

DIFFUSE REFLECTANCE INFRARED FOURIER TRANSFORM SPECTROSCOPY (DRIFT) AND COLOR CHANGES OF ARTIFICIAL WEATHERED WOOD

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ABSTRACT

Short-term (22.7 h) accelerated weathering was performed on black cherry (*Prunus serotina*), soft maple (*Acer saccharinum*), and red oak (*Quercus rubra*) using a 2-h ultraviolet (UV) light irradiation and 0.3-h water spray regime. Contributions to the wood surface color change from changes in lightness, chroma, and hue were observed, and variations existed among wood species. Chemical modifications on wood surfaces were monitored semi-quantitatively by using Diffuse Reflectance Infrared Fourier Transform spectroscopy (DRIFT). Band intensities at 1170 cm^{-1} , 1510 cm^{-1} , and 1740 cm^{-1} were used to follow the photodegradation on the wood surface during the 22.7-h accelerated weathering. Linear correlation was observed between the ratio of band intensity at 1740 cm^{-1} relative to the band intensity at 1170 cm^{-1} , and the color change or the lightness modification. Results from this study clearly indicated that the rates of weathering/photodegradation of wood are influenced by wood species. Soft maple and red oak exhibit similar weathering rate (0.048) and higher than that of black cherry (0.031).

Keywords: DRIFT, wood weathering rate, color change, lightness modification, semi-quantification.

INTRODUCTION

Wood used outdoors is subjected to weathering. The main factors inducing weathering during full exposure are sunlight, especially UV light, heat, and moisture (Kalnins and Feist 1991). Extractives and lignin absorb the visible and the UV compo-

nents of light, resulting in the initiation of photochemical reactions leading to wood degradation (Hon and Change 1984; Hon 1991). Weathering causes changes in wood properties such as weight loss (Feist and Mraz 1978), discoloration (Hon et al. 1985), surface erosion (Sell and Feist 1986; Williams et al. 2001), formation of checks and cracks (Williams and Feist 1994). Weathering may also make the wood substrate more susceptible to fungal growth (Evans and Banks 1986).

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The weathering of wood has been investigated with several techniques. Microscopy was used to observe the changes in wood microstructure (Derbyshire and Miller 1981; Owen et al. 1993), profilometer to monitor wood surface roughness (Kamdem and Grelier 2002; Nzokou and Kamdem 2002), UV-visible spectroscopy to analyze the extracts and the surface of weathered wood (Hon and Chang 1984; Liu et al. 1994), and spectrophotometry to follow the color changes (Hon et al. 1985; Grelier et al. 2000).

In order to understand the chemical changes involved in wood weathering, several studies reported the use of Fourier Transform Infrared Spectroscopy (FTIR) to monitor the modifications of some functional groups on weathered wood surface (Hon and Feist 1986; Németh and Faix 1990; Anderson 1991a,b; Sudiyan et al. 1999). Carbonyl groups, carboxyl groups, and carbon-carbon double bonds from the aromatic groups are reported to be most susceptible to photochemical reactions in wood weathering (Hon and Feist 1986; Németh and Faix 1990; Sudiyan et al. 1999). Hon and Feist (1986) used FTIR to monitor the modification on wood surface after a 40-day artificial weathering of yellow poplar. They ratioed the intensities of absorption band at 1740 cm^{-1} and 1510 cm^{-1} to 1160 cm^{-1} , and reported the increase in intensities of band at 1740 cm^{-1} and the decrease at 1510 cm^{-1} associated with the weathering time.

Color change is attributed partially to the migration/generation and/or removal of colored material such as wood extractives, colored low molecular weight lignin derivatives, and quinones formed during the weathering process. (Leary 1968; Fengel and Wegener 1984). An important color change has been observed on wood surface during the initial stage of accelerated weathering (Hon and Feist 1986; Németh and Faix 1990; Nzokou and Kamdem 2002).

The objectives of this study were to semi-quantitatively characterize the modification generated on wood surface by using Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFT) during the first 22.7 h of an artificial accelerated weathering regime, and to

correlate the changes in functional groups to the color changes developed on wood surface monitored by a reflectometer using CIELAB system. Black cherry (*Prunus serotina*), soft maple (*Acer saccharinum*), and red oak (*Quercus rubra*) were selected as test species for this study. These hardwood species are valuable in decorative furniture and joinery where discoloration is frequently noticed on wood surface exposed to light and/or rain (Hon and Feist 1986; Grelier et al. 2000).

