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Influence of Post-extraction on Photostability of Thermally Modified Scots Pine Wood during Artificial Weathering

Haiying Shen, Jinzhen Cao,* Wenjing Sun, and Yao Peng

The photo-stabilizing effect of post-extraction was evaluated for thermally modified wood. Extracted and non-extracted thermally modified Scots pine (*Pinus sylvestris* L.) samples were exposed in a xenon weather-ometer for 1008 h, and the surface color and chemical changes were characterized using a chroma meter, attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), and X-ray photoelectron spectroscopy (XPS). The results showed that: (1) the weight losses of thermally modified wood were higher than those of unmodified wood after extraction due to the leaching of some low molecular weight compounds that were generated during thermal modification; (2) the photodegradation of thermally modified wood during weathering was hindered by the presence of extractives; and (3) the color change during weathering was a little more severe in sapwood than in heartwood because more extractives were present in heartwood.

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INTRODUCTION

Wood is hygroscopic and vulnerable to biological attack due to its anatomical features and chemical constituents, which directly result in insufficient dimensional stability and biological resistance. Thermal modification of wood at relatively high temperatures (180 to 260 °C) is an effective method to improve the dimensional stability and decay resistance of wood without requiring any toxic chemicals (Petrič 2013). The thermal modification of wood has a long history (Stamm and Hansen 1937; Kollman and Schneider 1963; Rusche 1973), and extensive studies in this area have led to the development of various thermal modification technologies such as the ThermoWood, Retification, PLATO, and oil heat treatment (OHT) processes. The main differences between these processes are in heat-transferring media, temperature and duration of treatment, closed or open system (pressure), wet or dry system (humidity), and the use of catalyst. Of these processes, ThermoWood is a mature production technology; developed in Finland, it uses atmospheric pressure with a constant steam flow throughout the process. One effect of thermal treatment is that wood obtains an attractive darker color. However, when thermally modified wood is exposed outdoors, various surface problems appear, such as color fading, surface roughening, and checking. These changes could definitely influence the service life of the wood in terms of aesthetic and mechanical considerations, thus affecting the exploration of thermally modified wood in the market.

There have been some investigations concerning the weathering performance of thermally modified wood. Tomak *et al.* (2014) and Yildiz *et al.* (2013) observed that

natural or accelerated weathering led to a reduction in compression strength, modulus of rupture (MOR), and modulus of elasticity (MOE) in thermally modified wood. Although the color stability and photostability of thermally modified wood has improved (Ayadi *et al.* 2003; Nuopponen *et al.* 2004; Dubey *et al.* 2010; Huang *et al.* 2012a; Huang *et al.* 2013), the color of most thermally modified wood is lightened during UV exposure or solar irradiation (Srinivas and Pandey 2012; Huang *et al.* 2012b; Tomak *et al.* 2014). Yildiz *et al.* (2013) investigated the color change during artificial weathering of four heat-treated wood species (ash, iroko, Scots pine, and spruce) at 200 °C and suggested that the protective effect of heat-treatment was lost during longer weathering exposures. The color of thermally modified wood has shown little difference compared with untreated wood after a long exposure (Huang *et al.* 2012a,b; Yildiz *et al.* 2013). In addition, the contact angle of water droplets on thermally modified wood is much higher than on untreated wood, but it was shown that contact angle of water of thermally modified wood was comparable to untreated wood after artificial accelerated irradiation for 1500 h (Huang *et al.* 2012b). These observations reveal that thermal modification might not improve the resistance of the wood surface against UV and visible light irradiation.

The weathering performance of wood is closely related to its chemical changes during treatment. The formation of chromophoric products by lignin scission and the removal of extractives from the interior to the exterior of wood is responsible for the color change of wood (Chang *et al.* 1999; KačÍk *et al.* 2014). Huang *et al.* (2012b) found that photodegradation tended to occur in the middle lamella of the wood surface cells where the lignin concentration in the cell wall is the highest, demonstrating the high photosensitivity of lignin when exposed to weathering. Lignin is thought to degrade when the α-carbonyl absorbs radiation energy and enters an excited state, which initiates cleavage of the β-arylether linkage and several electron migration steps that form quinoid compounds (Kuo and Hu 1991). In addition to lignin degradation, extractives influence the weathering performance of wood. The natural durability of different wood species differs because of extractives (Williams and Feist 1999). Extractives are cell wall chemicals mainly consisting of fats, fatty acids, fatty alcohols, phenols, terpenes, steroids, resin acids, rosin, waxes, and many other minor organic compounds (Rowell *et al.* 2005). Their mechanisms of photodiscoloration are very complicated and include reactions between phenolic compounds as well as structural changes in the functional groups of wood extractive molecules (Chang *et al.* 2010a). For example, Chang *et al.* (2010b) noted that the rate of photodegradation for wood is retarded by the presence of extractives, which contain unsaturated phenolics capable of absorbing light energy and consequently degrading themselves before other wood components, thus protecting wood components from aging. Lin and Kringstad (1970) found that functional groups, radicals, and oxygen are involved in some photochemical reactions, and they are probably responsible for wood color changes during weathering *via* the oxidation of biphenyl and ring-conjugated double bonds and the formation of carboxyl groups.

After thermal modification, some extractives move to the wood surface, and new extractives with low molecular weights are generated during the degradation of wood components. Nuopponen *et al.* (2003) found that fats, waxes, and resin acids moved along the axial parenchyma cells to the surface of Scots pine during thermal modification. Water-soluble and alcohol-soluble extractives increase in pine and eucalyptus wood after thermal modification (Esteves *et al.* 2008, 2011). It is evident that thermal modification changes wood components, including extractives; however, the influence of extractives on the photo-degradation of thermally modified wood is unclear. Ahajji *et al.* (2009) indicated

that thermal modification increased the phenol contents and the concentration of stable phenoxyl-free radicals in beech and spruce, which improved the antioxidant activity of wood. However, it is unknown whether the changes in extractives during thermal modification protect wood from oxidation during weathering.

