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ORIGINAL ARTICLE

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Light source dependence of the photodegradation of wood

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Abstract The aim of this study was to determine whether artificial ultraviolet (UV) light sources are able to imitate properly the photodegradation of wood caused by sunlight. In this study, wood specimens were irradiated with a xenon lamp and a mercury lamp. The xenon light simulated sunlight only in the case of long-term irradiation. The photoinduced yellowing of wood was faster and greater in the case of short-term exposure to xenon light than that caused by sunlight. The number of UV light-generated carbonyl groups absorbing infrared light around $1700\,cm^{-1}$ showed good correlation with photoinduced yellowing. On the other hand, mercury light did not simulate sunlight. However, the mercury lamp, as a strong UV light emitter, can be applied to determine the valid limits of the Kubelka–Munk (K-M) equation. Our results show that the K-M equation cannot be applied to determine the absorption properties of the sample if the values of the K-M units exceed 50.

Key words Weathering · Sunlight · Artificial light · Color changes · DRIFT spectra

Introduction

The main factor that causes the greatest changes in the surface properties of wood during outdoor exposure is sunlight. Careful investigation of this type of degradation of wood is difficult using outdoor exposure, because weather conditions are not repeatable. Therefore, the light-induced degradation of wood is usually investigated under artificial conditions. The artificial light source most frequently used is the xenon lamp. Because of the thinning of earth's ozone layer, nowadays more ultraviolet (UV) radiation reaches the earth's surface than before. Therefore, the UV B wavelength region (280–315 nm) has to be taken into consideration. Xenon lamps have no emission in the UV B region, while the emission spectrum of the mercury lamp has a wider range of UV light.[1] To simulate the effect of this UV B radiation, a mercury lamp may be used.

Comparative studies of the effect of sunlight and artificial light sources on the weathering of wood are rare in the literature. Ota et al.[2] tested the colour stability of acetylated veneers of kiri (*Paulownia tomentosa Steud.*) irradiated by sunlight and light generated by a mercury lamp. Podgorski et al.[3] measured the effect of outdoor and artificial weathering of coated wood by glass transition temperature. The cycles of treatment consisted of immersion in distilled water, drying, and light irradiation with UV lamps. In our experiments the samples were brought out for sunlight exposure only on sunny days to determine the effect of the sunlight alone. This type of outdoor irradiation is not found in the literature at all. The aim of this study was to determine whether artificial light sources are able to properly imitate the photodegradation of wood caused by sunlight. The similarities and differences in the effects caused by natural and artificial light (xenon and mercury lamps) on wood were examined to determine which type of radiation simulates the effects of sunlight. As the intensity of sunlight changes continuously during the day and during the year, the comparison was made on the basis of irradiation time. In addition, the validity of the Kubelka–Munk equation was discussed in the case of photoirradiated wood.

