

NOTE

Yanni Sudiyani · Yuji Imamura · Shuichi Doi
Shigeru Yamauchi

Infrared spectroscopic investigations of weathering effects on the surface of tropical wood

Received: October 22, 2001 / Accepted: February 20, 2002

Abstract Two Fourier transform infrared spectroscopic techniques, photoacoustic and diffuse reflectance spectroscopy, were utilized to explore the physical and chemical changes in wood caused by weathering. Five tropical wood species (albizia, kapur, mahoni, nangka, puspa) were exposed to natural weathering for various periods. The contents of extracts, phenolics, and Klason lignin in unexposed samples of these wood species were determined by chemical analysis. Infrared spectra of the weathered surfaces were recorded by the two techniques. The photoacoustic spectra exhibited rapid decomposition and elusion of wood constituents containing benzene rings in the region closest to the exposed surface. Line maps of infrared spectra in the vertical direction obtained by diffuse reflectance infrared microspectroscopy were consistent with the view that the additive effects of water and ultraviolet irradiation play an important role in destroying the lignin-hemicellulose matrix of the cell wall. The infrared spectroscopic techniques are available for the analysis of weathered wood.

Key words Weathering · Surface · Infrared spectroscopy · Photoacoustic spectroscopy · Tropical wood

Introduction

Rapid deterioration with outdoor exposure is a major disadvantage to the use of wood and wood-based materials for engineering and structural applications. Indoors, the characteristic appearance of wood surfaces changes little in the short term. Outdoors, however, changes in color and texture proceed rapidly. The weathering of wood is caused by the combined effects of sunshine, rainfall, oxygen and other reactive species, dust, and variations of temperature and moisture.^{1,2} Solar irradiation containing ultraviolet (UV) rays is a dominant factor causing depolymerization of lignin in the cell wall matrix, and the subsequent washing away of decomposition products by rainfall facilitates erosion.

Clarification of the changes in wood properties caused by weathering is of fundamental importance to improved weatherability. We have investigated the weathering effects on sugi (*Cryptomeria japonica* D. Don), a softwood species cultivated in Japan, and albizia (*Paraserianthes falcata* Becker), a fast-growing hardwood species in the tropics.^{3,4} To explore the chemical changes of wood constituents near the weathered surface, infrared and electron spin resonance (ESR) spectroscopic techniques were employed in addition to chemical analysis. Significant findings have been reported.⁴ However, better use could not be made of infrared spectroscopy for analysis of wood surfaces, as the infrared spectra were obtained by a transmission method.

With improved spectrometers and accessories and establishment of a mathematical process utilizing the Fourier transformation, several infrared spectroscopic techniques such as diffuse reflectance,^{5–10} attenuated total reflectance,^{11,12} and photoacoustic method^{9,13} have been applied to studies of wood and wood-based materials.

In this study the infrared spectra of five tropical wood species were measured by photoacoustic and diffuse reflectance techniques to obtain more information about the weathered surfaces of wood. Reported herein are the infrared spectra for tropical wood species weathered in Indonesia. Also presented are line maps of the diffuse reflectance spectra in the vertical direction obtained by microscopy.

Y. Sudiyani
Research and Development Center for Applied Physics, LIPI,
Serpong, Tangerang 13510, Indonesia

Y. Imamura
Wood Research Institute, Kyoto University, Kyoto 611-0011, Japan

S. Doi · S. Yamauchi (✉)
Institute of Wood Technology, Akita Prefectural University,
Kaiaisaka, Noshiro, Akita 016-0876, Japan
Tel. +81-185-52-6984; Fax +81-185-52-6976
e-mail: sigeru@iwt.akita-pu.ac.jp

Materials and methods

Wood samples

Twenty-four heartwood blocks measuring 45 mm (L) × 45 mm (T) × 3 mm (R) were cut from each tropical wood species. Table 1 summarizes the common, scientific, and family names, densities, and original colors of wood species used in this study. The tangential surface of the blocks was flattened and smoothed with a planer machine and subsequently exposed to natural weathering. Figure 1 depicts the wood block and a sample cut from the block that was used for measuring the line map by diffuse reflectance infrared Fourier transform (DRIFT) microspectroscopy.

