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Depth profiling of weathered tropical wood using Fourier transform infrared photoacoustic spectroscopy

Abstract Depth profiling analysis of wood samples using Fourier transform infrared photoacoustic spectroscopy (FTIR-PAS) was carried out to obtain information on the chemical changes caused by weathering. The test samples used for PAS measurements were tropical wood species, puspa (*Schima wallichii* Korth) and kapur (*Dryobalanop lanceolata* Burck), that were exposed outdoors for periods of 2–32 weeks. FTIR-PAS spectra of the weathered surfaces were recorded at various moving-mirror velocities in the range from 0.081 to 0.56cm/s (linear-scan method) to provide the depth profiling analysis. The band intensity of vibrations attributed to phenyl groups clearly decreased as weathering proceeded and demonstrated a tendency to be reduced with a decrease in the photoacoustic probing depth during relatively short weathering periods. The bands of C $=$ O groups also exhibited remarkable spectral changes. The PAS spectra of the tropical wood changed considerably during the 32 weeks of weathering, and their spectral contours gradually approached that of pure cellulose (microcrystalline). It was noted that FTIR-PAS is very useful for depth profiling analysis of the wood surface in the early stages of deterioration.

Key words Weathering · Surface · Photoacoustic spectroscopy · Depth profiling · Tropical wood

Introduction

Weathering leads to undesirable changes in the properties of wood, such as discoloring, roughening, and checking of the surface. Outdoor usage brings about decomposition and the washout of wood constituents. The deterioration of wood is facilitated by a combination of sunshine, rainfall, temperature, moisture, oxygen, dust, and other factors.[1,2] Although it is generally agreed that solar irradiation containing ultraviolet (UV) rays is the dominant causative factor in the depolymerization of lignin and destruction of the cell wall matrix, the mechanisms of this degradation have still not been completely elucidated at the molecular level.

Clarification of the chemical reactions in wood during weathering is of fundamental importance to the improvement of weatherability. We have studied the weathering effects on chemical and physical properties of Japanese cedar (*Cryptomeria japonica* D. Don) and several tropical wood species.[3–5] In these studies, infrared spectra of the weathered wood were recorded with the use of transmission, diffuse reflectance, and photoacoustic spectroscopic techniques to examine the chemical changes of wood constituents near the surface. In the past decade, infrared spectroscopic techniques have been employed as the main analytical tool in studies on the weathering of wood[6–10] because of the development of the spectrometer and accessories.

Fourier transform infrared photoacoustic spectroscopy (FTIR-PAS) has several characteristic features that distinguish it from other infrared techniques. One of them is that information on polymer materials can be obtained as a function of depth from the surface. Several depth profile studies of biological substances have been reported.[11–13] However, to our knowledge, there is no study applying FTIR-PAS to depth profiling of wood or wood-based materials, although FTIR-PAS spectra of wood were published by Kuo et al.,[14] Pandey and Theagarajan,[15] and Ohkoshi.[16] The primary reason for the limited use of FTIR-PAS is likely to be uncertainty over the optical and thermal proper-

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ties of wood, which is due to opacity, pores, and anisotropy. These factors make it difficult to accurately determine the actual probing depth. It is, however, quite possible to roughly estimate the probing depth and to investigate the effect of weathering on wood in the depth direction through FTIR-PAS measurements.

In order to acquire more information on the weathering phenomena in wood, we carried out a depth profiling analysis of the deteriorated regions of puspa (*Schima wallichii* Korth) and kapur (*Dryobalanop lanceolata* Burck), which are frequently employed in construction and furniture, with the use of an FTIR-PAS technique. Reported herein are the PAS spectra measured at various photoacoustic probing depths of tropical wood exposed outdoors in Indonesia.

Materials and methods

Wood samples

Wood blocks measuring 45 (L) × 45 (T) × 3 mm (R) were cut from heartwood of kapur and puspa. The tangential surface of the blocks was flattened and smoothed with a planer machine and subsequently exposed to natural weathering. Microcrystalline cellulose was purchased from Merck and used for PAS measurements as received.