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Experimental

The investigated hardwood samples were: beech (*Fagus crenata*), black locust (*Robinia pseudoacacia*), poplar (*Populus cauesceus*), and zelkova (*Zelkova serrata*); the softwood samples were: Japanese cedar (*Cryptomeria* *japonica* D. Don), Japanese cypress (*Chamaecyparis obtusa*), Scots pine (*Pinus sylvestris*), spruce (*Picea abies*), and, as a unique wood, bamboo (*Phyllostachys pubescens*) was also investigated. Planed surfaces with a tangential orientation were prepared. The sample size was 50 × 10 × 2mm. The samples of different series were prepared from the same board. The changes suffered only by the earlywood part of sapwood are presented in this study. For black locust, the earlywood part of heartwood was investigated. All species were represented by a series of two samples, and five points of fixed location were measured. The data presented in this work are the averages of ten measurements. The natural sunlight irradiations were carried out between 5 May and 19 August 2003 [air temperature varied 16°–41°C, maximum relative humidity (RH) 80%, and the daily average of total solar power density was 436–459 W/m^2], and between 17 September and 5 December 2003 (air temperature varied 5°–38°C and maximum RH 71%, the daily average of total solar power density was 326–260 W/m^2, the exposure was stopped after 120h because of bad weather conditions) in Takayama, Gifu Prefecture, Japan. Geographical data for Takayama are: latitude 36°9.3′N, altitude 560m. The samples were exposed outside only on sunny days to determine the effect of the sunlight alone. After exposure, the samples were stored in total darkness in the laboratory. The other series of specimens were irradiated with a xenon lamp at 180 W/m^2, in the range of 300–400nm, for up to 200h, at 63°C (black panel) and 50% RH, in a commercial chamber (SX-75: Suga Test Instruments, Tokyo). There was a quartz glass filter around the lamp. A strong UV light emitter, a mercury lamp was also used to irradiate specimens (HAL 800NL, installed into a KBP 659 Nippon Denchi chamber). The total light emission of the mercury lamp was 320W, and the samples were located 64cm from the lamp. The air temperature in the chamber was 26°C. Total irradiation time was 200h for sunlight and xenon light, and 20h for mercury light.

The color and the infrared (IR) spectra of the wood specimens were measured before and after irradiation. The exposures were interrupted after 5, 10, 20, 30, 60, and 120h to measure the color and IR data. The color measurements were carried out with a colorimeter (SE-2000 Nippon Denshoku, Tokyo). The L^*, a^*, and b^* color co-ordinates were calculated based on a D_{65} light source. The IR spectral measurements were performed with a Jasco FTIR double beam spectrometer equipped with a diffuse reflectance unit (Jasco, DR-81). The resolution was 4cm^{-1} and 64 scans were obtained and averaged. The background spectrum was obtained against an aluminum plate. The spectral intensities were calculated in Kubelka–Munk (K-M) units. The spectra were normalized to the band between 1350cm^{-1} and 1405cm^{-1}, and a two-point baseline correction at 3800cm^{-1} and 1900cm^{-1} was carried out.

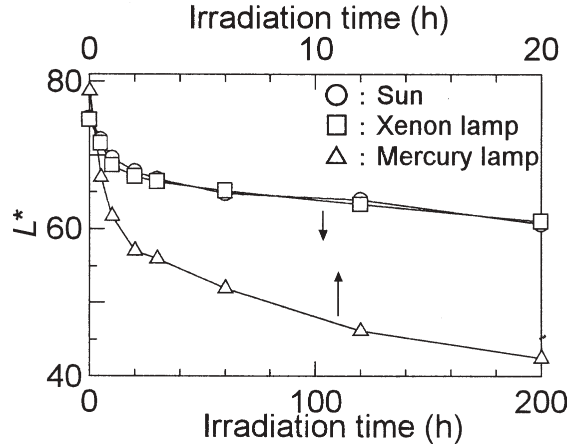

Fig. 1. Lightness change of beech wood during light irradiation. *Arrows* indicate appropriate irradiation time scale

