

Makoto Ohkoshi

FTIR-PAS study of light-induced changes in the surface of acetylated or polyethylene glycol-impregnated wood

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Abstract The objective of this study was to characterize the surface changes in acetylated and polyethylene glycol (PEG)-impregnated wood caused during light irradiation by Fourier transformed infrared photoacoustic spectroscopy analysis to determine their effects on the reduction of light deterioration. Light irradiation made the color of the chemically modified wood lighter or more vivid, whereas it deepened the color of the untreated wood. The color difference during light irradiation was less in the chemically modified wood than the untreated wood. The color difference of PEG-impregnated wood increased with increasing irradiation time. The light irradiation generated much carbonyl and significantly degraded lignin in the untreated wood. The generation of carbonyl and lignin degradation diminished in the acetylated wood in comparison with the untreated wood, indicating that acetylation restrained the photochemical degradation of wood. Deacetylation did not occur during light irradiation of the acetylated wood. The PEG impregnation decreased the generation of carbonyl and degradation of lignin during light irradiation. However, the irradiation occurred a little photochemical degradation of PEG, generating the carbonyl. Therefore, longer light irradiation should increase the degradation of PEG, thus reducing the effect of treatment. The correlation between the color difference and lignin degradation was high, indicating that the color changes during light irradiation significantly depended on lignin degradation. The chemical modification reduced the degradation of lignin and consequently decreased the color difference. Some of the compounds containing the carbonyl generated during light irradiation were water-soluble.

Key words Acetylation · PEG impregnation · Light irradiation · Color changes · FTIR-PAS spectra

Introduction

Many studies have focused on reducing light-induced deterioration of wood surfaces by chemical modification. Acetylation has been investigated most often among these modifications because of the relatively easy procedure and low cost. The acetyl substitution of phenolic hydroxyl groups in lignin should restrain the generation of phenoxy radicals, which cause light-induced deterioration. Feist et al.¹ showed that acetylation protected wood from photochemical degradation of lignin and hemicellulose during accelerated weathering. Plackett et al.² showed that acetylated wood was more color-stable than untreated wood in an accelerated weathering test with water spraying, and Owen et al.³ noted that acetylation of wood under mild conditions served to protect the surface from the weathering effects of light and water. Leary⁴ showed that acetylation retarded the yellowing of wood during light irradiation. Dawson and Torr⁵ reported that acetylation photostabilized the surface to a significant degree under light irradiation for 1000h, and the changes in color due to light irradiation decreased as the acetyl content of wood increased.

Some researchers showed that the longer light irradiation decreased the photostabilization effect of chemical modification of wood. Hon⁶ reported that acetylated wood exhibited a color stabilization effect for the initial 28 days of light irradiation, but its effect diminished steadily thereafter. He concluded that this diminished effect was due to deacetylation by prolonged light irradiation. Dunningham et al.⁷ showed that acetylation provided protection against color changes for the first 8 weeks of outdoor weathering exposure, but after 28 weeks' exposure the color of the untreated and acetylated wood was nearly the same (dark gray). This was thought to reflect the many factors present during natural exposure (e.g., dirt, fungal spores) in addition to light and water.

M. Ohkoshi (✉)
Forestry and Forest Products Research Institute, PO Box 16,
Tsukuba Norin Kenkyu Danchi-Nai, Ibaraki 305-8687, Japan
Tel. +81-298-73-3211; Fax +81-298-74-3720
e-mail: ohkoshi@ffpri.affrc.go.jp

In contrast, Kalnins⁸ showed that acetylated wood was not more resistant to photodegradation. Torr et al.⁹ showed that acetylated wood was not photostable to ultraviolet light.

On the other hand, Minemura and Umehara¹⁰ reported that a coating of polyethylene glycol (PEG) on whitish wood decreased the color changes after light irradiation, but the coating on some other woods, contrarily, increased the changes. PEG can associate with phenolic compounds at the position of etheric oxygen in polyethylene oxide chains or produce peroxide compounds during light irradiation. Thus, the light energy absorbed by wood should migrate to PEG and produce peroxide compounds in PEG to decompose the chromophore in wood.

It is not completely understood if chemical modification reduces the light-induced deterioration of wood, as mentioned above. Many studies have been carried out on the characterization of weathering of wood by means of Fourier-transformed infrared (FT-IR) transmission spectroscopy and diffuse reflectance spectroscopy (DRIFT).^{3,11} Pandey and Theagarajan¹² showed that FT-IR photoacoustic spectroscopy (PAS) spectra of wood were similar to the spectra obtained by the transmission and DRIFT techniques. PAS can nondestructively measure the changes in solid wood surface caused by light irradiation. The present study characterizes in detail the light-induced changes of the wood surface by FTIR-PAS measurements to examine the effects of chemical modification on the reduction of light deterioration.

Experimental

Wood samples

Four softwood species were used: heartwood of sugi (*Cryptomeria japonica* D. Don, density 0.37 g/cm³, abbreviation SG); hinoki (*Chamaecyparis obtusa* Endl., 0.43 g/cm³, HK), karamatsu (*Larix leptolepis* Gordon, 0.50 g/cm³, KM); and akamatsu (*Pinus densiflora* Sieb. et Zucc., 0.52 g/cm³, AM). The dimensions of the wood specimens were 14 cm (L) × 6.5 cm (R) × 0.8 cm (T) for the color difference measurements and 0.6 cm (L) × 0.6 cm (R) × 0.2 cm (T) for the PAS measurements.

Acetylation and impregnation with PEG

The wood specimens were extracted with an alcohol/benzene (1:2) mixture before acetylation. The dried specimens were reacted with acetic anhydride in the liquid phase without a catalyst for 24 h at 120°C. At the end of the reaction the specimens were fully washed with water and then oven-dried before weighing.