MATERIALS AND METHODS

Wood specimens

Defect-free, kiln-dried flatsawn planks of black cherry (*Prunus serotina*), soft maple (*Acer saccharinum*), and red oak (*Quercus rubra*) were selected for this study. Four replica of specimens, measuring 4 mm by 25 mm by 25 mm, were used for each species.

Artificial accelerated wood weathering

Weathering was conducted with an artificial accelerated weathering device (Model: QUV/Spray) from Q-Panel Lab Products, Cleveland, OH, equipped with eight UVA 340 nm fluorescent UV lamps and distilled water spray from twelve spray nozzles mounted between the UV lamps, capable of delivering 4 liters of water per minute at room temperature. The pH of the distilled water used was 6.2 ± 0.05 . The device was operated at an average irradiance of 0.85 W/m^2 , and at a temperature of 50°C .

The weathering cycle was carried out by following the procedure outlined in ASTM standard G154 (ASTM 2000). Each cycle included continuous UV light irradiation of 2 h followed by a 0.3-h water spray for a total of 2.3 h. Test specimens were mounted on panel holders 50 mm away from the UV lamps. DRIFT spectra and color data of weathered samples were collected after every 2-h UV irradiation and 0.3-h water spray interval during the first 22.7 h of weathering. To reduce the effect of moisture content variation on color and DRIFT, weathered samples were conditioned at 50°C for 2 h in

an oven to a moisture content of $5 \pm 0.5\%$ before the DRIFT and color measurements.

COLOR MEASUREMENTS

The surface color of wood samples was measured by following the procedure outlined in ASTM standard D2244 (ASTM 2000). A Microflash Elrepho model 200 Reflectometer from DataColor, Datacolor International, Charlotte, NC, was used to measure the L , a , and b values on each sample. The values of color change (ΔE) were calculated by reference to unweathered samples.

DRIFT MEASUREMENTS

DRIFT spectra of unweathered and weathered specimens were collected with a Nicolet Fourier Transform Infrared (FTIR) spectrophotometer (Model Protégé 460) from Nicolet Instruments Corporation, Madison, WI, equipped with a Spectra-Tech (Spectra Tech, INC. Shelton, CT) diffuse reflectance accessory. Spectra were recorded for a total of 128 scans in Kubelka-Munk units in the $4000\text{--}400\text{ cm}^{-1}$ wavenumber range, with a resolution of 4 cm^{-1} . Background spectra were collected with the use of dry KBr powder. The baseline was established at 1900 cm^{-1} in this study.

DATA ANALYSIS

Color change

The color coordinates/parameters L , a , and b were used to calculate the color change (ΔE). L is defined as the lightness, a and b are the chromaticity coordinates in the CIELAB system. ΔL is lightness modification, Δa and Δb are the changes in chromaticity coordinators a and b . The algebraic signs of ΔL , Δa , and Δb have the following meanings (ASTM 2000):

- + ΔL : lighter
- ΔL : darker
- + Δa : redder (less green)
- Δa : greener (less red)
- + Δb : yellow (less blue)
- Δb : bluer (less yellow)

The descriptions of the color change (ΔE) have been reported previously (Grelier et al. 2000; Kamdem and Grelier 2002). Color change (ΔE) is calculated using Eqs. (1) and (2), where X is L , a , or b , L_i , a_i , and b_i are the initial values of the L , a , and b parameters. L_f , a_f , and b_f are the final values.

$$\Delta X = X_f - X_i \quad (1)$$

$$\Delta E = \sqrt{(\Delta L^2 + \Delta a^2 + \Delta b^2)} \quad (2)$$

Hitka et al. (2001) used the value of color change (ΔE) to define the levels of perceived difference in color. ΔE varying for 0 to 0.5 is defined as negligible, between 0.5 and 1.5 is slightly perceivable, from 1.5 to 3.0 is noticeable, from 3.0 to 6.0 is appreciable, and from 6.0 to 12.0 is very appreciable.