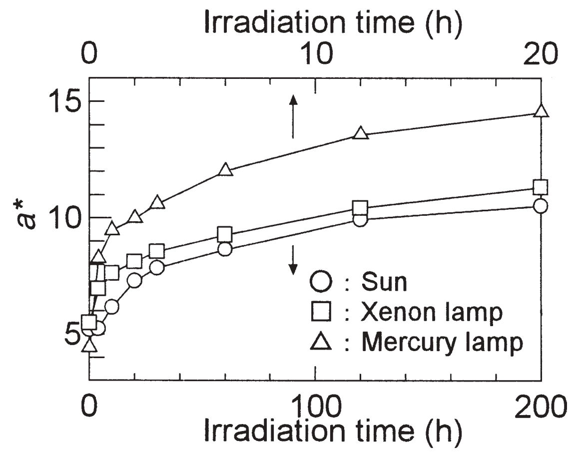

Fig. 2. Color change (red content) of beech wood during light irradiation

Results and discussion

Color changes

Color and color stability are important features of products made from wood. The color of wood is sensitive to light radiation and thermal treatment.[4,5] UV light in particular causes remarkable color changes.[5,6] Color changes were more pronounced initially during exposure than the change in IR spectra, for all treatments and samples. In some species this color change was notable and visible even with the naked eye after a few hours of radiation (e.g., black locust). In contrast, poplar suffered hardly any visible color change during the same period of time. During the first 30h of light irradiation by sun and xenon lamp, the color change was rapid, as is shown in Figs. 1–4 and in Table 1. Table 1 presents the color data of five representative wood species after exposure to sunlight and xenon light. Changes in lightness were particularly pronounced. The rapid period of lightness change caused by sunlight in the first 30h ac-

Table 1. Color data of the representative wood species

		Exposure time (h)							
		0	5	10	20	30	60	120	200
Black locust	*L**	73.75	69.64	67.66	67.16	66.87	67.22	68.21	64.87
heartwood	*a**	1.63	3.99	5.29	5.79	6.62	6.95	8.41	9.20
(sunlight)	*b**	24.82	27.11	28.44	29.40	32.08	32.63	35.90	36.18
Black locust	*L**	72.96	71.13	68.53	67.50	66.80	66.20	64.50	62.09
heartwood	*a**	1.61	7.28	8.64	9.32	10.24	11.14	10.92	11.24
(xenon light)	*b**	24.88	32.87	32.91	33.01	34.11	36.21	36.59	37.01
Poplar	*L**	75.20	73.40	73.11	72.48	72.96	72.80	71.16	68.25
sapwood	*a**	4.88	4.19	4.11	4.26	4.54	4.75	6.35	7.46
(sunlight)	*b**	23.40	22.81	23.66	26.07	28.07	29.76	32.69	33.45
Poplar	*L**	75.23	74.10	72.73	72.20	72.24	70.79	69.95	67.35
sapwood	*a**	5.34	5.13	5.32	5.73	6.38	8.05	8.07	8.96
(xenon light)	*b**	23.66	28.65	29.28	31.02	31.81	35.37	35.84	36.37
Japanese cedar	*L**	80.94	79.24	75.76	75.16	75.29	74.63	71.48	67.14
sapwood	*a**	1.54	0.79	1.06	1.63	2.56	3.58	6.74	8.11
(sunlight)	*b**	18.39	21.31	25.00	27.97	31.47	33.34	35.76	35.46
Japanese cedar	*L**	82.84	79.00	76.39	73.62	72.29	68.26	67.50	62.82
sapwood	*a**	1.20	1.35	2.76	3.79	5.97	8.69	9.21	10.11
(xenon light)	*b**	19.64	30.55	32.34	34.06	36.77	39.73	38.42	37.21
Spruce	*L**	81.98	80.84	76.85	75.75	75.29	74.83	70.57	65.9
sapwood	*a**	0.37	0.00	0.51	1.21	2.01	3.37	6.92	8.64
(sunlight)	*b**	17.19	20.60	24.82	27.91	31.48	33.78	37.25	36.75
Spruce	*L**	82.86	77.39	74.57	71.62	70.52	69.61	65.00	60.31
sapwood	*a**	0.21	0.20	1.76	3.02	4.31	7.25	8.09	9.14
(xenon light)	*b**	16.30	28.52	30.60	32.91	33.97	37.57	37.27	36.07
Bamboo	*L**	65.77	65.17	63.85	64.39	64.59	65.43	66.2	63.66
(sunlight)	*a**	5.98	5.64	5.45	5.48	5.70	5.75	7.01	8.08
	*b**	26.08	24.30	25.21	26.64	28.49	29.11	32.04	32.82
Bamboo	*L**	67.26	65.63	65.03	64.20	64.48	63.34	63.69	61.25
(xenon light)	*a**	6.15	6.20	6.63	6.94	7.85	8.87	8.49	8.98
	*b**	26.18	29.73	30.49	31.60	31.26	33.53	33.41	32.68

