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The Effects of Wavelength on Photodegradation Depth Profiles in Japanese Cedar (*Cryptomeria Japonica* D.Don) Earlywood

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Abstract

FT-IR microscopy was used to depth profile the photodegradation of Japanese cedar earlywood exposed to monochromatic light in the UV and visible ranges (band pass: 20nm). Parallel experiments assessed the transmission of the light through thin sections of Japanese cedar. The depth of photodegradation increased with wavelength up to and including the violet region of the visible spectrum, but decreased in the blue region. In contrast, penetration of light into Japanese cedar was positively correlated with wavelength. We concluded that violet light has sufficient energy to degrade wood and extends photodegradation into wood beyond the zone affected by UV radiation. Accordingly, surface treatment designed to protect wood used outdoors should protect wood from the effects of violet light.

Introduction

Exposure of wood to the weather results in rapid depolymerisation of lignin and cellulose and degradation of wood's cellular structure (Feist and Hon 1984; Evans et al. 1996). These changes cause wood to yellow as unsaturated photodegraded lignin compounds accumulate at exposed surfaces, and eventually become grey and rough due to leaching of photodegraded lignin and fibre fragments from wood by rain (Feist and Hon 1984). Surface degradation decreases adhesion of coatings (Ashton 1967; Williams and Feist 1994) and encourages surface colonization of weathered wood by the black coloured yeast *Aureobasidium pullulans* (de Bary) Arnaud (Schoeman and Dickinson 1997). These undesirable effects of weathering are confined to the wood surface, and the superficial nature of weathering is one of its defining features. This is linked to the limited penetration of sunlight into wood, since the other factors involved in the weathering of wood (water and heat), have the ability, in principle, to degrade wood to a much greater depth (Browne and Simonson 1957). Hence, beyond the zone immediately affected by light, the chemical and physical properties of weathered wood are 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 Japanese cedar (*Cryptomeria japonica* D. Don) 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 suggested that visible light may degrade wood beyond the zone affected by UV radiation. This accords with studies

that have shown that visible light is capable of photodegrading wood and other organic molecules (Derbyshire and Miller 1981; Kitamura et al. 1989; Hon and Minemura 1991; Young 1992; Xie et al. 2000). Visible light is less energetic than UV radiation and a critical wavelength must exist beyond which it has insufficient energy to photodegrade wood's structural components. Light falling within this critical value, however, would penetrate wood to a greater extent than shorter more energetic radiation, as predicted by the Beer-Lambert equation, and thus would be capable of extending photodegradation beyond the zone affected by UV radiation. 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.

Materials and methods

Wood samples

Air-dried Japanese cedar (*Cryptomeria japonica* D. Don) sapwood blocks measuring 2 (L) x 1 (R) x 1 (T) cm³ were used for FT-IR (Fourier-Transform infra-red) depth profile studies. The average density of earlywood in these blocks as measured by x-ray densitometry was 0.24 g cm⁻³. Radially-cut wood sections were prepared using a microtome from the same wood specimens used for depth profile studies. The thickness of these sections was measured using a calibrated digital microscope (Keyence VH 7000), as described previously (Kataoka et al. 2004), and they were then used for light transmission studies.

Irradiation at different wavelengths

Radially-cut faces and sections of wood blocks were exposed to monochromatic radiation emitted by a spectro-irradiator (MM-3, Bunkoh-Keiki Co., Ltd.) equipped with a 300 W xenon lamp and a diffraction grating. Separate individual specimens were irradiated with UV radiation 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) and a band pass width of 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 to be 132,233,298, 329,336,244,253,236, and 171 W m⁻², respectively. For light transmission 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 wavelength used, in order to expose each sample to the same number of photons ($3.66 \times 10^{25} \text{ m}^{-2}$). Thirty micrometer-thick

tangentially-orientated earlywood sections were cut from exposed surfaces and used for microscopic FT-IR measurements, as illustrated in Figure 1, and described previously (Kataoka et al. 2004, 2005).