Chemical analysis

Hot water extractions of wood samples were carried out according to ASTM-D 110–84.¹⁴ Wood powder passed

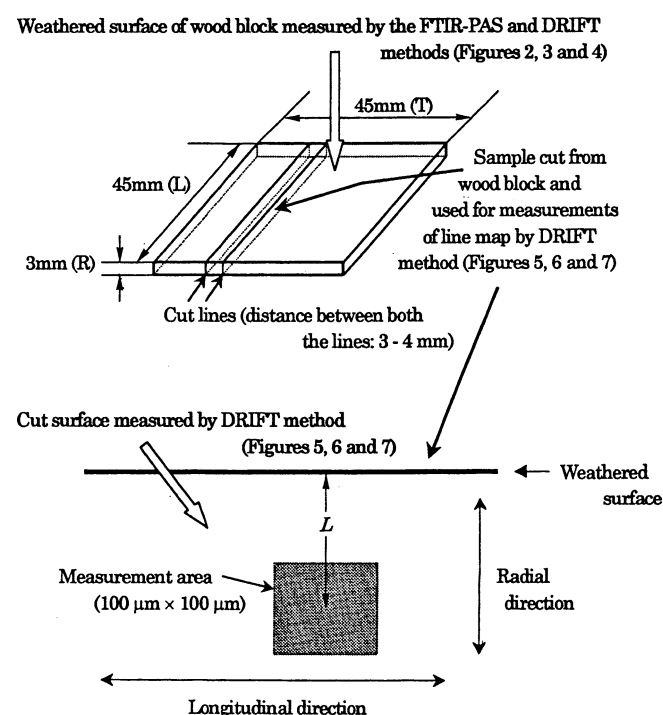


Fig. 1. Tested wood block and a sample cut from the block and used for measurements of the line map by diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy and measurement area on a cut surface of the sample. *L*, distance from the weathered surface to the center of the area; FTIR-PAS, Fourier transform infrared photoacoustic spectroscopy; *R*, radial; *T*, tangential

through an 80-mesh sieve was introduced together with deionized water into a flask attached to a reflux condenser. The flask was gently heated for 3 h. The yield of hot water extracts was calculated from the weight loss of the wood powder after the extraction.

Ethanol–benzene extracts were obtained by successive extraction of the wood powder in a Soxhlet extractor using an ethanol–benzene (1:2, v/v) mixture as a solvent for more than 24 h until the eluent became colorless. The yield of the extracts was measured after oven-drying at 105°C for 6 h.

For determining Klason lignin, the wood powder remaining after extraction by ethanol–benzene was hydrolyzed with sulfuric acid at ambient temperature for 2 h. The resulting mixture was diluted with water and autoclaved at 120°C for 2 h. Subsequently, the insoluble substance was separated with a glass filter and then dried at 105°C for 6 h.

The wood powder extracted by benzene was refluxed in water for 3 h, filtered, and then washed with boiling water six times. The whole filtrate was boiled with hydrochloric acid and formaldehyde solution for 30 min. To determine the phenolics content, the precipitate that resulted after boiling was filtered and dried at 105°C for 2 h. The mean value for each chemical analysis was obtained from three replications.

Natural weathering conditions

Test blocks of all the tropical wood species were exposed in Serpong, Indonesia for 2–32 weeks (September 2000 to April 2001) at an inclination of 5° from the horizontal facing east, at a height of 1 m above the ground. The meteorological data obtained during the exposure test are given in Table 2. The test blocks were set outside without any cover from the rain and wind. All the exposure tests started on September 1, 2000.

Infrared analysis

Fourier transform infrared photoacoustic spectroscopy

Fourier transform infrared photoacoustic spectroscopy (FTIR-PAS) spectra were measured using a JEOL JIR 7000 W spectrometer connected to an IR-PAS module (IR/PAS 1000). All the spectra were obtained at 100 times accumulation and with a spectral resolution of 4 cm⁻¹. A circular piece 9 mm in diameter (thickness about 1 mm) was cut from the midsection of the weathered surface of each wood block and set in a thin cell of 10 mm diameter. Photoacoustic signals were collected on purging a cell bench with

Table 1. Names, densities, and original colors of heartwood samples

Common name	Scientific name	Family name	Air-dried density (g/cm ³)	Original color
Albizia	<i>Paraserianthes falcata</i> Becker	Leguminosae	0.38	Light brown
Kapur	<i>Dryobalanop lanceolata</i> Burck	Dipterocarpaceae	0.77	Dark brown
Mahoni	<i>Swietenia macrophylla</i> King	Meliaceae	0.65	Bright brown
Nangka	<i>Artocarpus heterophyllus</i> Lamk	Moraceae	0.69	Yellow
Puspa	<i>Schima wallichii</i> Korth	Theaceae	0.70	Pale brown

Table 2. Meteorological data at Serpong, Indonesia during the exposure test

Measurement duration	Temperature(°C)			Average RH (%)	Rainfall (mm)		UV irradiation (kJ/m ²)	
	Min.	Max.	Ave.		Total	Per week	Total	Per week
Sept. 1–14, 2000 (2 weeks)	26.6	28.0	27.3	85.0	4	2	8 125	4063
Sept. 15–28, 2000 (2 weeks)	26.0	27.4	26.7	87.3	108	52	15 508	3692
Sept. 29–Oct. 12, 2000 (2 weeks)	25.7	27.0	26.4	90.1	211	52	23 248	3870
Oct. 13–26, 2000 (2 weeks)	26.0	27.6	26.9	89.0	296	43	31 638	4195
Oct. 27–Dec. 21, 2000 (8 weeks)	25.9	27.2	26.6	90.8	656	45	67 317	4460
Dec. 22, 2000–April 12, 2001 (16 weeks)	25.5	26.6	26.0	92.8	1807	72	135 265	4247