The wood specimens were extracted with hot water before impregnation with PEG. The dried specimens were put under vacuum and then impregnated with 30% aqueous solution of PEG 4000 (average molecular weight 3000–3700). The specimens were weighed after drying. Filter

papers (Advantec) were also impregnated with PEG to examine the changes in PEG caused by light irradiation.

Light irradiation

The untreated, acetylated, and PEG-impregnated wood specimens were irradiated with light using a Suga xenon fade meter FAL-25AXC-HC (2.5 kW) at a distance of 25 cm from the light source and a black-panel temperature of 63°C. The irradiation times were 100 and 1000 h for PAS analysis and color measurement, respectively. The average amount of light irradiated on the specimen surface was 1.11 MJ/m²/h at wavelengths of 300–700 nm. This indicates that the irradiation for 170 h by this apparatus is equivalent to the average amount of sunlight irradiated on the horizontal plane in Tokyo for 1 month, which was estimated from the value measured for 21 years from 1966 to 1986.¹³

Measurement of color difference

The colors (brightness L^* , chromaticity a^* , b^* , and chroma C^*) of the surface of light-irradiated wood specimens were measured by a Minolta CM-508i spectrophotometric colorimeter. The measured position was a circular area of diameter 8 mm at the center of the surface. The color difference ΔE_{ab}^* was estimated from the equation $[(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$.

FTIR-PAS measurement

The FTIR-PAS spectra of the light-irradiated wood specimens were measured by a Nicolet Magna 860-PAS300. The intensities of absorbance due to C—O—C stretching in polysaccharides at 1161 cm⁻¹, to C=O stretching at 1732 cm⁻¹, and to benzene ring stretching in lignin at 1508 cm⁻¹, were measured from the spectra. In addition, the intensities of absorbance due to CH₃ bending and C—O stretching in acetyl groups at 1369 cm⁻¹ and 1230 cm⁻¹, respectively, were measured in the acetylated wood. In the PEG-impregnated wood, the intensities of absorbance due to β -linkage in polysaccharides at 899 cm⁻¹ and to CH₂ rocking in PEG¹⁴ at 845 cm⁻¹ were also measured. It is known that polysaccharides are little degraded by light irradiation. Therefore, the ratio of the intensities at 1732, 1508, 1369, 1230, and 845 cm⁻¹ to those at 1161 or 899 cm⁻¹ was calculated from the measured values. We then estimated the ratios ($R_{C=O}$, R_{Lgn} , $R_{AcetylCH_3}$, $R_{AcetylC-O}$, R_{PEG}) after irradiation to those before irradiation. The ratio of the decrease in lignin (R_{Lignin}) by light irradiation was estimated from $1 - R_{Lgn}$. These ratios indicate changes in the amounts of carbonyl, lignin, acetyl, and PEG caused by light irradiation.

Removal of water-soluble compounds after light irradiation

After light irradiation and the subsequent PAS measurement, the specimens were submerged in stirred water for

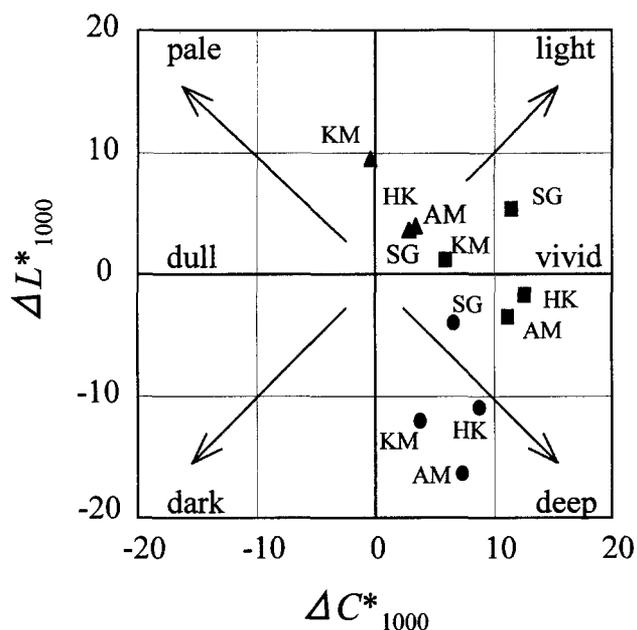


Fig. 1. Color changes of untreated, acetylated, and polyethylene glycol (PEG)-impregnated wood after light irradiation for 1000h. ΔL^*_{1000} and ΔC^*_{1000} , changes in brightness and chroma after light irradiation for 1000h; circles, untreated; triangles, acetylated; squares, PEG-impregnated. Other abbreviations are the same as described in the text

several days to remove water-soluble compounds produced by irradiation. After drying, the PAS spectra were measured. Some of the water-soluble extractives in wood should be also eluted away during the water treatment of untreated wood. Therefore, the specimens extracted previously with hot water were used for this experiment instead of untreated specimens.

Results and discussion

Acetylation and impregnation with PEG

The weight percent gains (WPG) of wood specimens due to acetylation were 22.5% in SG, 24.6% in HK, 15.1% in KM, and 20.2% in AM. The polymer loading (PL) due to PEG impregnation was 57.5% in SG, 54.6% in HK, 27.8% in KM, and 13.4% in AM. The low PL of the KM specimen may be attributed to its low penetrability. On the other hand, the reason for low PL in the AM specimen may be that pine resins obstruct penetration of PEG into wood because the resins had not been previously removed from the specimens.