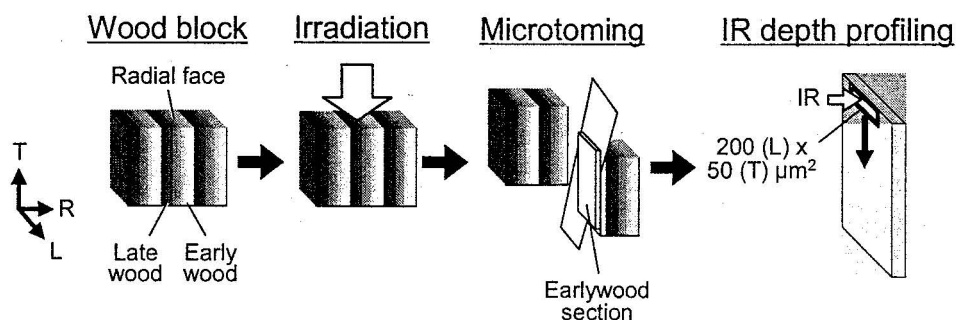


Figure 1 Method used to prepare and section wood for IR depth profile analysis

Light transmission measurements

A photo-detector that is part of the MM-3 spectro-irradiator was used to detect light transmitted through radially-cut wood sections of varying thicknesses. The transmission of light was measured immediately behind the sections, as described previously (Kataoka et al. 2004). It was possible to measure the transmission of light exclusively through earlywood because the aperture of the photo-detector was smaller (approximately 1.5 mm) than the width of earlywood bands in the wood sections.

FT-IR depth profile analyses

FT-IR spectra were taken at different depths on small areas ($200\text{ (L)} \times 50\text{ (T)}\ \mu\text{m}^2$) of photo-irradiated earlywood surfaces, using a Nicolet Magna 860 spectrometer coupled to a Nicplan microscope, as shown in Figure 1, and described previously (Kataoka et al. 2004, 2005). All the spectra obtained were the averages of 64 scans at 4 cm^{-1} resolution. Changes in absorption intensities at 1730 cm^{-1} were used to assess the effects of light on the chemical composition of wood. The height of the band at 1370 cm^{-1} due to CH deformation in polysaccharides was used as an internal standard in accordance with the method of Tolvaj and Faix (1995).

Results

Figure 2 illustrates the effect of irradiation wavelength from 246 to 496 nm on the percentage transmission of light through thin Japanese cedar earlywood sections of varying thickness. It is clear that the depth to which light penetrated the wood increased with increasing wavelength across the whole spectral range used here. In particular, pronounced increases in penetration were observed as the wavelength of light increased in the 340 to 434 nm range. Figure 2 also shows that the intensity of each wavelength decreased exponentially with increasing wood thickness. This made it possible to calculate the depths (thicknesses) at which 10%, 5% and 1% of the incident light are expected to be present in Japanese cedar earlywood (Table 1).

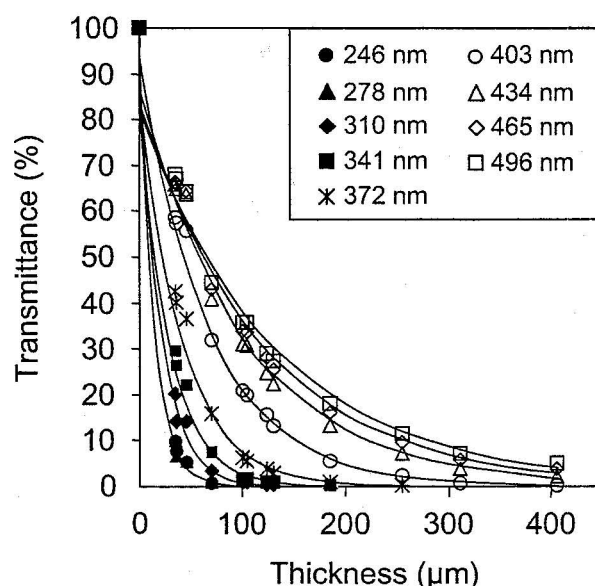


Figure 2. Percentage transmission of monochromatic light with wavelengths ranging from 246 to 496 nm through sections of varying thickness of Japanese cedar earlywood

Table 1. The depths at which 10%, 5% and 1% of light with wavelengths from 246 to 496 nm are expected to be present in photo-irradiated Japanese cedar sections

Wavelength (nm)	Depth of 10% transmittance (μm)	Depth of 5% transmittance (μm)	Depth of 1% transmittance (μm)
246 (UV)	33	43	66
278 (UV)	33	44	67
310 (UV)	48	63	99
341 (UV)	63	83	131
372 (UV)	87	114	178
403 (visible)	153	201	311
434 (visible)	224	296	463
465 (visible)	257	341	536
496 (visible)	279	371	585