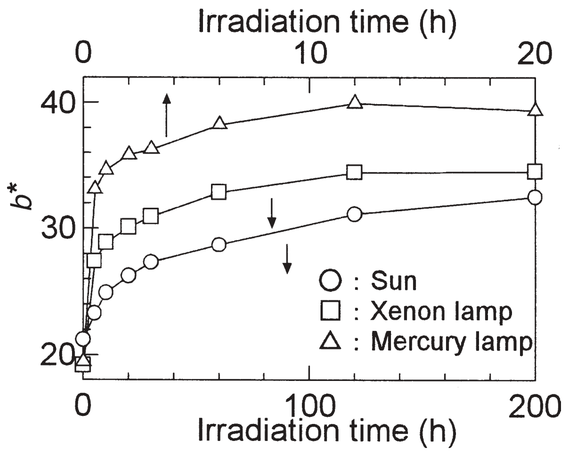

Fig. 3. Color change (yellowing) of beech wood during light irradiation

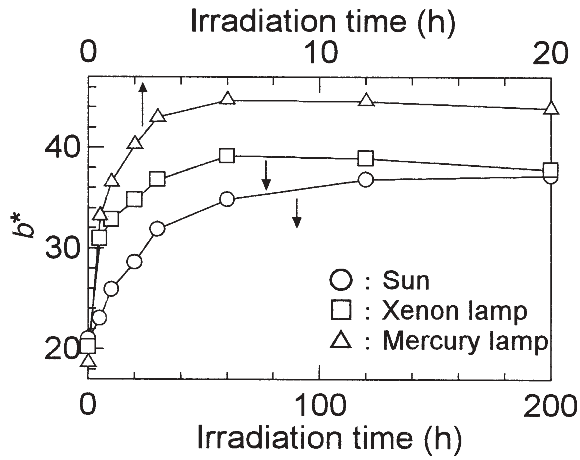

Fig. 4. Color change (yellowing) of Japanese cypress wood during light irradiation

counted for ca. 60% of the total change in hardwoods and 40%–50% of those in softwoods. The applied artificial light sources caused even faster changes in lightness than sunlight during the first 30h of exposure. The greatest difference in color caused by exposure to the xenon lamp compared with that caused by sunlight was observed for spruce. The difference in lightness after 30h of irradiation was 15%. After 50h of irradiation the trend changed and the trendlines converged or became parallel. The effects of exposure to the mercury lamp are discussed below.

The *a** coordinate represented in Fig. 2 for beech did not change significantly during the first few hours of exposure to sunlight. On the other hand, a^* decreased slightly in the cases of Japanese cedar and Japanese cypress. Repeated irradiation tests produced similar results. Only the black locust wood became redder during the first few hours of exposure to sunlight. In contrast, samples exposed to xenon light became redder during the first few hours of irradiation. The extraordinary behavior of black locust may be due to its high extractive content.[7] The robinetin in this species may be especially sensitive to UV light exposure. The third color coordinate b^* showed an even greater difference than a^* when sunlight exposure and xenon light exposure were compared (Figs. 3 and 4). The yellowing of the samples caused by xenon light was concentrated in the first 5h of irradiation. Color changes during this period account for 61% of the total yellowing of Japanese cypress and spruce samples. However, the changes caused by sunlight mainly occurred during the first 30h of irradiation. After 50h of irradiation, the intensity of change decreased and the trendlines converged or became parallel. During long-term exposure, the color changes in wood were similar for both irradiation types. From the viewpoint of color change, it can be concluded that the xenon lamp irradiation simulates natural exposure to sunlight only when wood is subjected to long-term exposure to xenon light. Short-term exposure to xenon light causes more rapid yellowing than sunlight. Another important result is that the xenon lamp can be used to accelerate color changes only in the first 100h of exposure. The acceleration effect by xenon light is about three times that of sunlight.

