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Violet light causes photodegradation of wood beyond the zone affected by ultraviolet radiation

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Abstract

The limited penetration of wood by light explains why the weathering of wood exposed outdoors is a surface phenomenon. Wood is rapidly degraded by short-wavelength UV radiation, but the penetration of light into wood is positively correlated with its wavelength. Hence, sub-surface degradation is likely to be caused by longer-wavelength light that still has sufficient energy to degrade wood. In this paper we test this hypothesis and determine the wavelengths of visible light that extend photodegradation into wood beyond the zone affected by UV radiation. Sugi (*Cryptomeria japonica*) earlywood was exposed to UV and visible light with narrow band gaps (20 nm) and the penetration of light into the wood was measured using a photodetector. Photodegradation was depth-profiled using FT-IR microscopy. There was a positive correlation between the penetration of light into sugi earlywood and the wavelength of the incident radiation within the range 246–496 nm. The depth of photodegradation also increased with wavelength up to and including the violet region (403 nm) of the visible spectrum. Blue light (434–496 nm) penetrated wood to a greater extent than violet light and was capable of bleaching the wood, but it did not significantly modify lignin, and hence it was not responsible for sub-surface photodegradation of wood. We conclude that violet light is the component of the visible spectrum that extends photodegradation into wood beyond the zone affected by UV radiation. Accordingly, surface treatments designed to protect wood used outdoors should shield wood from the effects of violet light.

Keywords: depth profile; FT-IR; photodegradation; sugi wood; ultraviolet radiation; violet light; visible light; wavelength.

Introduction

Exposure of wood to the weather results in rapid depolymerisation of lignin and cellulose, and degradation of the cellular structure of wood (Feist and Hon 1984; Evans et al. 1996). These changes cause wood to yellow, as unsaturated photodegraded lignin fragments accumulate at exposed surfaces, and eventually become grey and rough due to leaching of photodegraded lignin and fibre fragments from the wood by rain (Feist and Hon 1984). Surface degradation decreases the adhesion of coatings (Ashton 1967; Williams and Feist 1994) and encourages surface colonisation of weathered wood by the black-coloured yeast *Aureobasidium pullulans* (de Bary) Arnaud (Schoeman and Dickinson 1997). These apparent undesirable effects of weathering are confined to the wood surface. It is one of the definitions of weathering that it is a surface phenomenon and the limited penetration of sunlight with sufficient energy to degrade wood plays a pivotal role in this context. Water and heat, as other (less effective) factors of degradation, do not have the same penetration limits (Browne and Simonson 1957). Beyond the zone immediately affected by light, the chemical and physical properties of weathered wood are believed to be largely unchanged (Horn et al. 1994).

The intensity of light transmitted through wood decreases exponentially with depth, as predicted by the Beer-Lambert equation (Browne and Simonson 1957). Recently, we showed that this equation was useful in explaining why visible light penetrated sugi (*Cryptomeria japonica*) earlywood to a greater extent than UV radiation (Kataoka et al. 2004). In the same study we examined the photodegradation caused by UV and visible light and found that visible light degraded wood beyond the zone affected by UV radiation. This finding is in accord with studies that have demonstrated that visible light is capable of photodegrading wood and other organic molecules, in spite of its lower energy (Derbyshire and Miller 1981; Kitamura et al. 1989; Hon and Minemura 1991; Young 1992; Xie et al. 2000). It is clear that visible light penetrates wood more deeply than UV radiation. The extent to which visible light degrades wood beyond the zone affected by UV radiation is the focus of this paper.