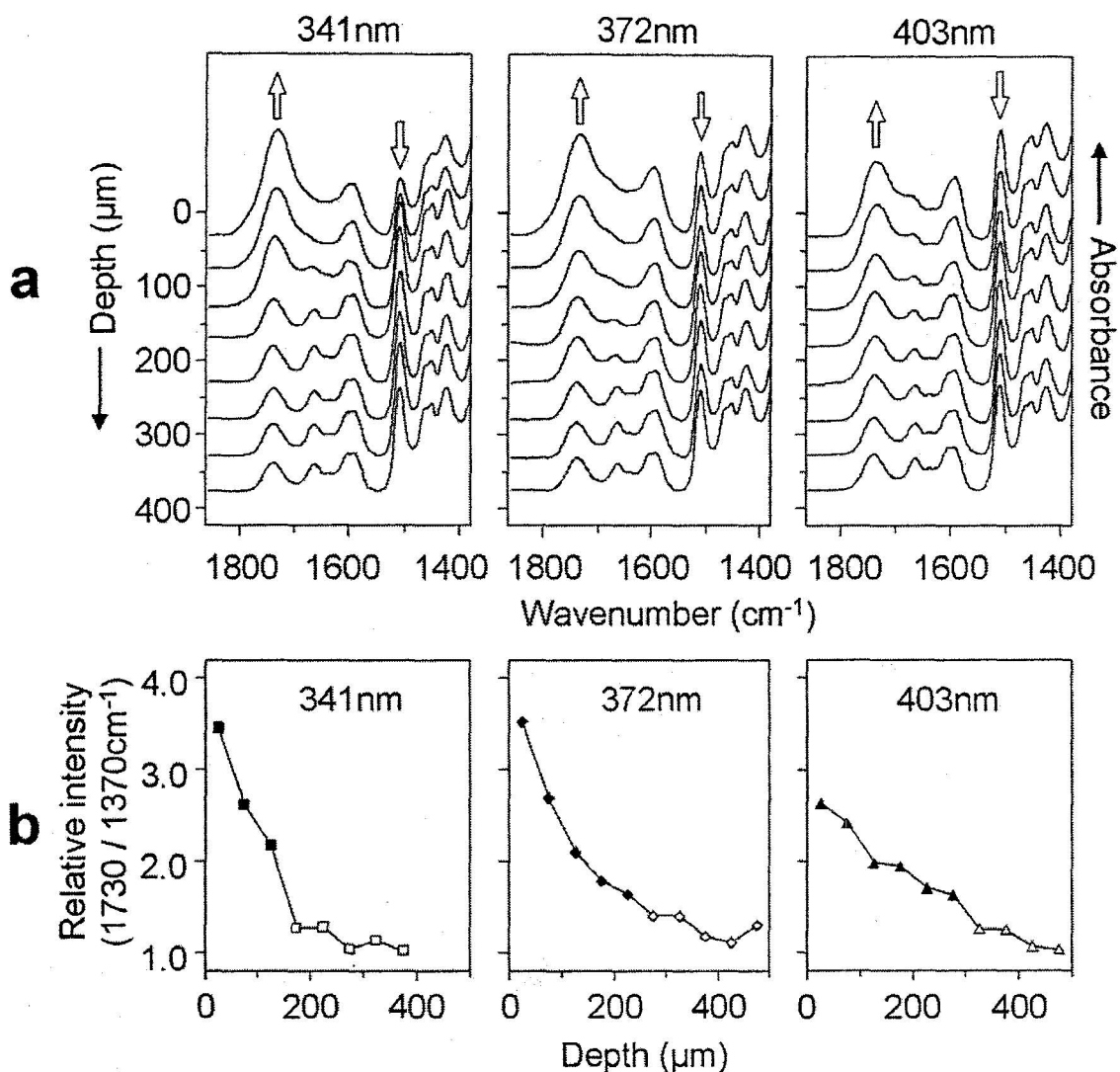


Figure 3 (a) FT-IR depth profile spectra in the range 1800 to 1400 cm^{-1} of Japanese cedar earlywood irradiated with UV radiation at 341 nm (left), 372 nm (middle) or violet light (403 nm, right). Arrows indicate where pronounced changes in peak heights occurred. (b) Changes in absorption at 1730 cm^{-1} as a function of depth obtained from a. 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 using Smirnov-Grubbs test at the 5% significance level).

