

RAPID COMMUNICATION

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Depth profiling of photo-induced degradation in wood by FT-IR microspectroscopy

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Wood undergoes rapid surface degradation during outdoor use owing to a combination of various weathering factors, such as solar radiation, water, temperature, and atmospheric gases. Among these factors, solar radiation is most damaging, as it initiates the formation of free radicals, which cause various chemical changes in wood. The depth at which these photoreactions take place is believed to be shallow in wood, although it is still difficult to determine how far from the surface wood can be photochemically penetrated. An earlier study¹ reported that the intensity of light in the ultraviolet (UV) and visible ranges greatly decreases after penetrating wood layers of 75 and 200 μm thickness, respectively. At the same time, the formation of free radicals¹ and decomposition of wood constituents^{2–4} caused by light are frequently observed within the upper 200 μm . However, evidence of photo-induced degradation of wood has also been found as far as 500–2500 μm from the surface.⁵ The latter case is usually explained as being a result of radical chain reactions whose secondary effects may migrate deeper into wood than the light itself.¹ This hypothesis seems to be widely accepted despite the fact that the rate of the migration is unknown, and there is no expla-

nation for why this migration is not always observed. In this study, we attempted to precisely monitor the penetration of photochemical effects into wood using Fourier transform infrared (FT-IR) microspectroscopic depth profile analysis. The results show a characteristic penetration behavior of certain chemical effects, suggesting that the direct influence of light on the phenomenon should be reexamined.

The wood specimens used were air-dried sugi (*Cryptomeria japonica* D. Don) sapwood pieces measuring 5 (L) \times 5 (R) \times 2 (T) cm and having a typical earlywood density of 0.22 $\text{g}\cdot\text{cm}^{-3}$ (determined by X-ray densitometry). The radially cut face was exposed to artificial sunlight from a xenon lamp ($>290\text{nm}$) at 375 $\text{W}\cdot\text{m}^{-2}$ (in the range of 300–700 nm at the wood surface) for up to 1500 h at 60°C (black panel) and 30% relative humidity in a commercial chamber (Suga FAL-25AXC-HC). The total energy was roughly equivalent to that of 10–11 months of natural weathering in the horizontal plane in Tokyo. After each exposure step at 50, 100, 300, 600, and 1500 h, 30 μm thick earlywood tangential sections cut vertical to the exposed surface were used for microscopic FT-IR measurements (Fig. 1). The depth profiling spectra were recorded on a Nicolet Magna 880 spectrometer coupled with a Nicplan microscopic unit in which the IR radiation was focused on small areas of 200 (L) \times 50 (T) μm or 200 (L) \times 100 (T) μm (Fig. 1). All the spectra employed averaged 64 scans at 4 cm^{-1} resolution. To examine the effects of irradiation, changes in absorption intensities at 1730 and at 1510 cm^{-1} were monitored because their photosensitive behaviors were known to reflect some important aspects of the wood photodegradation processes: The rise of the former indicates formation of a variety of carbonyl species; and the latter decreases owing to decomposition of aromatic moieties.^{2–4,6–8} For all intensity measurements, the height of the band at 1370 cm^{-1} due to CH deformation in polysaccharides was used as an internal standard.⁶

The FT-IR depth profiling spectra after 1500 h of irradiation are shown in Fig. 2a. It is apparent that the artificial solar radiation caused the most significant chemical changes in the outermost wood layer, although some intensity changes as far as 400–500 and 600–700 μm can be detected

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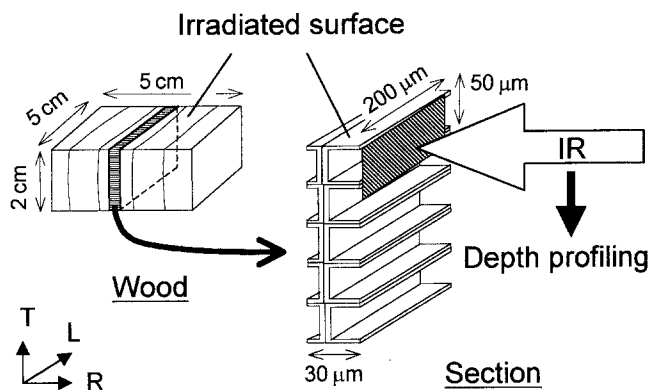


Fig. 1. Method of obtaining infrared (IR) spectra at various depths from a photoirradiated wood surface