Materials and methods

Wood samples

Air-dried sugi (*Cryptomeria japonica* D. Don) sapwood blocks measuring 2×1×1 cm (L×R×T) were used. The average density of earlywood in these blocks was 0.24 g cm^{-3}, as measured by X-ray densitometry. Radially cut wood sections were prepared using a microtome from the same wood specimens indicated above. The thickness of these sections was measured

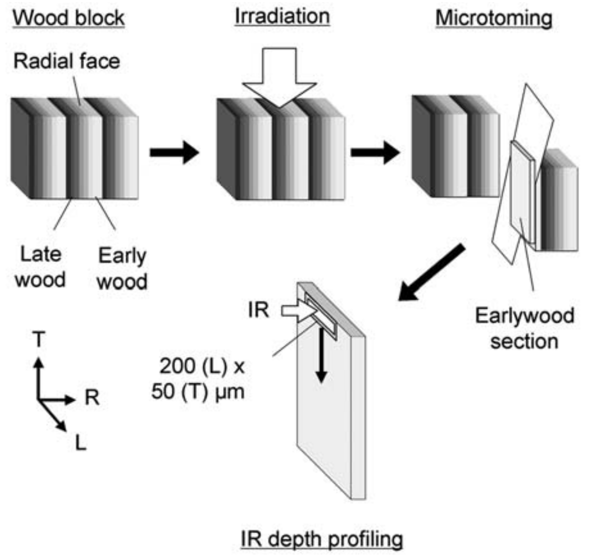

Figure 1 Method used to prepare and section wood for IR depth-profile analysis.

using a calibrated digital microscope (Keyence VH 7000), as previously described (Kataoka et al. 2004).

Irradiation at different wavelengths

Radially cut faces and sections of wood blocks were exposed to monochromatic radiation emitted from a spectro-irradiator (MM-3, Bunkoh-Keiki Co. Ltd.) equipped with a 300-W xenon lamp and a diffraction grating. UV radiation was applied with an average wavelength of 246, 278, 310, 341 or 372 nm, or visible light with an average wavelength of 403 (violet), 434, 465 or 496 nm (all blue). The bandpass width was set to 20 nm. The irradiance (or dose rate: energy per unit time received per unit area on a sample surface) of each of the aforementioned bands was measured as 132, 233, 298, 329, 336, 244, 253, 236, and 171 W m^{-2}, respectively. For light transmission and colour measurement studies, all wavelengths were used. For FT-IR depth-profile analyses, fewer wavelengths were employed (310, 341, 372, 403, 434 and 465 nm). The duration of exposure of samples prior to IR analyses varied from 16.2 to 21.9 h, depending on the irradiation wavelength, so that samples were exposed to the same number of photons (3.66×10^{25} m^{-2}). Tangentially orientated earlywood sections (30 μm thick) were cut from exposed surfaces and characterised by FT-IR microscopy, as illustrated in Figure 1 and previously described (Kataoka et al. 2004, 2005).

Light transmission measurements

Light transmitted through radially cut wood sections of varying thickness was detected with the photo-detector that is part of the MM-3 spectro-irradiator. Transmission measurements could be restricted to earlywood because the aperture of the photo-detector was smaller (approx. 1.5 mm) than the width of earlywood bands.

FT-IR depth-profile analyses

FT-IR spectra were taken at different depths on small areas (200×50 μm, L$\times$T) of photo-irradiated earlywood surfaces using a Nicolet Magna 860 spectrometer coupled to a Nicplan microscope, as shown in Figure 1 and previously described (Kataoka et al. 2004, 2005). Averages of 64 scans were taken at a resolution of 4 cm^{-1}. The irradiation effect was assessed based on the absorption intensities at 1730 cm^{-1} because photo-cleavage of lignin (the photolabile component of wood) generates carbonyl-containing compounds (Anderson et al. 1991; Horn et al. 1994; Pandey 2005). The intensity of the band at 1370 cm^{-1} (CH deformation in polysaccharides) was used as an internal standard, in accordance with the method of Tolvaj and Faix (1995).

Colour measurements

A spectrophotometer (NF-333, Nippon Denshoku Industries Co. Ltd.) was used to measure colour according to ISO 7724-2 (1984). Reflection spectra were measured in the range 400–700 nm and recalculated based on the *CIE*Lab system (10° standard observer and D65 illuminant) (Bekhta and Niemz 2003).