ΔE includes the contributions of modifications in lightness, chroma, and hue. Chroma (C) is the perpendicular distance from the lightness axis. The contribution of chroma difference to color change (ΔE) is expressed as ΔC and calculated by using Eq. (3) The hue difference (ΔH) is calculated by using Eq. (4) (ASTM 2000). Hue angle (h , in degree) indicates the direction on the chroma diagram and is calculated according to Eq. (5) (ASTM 2000). A 0° represents a location on the $+a$ (red) axis, a 90° on the $+b$ (yellow) axis, 180° on $-a$ (green), 270° on $-b$ (blue), and back to $360^\circ = 0^\circ$ (red).

$$\Delta C = \sqrt{(a_f^2 + b_f^2)} - \sqrt{(a_i^2 + b_i^2)} \quad (3)$$

$$\Delta H = \sqrt{(\Delta E^2 - \Delta L^2 - \Delta C^2)} \quad (4)$$

$$h = \arctg\left(\frac{b}{a}\right) \quad (5)$$

DRIFT

To facilitate the manipulation of the spectra obtained from the wood surface, DRIFT was used to collect the spectra in Kubelka-Munk units. The correlation between the band intensity and the concentration of corresponding func-

tional group is expressed in Eq. (6) (Smith 1996).

$$KM = \frac{2.303ac}{s} \quad (6)$$

where KM is the band intensity of a functional group in Kebelka-Munk units; a is the absorptivity of the sample; c is the concentration of the functional group; and s is the scattering factor of the sample. The scattering factor s for solid sample is a function of the uniformity of the sample such as particle size, the shape distribution, and the packing density. For solid wood, surface uniformity and homogeneity are important factors during the collection of DRIFT spectrum. To reduce the variability from one spectrum to another in the same specimen, special care was taken to collect DRIFT spectra almost at the same spot on the wood surface. To compensate for the spectral variations, a stable band with minimum modification after the 22.7-h weathering was selected as a reference band and used to ratio the intensity of bands of interest.

Statistic analysis

Regression analysis was performed to establish the correlation between the ratios of band intensity at 1740 cm^{-1} or 1510 cm^{-1} , and the weathering time, color change (ΔE), lightness

modification (ΔL), or changes in chromaticity coordinates (Δa and Δb).

Statistical analysis using F-test on a generalized linear model (GLM) was performed to test the effect of wood species on the wood weathering properties such as wood weathering rate, the correlation between the ratio of band intensity at 1740 cm^{-1} and ΔE or ΔL at 0.05 significant level (SAS version 8.0, SAS Institute, Cary, NC).

RESULTS AND DISCUSSION

Color changes

The color changes of black cherry, soft maple, and red oak with QUV weathering time are represented in Fig. 1. Based on the Hikita et al. (2001) definition, appreciable color changes occurred on the sample surface after the first 2-h UV irradiation. The most intensive color change was observed during the first two cycles (4.6 h) of the UV/water-spray application, in agreement with earlier studies (Grelier et al. 2000; Kamdem and Grelier 2002; Nzokou and Kamdem 2002). The values of ΔE after each 0.3-h water spray were lower than the values after the previous 2-h UV irradiation, producing a graph with a typical saw tooth pattern. The decrease in ΔE after the 0.3-h water spray was attributed to the removal of colored water-soluble material present on the wood surface.

Table 1 lists the values of L , a , b parameters of wood samples before and after the 22.7-h accelerated weathering regime. ΔL , Δa , Δb , and ΔE after the 22.7-h weathering were calculated using Eqs. (1) and (2) and reported in Table 2. The ratios of ΔL to L_i , Δa to a_i , and Δb to b_i in percentage defined as the rate of modification in lightness and chromaticity coordinates (a and b) are listed in Table 3. A negative $\Delta L/L_i$ reflects a change in lightness from light to dark, while a positive sign is from dark to light. A modification from green to red is expressed by a positive $\Delta a/a_i$, and a positive $\Delta b/b_i$ is from blue to yellow. After 22.7 h, the values of $\Delta L/L_i$ of all species used in this study were negative (Table 3), indicating that the surface became darker as compared to the initial surface color. As shown

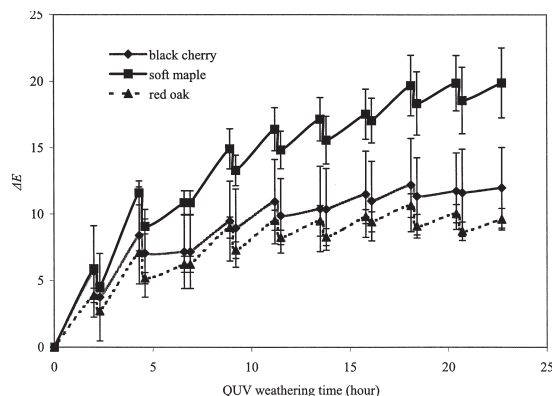


FIG. 1. Color changes (ΔE) after 22.7 h UV/water-spray weathering.