To clarify the role of extractives in thermally modified wood during the weathering process, thermally modified wood samples, both non-extracted and post-extracted using ethanol/toluene, were exposed to the same accelerated weathering conditions, and their color and chemical changes were evaluated at various intervals.

EXPERIMENTAL

Materials and Methods

Sample preparation

Samples measuring 75 mm (longitudinal) $\times$ 10 mm (tangential) $\times$ 3 mm (radial) were machined from air-dried Scots pine (*Pinus sylvestris* L.) sapwood or heartwood. The density of the Scots pine samples was 0.45×10^{-3} kg/m^3, and the average width of each annual ring was about 2.2 mm. The wood samples were divided into four groups. Labeling of wood samples was used for short as shown in Table 1, in which the number of 1 and 2 represents non-extracted and extracted wood. The letters "U", "T", "s", and "h" represent unmodified wood, thermally modified wood, sapwood, and heartwood, respectively. Six replicates were used for each treatment group.

Table 1. Labeling of Wood Sample Groups

Treatment	Position	Unmodified	Thermally Modified
Non-extracted	Sapwood	U1-s	T1-s
	Heartwood	U1-h	T1-h
Extracted	Sapwood	U2-s	T2-s
	Heartwood	U2-h	T2-h

The thermally modified specimens were subjected to thermal modification at 130 °C for 1 h followed by heating at 200 °C for 6 h in a temperature-controlled laboratory oven with a water vapor supplying system. The weight loss after thermal modification was calculated according to Eq. 1,

$$WL_1\ (\%) = \frac{m_0 - m_1}{m_0} \times 100\% \tag{1}$$

where m_0 and m_1 represent the oven-dry mass of the wood sample before and after thermal modification, respectively.

The thermally modified specimens were extracted in a Soxhlet apparatus for 24 h using an ethanol/toluene mixture (1:2, v/v) and then oven-dried at (103 $\pm$ 2) °C for 12 h. The weight loss after extraction was calculated according to Eq. 2,

$$WL_2(\%) = \frac{m_1 - m_2}{m_1} \times 100\% \tag{2}$$

where m_2 is the oven-dry mass of the thermally-modified sample after extraction. Other specimens were stored in dark conditions as control groups.

Artificial weathering test

The artificial sunlight exposure test was conducted using a xenon weather-ometer (SN-150, Tianjin Su Rui Technology Co., Ltd, Tianjin, China). This device is made up of a controlled irradiation water-cooled xenon arc lamp with a CIRA inner filter and a soda outer filter as the source of radiation to simulate sunlight. The test was performed according to the ASTM G155 standard (2005). Briefly, 102 min of xenon light irradiation was followed by 18 min of light irradiation with water spray (atmosphere not controlled) without a dark cycle, which was meant to simulate natural weathering with rain and to accelerate the weathering process. The black panel temperature was set at (63 ± 3) °C, and the irradiation level was $0.35/m^2$ at 340 nm. The irradiation was interrupted after 72, 168, 240, 336, 672, and 1008 h of exposure, and each set of samples was taken out for an evaluation of surface properties. All samples were stored in ambient conditions.

Color measurement

The surface color of the samples was measured using a chroma meter (Datacolour DF 110, Shenzhen 3NH Technology Co., Ltd, Shenzhen, China) according to the CIE LAB color system. The parameters $L*$, $a*$, and $b*$ were measured at intervals at five specific locations on the surface of each specimen, and the average value was calculated. $L*$ represents the lightness coordinate and varies from 100 (white) to 0 (dark). The $a*$ value represents the red $(+a)$ to green $(-a)$ coordinate, whereas $b*$ represents the yellow $(+b)$ to blue $(-b)$ coordinate. The CIELAB parameters of $\Delta L*$, $\Delta a*$, $\Delta b*$, and $\Delta E*$ were calculated according to the following equations,

$$\Delta L^* = L_t^* - L_i^* \tag{3}$$

$$\Delta a^* = a_t^* - a_i^* \tag{4}$$

$$\Delta b^* = b_t^* - b_i^* \tag{5}$$

$$\Delta E = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \tag{6}$$

where L_i*, a_i*, and b_i* are the parameters measured before weathering; L_t*, a_t*, and b_t* are the parameters measured after weathering; and $\Delta L*$, $\Delta a*$, $\Delta b*$, and $\Delta E*$ represent changes in lightness, red/green chromaticity, yellow/blue chromaticity, and the total color change, respectively.

Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR)

ATR-FTIR spectra were obtained directly from the wood surface using an attenuated total reflectance FTIR spectrometer (Bruker Vertex 70v, Ettlingen, Germany). The wood surfaces that were analyzed in contact with a ZnSe crystal had a 45° angle of incidence. The FTIR spectra were obtained in absorbance units from 2000 cm^{-1} to 1000 cm^{-1} using 100 scans at a resolution of 4 cm^{-1}. Normalization was carried out to obtain results to be reported. At set intervals of weathering, three replicates of the samples were taken out from the weathering machine and analyzed. A representative spectrum from each group was used to show the results.

X-ray photoelectron spectroscopy (XPS)

The chemical elements in the extracted and non-extracted thermally modified wood exposed to different periods of aging were compared. The samples were cut into slices with dimensions of 5 mm × 5 mm × 3 mm. X-ray photoelectron spectra were collected using an Escalab 250 Xi (Thermo Scientific, New York, NY, USA). The samples were analyzed at pressures between 10^{-9} and 10^{-8} Torr with a pass energy of 29.35 eV and a take-off angle of 45°.