Changes in color difference during light irradiation

Figure 1 shows the relation between the changes of brightness (ΔL^*) and chroma (ΔC^*) of wood specimens light-irradiated for 1000h. The direction of color changes due to light irradiation can be recognized in Fig. 1. The color of the untreated specimens deepened after light irradiation,

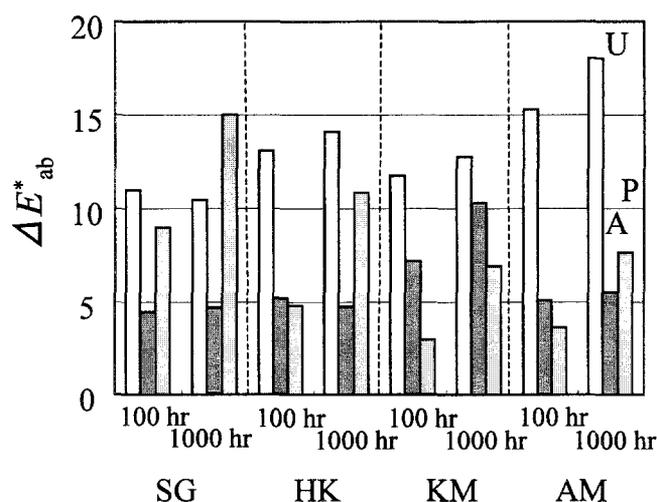


Fig. 2. Color differences of untreated (U), acetylated (A), and PEG-impregnated (P) wood after light irradiation for 100 and 1000h. Other abbreviations are the same as described in the text

whereas the color of the acetylated specimens became lighter, and one of the PEG-impregnated specimens became more vivid. These findings show that the direction of color change due to light irradiation differed between the untreated and treated specimens and between the two treatments.

The color differences ΔE^*_{ab} of the specimens after light irradiation for 100 and 1000h are shown in Fig. 2. The ΔE^*_{ab} of acetylated specimens was much smaller than that of the untreated specimens in all wood species tested. The increase in irradiation time from 100 to 1000h scarcely changed the ΔE^*_{ab} of acetylated specimens except the KM specimen. The ΔE^*_{ab} of acetylated KM specimen was still smaller than that of the untreated specimen after irradiation for 1000h. These results indicate that the acetylation of wood suppressed the color change caused by light irradiation.

The ΔE^*_{ab} in the acetylated KM wood specimen increased with the increase in irradiation time, as shown in Fig. 2. Dawson and Torr⁵ showed that the changes in color during light irradiation were reduced with increased acetyl content of wood. Based on this finding, the observed increase in ΔE^*_{ab} is thought to be because of low WPG due to acetylation attained in the KM wood specimen. On the other hand, Hon⁶ showed that acetylated wood exhibited a color stabilization effect for the initial 28 days of light irradiation, but its effect steadily diminished thereafter. He concluded that the decreased effect was due to the deacetylation caused by prolonged light irradiation. However, this decrease may be because of the low WPG of his specimens and not because of the deacetylation, as mentioned later.

Plackett et al.² showed that acetylated wood was more color-stable than untreated wood in an accelerated weathering test with water spraying. On the other hand, Dunningham et al.⁷ showed that acetylation protected against color changes for the first 8 weeks of outdoor weathering exposure, but after this period the acetylated wood

changed in a manner similar to that of the untreated wood. This is considered to reflect the many factors present during natural exposure (e.g., water, dirt, fungal spores) in addition to light.

The ΔE_{ab}^* of PEG-impregnated wood specimens after light irradiation for 100h was smaller than that of the untreated specimens even in KM and AM, with low PLs. Hon and Ifju¹⁵ reported that the penetration depth of ultraviolet light into wood was about 75 μm , and Kataoka and Kiguchi¹⁶ showed that the depth of the photo-induced degradation layer was about 100 μm after light irradiation for 100h. It is supposed from these findings that PEG in the surface to a depth of 75–100 μm effectively diminishes the color changes during light irradiation. The low PL of the KM and AM specimens can be explained by low penetrability into the wood. The PEG content on the surface should not have been much different from those of the other species (SG and HK) because PEG aqueous solution with the same concentration impregnated the wood. This PEG content may have been enough to suppress the color changes. Therefore, it is thought that the color changes of KM and AM specimens were small despite the low PL.

Increasing the irradiation time from 100h to 1000h increased the ΔE_{ab}^* of PEG-impregnated specimens of all species, in contrast to acetylation. Especially, the ΔE_{ab}^* of the PEG-impregnated SG specimen after 1000h of irradiation was larger than that of the untreated specimens. These results indicate that the effect of PEG on the suppression of color change decreased with the increase in irradiation time. This may be due to the degradation of PEG by light.

Effect of acetylation on photochemical degradation of wood surface

The FTIR-PAS spectra of light-irradiated HK specimens and nonirradiated specimens are shown in Fig. 3. Pandey and Theagarajan¹² and Kuo et al.¹⁷ applied PAS technology to wood analysis and concluded that the FTIR-PAS spectra of wood were similar to the spectra obtained by transmission and diffuse reflectance techniques. The depth sensed by PAS varies depending on the condition of the wood samples (density, coefficient of thermal conductivity, specific heat) and PAS measurement (moving mirror velocity, wave numbers). The depth was approximately 10–30 μm for wave numbers of 4000–400 cm^{-1} in this study. This indicates that PAS technology is suitable for analyzing light-irradiated wood surfaces because the sensed depth is smaller than the penetration depth (75 μm) of ultraviolet (UV) light or the depth of the photodegradation layer (100 μm).