TABLE 1. L , a , and b parameters and h in the QUV weathering.

Wood species	0 hour				22.7 hours			
	L_i	a_i	b_i	$h_i(^{\circ})$	L_f	a_f	b_f	$h_f(^{\circ})$
Black cherry	60.97	11.50	20.96	61.25	49.73	14.54	23.50	58.25
Soft maple	84.00	3.97	16.44	76.42	72.16	10.13	31.19	72.01
Red oak	73.65	7.43	18.21	67.80	67.36	9.34	25.23	69.69

TABLE 2. Δa , Δb , ΔC , ΔH , ΔL^2 , ΔC^2 , ΔH^2 , and ΔE after 22.7-h weathering.

Wood species	Δa	Δb	ΔL	ΔC	ΔH	ΔL^2	ΔC^2	ΔH^2	ΔE
Black cherry	3.04	2.55	-11.24	3.72	1.38	126.34	13.84	1.90	11.92
Soft maple	6.16	14.75	-11.83	15.88	1.87	139.95	252.17	3.50	19.89
Red oak	1.92	7.02	-6.29	7.23	0.84	39.56	52.27	0.71	9.62

in Tables 1 and 3, the largest rate of lightness modification was observed on black cherry with $\Delta L/L_i$ of -18.4% and a L_f value of 49.73. With a relatively high $\Delta L/L_i$ value of -14.0%, soft maple remained lighter with L_f value of 72.16 compared to black cherry and red oak. Red oak exhibited a relatively lower $\Delta L/L_i$ of -8.5% with a L_f value of 67.36. A value of $\Delta a/a_i$ of +155.2% was obtained from soft maple. This value was much higher than the values obtained from black cherry (+26.4%), and red oak (+25.8%), clearly suggesting that after 22.7 h, the rate of modification in chromaticity coordinate a on soft maple was more intensive than black cherry and red oak. This brought the chromaticity coordinate a of soft maple from a_i of 3.97 to a_f of 10.13. The a_f value of soft maple was slightly higher than that of red oak ($a_f = 9.34$) but lower than that of black cherry at an a_f value of 14.54. Red oak had the largest $\Delta b/b_i$ value (+38.6%) after the weathering, suggesting an important shift from blue to yellow. Black cherry and soft maple had similar $\Delta b/b_i$ values at +12.2% and +12.1%, respectively. However, the values of b_f for soft maple (31.19), red oak (25.23), and black cherry (23.50) indicated that, even though $\Delta b/b_i$ was higher with red oak, soft maple was more yellow than the other two species.

This observation was confirmed by the calculation of the hue angle (h) as listed in Table 1. An initial hue angle at 61.25° indicated that before weathering, the location of black cherry on the

chroma diagram was closer to red than soft maple (76.42) and red oak (67.80). The highest h_i value found in soft maple suggested more yellow than the other two species. After 22.7 h, black cherry and soft maple shifted toward red with h_f values of 58.25° and 72.01° , respectively. Red oak became yellow with a h_f value of 69.69° . Overall, black cherry located closer to red and soft maple to yellow, while red oak was in between.

Soft maple yielded the largest color change after 22.7 h with a ΔE value of 19.89, followed by black cherry with a ΔE value of 11.92. Red oak was the most color-stable test species with a ΔE value of 9.62 (Table 2). The contributions to the color change from lightness, chroma, and hue modifications were estimated using ΔL^2 , ΔC^2 , and ΔH^2 (Table 2) as defined in Eq. (4). For black cherry, the value of ΔL^2 at 126.34 was the most important parameter affecting the color change when compared to ΔC^2 at 13.84 and ΔH^2

TABLE 3. Rate of modification in L , a , and b parameters in the QUV weathering.

Wood species	$\Delta L/L_i^1$ (%)	$\Delta a/a_i^2$ (%)	$\Delta b/b_i^3$ (%)
Black cherry	-18.4	+26.4	+12.2
Soft maple	-14.0	+155.2	+12.1
Red oak	-8.5	+25.8	+38.6

¹ rate of modification in lightness.² rate of modification in chromaticity coordinate a ³ rate of modification in chromaticity coordinate b