RESULTS AND DISCUSSION

Weight Loss

The weight losses for the Scots pine samples during both thermal modification and extraction are listed in Table 2. Thermal modification led to weight losses of 10.31% and 10.62% for sapwood and heartwood, respectively. This result was attributed to the degradation of wood components and the removal of some volatile substances during thermal modification. After extraction, more substances were removed from thermally modified wood (T2-s and T2-h) than from the unmodified group (U2-s and U2-h). This was mainly due to the leaching of some organic substances, including both extractives and new compounds with low molecular weights that were generated during thermal modification (Esteves *et al.* 2008, 2011). More extractives were removed from heartwood than from sapwood, which was expected because heartwood originally contains more extractives than sapwood. The low amount of extractives in this study was mainly because the extraction was applied directly to wood slices rather than to wood flour, which kept the wood surface unbroken for further measurements. Thus, only the extractives at the wood surface or beneath the wood surface were extracted.

Table 2. Weight Losses of Scots Pine Samples after Thermal Modification (WL_1) and Ethanol/Toluene Extraction (WL_2)

Weight loss (%)	U2-s	U2-h	T1-s	T1-h	T2-s	T2-h
WL_1	—	—	10.47 (1.54*)	10.59 (1.94*)	10.31 (1.85*)	10.62 (2.04*)
WL_2	0.83 (0.21*)	1.22 (0.17*)	—	—	1.91 (0.14*)	2.21 (0.09*)

* Standard deviation of twelve replicates

Color Changes during Artificial Weathering

Table 3 shows the changes in redness (a^*), yellowness (b^*), and lightness (L^*) and the total color change (ΔE) of the non-extracted and extracted thermally modified Scots pine as a function of artificial sunlight irradiation time. A decreasing trend in the a^* and b^* values of the thermally modified wood was observed, suggesting that the thermally modified Scots pine surface was becoming more green and blue with increasing irradiation time. The L^* values of Scots pine increased after artificial sunlight irradiation, suggesting that the thermally modified wood surface became lighter during the weathering test, and all the chroma co-ordinate parameters (a^*, b^*, and L^*) changed dramatically during the first 72 h of exposure. After 72 h, these three parameters changed gradually and then stabilized towards the end of the test, indicating that the degradation of the wood components was more severe at the very beginning of weathering.

Table 3. Color Changes in Thermally Modified Wood Samples during the Artificial Weathering Test

Sample ID	Weathering Time (h)	Color Changes			
		L*	*a**	*b**	Δ*E*
T1-s	0	45.00 (1.27*)	9.20 (0.36*)	11.07 (0.74*)	0
	72	41.19 (1.08*)	4.76 (0.53*)	8.94 (0.54*)	3.95 (0.32*)
	336	40.91 (0.97*)	4.31 (0.43*)	8.14 (0.63*)	6.62 (0.41*)
	1008	42.28 (1.31*)	4.16 (0.61*)	7.54 (0.34*)	9.47 (0.52*)
T2-s	0	47.21 (1.23*)	9.80 (0.43*)	13.81 (0.65*)	0
	72	42.04 (1.04*)	4.97 (0.33*)	10.12 (0.68*)	4.64 (0.42*)
	336	42.93 (1.02*)	5.13 (0.28*)	9.71 (0.59*)	8.94 (0.27*)
	1008	42.28 (1.32*)	4.27 (0.31*)	9.58 (0.42*)	9.93 (0.54*)
T1-h	0	42.00 (1.01*)	8.00 (0.51*)	9.00 (0.54*)	0
	72	41.45 (0.99*)	4.76 (0.36*)	8.34 (0.47*)	4.21 (0.33*)
	336	41.66 (0.72*)	3.95 (0.24*)	8.50 (0.37*)	4.98 (0.24*)
	1008	41.19 (1.08*)	3.74 (0.14*)	6.58 (0.49*)	6.55 (0.43*)
T2-h	0	43.01 (1.34*)	7.59 (0.39*)	9.14 (0.52*)	0
	72	42.87 (1.11*)	4.87 (0.27*)	8.15 (0.66*)	4.42 (0.55*)
	336	41.54 (1.01*)	4.08 (0.30*)	8.48 (0.31*)	5.98 (0.34*)
	1008	41.14 (1.00*)	3.88 (0.12*)	7.62 (0.46*)	7.55 (0.41*)

* Standard deviation of five replicates
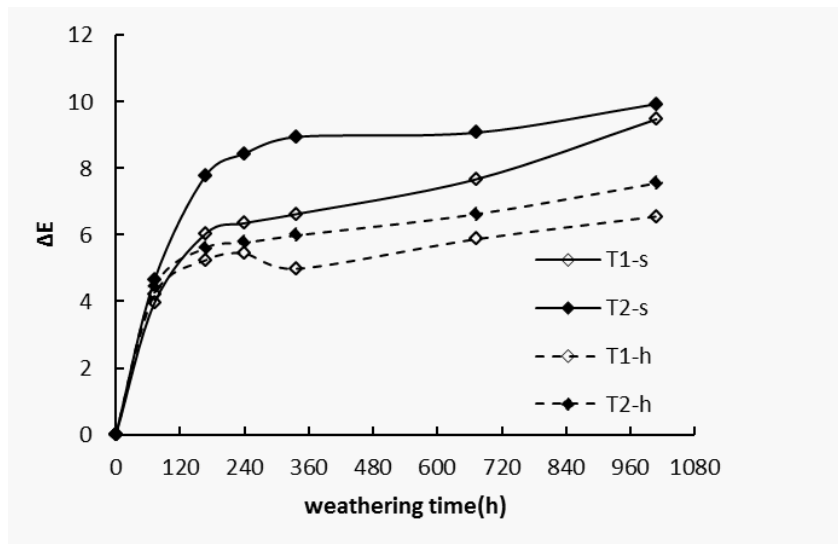
Fig. 1. Total color changes in thermally modified sapwood and heartwood samples during artificial weathering