In the untreated specimen the absorbance due to C=O stretching at 1732 cm^{-1} increased significantly, and that due to benzene ring stretching in lignin at 1508 cm^{-1} decreased significantly with increasing irradiation time. These results indicate that the generation of carbonyl and the degradation of lignin progressed as light irradiation continued.

In the acetylated specimen, the absorbance at 1732 cm^{-1} was high because of the overlapping with the carbonyl in

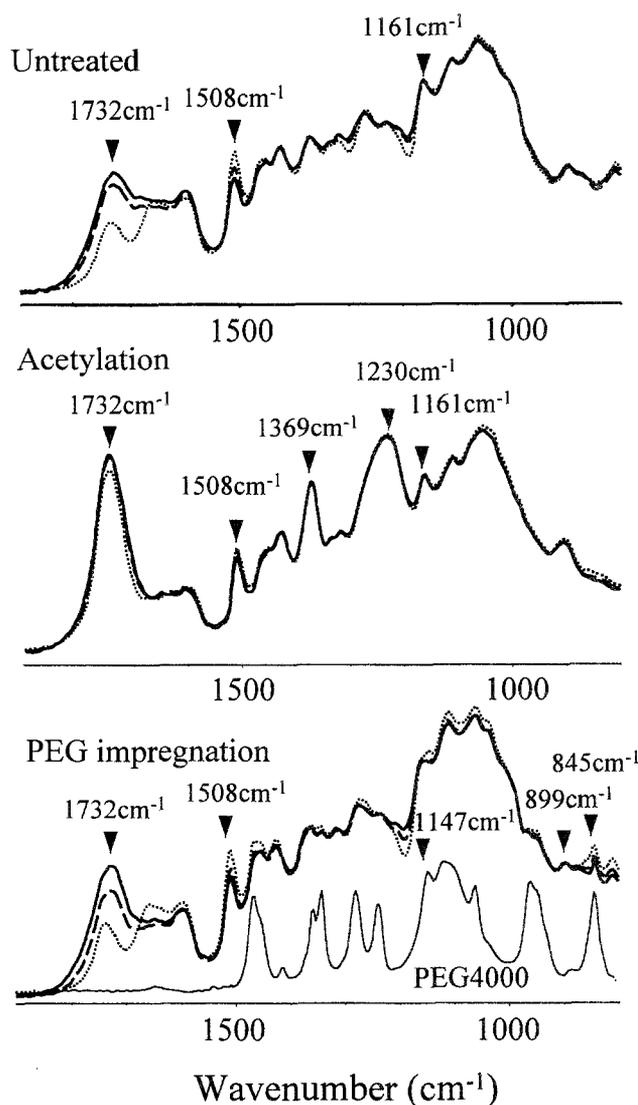


Fig. 3. Fourier transformed infrared-photoacoustic spectroscopy (FTIR-PAS) spectra of untreated, acetylated, and PEG-impregnated hinoki wood before and after light irradiation. *Dotted line*, nonirradiated; *broken and thick lines*, irradiated for 50 and 100h, respectively; *thin line*, PEG4000

acetyl groups. The increase of absorbance at 1732 cm^{-1} and the decrease at 1508 cm^{-1} in the acetylated specimen after light irradiation were much smaller than in the untreated specimen. Owen et al.³ obtained a similar result using diffuse reflectance spectroscopy. The small increase at 1732 cm^{-1} may include the changes in acetyl carbonyl, as there is a possibility of deacetylation during light irradiation. The changes in absorbance of both CH₃ and C—O in acetyl groups at 1369 and 1230 cm^{-1} were small in the PAS spectra after light irradiation, as shown in Fig. 3. The changes in R_{AcetylCH_3} and $R_{\text{AcetylC—O}}$ with irradiation time are shown in Fig. 4. These ratios changed little with increasing irradiation time. The means of R_{AcetylCH_3} and $R_{\text{AcetylC—O}}$ of the four wood species after irradiation for 100h were 0.99 and 0.97, respectively. This indicates that the acetyl groups were not easily removed from wood during light irradiation. The deacetylation was unlikely to have been caused by the long