Natural weathering conditions

A tangential sectional surface of kapur and puspa samples was 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. A sample block of both the species for FTIR-PAS measurements was prepared for each weathering period. The data on rainfall and sunlight irradiation are summarized in Table 1. The temperature and relative humidity during the exposure test ranged from 25.5°C to 28.0°C and from 85.0% to 92.8%, respectively. The meteorological data were described in detail previously.[5] The test samples were set outdoors without any cover from the rain and wind. After the natural weathering, the weathered and control samples were stored in the dark at ambient temperature and humidity. The moisture contents of wood samples and

Table 1. The data for rainfall and sunlight irradiation at Serpong, Indonesia during the exposure test

Measurement duration	Total rainfall (mm)	Total sunlight irradiation (kJ/m²)
September 1–14, 2000 (2 weeks)	4	8 125
September 15–28, 2000 (2 weeks)	108	15 508
September 29, 2000–April 12, 2001 (28 weeks)	1807	135 265

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

cellulose powder were 8%–12% and 5%, respectively, when the materials were used for the PAS measurements.

Fourier transform infrared photoacoustic spectroscopy (FTIR-PAS)

FTIR-PAS spectra were recorded using a Jeol JIR 7000W spectrometer equipped with an IR-PAS module (IR/PAS 1000). All the spectra were obtained with a spectral resolution of 4 cm⁻¹. For the unexposed test samples and those weathered for 2, 4, and 32 weeks, the PAS measurements were made with the moving-mirror velocities of 0.081, 0.16, 0.32, and 0.56 cm/s (linear-scan method). A circular piece, 9 mm in diameter (thickness: about 1 mm), was prepared from the midsection of the weathered surface of each wood sample and set in a thin cell 10 mm in diameter. The cellulose powder was packed in the thin cell. Photoacoustic signals were collected by purging a cell bench with dry nitrogen. The PAS spectra were ratioed against a carbon black background. Bands due to water vapor were eliminated by the use of a difference spectrum method. The PAS spectra shown in Figs. 3–7 were approximately normalized by the intensity (height) of the band at 1370 cm⁻¹ due to C—H bending vibrations.[17,18]

Results and discussion

FTIR-PAS spectra of cellulose recorded at the moving-mirror velocity of 0.16 cm/s are displayed in Fig. 1. It is well known that cellulose is the most difficult wood constituent polymer to decompose by weathering. The assignments of the strong or medium vibrational bands observed at 1426,
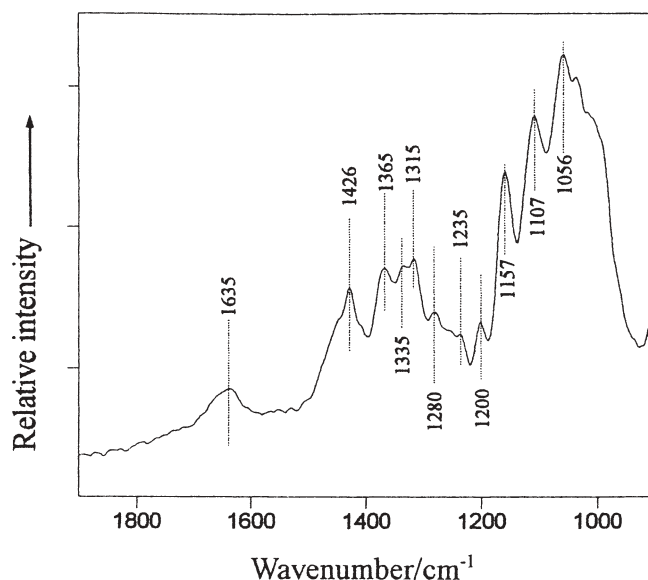
Fig. 1. Fourier transform infrared photoacoustic spectroscopy (FTIR-PAS) spectra of microcrystalline cellulose in the wavenumber range of 1900–900 cm⁻¹ at a moving-mirror velocity of 0.16 cm/s
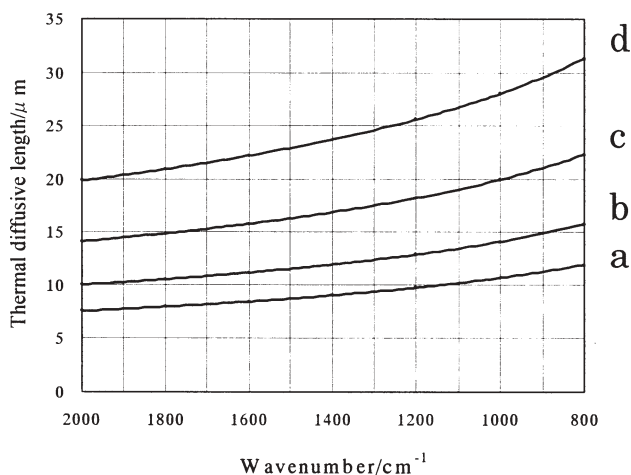
Fig. 2. Plots of thermal diffusion length of wood calculated from the typical thermal diffusivity of wood (2.0×10^{-3} cm²/s) against the infrared frequency in wavenumber at various moving-mirror velocities *a*, 0.56 cm/s; *b*, 0.32 cm/s; *c*, 0.16 cm/s; *d*, 0.081 cm/s