As shown in Fig. 1, the total color change (Δ*E*) of all thermally modified Scots pine samples increased with increasing weathering time, and this change was slighter in non-extracted specimens (T1-s and T1-h) compared to that of extracted samples (T2-s and T2-h). A larger Δ*E* value in the extracted samples presented at the beginning of the weathering

process in the sapwood groups, while this trend occurred after 336 h of exposure in the heartwood groups. The total color change of the heartwood tended to be lower than the sapwood due to the decreased permeability of sapwood. Extractives can protect wood against weathering to some extent (Chang *et al.* 1999, 2001, 2010a,b). Pietta (2000) found that phenolics in plant extractives absorb free radicals and have effective antioxidant activity. Kishino and Nakano (2004) attributed the improved antioxidant ability of thermally modified wood to the increased phenol content and the higher concentrations of stable phenoxyl-free radicals. Hence, it is likely that the presence of phenolics extractives had a protective effect against the degradation of thermally modified Scots pine.

Structural Analyses with FTIR Spectroscopy

Figure 2 shows changes in the FTIR spectra from 2000 to 1000 cm^{-1} of Scots pine sapwood after thermal modification and extraction. Comparing unmodified wood (U1-s and U2-s) with thermally modified samples (T1-s and T2-s), the relative intensity of the band at 1740 cm^{-1}, assigned to carbonyl groups and C=O stretching vibration of acetyl or carboxylic acid of hemicelluloses (Gérardin *et al.* 2007; Esteves *et al.* 2008), decreased after thermal modification, demonstrating the degradation of hemicelluloses.
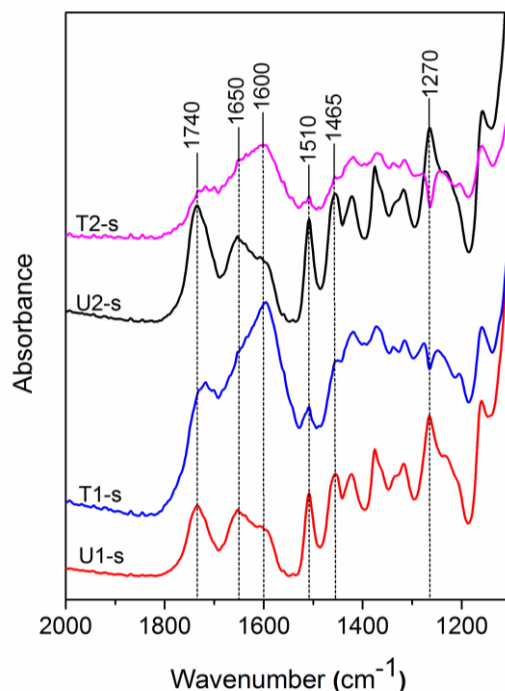

Fig. 2. Changes in the FTIR spectra of non-extracted and extracted Scots pine sapwood before and after thermal modification

The degradation of hemicelluloses can decrease water adsorption, which was confirmed by the decreased relative intensity of the band at 1650 cm^{-1} after thermal modification. The characteristic bands of lignin at 1510 cm^{-1}, 1465 cm^{-1}, and 1270 cm^{-1} decreased, indicating that lignin degradation also occurred during thermal modification. The increase in the band at 1600 cm^{-1} was mainly due to the increase in the aromatic rings in the wood components as a result of degradation. Huang *et al.* (2012b) found that photodegradation tended to occur in the middle lamella of the wood surface cells where the lignin concentration in the cell wall is the highest, demonstrating the high photosensitivity of lignin when exposed to weathering. Lignin is thought to degrade when

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the α-carbonyl absorbs radiation energy and enters an excited state, which initiates cleavage of the β-arylether linkage and several electron migration steps that form quinoid compounds (Kuo and Hu 1991).The increase in the band at 1600 cm^{-1} was mainly due to the increase in the aromatic rings in the wood components as a result of degradation.

Because most of the changes in characteristic bands were very small and not easy to compare visually, a ratio of 1510 cm^{-1} to 1370 cm^{-1} (I_{1510}/I_{1370}) was proposed to quantitatively denote the ratio of phenolic compounds to cellulose (Chang *et al.* 2010b). The I_{1510}/I_{1370} ratio of non-extracted thermally modified samples (T1-s) and non-extracted unmodified samples (U1-s) was 0.6667 and 0.6067, respectively. After the ethanol/toluene extraction, the ratio decreased to 0.5730 and 0.5849, respectively, suggesting that phenolic extractives were removed during extraction, especially in thermally modified wood. Esteves *et al.* (2008) found that some new extractives, such as phenolic compounds, were generated by the hydrolysis or degradation of wood components, especially lignin, during thermal modification. Similar trends were observed in the Scots pine heartwood samples.

Changes in the FTIR spectra for the non-extracted and extracted thermally modified Scots pine sapwood during weathering are shown in Fig. 3. After artificial weathering, the intensities of many bands decreased to different extents. After 1008 h of artificial weathering, the relative ratio of carbonyl groups in hemicelluloses (1740 cm^{-1}) and fatty acid esters (1730 cm^{-1}) (Back and Allen 2000) had almost disappeared in both non-extracted and extracted specimens, suggesting the removal of hemicellulose and fatty acid esters during weathering. For the thermally modified Scots pine, bands at 1510 cm^{-1} almost disappeared at the end of weathering test, which indicated the degradation of lignin. The bands at 1267 cm^{-1} were diminished after a long weathering time, which indicated C-O stretching in lignin and hemicellulose.
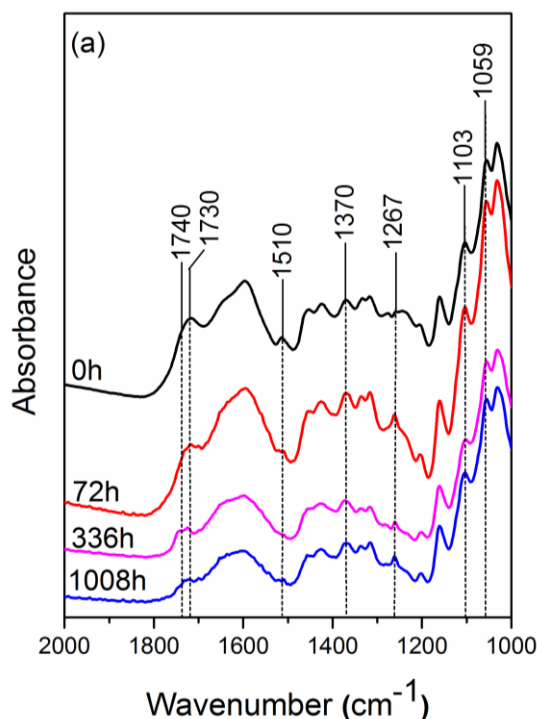