Total rainfall and UV irradiation are cumulative values from September 1, 2000 to the last day of the duration

Min., minimum; Max., maximum; Ave., average; RH, relative humidity; UV, ultraviolet

dry nitrogen. The velocity of the moving mirror was fixed at 1.6 mm/s through all the measurements. Carbon black was used as a reference sample.

DRIFT microspectroscopy

DRIFT spectra were recorded using the spectrometer equipped with a liquid nitrogen-cooled MCT detector and through a Nikon optical microscope (total magnification 400×). The apertures and step size were set at 100 × 100 μm and 50 μm, respectively. Fifty scans were summed in each spectrum at 4 cm⁻¹ resolution. The spectra were obtained by measuring the center of the weathered surface of the circular piece used for the PAS measurement. The line map of diffuse reflectance spectra was measured on a cut surface in the vertical direction (Fig. 1). The spectra were ratioed against an Au mirror background.

Results and discussion

FTIR-PAS

The FTIR-PAS technique probes mainly wood samples within a short distance from the surface. The distance is determined by the shorter of two lengths (thermal and optical wave decay lengths). The former (thermal sensing depth d) is controllable by the moving mirror velocity and for an opaque sample such as wood is calculated^{9,13} by $d = 1/a_s = (D/\pi g \nu)^{1/2}$, where a_s is the thermal wave decay coefficient, D is the thermal diffusivity of the sample, g is the moving mirror velocity, and ν is the frequency. The velocity of the moving mirror in this study was adjusted to 1.6 mm/s, and the typical thermal diffusivity of wood is 2.0×10^{-3} cm²/s.¹³ According to calculations with these values, the thermal sensing depth ranges between 14 μm (2000 cm⁻¹) and 22 μm (800 cm⁻¹).

The latter length, the optical sensing depth ($1/\alpha$), is represented as a reciprocal of the optical wave decay coefficient (α) depending on the wavenumber; it ranges from about 5 μm (2000 cm⁻¹) to 12–13 μm (800 cm⁻¹) for a typical wood sample.¹³ In practice, it is difficult to evaluate the actual thermal and optical sensing depths accurately because wood is a porous, anisotropic material and the D

value varies with weathering in the neighborhood of the surface. It is possible, however, to use the d and $1/\alpha$ values as tentative criteria for surface analysis of weathered wood. Thus the weathering effects were investigated on the assumption that the FTIR-PAS spectra in the wavenumber region probed the samples within a depth of about 20 μm from the weathered surface.

The results of chemical analysis of the unexposed wood samples are summarized in Table 3. Nangka and mahoni have more extracts and phenolics than the other three species, so the tropical wood species used in this study can roughly be divided into two groups based on extract contents.

Figures 2 and 3 show the FTIR-PAS spectra of the surfaces of puspa and nangka weathered for various periods, respectively. The unexposed samples were similar to each other in terms of spectral contour except for the relative intensity of the bands at about 1650 cm⁻¹, which are attributed to a stretching vibration of C=O conjugated with an aromatic ring,^{15,16} and at 1460 cm⁻¹, which is assigned to deformation of CH₃ and CH₂. Other wood species closely resembled puspa in terms of the spectral outline, and their bands at 1650 cm⁻¹ were not as strong as that of nangka. The large total amount of ethanol–benzene extract, lignin, and phenolics in nangka (Table 3) is presumably one reason for such a strong band at 1650 cm⁻¹.

Inspection of the spectra in Figs. 2 and 3 reveals that the two wood species show the same spectral changes on weathering. The intensities of the bands at 1735, 1592, 1503, 1460, and 1235 cm⁻¹ apparently decrease; and some nearly disappear as exposure proceeds. According to previous studies,^{17–19} the band at 1735 cm⁻¹ is mainly due to xylan, the bands at 1460 and 1235 cm⁻¹ are caused by both lignin and xylan, and the bands at 1592 and 1503 cm⁻¹ are attributed to the benzene ring in lignin. By contrast, the vibrations at 1422, 1370, and 1315 cm⁻¹, which are primarily due to cellulose, demonstrate no marked change in the FTIR-PAS spectra. In addition, a weak band seems to appear at about 1200 cm⁻¹.