Fig. 3. FTIR-PAS spectra of unexposed puspa *a*, 0.56 cm/s; *b*, 0.32 cm/s; *c*, 0.16 cm/s; *d*, 0.081 cm/s

1365, 1335, 1315, 1157, 1107, and 1056 cm⁻¹ have already been reported and summarized.[14] In addition to these bands, weak bands were detected at 1280, 1235, and 1200 cm⁻¹. The bands at 1280 and 1200 cm⁻¹ were of great use to estimate the degree of deterioration in the surface layers of wood, although their vibrational modes have not been determined yet.

The photoacoustic probing depth should be determined from the shorter of the thermal diffusive length (μ_S) and the optical wave decay length (μ_β). The thermal diffusive length can be controlled by the moving-mirror velocity, because μ_S is given by
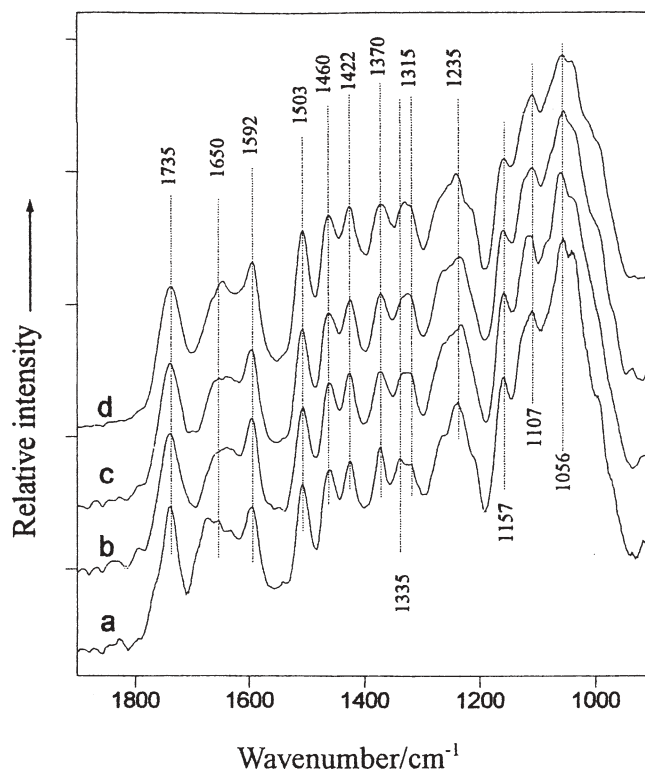
$$\mu_s = \left(D/\pi V \nu\right)^{1/2}$$

for an opaque sample such as wood, where D is the thermal diffusivity of sample, V the moving-mirror velocity, and ν the frequency of infrared radiation. Therefore, depth profiling is possible for the weathered samples provided that μ_S is shorter than μ_β. In this study, most of the weathered tropical wood samples demonstrated photoacoustic spectral changes with the moving-mirror velocity.