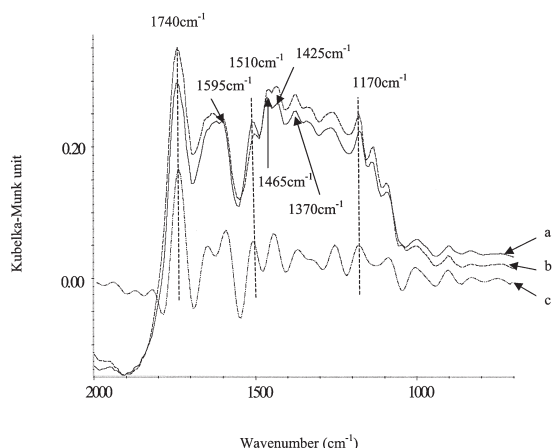


FIG. 2. DRIFT spectrum of black cherry (a) before, (b) after 22.7-h QUV weathering, and (c) after Fourier self-deconvolution.

at 1.90. For soft maple, ΔC^2 of 252.17 and ΔL^2 of 139.95 contributed more to the color change than ΔH^2 of 3.50. For red oak, ΔC^2 of 52.27 followed by ΔL^2 of 39.56 were the most important parameters affecting the color change.

DRIFT

DRIFT spectra of unweathered wood (Fig. 2a) and weathered wood (Fig. 2b) are represented in Fig. 2. The band assignment was performed based on previous work (Morohoshi 1991; Sakakibara 1991; Jin et al. 1991; Dawson and Torr 1992; Zhang and Kamdem 2000). The summarized IR absorption bands associations with the functional groups in wood components are listed in Table 4. A notable broad band was

observed at 1740 cm^{-1} . Fourier “self-deconvolution” at bandwidth of 90 and enhancement of 2.3 was performed to enhance the resolution, using OMINC software from Nicolet Instrument Corp. After the deconvolution, only one band at 1740 cm^{-1} was obtained (Fig. 2c). The intensity of band at 1740 cm^{-1} , which corresponds to carbonyl (C=O) stretching, was observed to increase after the weathering (Fig. 2b), and a decrease was observed on band intensity at 1510 cm^{-1} , which was associated with the aromatic skeletal vibration of benzene ring. The increase at 1740 cm^{-1} and the decrease at 1510 cm^{-1} after the weathering were in agreement with previous reports (Leary 1968; Hon and Feist 1986; Németh and Faix 1990; Sudiyani et al. 1999).

In order to characterize the changes in FTIR absorption bands quantitatively, Hon and Feist (1986) used the band at 1170 cm^{-1} as the reference band in their 40-day artificial accelerated wood-weathering test. The energy of UVA lamp with λ at 340 nm used in this study was 352 kJ/mole. This energy level was slightly lower than the energy needed to dissociate C-O bond (389 kJ/mole) in cellulose (Hon 1976). Therefore, the band at 1170 cm^{-1} from the C-O-C antisymmetric bridge stretching of polysaccharides was considered to be stable in this 22.7-h weathering. The band intensities in Kubelka-Munk units at 1740 cm^{-1} and 1510 cm^{-1} were ratioed against the band intensity at 1170 cm^{-1} to extrapolate information for semi-quantitative study.

An increase in the band intensity at 1740 cm^{-1} was observed during the UV irradiation. After the

TABLE 4. Infrared bands associated with functional groups in hardwood components (Dawson and Torr 1992; Morohoshi 1991; Sakakibara 1991; Jin et al. 1991; Zhang and Kamdem 2000).

Wavenumber (cm^{-1})	Assignment
1735 \pm 5	Carbonyl (C = O) stretching, unconjugated ketone and carboxyl group
1595 \pm 5	Aromatic skeletal vibrations of benzene ring
1510 \pm 5	Aromatic skeletal vibrations of benzene ring
1465 \pm 5	CH ₂ bending in lignin and CH ₂ bending on pyran ring in lignin
1425 \pm 5	CH ₂ scissor in cellulose (mainly), and CH ₃ bending in lignin
1370 \pm 5	CH ₃ bending in hemicelluloses
1165 \pm 5	C-O-C antisymmetric bridge stretching

water spray, the band intensity at 1740 cm⁻¹ decreased. The decrease was attributed to the removal of water-soluble compounds containing C=O group (Hon and Feist 1986). In order to evaluate the compounds with C=O groups present on wood surface during UV irradiation, the ratios of the band intensity at 1740 cm⁻¹ (relative to 1170 cm⁻¹) were adjusted by using Eq. (7) to reduce the effect of water spray, and the adjusted results are reported in Table 5. The values of *L*, *a*, and *b* were also adjusted to calculate the corresponding Δ*L*, Δ*a*, Δ*b*, and Δ*E* as shown in Table 6.