Figure 3a shows the FT-IR depth-profile spectra of Japanese cedar earlywood irradiated with UV radiation with wavelengths of 341 nm and 372 nm and violet light (403 nm), using a constant number of photons. 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. Hence, spectra of wood irradiated with light with average wavelengths of 341 and 372 nm show greater changes than the spectra of wood irradiated with violet light. Differences were most pronounced at the surface of

irradiated specimens, again as expected. Violet light, however, caused greater chemical changes in sub-surface layers despite the more pronounced effect of shorter wavelength UV radiation at the wood surface (Figure 3a).

The maximum depth of photodegradation for each wavelength was assessed by plotting changes in peak height at 1730 cm^{-1} against the reference peak at 1370 cm^{-1} , as illustrated in Figure 3b. The filled symbols in Figure 3b indicate statistically significant changes in intensity, and provide a measure of the maximum depth of photodegradation. Table 2 shows the maximum depth of photodegradation for specimens irradiated with light with wavelengths of 310, 341, 372, 403 or 434 nm. Significant changes in the carbonyl band were detected at depths of up to 100, 150, 250, 300 and 50 μm , respectively. No significant changes in the carbonyl band were observed in spectra obtained from wood irradiated with light with wavelengths greater than 434 nm. These results indicate that the maximum depth of photodegradation in Japanese cedar earlywood was positively correlated with the wavelength of the incident light for wavelengths in the range from 310 to 403nm, but light with wavelengths longer than 403nm did not extend photodegradation into wood beyond the zone affected by UV radiation.

Table 2. *Maximum depth of photodegradation (to which significant changes in the carbonyl band (1730 cm^{-1}) were detected) in Japanese cedar earlywood irradiated with wavelength from 310 to 465 nm*

Wavelength (nm)	Maximum depth of photodegradation (μm)
310 (UV)	100
341 (UV)	150
372 (UV)	250
403 (visible)	300
434 (visible)	50
465 (visible)	0

The increased depth of photodegradation caused by longer wavelength light in the spectral range from 310 to 403 nm accords with its increased penetration into wood. Figure 4 illustrates the relationship between depth of photodegradation and the penetration of light with different wavelengths into Japanese cedar earlywood. There appeared to be a good relationship between penetration of light in the spectral range from 310 to 403 nm and maximum depth of photodegradation. Light with wavelengths longer than 434 nm penetrated earlywood to a greater depth than shorter

wavelengths, but did not cause any detectable chemical changes to the wood's chemical composition. As mentioned earlier, the changes in the non-conjugated carbonyl (1730 cm^{-1}) and aromatic (1510 cm^{-1}) peaks in the IR spectra of irradiated wood became smaller with increasing wavelength of the incident light.

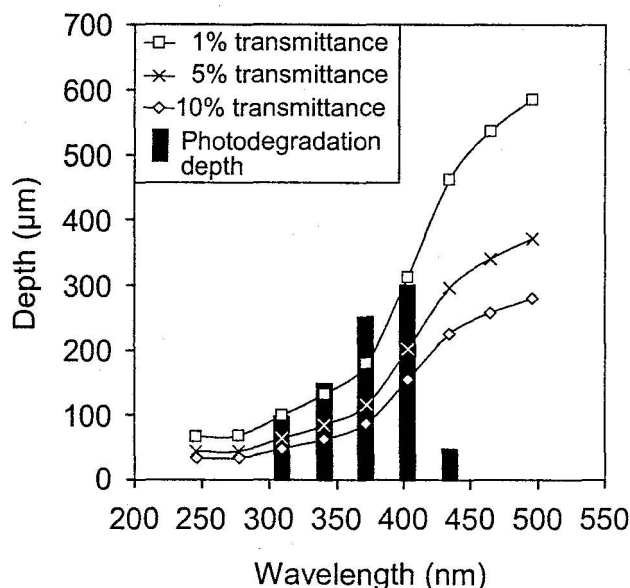


Figure 4. Changes in depth of penetration of light and the maximum depth of photodegradation (to which significant changes in the carbonyl band (1730 cm^{-1}) were detected) in Japanese cedar earlywood as a function of wavelength of light used to irradiate specimens.