Results

Figure 2 shows the effect of irradiation wavelength from 246 to 496 nm on the transmission of light through thin sugi earlywood sections of varying thickness. As expected, the depth to which light penetrated the wood increased with increasing wavelength across the whole spectral range investigated. In particular, pronounced increases in penetration were observed as the wavelength of light increased in the range 310–465 nm. Figure 2 also demonstrates that the intensity of each wavelength decreased exponentially with increasing wood thickness. This made it possible to calculate the depth (thickness) at which 10% and 1% of the incident light is expected to be present in sugi earlywood (Table 1).

The FT-IR depth-profile spectra of sugi earlywood irradiated with wavelengths of 341, 372 and 403 nm at a constant number of photons are presented in Figure 3. Weakening of the IR absorption band at 1510 cm^{-1} (due to photodegradation of lignin) and strengthening of the band at 1730 cm^{-1} (formation of non-conjugated carbonyl groups) are notable features of the spectra. UV irradiation degraded wood surfaces to a greater extent than visible (violet) light, as expected. However, violet light caused

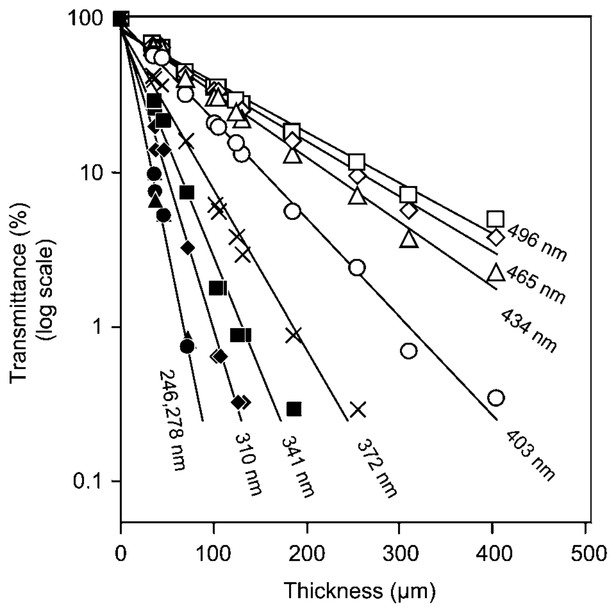

Figure 2 Percentage transmission of monochromatic light with wavelengths ranging from 246 to 496 nm through sections of varying thickness of sugi earlywood (semi-logarithmic scale).

Table 1 The depths at which 10% and 1% of light with wavelengths of 246–496 nm are expected to be present in photoirradiated sugi sections.

Wavelength (nm)	Depth of 10% transmittance (μm)	Depth of 1% transmittance (μm)
246 (UV)	33	66
278 (UV)	33	67
310 (UV)	48	99
341 (UV)	63	131
372 (UV)	87	178
403 (visible)	153	311
434 (visible)	224	463
465 (visible)	257	536
496 (visible)	279	585

greater chemical changes in sub-surface layers, despite the more pronounced effect of shorter-wavelength UV radiation at the wood surface (Figure 3).

The maximum depth of photodegradation for each wavelength was assessed by plotting changes in absorbance measured at 1730 cm^{-1} against the reference band at 1370 cm^{-1}, as shown in Figure 4. The filled symbols in Figure 4 indicate statistically significant changes in intensity, and provide a measure of the maximum depth of photodegradation. Significant changes in this carbonyl band were detected at depths of up to 100, 150, 250, 300 and 50 μm for specimens irradiated with light of wavelengths of 310, 341, 372, 403 and 434 nm, respectively. No significant changes in the carbonyl band were observed in spectra obtained from wood irradiated with light of wavelengths greater than 434 nm. Accordingly, the maximum depth of photodegradation was positively correlated with the wavelength in the range from 310 to 403 nm, but light with wavelengths above this limit did not extend photodegradation into wood.