$$X_{(2+2.3n,adjusted)} = X_{(2+2.3n,measured)} + \sum_{i=0}^n [(X_{2+2.3i}) - (X_{2.3+2.3i})] \quad (7)$$

where *X* represents either the lightness *L*, the color chromaticity coordinates *a* or *b*, or the ratio

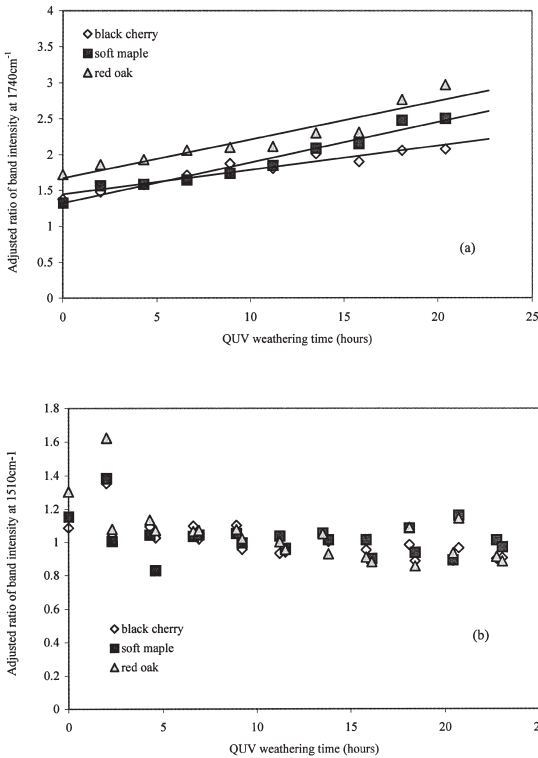


FIG. 3. Adjusted ratio of band intensity versus artificial weathering hours (a) ratio of band intensity at 1740 cm⁻¹, (b) ratio band of intensity at 1510 cm⁻¹.

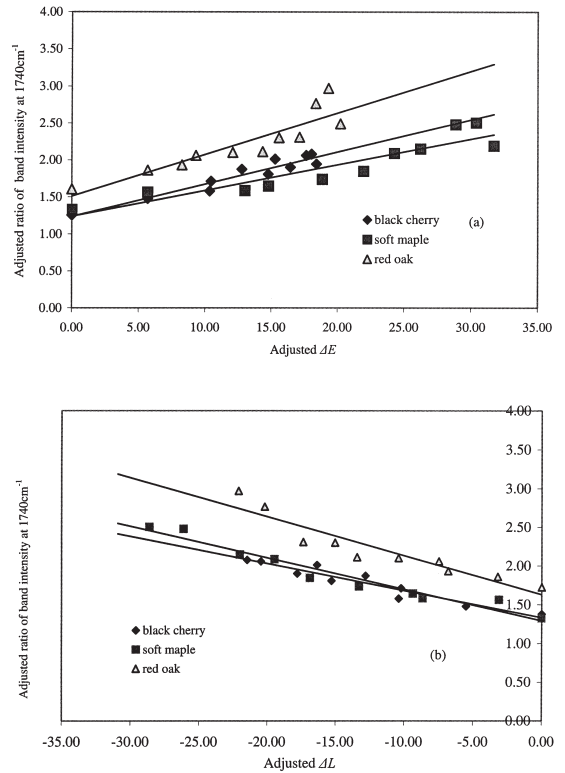


FIG. 4. Adjusted ratio of band intensity at 1740 cm⁻¹ versus color parameters after 22.7 h of QUV weathering (a) adjusted Δ*E*, (b) adjusted Δ*L*.

of the band intensity at 1740 cm⁻¹; and *n* is the number of UV/water spray cycles. $X_{(2+2.3n,adjusted)}$ is the adjusted parameter during the UV/water spray cycle, and $X_{(2+2.3n,measured)}$ the parameter measured after each UV irradiation. The difference before and after each 0.3-h water spray is $[(X_{2+2.3i}) - (X_{2.3+2.3i})]$, and the cumulative difference caused by all the previous water spray applications is expressed as

$$\sum_{i=0}^n [(X_{2+2.3i}) - (X_{2.3+2.3i})]$$

A regression was performed to establish any correlation between the weathering time (*x*) and the ratio of band intensity at 1740 cm⁻¹ or 1510 cm⁻¹ (*y*). The results are listed in Table 5 and plotted in Figure 3. The ratio of band intensity at 1740 cm⁻¹ increased with the weathering time (Fig. 3a), with the linear correlation coeffi-

TABLE 5. Regression analysis for the relationship between ratio of band intensity at 1740 cm⁻¹ or 1510 cm⁻¹, and the weathering duration.