The same spectral changes were also observed for other wood species and are compatible with the results of the infrared analysis by the transmission method for weathered albizia.⁴ Hence the chemical changes of wood constituents indicated in our previous report fundamentally apply to all the wood species in this study. However, the changes in

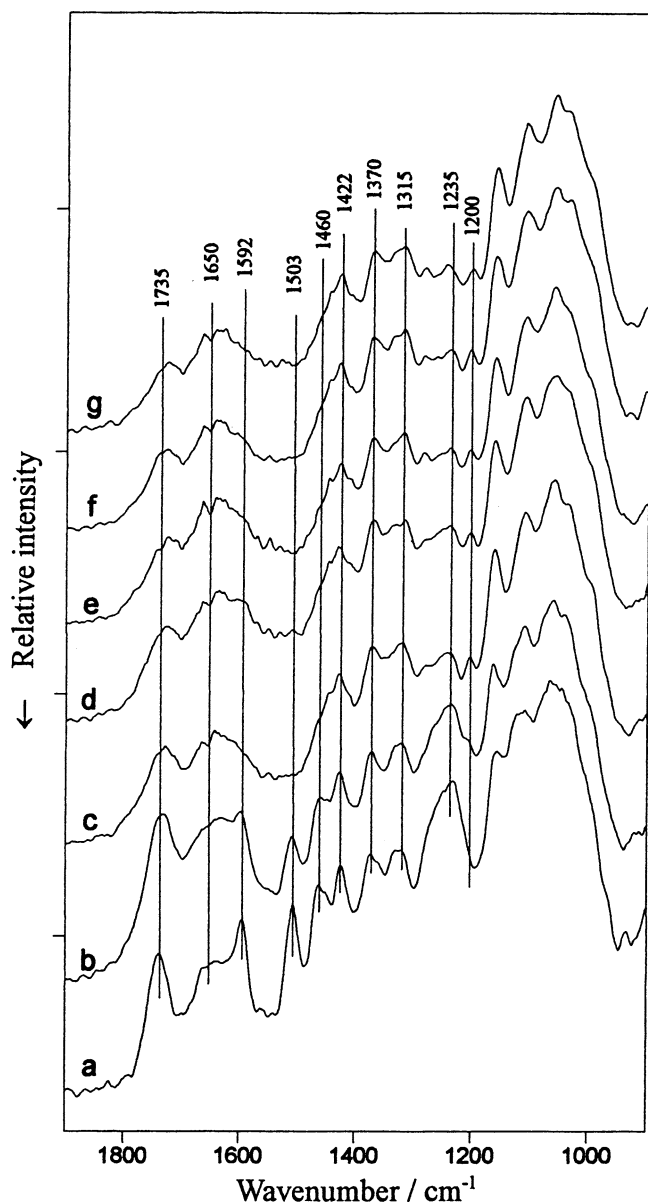


Fig. 2. FTIR-PAS spectra of the surfaces of puspa weathered for various periods. *a*, Unexposed; *b*, 2 weeks; *c*, 4 weeks; *d*, 6 weeks; *e*, 8 weeks; *f*, 16 weeks; *g*, 32 weeks

FTIR-PAS spectra are more marked than those in the transmission spectra and are observable in the samples weathered for only 2 weeks, as shown in Fig. 2b. This suggests that FTIR-PAS provides us with information on the region closest to the surface and is a useful, convenient technique for exploring the effects of weathering on wood.

As mentioned above, the bands at 1503 and 1460cm^{-1} for puspa are markedly reduced, and the band at 1592cm^{-1} also decreases during the second week. Such spectral changes, despite only a small amount of rainfall (4mm), indicate that the photochemical decomposition caused by sunlight occurs readily at a depth of about $20\mu\text{m}$. The reduction of these bands is nearly completed by the fourth week. Compared with these rapid decreases, the band at 1735cm^{-1} due to a C=O stretching vibration¹⁷⁻¹⁹ diminishes moderately, shifting to lower wavenumbers and broadening slightly with weathering. The shift and broadening may be due to the break and regeneration of a hydrogen bond $\text{C}=\text{O}\cdots\text{H}$ brought about through chemical change and the disruption of wood constituents. Moreover, the line