The effect of mercury lamp irradiation differed to those of xenon or natural light exposure. Mercury light irradiation was carried out for up to 20h. All data for this type of irradiation are presented in Figs. 1–4. This treatment caused much greater color changes than the other types of irradiation. The emission spectrum of the mercury lamp (supplied by the lamp manufacturer) is located mainly in the UV region (80%). It contains 31% UV-A (315–380nm) radiation, 24% UV-B (280–315nm), and 25% UV-C (>280nm) radiation. The photons of the UV-C range have sufficient energy to split almost all chemical bands existing in wood.[8] The sunlight reaching the surface of the Earth does not contain UV-C. Therefore, the use of a mercury lamp can provide valuable results for understanding the nature of the UV photodegradation of wood, but it is unable to simulate the effects of sunlight.

Changes in DRIFT spectra

Infrared spectroscopy is a useful method for studying the chemical changes in wood caused by light irradiation. The differences in the changes of IR spectra caused by the two types of irradiation in this study are qualitative rather than quantitative. The difference IR spectra were calculated to clearly show the changes. There was deviation between hardwoods and softwoods. These are represented by the spectra of Japanese cypress and beech in Figs. 5 and 6, respectively. Only the fingerprint area (900–1900 cm^{-1}) is presented because differences were found only in this

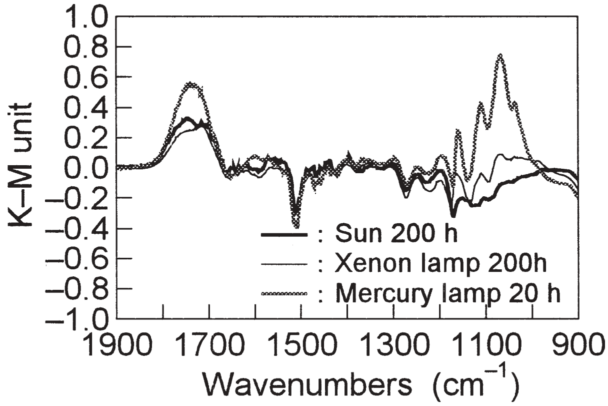

Fig. 5. Difference IR spectra of Japanese cypress wood caused by light irradiation

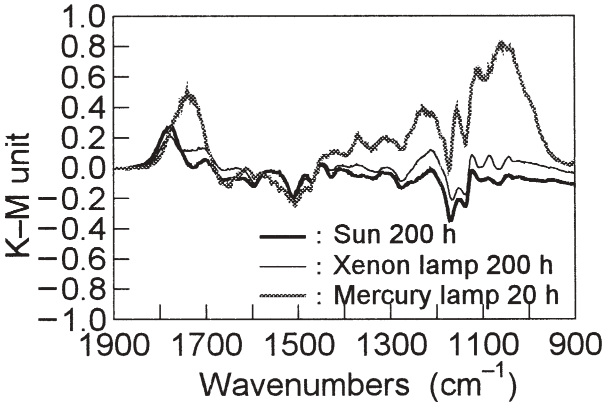

Fig. 6. Difference IR spectra of beech wood caused by light irradiation

region. The band assignments can be found in a previous work.[5] After irradiation, the carbonyl band between 1680 and 1900 cm^{-1} increased and the peak of the aromatic skeletal vibration arising from lignin (1510 cm^{-1}) decreased together with the guaiacyl vibrations at 1275 cm^{-1}, as has been noted in previous studies.[5–6,9–12] The band for the aromatic skeletal vibration at 1600 cm^{-1} also decreased in the case of hardwoods. The changes in the wavenumber region of 900–1200 cm^{-1} are not obvious, and these are discussed later. The effect of the two irradiation types (i.e., sunlight and xenon light) on peaks in the wavenumber region of 1680–1900 cm^{-1} were different. Two peaks usually develop in this region during the exposure of wood to UV radiation. In softwoods, these peaks are close to each other. These highly overlapped bands are sometimes visible as one broad band if the irradiation is strong enough or prolonged. This is well demonstrated in Fig. 7. After 1h of mercury lamp irradiation, the two bands are well separated, but after 6h they have already merged to create one peak. In hardwoods, these bands are usually more separated, and the intensity difference between the two bands changed more heavily than for softwoods (Figs. 5, 6, and 8).