Species and wavenumber	Artificial weathering (hours)										Regression analysis			
	0	2	4.3	6.6	8.9	11.2	13.5	15.8	18.1	20.4	22.7	A	B	R ²
Black cherry (1740 cm ⁻¹)*	1.26	1.48	1.58	1.71	1.87	1.81	2.01	1.90	2.06	2.08	1.95	0.031	1.44	0.81
Soft maple (1740 cm ⁻¹)*	1.61	1.86	1.93	2.06	2.10	2.11	2.30	2.31	2.77	2.97	2.49	0.048	1.69	0.83
Red oak (1740 cm ⁻¹)*	1.33	1.57	1.59	1.65	1.74	1.85	2.09	2.15	2.48	2.51	2.19	0.048	1.38	0.88
Black cherry (1510 cm ⁻¹)**	1.09	1.35	1.09	1.10	1.10	0.93	1.05	0.95	0.98	0.89	0.90	no meaningful linear regression possible		
Soft maple (1510 cm ⁻¹)**	1.15	1.38	1.04	1.03	1.05	1.04	1.05	1.01	1.08	0.89	1.01			
Red oak (1510 cm ⁻¹)**	1.27	1.56	1.12	1.07	1.07	1.00	1.04	0.92	1.07	0.93	0.92	(R ² <0.5)		

* Band intensity at 1740 cm⁻¹ divided by the intensity at 1170 cm⁻¹.
 ** Band intensity at 1510 cm⁻¹ divided by the intensity at 1170 cm⁻¹.
 Regression equation: y = Ax + B.
 R²: correlation coefficient.

TABLE 6. ΔE, ΔL, Δa, and Δb values versus hours of QUV weathering.

Parameters	Species	QUV hrs												
		0	2	4.3	6.6	8.9	11.2	13.5	15.8	18.1	20.4	22.7		
ΔE*	Black cherry	0	5.57	10.29	10.41	12.75	14.81	15.36	16.50	17.74	18.15	18.52		
	Soft maple	0	5.89	12.99	14.78	18.84	20.79	23.10	25.06	27.69	29.22	30.54		
	Red oak	0	3.87	8.27	9.33	12.11	14.37	15.61	17.17	18.40	19.36	20.28		
ΔL*	Black cherry	0	-5.51	-10.39	-10.21	-12.81	-15.30	-16.36	-17.81	-20.46	-21.48	-22.32		
	Soft maple	0	-3.13	-8.65	-9.36	-13.30	-16.88	-19.48	-22.02	-26.14	-28.62	-30.92		
	Red oak	0	-3.19	-6.80	-7.46	-10.40	-13.42	-15.04	-17.36	-20.19	-22.10	-24.03		
Δa*	Black cherry	0	0.80	1.04	1.40	1.25	1.33	0.69	0.27	-1.00	-1.93	-2.73		
	Soft maple	0	0.35	2.58	3.14	4.78	6.19	7.17	7.79	8.99	9.34	9.69		
	Red oak	0	0.36	1.08	1.33	1.76	2.25	2.52	2.68	2.59	2.54	2.49		
Δb*	Black cherry	0	0.14	0.85	1.27	1.56	1.33	0.84	0.70	-0.86	-1.70	-2.40		
	Soft maple	0	4.98	10.24	11.81	14.10	14.10	15.05	15.66	15.87	15.93	15.85		
	Red oak	0	2.16	4.94	5.78	7.17	7.90	8.30	8.59	8.30	8.15	7.90		

* data calculated from adjusted L, a, and b.

cient R^2 varying from 0.81 to 0.88 in function of the wood species. The slope of the regression equation was used as an indication of the artificial weathering rate. Soft maple and red oak exhibited a higher weathering rate with a slope of 0.048 than black cherry (0.031).

No significant linear correlation was found between the ratio of band intensity at 1510 cm^{-1} and the weathering time. The decrease in ratio of band intensity at 1510 cm^{-1} (Fig. 3b) suggested the removal/decomposition of compounds containing benzene ring on wood surface. However, an initial increase in ratio of band intensity at 1510 cm^{-1} was observed after the first 2 h or UV irradiation without water spray, suggesting the migration of benzene ring containing compounds onto the wood surface. Further water spray and UV irradiation promoted the removal/decomposition of these compounds.