Fig. 3. Changes in FTIR spectra of (a) non-extracted (T1-s) and (b) extracted (T2-s) thermally modified Scots pine sapwood after different intervals of weathering

After 1008 h of weathering, the relative peaks of the bands at 1103 cm^{-1} and 1059 cm^{-1} corresponding to the non-extracted specimens that were assigned to the C-H in lignin and carbohydrates, respectively, were slightly higher than those of extracted specimens. This result provided some evidence that the C-H bonds in syringyl lignin might be protected during weathering by the original organic extractives.

The I_{1510}/I_{1370} ratios of non-extracted and extracted thermally modified wood after different durations of weathering are compared in Fig. 4. For both unmodified and thermally-modified groups, the I_{1510}/I_{1370} ratios of the non-extracted Scots pine (U1-s/h, T1-s/h) were always higher than those of the extracted specimens (U2-s/h, T2-s/h) for the same irradiation time, meaning that the lignin was degraded less during weathering in wood specimens containing extractives. In particular, the I_{1510}/I_{1370} ratio of non-extracted thermally modified wood (T1-s/h) showed the least reduction during weathering. Therefore, compared with unmodified wood, the photoprotective effects of extractives on thermally modified wood were more obvious.
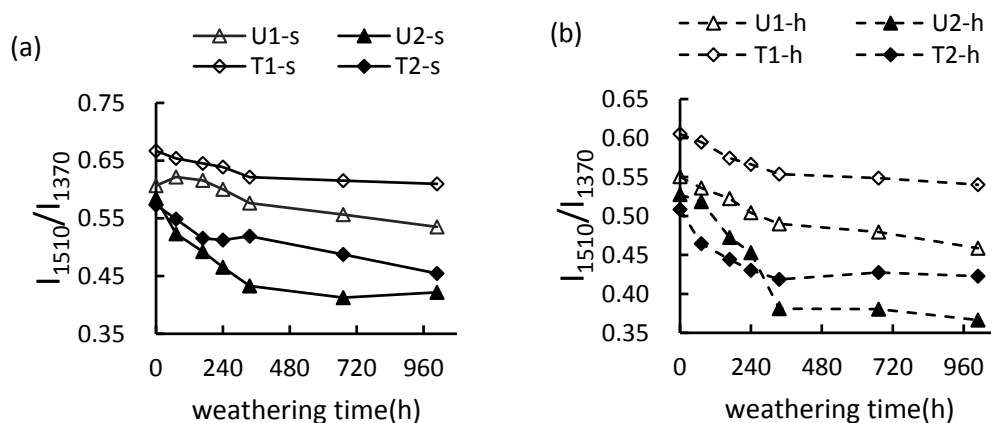

Fig. 4. Changes in the relative peak ratio of 1510 cm^{-1}/1370 cm^{-1} in the FTIR spectra of Scots pine (a) sapwood and (b) heartwood during artificial weathering

XPS Analysis

X-ray photoelectron spectroscopy (XPS) is a surface analysis method of evaluating materials. The intensities of different chemical elements and their ratios reflect chemical changes at the material surface. The typical survey spectra changes in carbon and oxygen after degradation are shown in Fig. 5. The intensity of O1s increased after extraction due to the removal of carbon-rich extractives such as terpenes, phenolics, and fatty acids (Kocaefe *et al.* 2013), which was also confirmed by the results of ratio of 1510 cm^{-1} to 1370 cm^{-1}, as discussed in the section on FTIR. Back and Allen (2000) found that the canal resin of Scots pine mainly consists of acidic diterpenes (resin acids) and volatile monoterpenes. This phenomenon is in good accordance with the survey spectra changes of *A. confusa* wood (Chang *et al.* 2010a).

Because extractives are rich in carbon, both the change in extractives and in oxygen content could change the O/C ratio. The O/C ratio can be used as an indicator of oxidation reactions on the wood surface as a result of extractive degradation (Chang *et al.* 2010b); namely, if the oxidation reaction is severe, then a higher O/C ratio is expected. The O/C ratios increased more noticeably with weathering in the non-extracted groups (U1, T1) than in the extracted groups (U2, T2), especially in the Scots pine heartwood samples, which