As shown in Fig. 2, the relationships between μ_S and ν calculated with the typical thermal diffusivity of wood (2.0×10^{-3} cm²/s)[14] are shown for the same moving-mirror velocities as chosen in the FTIR-PAS measurements in this work. The calculations reveal that μ_S decreases as V increases and as ν increases, although μ_S is difficult to estimate accurately over the whole mid-infrared frequency region because of opacity, pores (lumen and intercellular space), anisotropy and other factors.

The spectral changes with weathering and moving-mirror velocity in the two wood species were very similar to each other. Therefore, in this article, we show mainly the FTIR-PAS spectra of puspa to discuss the deterioration caused by natural weathering.

Figure 3 depicts the FTIR-PAS spectra measured at the various moving-mirror velocities in the 1900–900 cm⁻¹ region for unexposed puspa. The spectral outline and band positions show no significant change with moving-mirror velocity except the unresolved bands around 1650 cm⁻¹. However, there is a tendency for the intensities of bands at lower wavenumbers to increase relative to those at higher wavenumbers as the moving-mirror velocity increases. A likely explanation for this tendency is saturation of the photoacoustic signal caused by an increase in the probing depth, which equates to an increase of sample thickness. Although the results described here provide no conclusive evidence to account for these changes of relative intensity with moving-mirror velocity, such changes can be, if the photoacoustic saturation occurs, regarded as proof that the FTIR-PAS spectra include a depth profile on the region closest to the surface of wood samples.
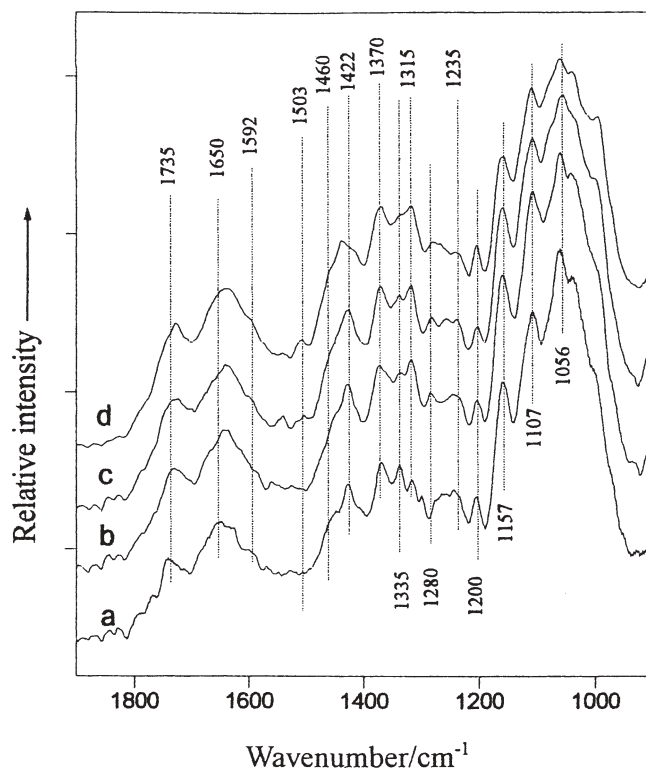
The overall spectral contour was nearly independent of the measurement location on the surface of the unexposed puspa; however, the line shape around 1650 cm⁻¹, especially in the spectrum obtained at 0.56 cm/s, varied significantly. The bands around 1650 cm⁻¹ that appeared as a broad peak are assigned to stretching vibrations of $C = O$ conjugated with an aromatic ring[19] and hence arise from lignin or phenolics molecules. In addition, $O-H$ bending vibrations of water molecules should be a component of the bands around 1650 cm⁻¹.[17] This may make the line shape around 1650 cm⁻¹ more changeable. In contrast, the band at 1735 cm⁻¹ due to stretching vibrations of $C = O$ groups in xylan[17,18,20] demonstrates no remarkable change with the moving-mirror velocity.
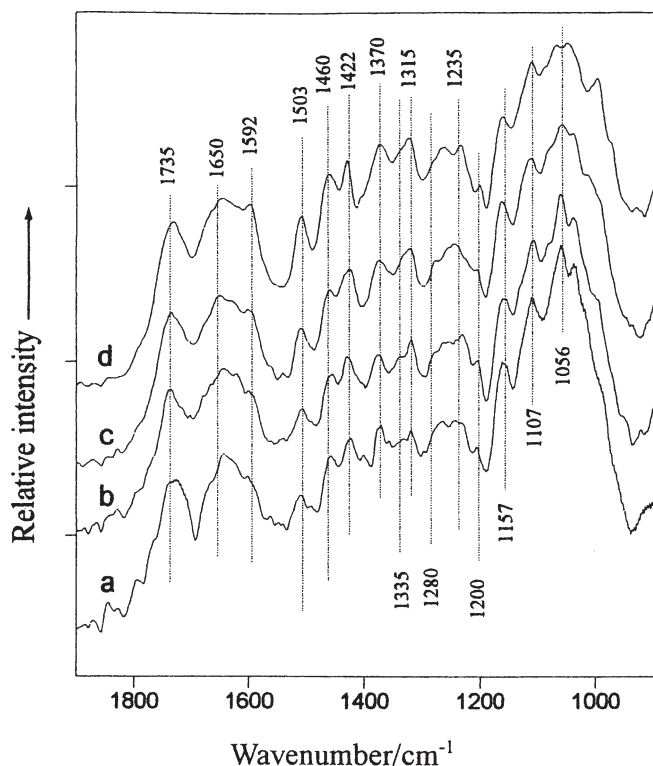
Fig. 4. FTIR-PAS spectra of puspa weathered for 2 weeks *a*, 0.56 cm/s; *b*, 0.32 cm/s; *c*, 0.16 cm/s; *d*, 0.081 cm/s
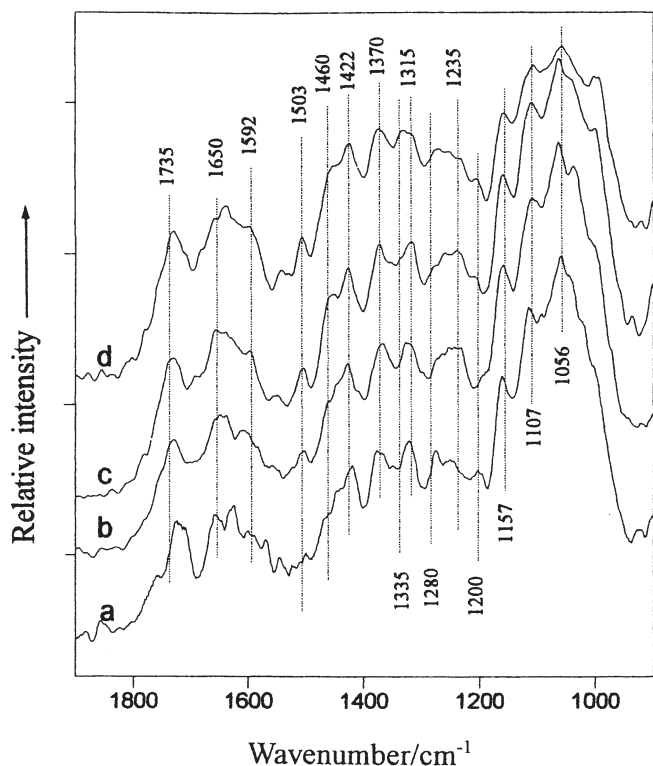