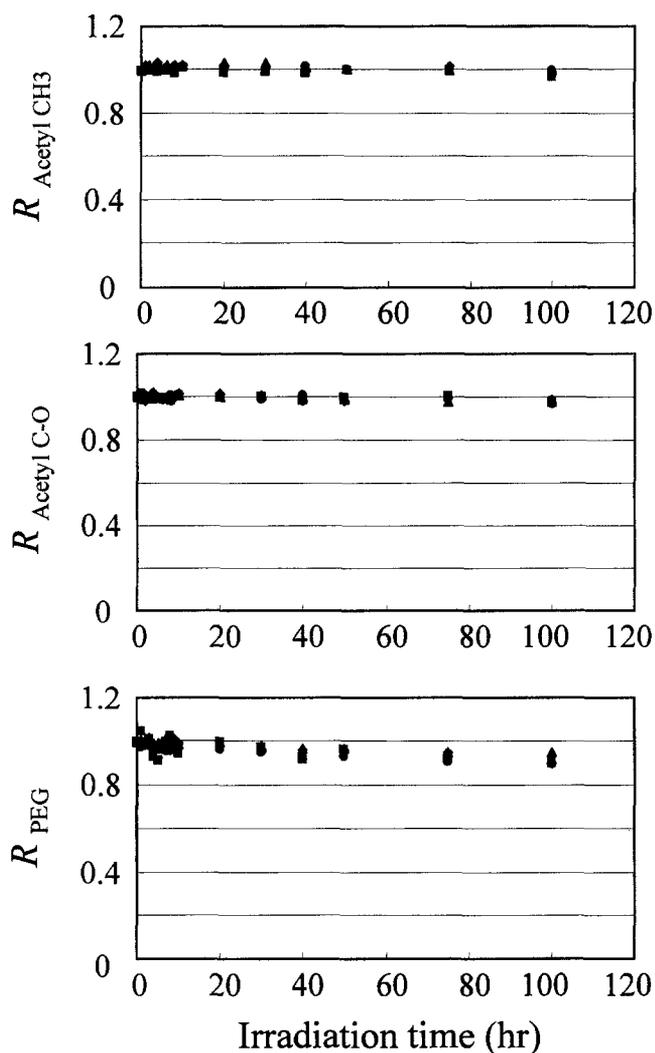


Fig. 4. Changes in the ratios of acetyl (R_{AcetylCH_3} and $R_{\text{AcetylC-O}}$) and PEG (R_{PEG}) in acetylated and PEG-impregnated wood with light irradiation times. Rhombi, sugi; circles, hinoki; triangles, karamatsu; squares, akamatsu

irradiation times because the color change did not increase with increasing irradiation time, as mentioned above. Therefore, it is concluded that the small change in absorption at 1732 cm^{-1} after light irradiation was mostly due to the photochemical degradation of wood components. These results indicate that acetylation restrained the photochemical degradation of wood.

The ratios ($R_{\text{C=O}100}$) of carbonyl generation after irradiation for 100h are shown in Fig. 5. In the untreated specimens, the $R_{\text{C=O}100}$ of SG was the largest, being 2.5. This indicates that the amount of carbonyl after irradiation was 2.5 times as large as that before irradiation. The ratios for the other species ranged from 1.7 to 1.9. On the other hand, the ratios of all the acetylated specimens were about 1.05, ranging from 1.0 to 1.1. This indicates that less carbonyl was generated in the acetylated wood specimens than in the untreated ones during light irradiation.

Figure 6 shows the ratios of the decrease in lignin ($R_{\text{Lignin}100}$) after light irradiation for 100h. The $R_{\text{Lignin}100}$ of the

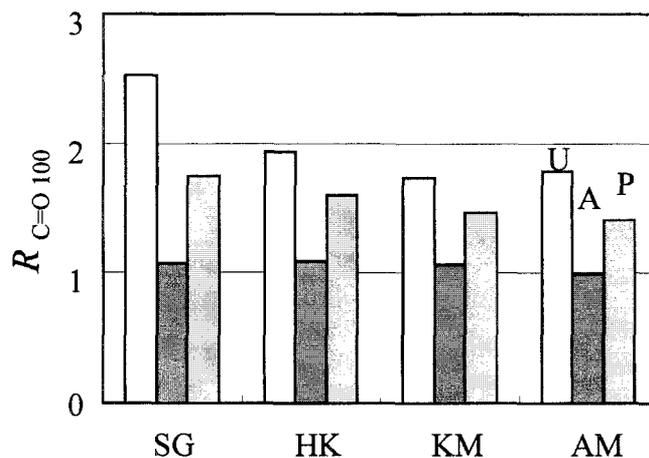


Fig. 5. Ratios ($R_{\text{C=O}100}$) of carbonyl generation in untreated, acetylated, and PEG-impregnated wood after light irradiation for 100h. Abbreviations are the same as described in the text and in Fig. 2

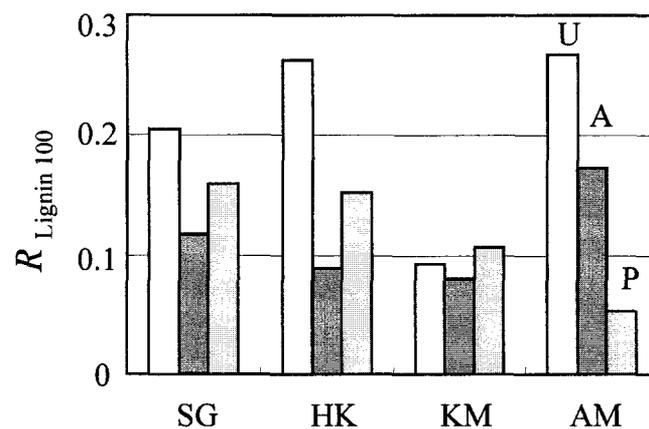


Fig. 6. Ratios ($R_{\text{Lignin}100}$) of lignin degradation in untreated, acetylated, and PEG-impregnated wood after light irradiation for 100h. Abbreviations are the same as described in the text and in Fig. 2.

KM specimen was smaller than that of other species. This small degradation of lignin may be characteristic of KM wood. The $R_{\text{Lignin}100}$ in the acetylated specimens of the other wood species was much smaller than in untreated ones, which indicates that the acetylation restrained lignin degradation caused by light. This may be related to the small degree of carbonyl generation.

Effect of PEG impregnation on photochemical degradation of wood surface

In the PEG-impregnated specimens, absorption due to C—O—C stretching in polysaccharides at 1161 cm^{-1} overlapped the out-of-phase stretching of C—O in PEG¹³ at 1147 cm^{-1} , as shown in Fig. 3. Therefore, the absorbance due to β -linkage in polysaccharides at 899 cm^{-1} was taken as standard instead of the absorption at 1161 cm^{-1} . The absorption of carbonyl at 1732 cm^{-1} increased and that of lignin at