Discussion

Changes in the IR spectra of Japanese cedar earlywood irradiated with violet light (403 nm) are evidence that violet light possesses sufficient energy to degrade lignin. These observations and measurements of the depth of penetration of wood by violet light strongly suggest that it is this component of the visible spectrum that extends photodegradation into wood beyond the zone affected by UV radiation. Blue light with longer wavelengths (430 to 500 nm) was unable to significantly degrade lignin and hence did not extend photodegradation into wood despite its ability to penetrate wood to a greater depth than violet light. These findings indicate that violet light plays a key role in the development of the photodegraded layer in weathered wood, and add to the growing body of evidence that it has an important role in degrading organic materials (Young 1992; Xie et al. 2000).

The findings here are also useful in explaining our previous observations of the growth of the photodegraded layer in Japanese cedar earlywood over time (Kataoka et al. 2004). Based on light transmission measurements here (Figure 2), the intensity of photo-active violet light (403 nm) is expected to decrease to 1% of its initial value (incident light) after penetrating Japanese cedar earlywood to a depth of approximately 310 μm (Table 1). This small intensity of light, however, may still produce 10% of the degradation that occurs at the surface, assuming that the primary photo-oxidation rate is proportional to the square root of the light intensity (Vink 1979). These findings are consistent with our previous observations that growth of the photodegraded layer in Japanese cedar earlywood over time was logarithmic, and a ten-fold increase in irradiation time was required to increase its thickness by 330 μm (Kataoka et al. 2004). They also explain previous observations that wood exposed to natural or artificial weathering is degraded well beyond the zone affected by UV radiation (Browne and Simonson 1957; Bamber and Summerville 1980; Yata and Tamura 1995; Kataoka et al. 2004, 2005).

Previous research also concluded that visible light can penetrate wood to a greater depth than UV radiation (Browne and Simonson 1957; Hon and Ifju 1978; Jirous-Rajkovic et al. 2004). There are some discrepancies, however, between our results and these previous studies. Based on our measurements, 1% of UV radiation in the range of 246 to 372 nm will penetrate Japanese cedar earlywood to depths of 66 to 178 μm , respectively (Table 1). In contrast, Browne and Simonson (1957) reported that UV showed 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 (340 nm peak) penetrated silver fir (*Abies alba* Mill.) wood to a depth greater than 70 μm . Much larger 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 (with wavelengths from 400 to 750 nm) penetrated redwood (*Sequoia sempervirens* (D. Don) Endl) 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 to 150 μm . Penetration depths observed here were 153 to 279 μm in the spectral range of 403 to 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 the differences in the methods used to assess the

transmission of light into wood and variation in the chemical composition and density of the wood samples employed in previous studies and those used here.

The finding that violet light is the component of the visible spectrum that extends photodegradation in wood beyond the zone affected by UV radiation has important implications for the development of improved protection systems for wood used outdoors. It is clear that such systems will need to employ chemicals that screen violet light (380 to 430 nm) from wood as well as UV radiation. These chemicals will be pigmented since they absorb visible light, however, the human eye has difficulty in discerning wavelengths in the violet region of the visible spectrum and pigments that absorb strongly in this region of the visible spectrum are a pale yellow colour (Goldsmith 1986; Tomoda et al. 1990). Hence, they may not dramatically affect the colour of lighter coloured wood species, and impose a great limitation on the use of natural finishing systems with such woods.

Conclusions

There was a positive correlation between the penetration of light into Japanese cedar earlywood and the wavelength of the incident radiation within the 246 to 496 nm range. The depth of photodegradation also increased with wavelength up to and including the violet region of the visible spectrum. Blue light (434 to 496 nm) penetrated wood to a greater depth than violet light, but it did not significantly modify lignin, and hence it was not responsible for sub-surface photodegradation of wood. The photodegradation depth profile of wood exposed to light, which is characterised by a gradient of degradation that decreases in severity from the surface to sub-surface layers, appeared to be a product of the ability of light to penetrate wood and degrade its structural components. We conclude that violet light (380 to 430 nm) is the component of the visible spectrum that extends photodegradation into wood beyond the zone affected by UV radiation. Surface treatments designed to protect wood used outdoors will therefore need to screen wood from the effects of violet light radiation or block the photo-catalytic reactions that are responsible for the degradation of wood by visible light.

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