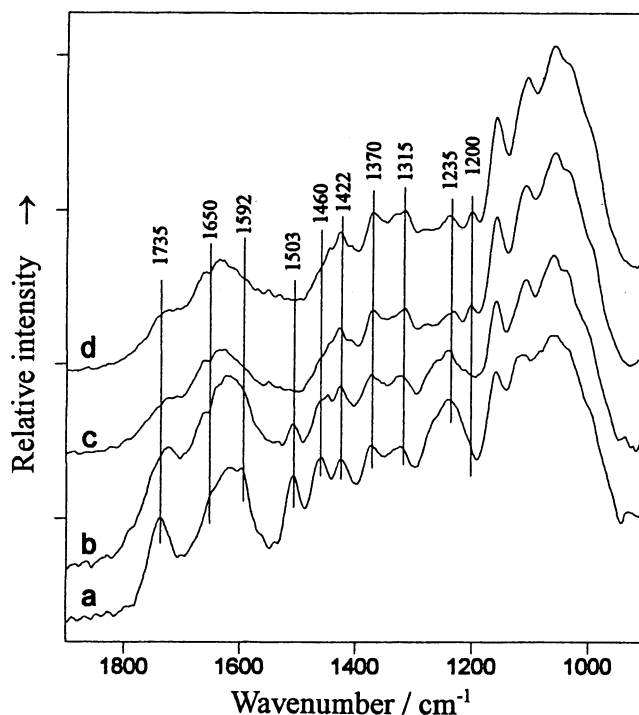


Fig. 3. FTIR-PAS spectra of the surfaces of nangka weathered for various periods. *a*, Unexposed; *b*, 8 weeks; *c*, 16 weeks; *d*, 32 weeks

Table 3. Chemical analysis of five wood species

Wood species	Hot water extracts (%)	EtOH-benzene extracts (%)	Klason lignin (%)	Phenolics (%)
Albizia	4.30 (0.15)	2.28	22.69 (1.82)	1.16 (0.05)
Kapur	4.62 (0.38)	2.30	29.79 (0.51)	1.77 (0.10)
Mahoni	8.06 (0.08)	5.73	25.73 (0.04)	7.16 (0.18)
Nangka	8.63 (0.28)	12.08	28.01 (0.11)	7.98 (0.35)
Puspa	4.38 (0.51)	1.98	24.28 (0.85)	0.25 (0.05)

Values in parentheses are standard deviations
Ethanol-benzene extracts have no replication

shapes at 1735 and 1235 cm^{-1} seem to vary continuously with outdoor exposure after the fourth week.

The bands at 1592, 1503, and 1460 cm^{-1} for albizia and kapur were observed to disappear rapidly with weathering. For albizia, even the bands at 1735 and 1235 cm^{-1} showed little spectral change after the eighth week.

It is well known that a band position at about 1600 cm^{-1} due to skeletal stretching vibration of the benzene ring is not particularly susceptible to substituent groups. Therefore, reduction of the band intensity at 1592 cm^{-1} indicates removal or decomposition of an aromatic ring rather than a chemical change in atomic groups on or around the aromatic ring. By contrast, the variations of line shapes at 1735 and 1235 cm^{-1} correspond to the various changes at the molecular level, decomposition, disordering, rearrangement, and elusion of wood constituent polymers because they show not only a reduction of band intensity but also a shift in band position.

The FTIR-PAS spectra of nangka (Fig. 3) demonstrate the same changes as those of puspa, described earlier. In contrast to puspa, however, the bands at 1503 and 1460 cm^{-1} , prominently due to lignin and phenolics, still decrease clearly from the 8th to the 16th week. During this period a similar but smaller decrease in the bands was observed for mahoni.

Based on the results of FTIR-PAS, the order in terms of spectrum-changing duration by weathering can be assumed to be as follows: nangka > mahoni > puspa, kapur > albizia. This order is almost in agreement with that for the total amount of lignin, phenolics, and extracts summarized in Table 3. Albizia presumably has the smallest amount because it has by far the lowest density (Table 1). Thus it can be presumed that the primary spectral changes correspond to the elusion of extracts and phenolics and the partial decomposition of a lignin polymer at a relatively early stage of weathering because FTIR-PAS spectra provide information on only the region closest to the weathered surface, although the chemical changes in other wood constituents certainly have some effect on the spectra.

DRIFT microspectroscopy

Figure 4 shows the DRIFT spectra of the weathered surface of puspa for various durations. Some of the DRIFT spectra, especially in the 1450–1200 cm^{-1} region, are not well resolved owing to spectral collapse, making it difficult to recognize a delicate spectral change by visual inspection. It was therefore mainly the bands at 1738, 1594, and 1508 cm^{-1} that distinctly showed the same changes with weathering as the corresponding bands in the FTIR-PAS spectra.

Line maps in the depth direction of the DRIFT spectra of puspa weathered for 2, 4, and 32 weeks are depicted in Figs. 5, 6, and 7, respectively. For the sample at the second week, the spectral features seem to be independent of the depth from the surface; furthermore, there is no distinct difference between the spectra of the weathered and unexposed puspa. In other words, the spectral contour is little influenced by weathering even in the spectrum obtained at

