²

Potential problems with using chromium trioxide as a pretreatment include its toxicity to workers pretreating wood and its environmental fate. However, the use of very low concentrations as in this study minimizes such concern.

Of the other compounds, ferric chloride offers promise as a pretreatment, because it also restricts colonization by stain fungi. The interaction of Fe(III) compounds with both wood model compounds and solid pine were studied.²³ Ferric nitrate was used and Fe^{3+} was shown to mainly complex with guaiacyl moieties in lignin and less with carbohydrates. The authors showed good dimensional stabilization of ferric nitrate treated wood when weathered than Cr(VI) treatments, which may account for its improved resistance to colonization by stain fungi. No work was undertaken with ferric chloride, and its high resistance to stain observed in this study may also be mirrored in an increase in dimensional stabilization when weathered.

Weathering of Acetylated Wood

Treatment of wood with acetic anhydride resulted in a significant increase in the peak intensity of carbonyl absorption at 1740 cm^{-1} , C—CH₃ symmetrical deformation band at 1375 cm^{-1} , and C—O vibration band at 1220 cm^{-1} (Fig. 8, curve b). The intensity and width of strong O—H stretching vibration at 3400 cm^{-1} (between 3600

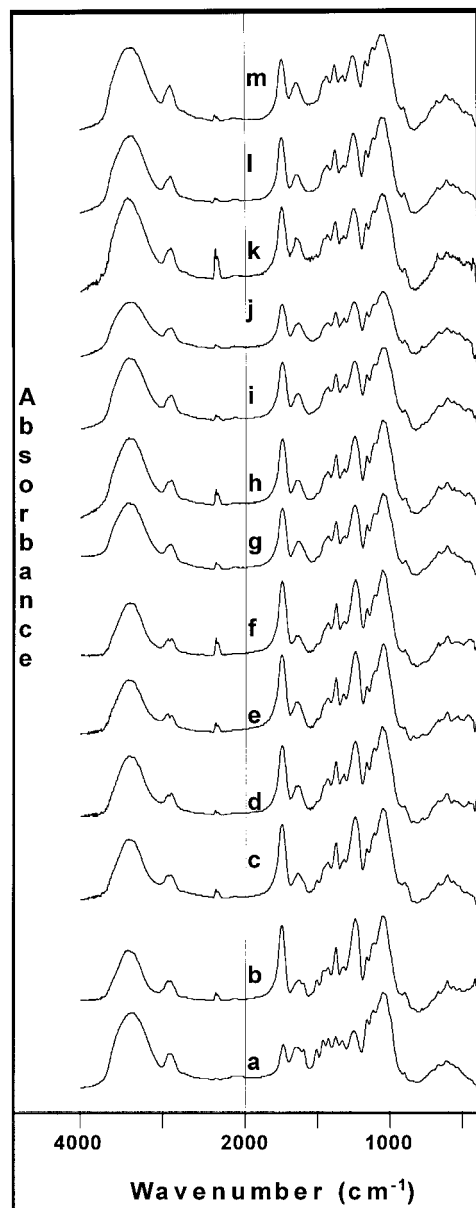


Figure 8 FTIR spectra of acetylated wood weathered for (b) 0 days; (c) 8 days; (d) 14 days; (e) 22 days; (f) 34 days; (g) 50 days; (h) 72 days; (i) 98 days; (j) 125 days; (k) 150 days; (l) 175 days; (m) 222 days. Curve (a) corresponds to the untreated and unweathered wood.

and 3200 cm^{-1}) reduces [Fig. 8(a,b)]. These changes can be attributed to the replacement of reactive O—H groups present in wood polymer matrix by acetyl groups. There is also a small decrease in the intensity of lignin-associated peak at 1505 cm^{-1} , indicating a modification of the aromatic ring in lignin. Boonstra et al.²⁴ also reported modification of the aromatic nuclei of lignin following acetylation by using ^{13}C -NMR

cross-polarizationmagic angle spinning (CP/MAS). Reduction in the intensity of O—H stretching vibration accompanied by enhancement in the intensity of C=O and C—O band provides evidence for chemical reaction between anhydride and hydroxyl groups associated with wood cell-wall polymers. The treatment of wood with acetic anhydride is a single-site reaction leading to ester formation with the hydroxyl groups of cellulose, hemicellulose, and lignin and with acetic acid as a by-product: $\text{Wood—OH} + (\text{CH}_3\text{CO})_2 \rightarrow \text{Wood—O—C—CH}_3 + \text{CH}_3\text{COOH}$. The reactivity is maximum with lignin and least with structural carbohydrates.²⁴ Thus, acetylated wood reduces its hydrophilicity.

Though weathering of acetylated wood also shows some changes in IR spectra, changes are less pronounced when compared to untreated wood exposed for the same duration, as can be seen from Figure 8. Most of the changes occur for the bands at 1600 , 1505 , and 1465 cm^{-1} . Other bands in the fingerprint region, including C=O and C—O bands, remain almost unchanged. Although the band at 1505 cm^{-1} disappears after about 50 days of exposure, the relative intensity of other peaks in the fingerprint area remain unchanged. Also, there is less fungal staining and surface degradation in acetylated wood than with untreated wood after the same exposure period [Fig. 4 (23)], although its color is somewhat lighter.

CONCLUSION

In rubberwood, natural weathering causes rapid and substantial surface delignification and loss of hemicellulose. The process is rapid, with some delignification following 1 days' exposure and complete delignification of wood at the surface within 1 week, indicated by the decrease in the intensities of IR bands at 1505 , 1600 , 1465 , and 1245 cm^{-1} . Fungal staining occurs within 1 month of outdoor exposure, although pretreatment of surfaces with chromium and ferric salts reduced this deterioration.

Chromium trioxide (chromium VI compound) proved most effective in imparting weathering resistance to the wood surface, probably because of the formation of a water insoluble and photostable complex between chromium trioxide and lignin present in the wood. The degree of reaction between wood and chromium (III) compound and ferric salts is less. Although treatment with these

compounds does not check delignification completely, they do provide resistance to staining, ferric chloride being the most effective. Acetylation also improves the weathering performance of wood.

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