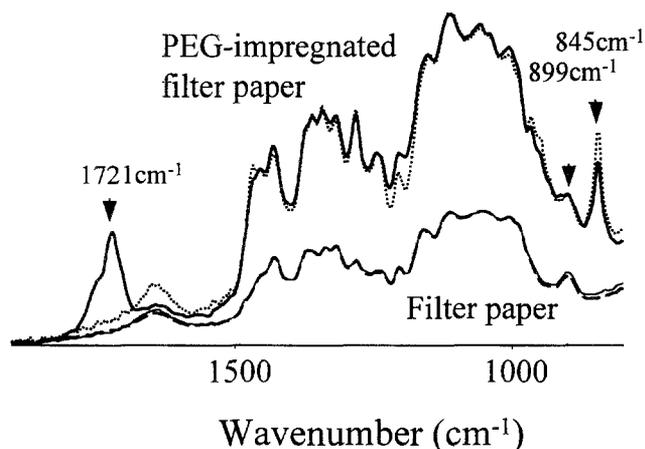


Fig. 7. FTIR-PAS spectra of the filter paper and PEG-impregnated filter paper before and after light irradiation for 100h. Dotted and thin lines, nonirradiated; thick and broken lines, irradiated for 100h

1508cm^{-1} decreased in the PEG-impregnated specimens with the increase in light-irradiation times. These results indicate that the generation of carbonyl and the degradation of lignin progressed with the duration of light irradiation.

The absorption due to out-of-phase rocking of CH_2 in PEG at 845cm^{-1} decreased also during the light irradiation. The changes of R_{PEG} with light-irradiation time are shown in Fig. 4. The R_{PEG} decreased a little with the increase in irradiation time. The mean of R_{PEG} in four species was 0.91 after 100h of irradiation. This decrease is supposedly due to the degradation of PEG during light irradiation. Longer light irradiation should degrade more PEG, thereby reducing the effect of PEG treatment. This is thought to be the reason for the increase in ΔE_{ab}^* brought about by the increase in irradiation time from 100 to 1000h, as shown in Fig. 2.

The PEG degraded by light may have produced the carbonyl. Figure 7 shows the PAS spectra of the PEG-impregnated filter paper before and after light irradiation for 100h versus the spectra of filter paper alone. The spectrum of filter paper without PEG did not change after light irradiation. On the other hand, the absorption of CH_2 in PEG at 845cm^{-1} was decreased after irradiation in the PEG-impregnated filter paper, similar to the PEG-impregnated wood. The absorption of carbonyl at 1721cm^{-1} was observed after light irradiation in the PEG-impregnated filter paper. Turi¹⁸ reported that heated PEG was at first broken down into lower-molecular-weight compounds and then produced acetaldehyde. The same reaction is thought to occur during light irradiation; that is, PEG was degraded by light, and the carbonyl was generated as a by-product. The same reaction should occur also in the PEG-impregnated wood. Therefore, the carbonyl produced by degradation of PEG should have been included in the increase of carbonyl with irradiation, as shown in Fig. 3.

The ratios of carbonyl generation in the PEG-impregnated specimens after light irradiation for 100h ($R_{\text{C=O}100}$) are shown in Fig. 5. These $R_{\text{C=O}100}$ ratios were smaller than those of untreated specimens. The ratios due only to the

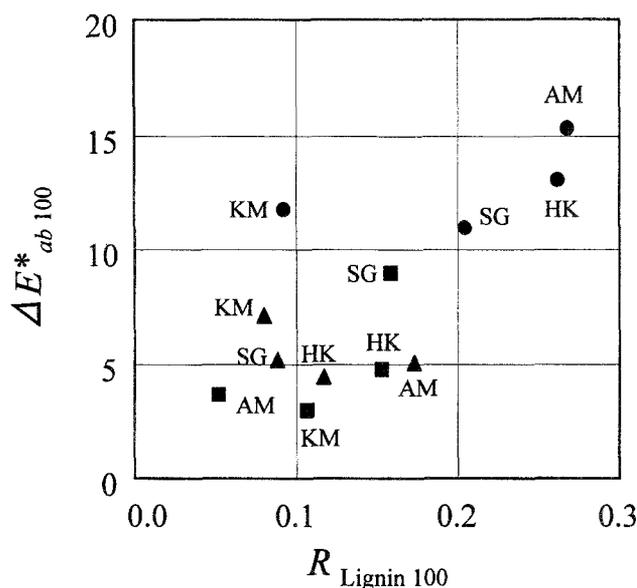


Fig. 8. Relation between the color difference ($\Delta E_{\text{ab}100}^*$) and the ratio of lignin degradation ($R_{\text{Lignin}100}$) of untreated, acetylated, and PEG-impregnated wood after light irradiation for 100h. Symbols are the same as in Fig. 1; abbreviations are the same as described in the text

degradation of wood components should be smaller than the observed ratios for the reason mentioned above. Based on these facts, it is clear that PEG impregnation decreased the generation of carbonyl during light irradiation.

The absorbance of lignin at 1508cm^{-1} did not overlap that due to PEG in PEG-impregnated specimens, as shown in Fig. 3. Therefore, the absorbance is related only to lignin in wood. Figure 6 shows the ratios of the decrease in lignin after light irradiation for 100h ($R_{\text{Lignin}100}$). In the PEG-impregnated specimens, $R_{\text{Lignin}100}$ was smaller than that of the untreated one except for KM, which exhibited little degradation of lignin even in the untreated specimen. This indicates that PEG impregnation restrained lignin degradation during light irradiation, but the effect should be reduced by the increase in PEG degradation with increased irradiation time. This would explain the increased color changes with increasing irradiation time.