showed a much more severe oxidation reaction for the non-extracted groups during the weathering test (Table 4). Phenolics in heartwood extracts show good antioxidant activity (Chang *et al.* 2001). This effect may be due to their ability to trap reactive oxygen (Pietta 2000). Thus, extractives in non-extracted specimens were oxidized easily during artificial irradiation.
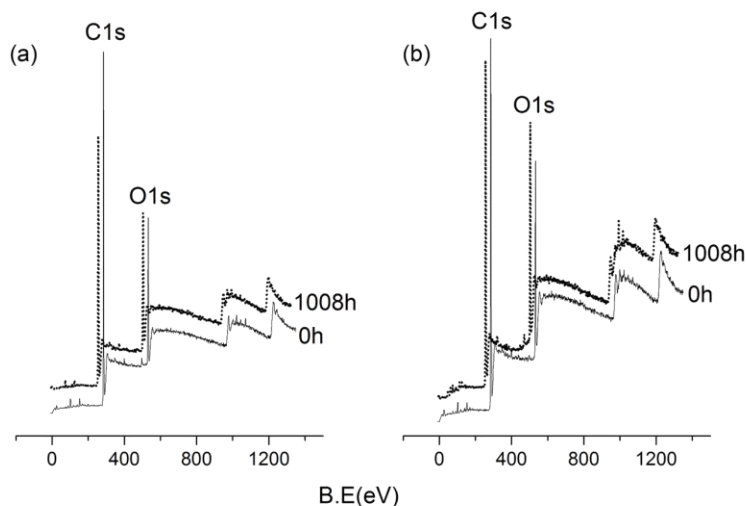

Fig. 5. XPS survey spectra of (a) non-extracted (T1-s) and (b) extracted (T2-s) thermally modified Scots pine sapwood after 1008 h of irradiation

Table 4 shows that the O/C ratios of extracted samples (U2, T2) were higher after 1008 h of weathering, with values close to 0.88 for the O/C ratio of cellulose and above 0.33 for lignin (Hon 1984). This data suggested that the surface of the extracted wood was richer in cellulose and poorer in lignin after weathering, which reflected the protective effect of extractives against lignin degradation. This result was in agreement with the ATR-FTIR results mentioned above. After 1008 h of weathering, non-extracted Scots pine heartwood (T1-h) had a lower ratio of O/C than sapwood (T1-s), indicating that the higher content of extractives in the heartwood protected the other wood components, especially lignin, from oxidation during weathering.

Table 4. Changes of O/C Ratio Calculated from the XPS Spectra of Scots Pine after Artificial Weathering

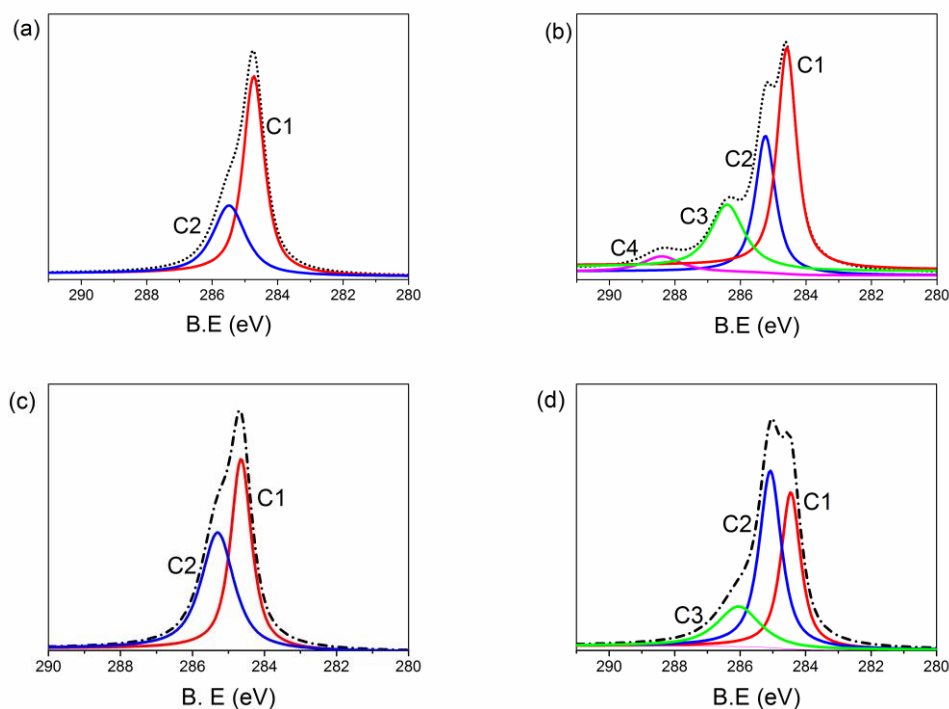| Weathering Time (h)	O/C ratio							
	U1-s	U2-s	T1-s	T2-s	U1-h	U2-h	T1-h	T2-h
0	0.59	0.71	0.52	0.67	0.50	0.77	0.41	0.70
72	0.64	0.75	0.56	0.70	0.55	0.80	0.47	0.72
168	0.67	0.78	0.59	0.73	0.58	0.81	0.51	0.76
240	0.70	0.82	0.62	0.75	0.62	0.85	0.56	0.79
336	0.75	0.84	0.66	0.77	0.68	0.87	0.60	0.82
672	0.78	0.85	0.69	0.80	0.76	0.89	0.65	0.85
1008	0.81	0.87	0.73	0.82	0.80	0.91	0.69	0.88

Fig. 6. C1 spectra of non-extracted and extracted Scots pine sapwood before and after 1008 h of exposure to weathering: (a) non-extracted, before weathering; (b) non-extracted, after weathering for 1008 h; (c) extracted, before weathering; (d) extracted, after weathering for 1008 h

To further investigate the changes in chemical bonds in thermally modified Scots pine after weathering, the C1 spectra were deconvoluted (Fig. 6). Before weathering, the C1 spectra were deconvoluted into C1 and C2 for both non-extracted and extracted thermally modified wood. The C1 peak was assigned to C-C and C-H bonds, which were closely related to the amount of lignin and extractives in the wood. The C2 peak was attributed to C-O bonding, which primarily originated from polysaccharides and, to a lesser extent, lignin. Figs. 6a and 6c show that after extraction, C1 decreased while C2 increased, suggesting the reduction in extractives.