Figure 5 illustrates the good relationship between depth of photodegradation in earlywood and the penetration of light (<434 nm) into wood. Light of wavelengths longer than 434 nm penetrated earlywood to a greater depth, but did not cause any detectable chemical changes. Figure 6 shows changes in the colour coordinates (ΔL^*, Δa^* and Δb^*) of irradiated wood (4 and 8 h)

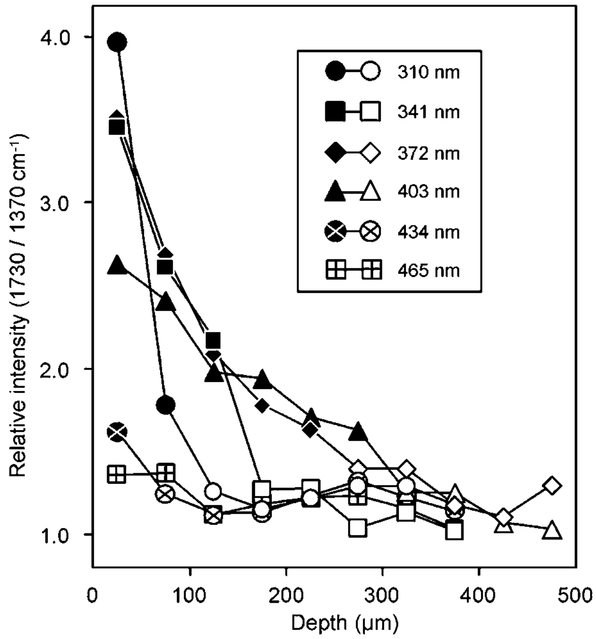

Figure 4 Changes in absorption at 1730 cm^{-1} as a function of depth for sugi earlywood exposed to light of different wavelengths from 310 to 465 nm. Filled symbols indicate that significant changes in peaks occurred as a result of exposure of wood to light (difference between unexposed controls and exposed specimens assessed by Smirnov-Grubbs test at the 5% significance level).

for light of different wavelengths. A transition from photoyellowing to photobleaching was observed at wavelengths between 403 nm (violet) and 434 nm (blue): the changes in L^* (+, bright; –, dark) changed from negative to positive, and those for a^* (+, red; –, green) and b^* (+, yellow; –, blue) changed from positive to negative.

Discussion

Violet light (403 nm) caused photoyellowing; carbonyl groups and quinone structures arise via the formation of ketyl and phenoxy radicals (Leary 1994). Photoyellowing

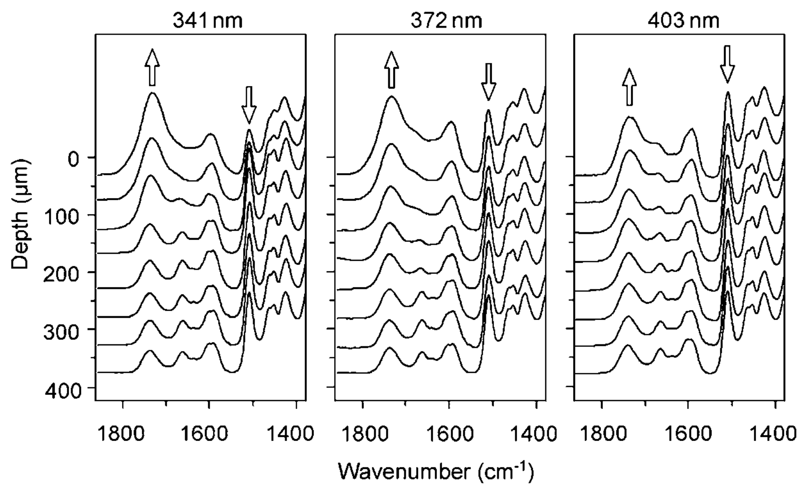

Figure 3 FT-IR depth profile spectra in the range 1800–1400 cm^{-1} of sugi earlywood irradiated with UV radiation at 341 nm (left), 372 nm (middle) or violet light (403 nm, right). Spectra are shown in absorbance units. Arrows indicate where pronounced changes in peak heights occurred.