Fig. 5. FTIR-PAS spectra of puspa weathered for 4 weeks *a*, 0.56 cm/s; *b*, 0.32 cm/s; *c*, 0.16 cm/s; *d*, 0.081 cm/s

FTIR-PAS spectra of puspa weathered for 2 weeks are demonstrated in Fig. 4. There are distinct spectral differences in several bands between the unexposed and 2-week weathered samples. The intensities of the bands at 1592 and 1503 cm^{-1} due to the benzene ring are apparently reduced by the 2 weeks of weathering. Moreover, in a series of PAS spectra, both the band intensities decrease with increasing moving-mirror velocity. In other words, the intensities of the bands assigned to the phenyl group decrease as the thermal sensing length becomes shorter. The same dependence upon moving-mirror velocity was observed in the PAS spectra of kapur weathered for 2 weeks, although it was not as clear as in puspa. The spectral changes around 1592 and 1503 cm^{-1} indicate that the decomposition of the benzene ring proceeded in the exposed surface and are evidence of the photolysis of lignin and phenolics resulting from natural weathering. Because rainfall was only 4 mm in the first 2-week period, it is unlikely to be a significant contributor to weathering.

The band at 1735 cm^{-1} is also influenced by weathering, and it seems that the band in Fig. 4a broadens and shifts to slightly lower wavenumbers. However, a dependence upon the moving-mirror velocity was not clearly observed for band intensity. The weak peak at about 1200 cm^{-1} attributed to cellulose is detectable in all the spectra. For kapur samples, at a moving-mirror velocity of 0.56 cm/s, the broad band around 1650 cm^{-1} was slightly split into two components.

FTIR-PAS spectra of puspa and kapur that was exposed outdoors for 4 weeks are shown in Figs. 5 and 6, respectively. The test samples were exposed to 104 mm of rainfall in the second 2 weeks, whereas the rainfall of the first 2 weeks was very low. It is, therefore, expected that part of the photolysis products were washed out from the samples and sunlight reached the deeper region in the cell wall. The PAS spectra in Fig. 5 reveal that the intensity of the band at 1503 cm^{-1} decreases further at each moving-mirror velocity as compared with the sample of puspa weathered for 2 weeks (Fig. 4). It is evident that the band intensity at 1503 cm^{-1} decreases with increasing moving-mirror velocity in both wood species and that the band disappears completely at 0.32 and 0.56 cm/s in puspa and at 0.56 cm/s in kapur. The band at 1592 cm^{-1} also decreases and remains as a shoulder in the spectra of both the wood species. These results confirm that the photolysis of the benzene ring caused by sunlight proceeded further and occurred in the region at a greater depth from the weathered surface during the second 2 weeks, and suggest that the rainfall contributed to the photolysis.

As can be seen in Fig. 5, it is clear that both the bands at about 1735 and 1650 cm^{-1} are reduced through a further 2-week exposure, although the band shapes seem to be almost independent of the moving-mirror velocity. For the carbonyl groups, it is commonly recognized that sunlight irradiation leads to not only decomposition but also formation. Actually, an increase in the band intensity at 1735 cm^{-1} after artificial sunlight irradiation from a xenon lamp has been verified experimentally.[10] Hence, the natural weathering

Fig. 6. FTIR-PAS spectra of kapur weathered for 4 weeks *a*, 0.56 cm/s; *b*, 0.32 cm/s; *c*, 0.16 cm/s; *d*, 0.081 cm/s
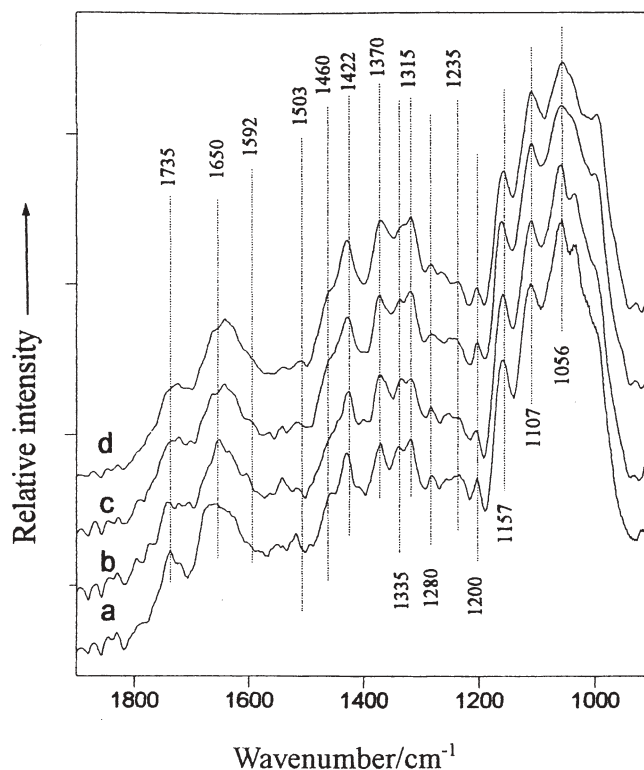
Fig. 7. FTIR-PAS spectra of puspa weathered for 32 weeks *a*, 0.56 cm/ s; *b*, 0.32 cm/s; *c*, 0.16 cm/s; *d*, 0.081 cm/s

effects on the carbonyl groups would be more intricate than those on the phenyl groups.