The spectra that correspond to after weathering were divided into four peaks, namely, C1, C2, C3, and C4. C3 represents the C=O and O-C-O bonds; these groups come mainly from polysaccharides and extractives. The C4 peak corresponds to the O-C=O bonding of carboxylic derivatives (Hon 1984; Chang *et al.* 2001; Sinn *et al.* 2001; Fardim and Durán 2002; Shchukarev *et al.* 2002; Nzokou and Kamdem 2005). For both non-extracted and extracted thermally modified wood, after weathering, the C1 peak shrank and the C2 peak became higher, suggesting a significant decrease in both lignin and extractive contents for the surface of the thermally modified wood during weathering. The C3 peaks in Figs. 6b and 6d are very small, which suggests that a small amount of new polysaccharides or extractives was generated after weathering. The occurrence of C4 on the weathered surface might be explained by the presence of carboxylic derivatives after weathering as a result of the degradation of lignin and extractives.

Although degradation occurred in both non-extracted and extracted wood samples, some differences were observed that clarify the role of extractives in thermally modified wood during weathering. Comparing Figs. 6b and 6d, the C1 peak area of the non-extracted wood (T1-s) was much larger than that of extracted wood (T2-s), suggesting that

more lignin existed in the non-extracted samples after 1008 h of weathering. This result demonstrated again that extractives hindered lignin degradation and slowed the weathering thermally modified wood, which agreed with the FTIR results. Given the complex constituency of the extractives, some further research is needed with regard to the extractive degradation mechanism.

CONCLUSIONS

1. Some low molecular weight compounds were generated during thermal modification, which was confirmed by the higher weight losses of thermally modified wood than those of unmodified wood after extraction.

2. When comparing the weathering behavior of non-extracted to extracted thermally modified wood by XPS and FTIR method, it was found that the degradation of thermally modified wood during weathering was hindered by extractives that originally exist or are newly-generated during thermal modification.

3. The color change during weathering was a little more severe in sapwood than in heartwood because more extractives were present in heartwood.

ACKNOWLEDGMENTS

REFERENCES CITED

Ahajji, A., Diouf, P. N., Aloui, F., Elbakali, I., Perrin, D., Merlin, A., and George, B. (2009). "Influence of heat treatment on antioxidant properties and color stability of beech and spruce wood and their extractives," *Wood Sci. Technol.* 43(1-2), 69-83. DOI: 10.1007 /s00226-008-0208-3

ASTM G155-05a. (2005). "Standard practice for operating xenon arc light apparatus for exposure of non-metallic materials," ASTM Intl., West Conshohocken, PA, USA.

Ayadi, N., Lejeune, F., Charrier, F., Charrier, B., and Merlin, A. (2003). "Color stability of heat-treated wood during artificial weathering," *Holz Roh-Werkst* 61(3), 221-226. DOI: 10.1007/s00107-003-0389-2

Back, E. L. (2000). "The locations and morphology of resin components in the wood," in: Back, E. L., and Allen, L. A. (eds.), *Pitch Control, Wood Resin, and Deresination*, Atlanta, GA, USA, TAPPI Press, pg. 1-28.

Chang, S. T., Wang, S. Y., Su, Y. C., Huang, S. L., and Kuo, Y. H. (1999). "Chemical constituents and mechanisms of discoloration of taiwania (*Taiwania cryptomerioides Hayata*) heartwood I. The structure reconfirmation and conversion mechanism of taiwanin," *Holzforschung* 53(2), 142-146. DOI: 10.1515/HF.1999.023

Chang, S. T., Wu, J. H., Wang, S. Y., Kan, P. L., Yang, N. S., and Shyur, L. F. (2001). "Antioxidant activity of extracts from *Acacia confusa* bark and heartwood," *J. Agric. Food Chem.* 49(7), 3420-3424. DOI: 10.1021/jf0100907

bioresources.com

Chang, T. C., Chang, H. T., Wu, C. L., Lin, H. Y., and Chang, S. T. (2010a). "Stabilizing effect of extractives on the photo-oxidation of *Acacia confusa* wood," *Polym. Degrad. Stab.* 95(9), 1518-1522. DOI: 10.1016/j.polymdegradstab.2010.06.012

Chang, T. C., Chang, H. T., Wu, C. L., and Chang, S. T. (2010b). "Influences of extractives on the photodegradation of wood," *Polym. Degrad. Stab.* 95(4), 516-521. DOI: 10.1016/ j.polymdegradstab.2009.12.024

Dubey, M. K., Pang, S., and Walker, J. (2010). "Color and dimensional stability of oil heat-treated radiata pinewood after accelerated UV weathering," *Forest Prod. J.* 60(5), 453-459. DOI: 10.13073/0015-7473-60.5.453

Esteves, B., Graça, J., and Pereira, H. (2008). "Extractive composition and summative chemical analysis of thermally treated eucalypt wood," *Appl. Surf. Sci.* 62(3), 344-351. DOI: 10.1515/HF.2008.057

Esteves, B., Videira, R., and Pereira, H. (2011). "Chemistry and ecotoxicity of thermally modified pine wood extractives," *Wood Sci. Technol.* 45(4), 661-676. DOI: 10.1007 /s00226-010-0356-0

Fardim, P., and Durán, N. (2002). "Surface chemistry of eucalyptus wood pulp fibers: Effects of chemical pulping," *Holzforchung* 56(6), 615-622. DOI: 10.1515/HF.2002.094

Gérardin, P., Petrič, M., Petrissans, M, Lambert, J., and Ehrhrardt, J. J. (2007). "Evolution of wood surface free energy after heat treatment," *Polym. Degrad. Stab.* 92(4), 653-657. DOI: 10.1016/j.polymdegradstab.2007.01.016

Hon, D. N. S. (1984). "ESCA study of oxidized wood surfaces," *Appl. Surf. Sci.* 29 (9), 2777-2784. DOI: 10.1002/app.1984.070290908