The difference in the effects of the two types of irradiation is moderate in the case of softwoods after 200h of

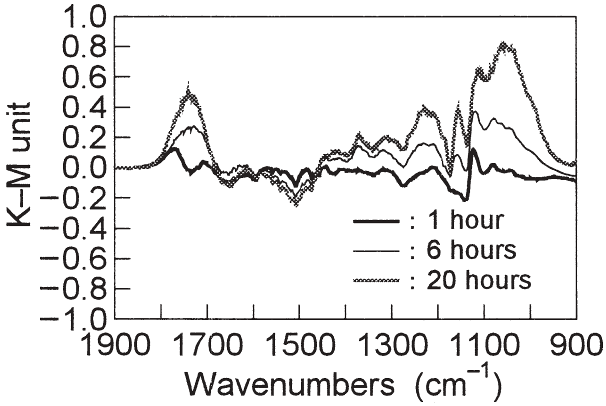

Fig. 7. Difference IR spectra of beech wood caused by mercury light irradiation

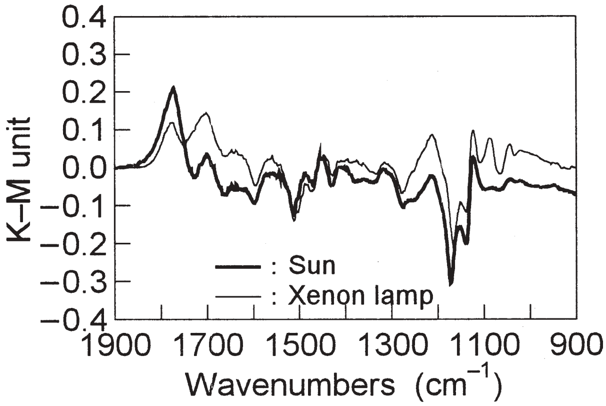

Fig. 8. Difference IR spectra of beech wood after 60h of light irradiation

irradiation (Fig. 5). The xenon light causes a slightly greater increase in the peak at 1716cm^{-1} than at 1748cm^{-1}. The absorption wavenumbers of the CO stretching in unconjugated ketones, carboxyl groups, and lactones are between 1730cm^{-1} and 1780cm^{-1}, and the nonconjugated aliphatic carbonyls absorb between 1700cm^{-1} and 1750cm^{-1}. As a single measure of the deviation between these two peak intensities, their ratio was calculated on the basis of the higher wavenumber. The 1716cm^{-1}/1748cm^{-1} ratio following exposure to xenon light was 1.15. On the other hand, exposure to sunlight for 200h created the opposite change in intensity: the 1716cm^{-1}/1748cm^{-1} ratio was 0.85. This deviation was little greater at shorter irradiation times. In the case of hardwoods, the deviation was more pronounced, shown for beech samples after 200h and after 60h of irradiation in Figs. 6 and 8, respectively. Here the two carbonyl peaks are well separated with maximums at 1700cm^{-1} and 1773cm^{-1}. After 200h of irradiation, there is little difference in the effect of sunlight and xenon light (Fig. 6). The relation of the two created peaks is similar to that of softwoods at 200h of irradiation. Only the peak at 1700cm^{-1} is smaller in every case. The 1700cm^{-1}/1773cm^{-1} ratio was 0.63 and 0.2 for xenon light and sunlight, respectively. These ratios changed during exposure. In the first few hours of exposure the deviation in the peak intensity ratio increased, mainly because of the rapid increase of the peak at 1700cm^{-1} in the case of xenon light. After 60h the deviation decreased. The biggest deviation was found at 60h of irradiation. Here the 1700cm^{-1}/1773cm^{-1} ratio was 1.2 and 0.17 for xenon light and sunlight, respectively. The increase of the band at 1700cm^{-1} was rapid at the beginning of xenon light irradiation and stayed the same after 60h of irradiation. In contrast, this band increased continuously during the 200h of irradiation with sunlight. Thus, the difference in the intensity ratios decreased continuously after 60h of exposure. Xenon light may not reproduce the change of energy for every wavelength in sunlight. The change of the band at 1700cm^{-1} was similar to the changes of the color coordinates a^* and b^*. These findings strengthen our conclusion suggested by color measurements that the xenon light irradiation can simulate the effects of sunlight only after long-term irradiation.