Relation between color difference and lignin degradation

The color changes of wood during light irradiation are related to the photooxidation of lignin and wood extractives.¹⁹ Figure 8 shows the relation between the color difference ($\Delta E_{\text{ab}100}^*$) and the ratios of lignin degradation of untreated, acetylated, and PEG-impregnated wood specimens after light irradiation for 100h ($R_{\text{Lignin}100}$). The correlation coefficient between these factors was 0.72. The KM specimens showed a tendency different from that of the other specimens. Although the $\Delta E_{\text{ab}100}^*$ of two treated KM specimens was smaller than that of the untreated one, the $R_{\text{Lignin}100}$ was almost the same among these KM specimens. This indicates that the color change of KM specimens during light irradiation was not related to lignin degradation. The extractives may have influenced the color changes of

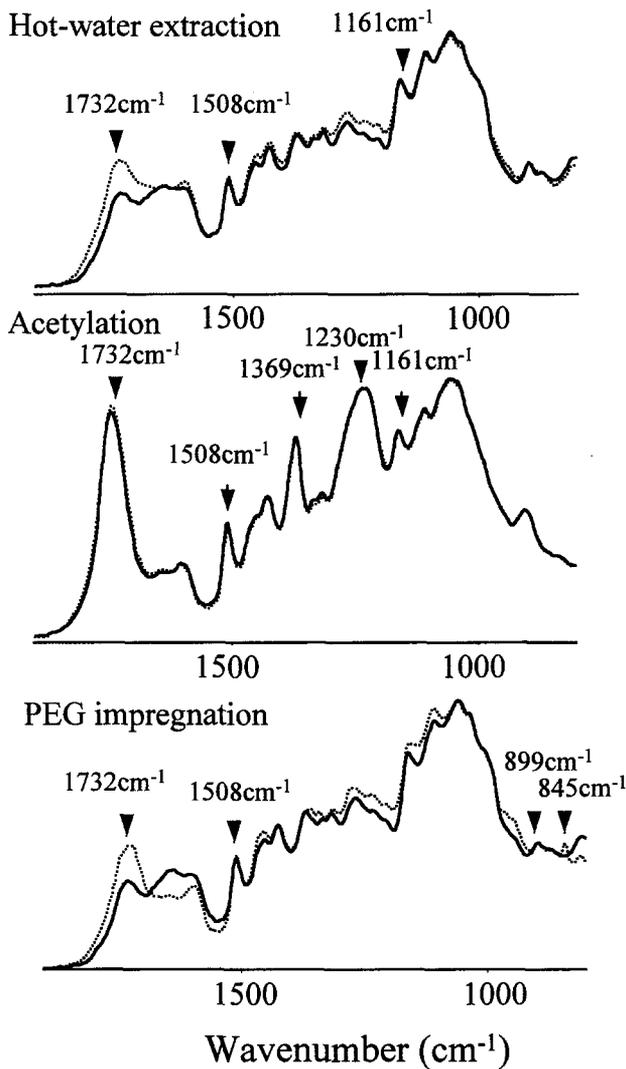


Fig. 9. FTIR-PAS spectra of hot-water-extracted, acetylated, and PEG-impregnated hinoki wood after light irradiation for 100h and subsequent water treatment. *Dotted lines*, light-irradiated for 100h; *solid lines*, water-treated after light irradiation for 100h

KM specimens due to light irradiation. Except for the KM specimens, the estimated correlation coefficient was 0.90. This high value indicates that the color changes during light irradiation significantly depend on lignin degradation in softwoods, except KM. Thus, the chemical modification reduced lignin degradation due to light irradiation and consequently decreased the color difference.

Changes in carbonyl contents by water treatment after light irradiation

The PAS spectra of water-treated HK specimens are shown in Fig. 9. The absorbance of lignin at 1508cm^{-1} was not decreased by the water treatment in the hot water-extracted, acetylated, and PEG-impregnated specimens. This indicates that the lignin remaining after light irradiation was insoluble in water.

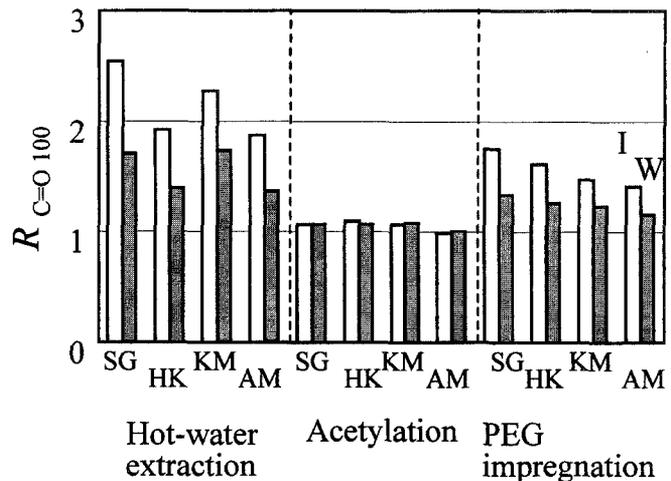


Fig. 10. Ratios ($R_{C=O100}$) of carbonyl generation in hot-water-extracted, acetylated, and PEG-impregnated wood after light irradiation for 100h and subsequent water treatment. *I*, light irradiation for 100h; *W*, water treatment after irradiation for 100h. Abbreviations are the same as described in the text

On the other hand, the absorbance of carbonyl at 1732cm^{-1} was largely decreased in the hot water-extracted specimens by the water treatment, as shown in Fig. 9. The $R_{C=O100}$ values before and after water treatment are shown in Fig. 10. In the hot water-extracted specimens, the proportion of $R_{C=O100}$ after water treatment relative to that before treatment was 0.76, on average, for four wood species (range 0.67–0.89). This indicates that light irradiation partly produced the water-soluble compounds containing the carbonyl.²⁰ These compounds should have been produced from lignin and extractives degraded by light. Such results suggest that the following situation occurs in the weathermeter test or during outdoor weathering of wood: The water-soluble compounds produced during light irradiation are flushed away by sprayed water or rainwater. The fresh wood surface thus revealed is photochemically degraded by light. The repetition of this process weathers wood.