Huang, X., Kocaefe, D., Kocaefe, Y., Boluk, Y., and Pichette, A. (2012a). "A spectrocolori-metric and chemical study on color modification of thermally modified wood during artificial weathering," *Appl. Surf. Sci.* 258(14), 5360-5369. DOI: 10.1016/j.apsusc. 2012.02.005

Huang, X., Kocaefe, D., Kocaefe, Y., Boluk, Y., and Pichette, A. (2012b). "A study of the degradation behavior of heat-treated jack pine (*Pinus banksiana*) under artificial sunlight irradiation," *Polym. Degrad. Stab.* 97(7), 1197-1214. DOI: 10.1016/j.poly mdegradstab.2012.03.022

Huang, X., Kocaefe, D., Kocaefe, Y., Boluk, Y., and Krause, C. (2013). "Structural analysis of heat-treated birch (*Betule papyrifera*) surface during artificial weathering," *Appl. Surf. Sci.* 264, 117-127. DOI: 10.1016/j.apsusc.2012.09.137

Kačĺk, F., Šmĺra, P., and Kačĺková, D. (2014). "Chemical changes in fir wood from old buildings due to ageing," *Cellulose Chem. Technol.* 48, 79-88. DOI: 10.1016/j.carb pol.2014.10.065

Kishino, M., and Nakano, T. (2004). "Artificial weathering of tropical woods. Part 2: Color change," *Holzforschung* 58(5), 558-565. DOI: 10.1515/HF.2004.085

Kocaefe, D., Huang, X., Kocaefe, Y., and Boluk, Y. (2013). "Quantitative characterization of chemical degradation of heat-treated wood surfaces during artificial weathering using XPS," *Surf. Interface Anal.* 45(2), 639-649. DOI: 10.1002/sia.5104

Kollman, F., and Schneider, A. (1963). "Über das Sorptionsverhalten wärmebehandelter Hölzer," *Holz Roh-Werkst* 21(3), 77-85. DOI: 10.1007/BF02609705

Kuo, M. L., and Hu, N. (1991). "Ultrastructural changes of photodegradation of wood surface exposed to UV," *Holzforschung* 45, 347-353. DOI: 10.1515/hfsg.1991.45.5.347

Lin, S. Y., and Kringstad, K. P. (1970). "Photosensitive groups in lignin and lignin model compounds," *TAPPI* 53, 663-685.

Nuopponen, M., Vuorinen, T., Jǎmsǎ, S., and Viitaniemi, P. (2003). "The effects of a heat treatment on the behavior of extractives in softwood studied by FTIR spectroscopic methods," *Wood Sci. Technol.* 37(2), 109-115. DOI: 10.1007/s00226-003-0178-4

Nuopponen, M., Wikberg, H., Vuorinen, T., Maunu, S. L., Jamsa, S., and Viitaniemi, P. (2004). "Heat-treated softwood exposed to weathering," *J. Appl. Polym. Sci.* 91(4), 2128-2134. DOI: 10.1002/app.13351

Nzokou, P., and Kamdem, P. (2005). "X-ray photoelectron spectroscopy study of red oak (*Quercus rubra*), black cherry (*Prunus serotina*) and red pine (*Pinus resinosa*) extracted wood surfaces," *Surf. Interface Anal.* 37(8), 689-694. DOI: 10.1002 /sia.2064

Petrič, M. (2013), "Surface modification of wood," *Reviews of Adhesion and Adhesives*, 1(2), 216-247. DOI: 10.7569/RAA.2013.097308

Pietta, P. G. (2000). "Flavonoids as antioxidant," *J. Nat. Prod.* 63, 1035-1042. DOI: 10.1021/np9904509

Rowell, R. M., Pettersen, R., Han, J. S., Rowell, J. S., and Tshabalala, M. A. (2005). "Part 3 Wood Cell Wall Chemistry," in: *Handbook of Wood Chemistry and Wood Components*, CRC Press, United States.

Rusche, H. (1973). "Thermal degradation of wood at temperatures up to 200°C – Part I: Strength properties of dried wood after heat treatment," *Holz Roh-Werkst* 31(7), 273-281.

Shchukarev, A., Sundberg, B., Mellerowicz, E., and Persson, P. (2002). "XPS study of living tree," *Surf. Interface Anal.* 34(1), 284-288. DOI: 10.1002/sia.1301

Sinn, G., Reiterer, A., and Stanzl-Tschegg, S. E. (2001). "Surface analysis of different wood species using X-ray photoelectron spectroscopy (XPS)," *J. Mater. Sci.* 36(19), 4673-4680. DOI: 10.1023/A:1017954300015

Srinivas, K., and Pandey, K. K. (2012). "Photodegradation of thermally modified wood," *Photochem. Photobiol. B: Biology* 117, 140-145. DOI: 10.1016/j.jphotobiol.2012.09.013

Stamm, A. J., and Hansen, L. A. (1937). "Minimizing wood shrinkage and swelling. Effect of heating in various gases," *Ind. and Eng. Chem. Res.* 29(7), 831-833. DOI: 10.1021/ie50331a021

Tomak, E. D., Ustaomer, D., Yildiz, S., and Pesman, E. (2014). "Changes in surface and mechanical properties of thermally modified wood during natural weathering," *Measurement* 53, 30-39. DOI: 10.1016/j.measurement.2014.03.018

Williams, R. S., and Feist, W. C. (1999). *Water Repellents and Water-Repellent Preservatives for Wood*, U. S. Department of Agriculture, Forest Products Laboratory, Madison, WI, USA.

Yildiz, S., Tomak, E. D., Yildiz, U. C., and Ustaomer, D. (2013). "Effect of artificial weathering on the properties of heat treated wood," *Polym. Degrad. Stab*. 98(8), 1419-1427. DOI: 10.1016/j.polymdegradstab.2013.05.004