Radiation emitted by a mercury lamp contains much more UV light than a xenon light source or sunlight as mentioned above. Müller et al.[6] compared the effect of two types of xenon lamps emitting different wavelengths of UV light. They measured the yellowing and the IR spectrum of spruce veneers and found that the reaction rate was faster under low-intensity irradiation at short wavelengths than at high intensity and long wavelengths. The UV-B and UV-C parts of the spectrum were particularly damaging to wood. Therefore, degradation caused by a mercury lamp is greater and different to that caused by sunlight or light emitted by a xenon lamp. This is confirmed by results presented in Figs. 5–7. It can be concluded that the mercury lamp is not able to simulate the degradation caused by sunlight. However, the results provide an insight to the mechanism of the photodegradation of wood. The broad carbonyl band (1680–1900cm^{-1}) is believed to consist of two section bands. However, in Fig. 6, the IR curve generated by mercury light differs from the others around 1800cm^{-1}. It seems that one band is missing, which is present in the IR spectra for wood exposed to sunlight and xenon-arc light. This suggests that the band with a maximum at 1773cm^{-1} may actually consist of two peaks. The width of this band is large enough to accommodate two peaks. Further research is needed to clarify this.

The wavenumber region of 900–1200cm^{-1} is a critical area of the diffuse reflectance spectrum of wood. The anomalous behavior of this wavenumber region was already reported in previous articles.[13–15] The validity of the Kubelka–Munk equation is questionable in this region. The surface roughness of wood increases as it is photodegraded. This phenomenon increases the light scattering and the number of the photons collected by the detector decreases. The Kubelka–Munk equation gives increasing numbers with decreasing reflectance. When the surface reflects poorly, the K-M function is extremely steep. Therefore, in this region a small increment in absorption causes a disproportionately high increase of K-M units. This is visible in Fig. 7 in which the whole curve is lifted, but not proportionately, at increasing irradiation time in this wavenumber range. Therefore, the K-M units do not represent the real absorption in this region. Recording many IR spectra for irradiated wood samples, our experiences show that the K-M equation cannot be applied to determine the absorption properties of the sample if the values of K-M unit exceed 50. This is because the values of the Kubelka–Munk function sharply increase above this limit if the reflection properties of the sample decrease.[16]

Conclusions

Xenon light is able to simulate the effect of sunlight during weathering only at long exposure times. In the short term, the yellowing of wood is faster and greater in the case of xenon light irradiation than in the case of sunlight. The acceleration effect by xenon light is about three times that of sunlight. During exposure to xenon light or sunlight, the number of UV light-generated carbonyl groups absorbing the infrared light around $1700\,cm^{-1}$ appears to be correlated with the yellowing of wood. Light emitted by a mercury lamp cannot be used to simulate sunlight. However, the mercury lamp, as a strong UV light emitter, can be applied to determine the validity limits of the Kubelka–Munk equation.

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