The results of the correlation analysis among the ratio of band intensity at 1740 cm^{-1} , color change (ΔE), lightness modification (ΔL), changes in chromaticity coordinates (Δa and Δb) are summarized in Table 7. The regression curves between the ratio of band intensity at 1740 cm^{-1} and ΔE as well as ΔL are plotted in Fig. 4.

A R^2 of 0.92 was obtained between the ratio of band intensity at 1740 cm^{-1} and ΔE for black cherry, 0.85 for soft maple, and 0.80 for red oak. The values of R^2 indicated a good linear correlation between the color change and the carbonyl group contents on wood surface. A slightly better correlation exists between the ratio of band intensity at 1740 cm^{-1} and ΔL rather than ΔE , with the R^2 s at 0.92, 0.95, and 0.88 for black cherry, soft maple, and red oak, respectively. The relationship between the ratio of band intensity at 1740 cm^{-1} and Δa or Δb was not as good as those observed with ΔE and ΔL . Linear correlation was found in soft maple with R^2 value between 0.65 and 0.73, and red oak with R^2 value from 0.52 to 0.65.

The band at 1740 cm^{-1} from carbonyl group is capable of absorbing light (Dyer 1965). A direct impact on the wood surface is the shift from light to dark with the increase of carbonyl group contents in weathering. Nassau (1983) reported that variations in structure of carbonyl-containing compounds affect the endpoints in the chro-

TABLE 7. Regression analysis for the relationship between the adjusted ratio of band intensity at 1740 cm^{-1} and the color parameters (ΔE , ΔL , Δa , and Δb).

Parameters (x)	ΔE			ΔL			Δa			Δb		
	A	B	R^2	A	B	R^2	A	B	R^2	A	B	R^2
Black cherry	0.044	1.24	0.92	-0.035	1.33	0.92	No meaningful linear regression possible ($R^2 < 0.5$)	1.46	0.73	0.06	1.19	0.65
Soft maple	0.035	1.24	0.85	-0.041	1.29	0.95	No meaningful linear regression possible ($R^2 < 0.5$)	1.57	0.65	0.086	1.65	0.52
Red oak	0.056	1.51	0.80	-0.050	1.63	0.88						

Regression equation: $y = Ax + B$.
 R^2 : correlation coefficient.

maticity diagram. Therefore, a better linear correlation was observed between the ratio of band intensity at 1740 cm^{-1} and the lightness modification (ΔL) rather than color change (ΔE), which include the contributions from lightness, chroma, and hue modifications.

Results from the GLM confirm that weathering properties were influenced by wood species. The weathering rate of soft maple and red oak was not significantly different at significant level of 0.05 (P-value = 0.99), but significantly different from black cherry (P-value = 0.03). Analysis of the correlation between the ratio of band intensity at 1740 cm^{-1} and ΔE or ΔL suggested that there was no significant difference between soft maple and red oak (P-value = 0.18) or between black cherry and red oak (P-value = 0.11); significant difference existed between black cherry and soft maple (P-value = 0.04).

CONCLUSIONS

This study confirms that a 22.7-h accelerated weathering with UV and water spray generate chemical modifications on wood components and induce color changes on the exposed wood surface of black cherry, soft maple, and red oak. The color change of black cherry was affected mainly by lightness modification, while the color change of soft maple and red oak resulted from changes in both chroma and lightness.

Artificial accelerated wood weathering phenomena could be described semi-quantitatively by using band intensity at 1170 cm^{-1} as the reference of each spectrum. The slope of the ratio of band intensity at 1740 cm^{-1} (relative to 1170 cm^{-1}) versus the weathering time could be used to estimate the rate of wood weathering in terms of the increase in carbonyl group contents with the duration of weathering. Soft maple and red oak showed a higher rate of increase in the carbonyl group contents; black cherry exhibited a relatively lower rate. Statistical analysis suggested that the weathering rate of soft maple and red oak was significantly different from black cherry.

There was a linear correlation between ΔL , ΔE , and the ratio of band intensity at 1740 cm^{-1} , indicating that the formation/presence of carbonyl-

containing compounds on the weathered wood surface also influence the lightness modification and the color change. The correlation between the ratio of band intensity at 1740 cm^{-1} and ΔL or ΔE was influenced by wood species as well. Significant difference was observed between black cherry and soft maple.

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