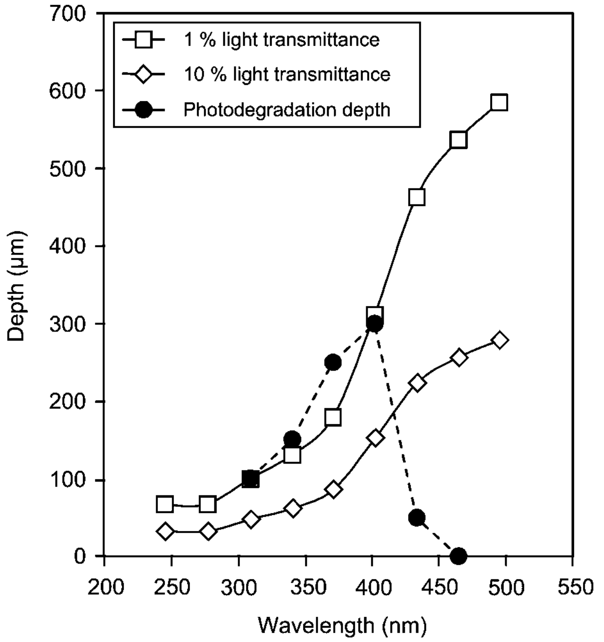

Figure 5 Changes in the depth of penetration of light and the maximum depth of photodegradation [to which significant changes in the carbonyl band (1730 cm^{-1}) were detected] in sugi as a function of the wavelength of light used to irradiate specimens.

at wavelengths between 403 and 434 nm is evidence that violet light possesses sufficient energy to degrade lignin (Figures 3 and 6). Blue light (430–500 nm) penetrated wood, but did not degrade lignin significantly. We suggest, based on these FT-IR and spectrophotometric observations, that violet light extends photodegradation into wood beyond the zone affected by UV radiation. These findings are in accordance with previous studies that have shown that visible light can degrade organic materials (Young 1992; Xie et al. 2000). Additional experimentation, however, would be desirable to further clarify the action of violet light on the chemical composition of wood. A good approach would be to analyse the same specimens to measure the penetration of photodegradation, as Tolvaj and Faix (1995) did in their IR difference spectral analysis of irradiated wood.

Based on light transmission measurements (Figure 2), the intensity of photoactive violet light (403 nm) is expected to decrease to 1% of its initial value after penetrating the wood to a depth of approximately 310 μm (Table 1). This small intensity of light, however, may still be responsible for 10% of the degradation that occurs at the surface, because the primary photo-oxidation rate is proportional to the square root of the light intensity (Vink 1979). This confirms our previous finding that a 10-fold increase in irradiation time causes photodegradation to extend into sugi earlywood by 330 μm (Kataoka et al. 2004). Our results also accord with the previous observations of Browne and Simonson (1957), Bamber and Summerville (1980), Yata and Tamura (1995) and Kataoka et al. (2004) that wood exposed to natural or artificial weathering is degraded well beyond the zone affected by UV radiation.