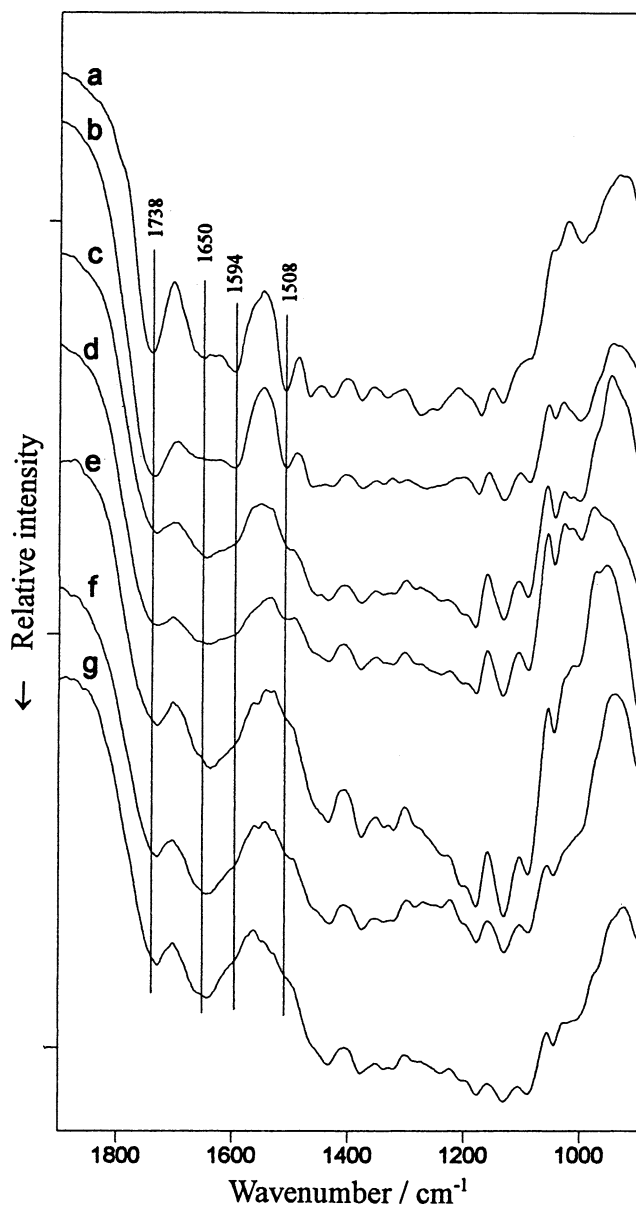


Fig. 4. DRIFT spectra of the surfaces of puspa weathered for various periods. a, Unexposed; b, 2 weeks; c, 4 weeks; d, 6 weeks; e, 8 weeks; f, 16 weeks; g, 32 weeks

the point nearest the surface (the first spectrum, $L = 50$). Because the first spectrum provides information from the surface to a depth of 100 μm , it is evident that the physical and chemical changes of wood constituents stopped at a depth much less than 100 μm .

The effects of weathering in the sample exposed for 4 weeks appear clearly in the first and second ($L = 100 \mu\text{m}$) spectra as a decrease in the bands at 1594 and 1508 cm^{-1} , respectively; It is likely that the same spectral changes occur even in the third ($L = 150 \mu\text{m}$) spectrum, although to a lesser degree. This reveals that the weathering effects reach much deeper during the fourth week than during the second week.

Most notable from the meteorological data is the marked increase in rainfall from the second to the fourth week. The

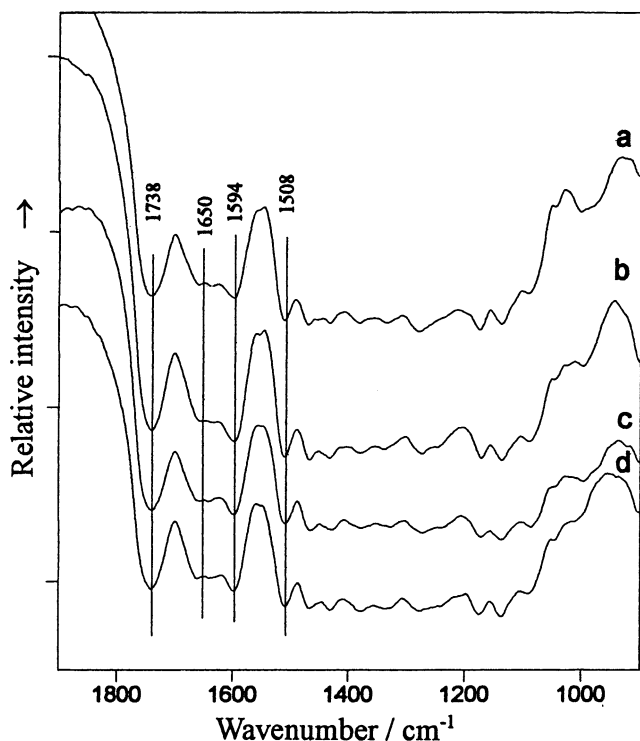


Fig. 5. Line map of DRIFT spectra of pupsa weathered for 2 weeks in the vertical direction. *a*, Unexposed; *b*, $L = 50\mu\text{m}$; *c*, $L = 100\mu\text{m}$; *d*, $L = 150\mu\text{m}$