In the acetylated specimens, the absorption at 1732cm^{-1} was little decreased by water treatment, as shown in Fig. 9. The $R_{C=O100}$ ratio after water treatment compared to that before treatment was 1.00, on average, for four wood species (range 0.98–1.01). The absorption due to acetyl carbonyl overlapping with carbonyl at 1732cm^{-1} should not have been decreased by water treatment, because the absorption of acetyl groups at 1369 and 1230cm^{-1} did not change. There was little carbonyl generated in acetylated wood during light irradiation, as shown in Fig. 5. This is thought to be the reason for the small change in $R_{C=O100}$ due to the water treatment. These results suggest that acetylation has an effect on weatherability in the weathermeter test and during outdoor weathering.

In the PEG-impregnated specimens, the absorbance of carbonyl at 1732cm^{-1} was largely decreased by the water treatment, as shown in Fig. 9. The $R_{C=O100}$ ratio after water treatment compared to that before treatment was 0.80, on average, for four wood species (range 0.76–0.84). The

carbonyl was generated not only by degradation of the wood components but also by degradation of PEG during light irradiation, as mentioned above. The PEG in wood should have been flushed away during water treatment because PEG is water-soluble. This is clear from the disappearance of the absorption of PEG at 845cm^{-1} after water treatment, as shown in Fig. 9. Therefore, the decrease of carbonyl observed after water treatment should include the flushing away of both degraded products containing carbonyl. These findings suggest that sprayed water or rainwater flushes away PEG during the weathermeter test or outdoor weathering, thereby decreasing the effect of PEG impregnation on weatherability. The PEG-impregnated wood surface should be coated with paint to protect against the flushing away of PEG.

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References

1. Feist WC, Rowell RM, Ellis WD (1991) Moisture sorption and accelerated weathering of acetylated and methacrylated aspen. *Wood Fiber Sci* 23:128–136
2. Plackett DV, Dunningham EA, Singh AP (1992) Weathering of chemically modified wood: accelerated weathering of acetylated radiata pine. *Holz Roh Werkstoff* 50:135–140
3. Owen JA, Owen NL, Feist WC (1993) Scanning electron microscope and infrared studies of weathering in southern pine. *J Mol Struct* 300:105–114
4. Leary GJ (1968) The yellowing of wood by light. Part II. *TAPPI* 51:257–260
5. Dawson B, Torr K (1992) Spectroscopic and colour studies on acetylated radiata pine exposed to UV and visible light. *Bulletin of the Pacific Rim Bio-based Composites Symposium, Chemical Modification of Lignocellulosics* in Lotolua, pp 41–51
6. Hon DN-S (1995) Stabilization of wood color: is acetylation blocking effective? *Wood Fiber Sci* 27:360–367
7. Dunningham EA, Plackett DV, Singh AP (1992) Weathering of chemically modified wood: natural weathering of acetylated radiata pine: preliminary results. *Holz Roh Werkstoff* 50:429–432
8. Kalnins MA (1984) Photochemical degradation of acetylated, methylated, phenylhydrazine-modified, and ACC-treated wood. *J Appl Polym Sci* 29:105–115
9. Torr KM, Dawson BSW, Ede RM, Singh J (1996) Surface changes on acetylation and exposure to ultraviolet radiation of *Pinus radiata* using X-ray photo-electron spectroscopy. *Holzforschung* 50:449–456
10. Minemura N, Umehara K (1979) Color improvement of wood. I. Photoinduced discoloration and its control (in Japanese). *Rep Hokkaido For Prod Res Inst* 68:92–145
11. Anderson EL, Pawlak Z, Owen NL, Feist WC (1991) Infrared studies of wood weathering. I. Softwoods. *Appl Spectrosc* 45:641–647
12. Pandey KK, Theagarajan KS (1997) Analysis of wood surfaces and ground wood by diffuse reflectance (DRIFT) and photoacoustic (PAS) Fourier transform infrared spectroscopic techniques. *Holz Roh Werkstoff* 55:383–390
13. Suga T (1988) Taikoukou to shikisai (in Japanese). Suga Shikenki, Tokyo, pp 17–34
14. Matsui Y, Kubota T, Tadokoro H, Yoshihara T (1965) Raman spectra of polyethers. *J Polym Sci A* 3:2275–2288
15. Hon DN-S, Ifju G (1978) Measuring penetration of light into wood by detection of photo-induced free radicals. *Wood Sci* 11:118–127
16. Kataoka Y, Kiguchi M (2001) Depth profiling of photo-induced degradation in wood by FT-IR microspectroscopy. *J Wood Sci* 47:325–327
17. Kuo M-L, McClelland JF, Luo S, Chien P-L, Walker RD, Hse C-Y (1988) Application of infrared photoacoustic spectroscopy for wood samples. *Wood Fiber Sci* 20:132–145
18. Turi CJ (1959) Ricerche analitiche sui tensioattivi.—Nota I.—I Poliosietilenglicoli. *Rend Ist Super Sanita* 22:174–188
19. Feist WC, Hon DN-S (1984) Chemistry of weathering and protection. In: Rowell RM (ed) *The chemistry of solid wood*. American Chemical Society, Washington DC, pp 401–451
20. Tolvaj L, Faix O (1995) Artificial ageing of wood monitored by DRIFT spectroscopy and CIE $L^*a^*b^*$ color measurements. *Holzforschung* 49:397–404