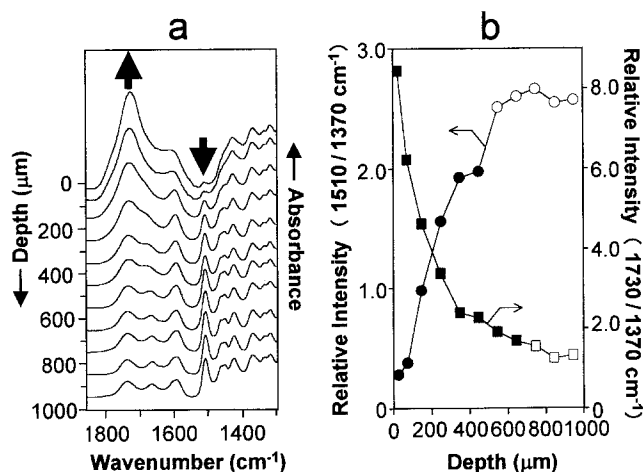


Fig. 2. **a** Fourier transform infrared (FT-IR) depth profile spectra in the region of $1800\text{--}1300\text{cm}^{-1}$ of photoirradiated sugi (*Cryptomeria japonica*) sapwood after 1500 h of exposure. **b** Changes in absorption intensities at 1510cm^{-1} (circles) and 1730cm^{-1} (squares) with depth obtained from **a**. Filled circles and squares out of the intensity variation range observed for reference spectra ($n = 35$) were from unexposed wood as determined by the Smirnov-Grubbs test at the 0.05 significance level

for the aromatic (1510cm^{-1}) and carbonyl (1730cm^{-1}) bands, respectively (Fig. 2b).

The results of monitoring the aromatic band to show how the photo-induced chemical changes reached this depth are illustrated in Fig. 3. It appears that the destructive effect on aromatic moieties continuously penetrated the wood to form a thick degraded layer, although the penetration rate became increasingly restricted with exposure time. A similar result was seen for the carbonyl band (not shown) except that the degraded layer was somewhat thicker. These results may explain why various depths or thicknesses have been reported for this phenomenon. It is probably because different penetration stages were also observed owing to a variation in the density of the wood specimens used. This also suggests that the formation of $400\text{-}\mu\text{m}$ -thick degraded layers reported for naturally weathered woods^{9,10} may be attributed mainly to photochemical

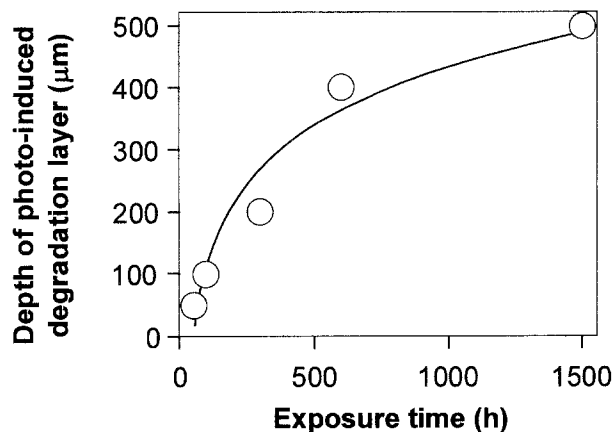


Fig. 3. Growth of photo-induced degradation layer according to the exposure time. Results of monitoring the IR absorption at 1510cm^{-1} are shown. The plot is approximated by a logarithmic curve ($R^2 = 0.96$)

effects. Moreover, it is notable that the plot in Fig. 3 is well approximated by a logarithmic curve (0.96 for R^2).

Although there might be some other explanations, it is worthy of note what this kinetic curve suggests: It would take an exponentially long irradiation time to continue to affect a series of underlying wood layers (about 10 times as long for the next $300\text{-}\mu\text{m}$ -thick layer). This is not surprising because the intensity of light that penetrates wood falls off exponentially as shown by the Beer-Lambert equation.^{1,5} In addition, although the light intensity in wood is supposed to be quickly lost by the first 75 or $200\text{-}\mu\text{m}$ -thick layer,¹ its ability to promote primary photoreactions could persist through a double-thick layer. This is because the steady-state rate of primary photooxidation processes to form some relatively stable oxidation products is known theoretically to be proportional to the square root of the light intensity (if the initiation reaction rate is proportional to the light intensity).^{11,12} Thus, it is imperative to study the light-transmitting property of the same wood for various spectral ranges to simulate the direct influence of light on the chemical changes observed deeper than $200\text{ }\mu\text{m}$.

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