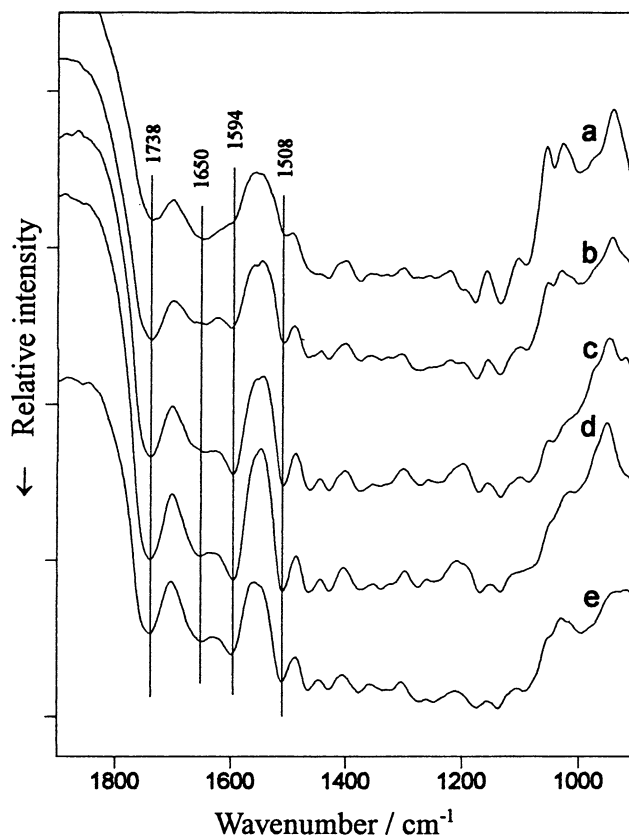


Fig. 7. Line map of DRIFT spectra of pupsa weathered for 32 weeks in the vertical direction. *a*, $L = 50\mu\text{m}$; *b*, $L = 100\mu\text{m}$; *c*, $L = 150\mu\text{m}$; *d*, $L = 200\mu\text{m}$; *e*, $L = 250\mu\text{m}$

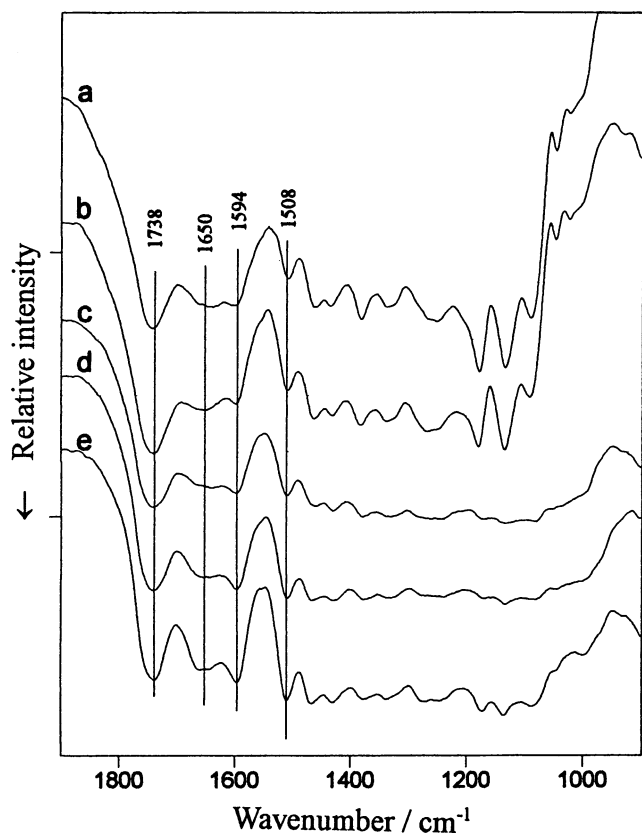


Fig. 6. Line map of DRIFT spectra of pupsa weathered for 4 weeks in the vertical direction. *a*, $L = 50\mu\text{m}$; *b*, $L = 100\mu\text{m}$; *c*, $L = 150\mu\text{m}$; *d*, $L = 200\mu\text{m}$; *e*, $L = 250\mu\text{m}$

rainfall was only 4mm for the first 2 weeks (September 1–14, 2000) compared with 104mm for the second period (September 15–28, 2000), although there was no significant difference in UV irradiation between the two periods. These results support the idea that water flashing accelerated the degradation of lignin polymer, causing further destruction of the lignin–hemicellulose matrix in cell walls.