There are some discrepancies, however, between our results and previous studies by Browne and Simonson (1957), Hon and Ifju (1978) and Jirous-Rajkovic et al. (2004). We found that 1% of UV radiation in the range 246–372 nm penetrated sugi earlywood to depths of 66–178 μm, respectively (Table 1). In contrast, Browne and Simonson (1957) reported that UV had little penetration into wood, and Hon and Ifju (1978) also concluded that the penetration of UV radiation into wood was negligible beyond a depth of 75 μm. Our results more closely agree with the findings of Jirous-Rajkovic et al. (2004) that UV (at 340 nm) penetrates silver fir (*Abies alba* Mill.) wood to a depth greater than 70 μm. Much greater discrepancies between our observations and those of previous studies exist in the visible range. Browne and Simonson (1957) observed that 11.5% of visible light (400–750 nm) penetrated redwood (*Sequoia sempervirens*) to a depth of 508 μm. An alternative way of expressing this result is that 10% of visible light is expected to be present at a depth of 540 μm. Hon and Ifju (1978) observed that 10% of visible light (520 nm) penetrated redwood to a depth of 125–150 μm. Penetration depths observed here were 153–279 μm for the spectral range 403–496 nm, which fall between the values reported by Browne and Simonson (1957) and Hon and Ifju (1978). These discrepancies may be due in part to methodological differences and partly to density differences of the wood samples investigated.

It is becoming increasingly clear that wood protection systems need to have components that absorb both violet light (380–430 nm) and UV radiation. Pigments that absorb strongly in the violet range have a pale yellow colour (Goldsmith 1986; Tomoda et al. 1990). The appearance of light-coloured wood species may be influenced by such additives, but not dramatically. Our results

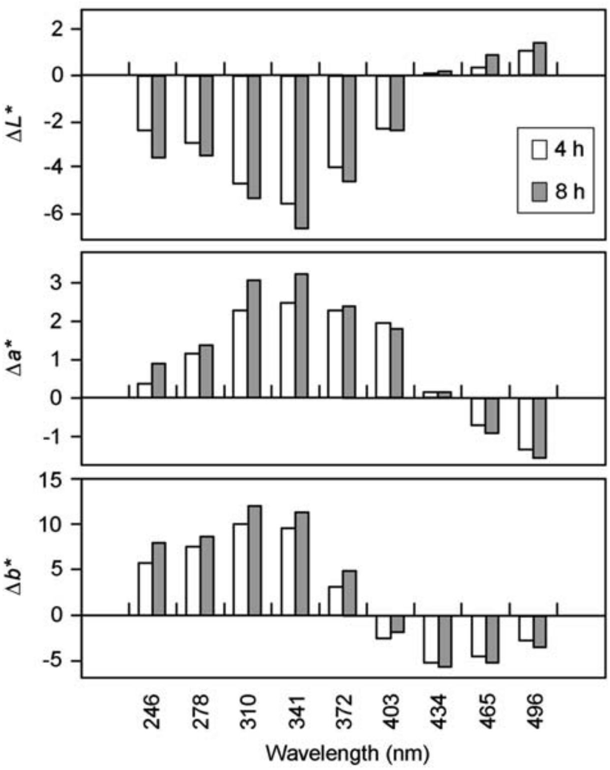

Figure 6 Changes in colour parameters (ΔL^*, Δa^* and Δb^*) of sugi after 4 and 8 h of exposure to light of different wavelengths.

also demonstrate that blue light can bleach wood, although IR spectra did not reveal chemical changes after photo-bleaching. It is also a challenge to find additives to prevent photobleaching of dark wood species. This can perhaps be achieved by a better understanding of the underlying mechanisms.

Conclusions

There was a positive correlation between the penetration of light into sugi earlywood and the wavelength of the incident radiation within the range 246–496 nm. The depth of photodegradation also increased with wavelength up to and including the violet region of the visible spectrum. Blue light (434–496 nm) penetrated wood to a greater depth than violet light and caused bleaching, without significantly modifying the IR spectra of lignin. The photodegradation depth profile of wood exposed to light is characterised by a severe decrease from the surface to sub-surface layers. Violet light (380–430 nm) extends photodegradation into wood beyond the zone affected by UV radiation. Surface treatments designed to protect wood used outdoors should also have absorbing properties in this wavelength range.

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