It is not easy to determine from the FTIR-PAS spectra in Fig. 4 after the first 2-week duration, having only 4 mm of rainfall, whether reduction of carbonyl groups occurs. However, the PAS spectra after the 4-week weathering, having 108 mm of rainfall, show remarkable decreases in the bands at 1735 and 1650 cm^{-1}. The amounts of sunlight irradiation during the first and second 2 weeks are 8125 and 7383 kJ/m^2, respectively. It can be, therefore, presumed that the leading cause of the decreases in C$=$O groups is not the photolysis by sunlight but the elution with rainfall of the products that are depolymerized through the decomposition of benzene rings. These products have relatively low molecular weights and are soluble in water.

In contrast to puspa, the spectra of kapur demonstrate the changes in the band shapes attributable to stretching vibrations of C$=$O groups with the velocity as shown in Fig. 6. For the spectrum of kapur at 0.56 cm/s, the band assigned to the C$=$O group in xylan is observed at a lower frequency than the spectra recorded at other velocities, and the spectral contour in the 1670–1530 cm^{-1} region splits into several components. There are two possible explanations for this shift and splitting. One is the formation of quinonoid structures containing new C$=$O groups after UV irradiation.[1] Another is a change in the hydrogen bond C$=$O$\cdots$H strength with rearrangement at the molecular level caused by weathering, because it is well known that a stretching vibrational band of the C$=$O group shifts to lower wavenumbers as the hydrogen bond length becomes

shorter. Further investigation is required to elucidate why the shift and splitting are observed. The bands at 1200 cm^{-1} in Fig. 5 appear more clearly than those in Fig. 4, suggesting that decomposition and elution of constituents other than cellulose proceeded significantly in the region near the weathered surface of puspa during the second 2 weeks.

Figure 7 shows the FTIR-PAS spectra of puspa weathered for 32 weeks. The band due to the benzene ring remains at 1503 cm^{-1} in the spectrum at 0.081 cm/s despite the long exposure, although it is only a trace. The weak band was also observed in the spectrum of kapur at 0.081 cm/s. In each spectrum, the bands at about 1735 and 1650 cm^{-1} remain distinct, although their relative intensities decrease further owing to photolysis and washout by rainfall. Similar decreases in these band intensities also appeared in each PAS spectrum of kapur weathered for 32 weeks. The bands at 1280 and 1200 cm^{-1} are obvious in all the spectra of puspa and were also detectable in kapur. No remarkable spectral change was observed at any moving-mirror velocity up to 32 weeks for both wood species in the bands at 1422, 1370, 1315, 1157, 1107, and 1056 cm^{-1} that are mainly attributable to cellulose molecules.

All the PAS spectral contours of puspa weathered for 32 weeks in Fig. 7 are similar to that of microcrystalline cellulose (Fig. 1) except the 1800–1500 cm^{-1} region. The results support the suggestion that cellulose polymer scarcely decomposes chemically as a result of natural weathering. It is, strictly speaking, necessary to estimate the contribution from the O—H bending vibrations of water molecules. However, the observation of the bands at about 1735 and

$1650\,cm^{-1}$ allows us to postulate that some degradation products containing C=O groups originating from both hemicellulose and lignin remain in the region from the weathered surface to a depth of several tens of microns.

Conclusion

We obtained valuable information on the deterioration of puspa and kapur caused by natural weathering from the depth profiling analysis through FTIR-PAS. The profiling supported the notion that the phenyl groups are rapidly degraded by a photochemical mechanism and suggested that the carbonyl groups are removed from the surface layers of wood due to a combination of photolysis of the phenyl groups and elution of the depolymerized products with rainfall. Moreover, our results indicated that cellulose polymer shows little chemical change by natural weathering.

From the viewpoint of methodology, FTIR-PAS is a useful tool for exploring the chemical changes in weathered wood, especially in the early stages of deterioration.

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