The band intensities at 1594 and 1508 cm^{-1} in the first spectrum decrease more notably in the sample weathered for 32 weeks than in that weathered for 4 weeks (Figs. 6a, 7a). This proves that the chemical change and decomposition of wood constituents proceeded in the region closest to the surface. However, for both weathered samples, there appears to be no obvious change in the intensity of either band measured at deeper points ($L \geq 200\mu\text{m}$) than in the unexposed pupsa. The same tendency was observed in the other four species. A possible explanation for the unexpected results is the absence of UV light in deeper regions. It can be assumed that decomposition of lignin polymer does not proceed rapidly in regions UV rays cannot reach.

The weathering of wood is a complicated phenomenon involving many factors. In the present study this phenomenon was investigated using two infrared spectroscopy techniques: FTIR-PAS and DRIFT microspectroscopy. Based on the infrared measurements, further evidence was obtained that the combined effects of UV irradiation and water flashing play an important role in the destruction of

the cell wall matrix. Moreover, it was demonstrated that these spectroscopic techniques are suitable for analyzing weathered wood.

To obtain more information on the effects of weathering, we are currently studying depth profiling by FTIR-PAS and exploring refinement and two-dimensionalization of mapping by DRIFT microspectroscopy.

References

- Hon DNS (1991) Photochemistry of wood. In: Hon DN-S, Shiraishi N (eds) Wood and cellulosic chemistry. Marcel Dekker, New York, pp 525–555
- Evans PD, Michell AJ, Schmalzl KJ (1992) Studies of the degradation and protection of wood surface. Wood Sci Technol 26:151–163
- Sudiyani Y, Takahashi M, Imamura Y, Minato K (1999) Physical and biological properties of chemically modified wood before and after weathering. Wood Res 86:1–6
- Sudiyani Y, Tsujiyama S, Takahashi M, Imamura Y, Minato K, Kajita H (1999) Chemical characteristics of surface of hardwood and softwood deteriorated by weathering. J Wood Sci 45:348–353
- Yamauchi S, Matsuki Y, Ohta S, Okuno T, Tamura Y (2000) Vibrational spectroscopic studies on wood and wood-based materials. V. Infrared spectroscopic investigation for penetration behavior of isocyanate adhesives at wood-dowel joints (in Japanese). J Adhes Soc Jpn 36:250–258
- Evans PD, Wallis AFA, Owen NL (2000) Weathering of chemically modified wood surfaces: natural weathering of Scots pine acetylated to different weight gains. Wood Sci Technol 34:151–165
- Zanuttini M, Citroni M, Martinez MJ (1998) Application of diffuse reflectance infrared Fourier transform spectroscopy to the quantitative determination of acetyl groups in wood. Holzforschung 52:263–267
- Pandey KK, Khali DP (1998) Accelerated weathering of wood surfaces modified by chromium trioxide. Holzforschung 52:467–471
- Pandey KK, Theagarajan KS (1997) Analysis of wood surface and ground wood by diffuse reflectance (DRIFT) and photoacoustic (PAS) Fourier transform infrared spectroscopic technique. Holz Roh Werkst 55:383–390
- Kataoka Y, Kiguchi M (2001) Depth profiling of photo-induced degradation in wood by FT-IR microspectroscopy. J Wood Sci 47:325–327
- Jensen ES, Gatenholm P, Sellitti C (1992) An ATR-FTIR study on penetration of resins in wood. Angew Makromol Chem 200:77–92
- Denes AR, Tshabalala MA, Rowell R, Dens F, Young RA (1999) Hexamethyl-disiloxane-plasma coating of wood surface for creating water repellent characteristics. Holzforschung 53:318–326
- Kuo ML, McClelland JF, Luo S, Chien PL, Walker RD, Hse CY (1988) Applications of infrared photoacoustic spectroscopy for wood samples. Wood Fiber Sci 20:132–145
- ASTM standard D 1110–84 (1981; reapproved 1990) Annual book of ASTM, Philadelphia
- Bolker NI, Somerville NG (1963) Infrared spectroscopy of lignins. Part II. Lignins in unbleached pulps. Pulp Pap Mag Can 64: T187–193
- Sarkanen K, Chang HM, Ericsson B (1967) Species variation in lignins. I. Infrared spectra of guaiacyl and syringyl models. TAPPI 50:572–575
- Harrington KJ, Higgins HG, Michell AJ (1964) Infrared spectra of *Eucalyptus regnans* F. Muell and *Pinus radiata* D. Don. Holzforschung 18:108–113
- Michell AJ, Watson AJ, Higgins HG (1965) An infrared spectroscopic study of delignification of *Eucalyptus regnans*. TAPPI 48:520–532
- Lang CY, Bassett KH, McGinnes EA, Marchessault RH (1960) Infrared spectra of crystalline polysaccharides. VII. Thin wood sections. TAPPI 43:1017–1024