

Heat-Treated Softwood Exposed to Weathering

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ABSTRACT: Scots pine samples, heat-treated (225°C under steam) and reference (kiln-dried), were exposed to natural weathering for 7 years in Espoo, Finland. The weathered and unweathered samples were examined with FTIR, UV resonance Raman, and ¹³C CPMAS NMR spectroscopies. The spectroscopic results revealed that the lignin contents of the weathered heat-treated and especially of the weathered reference softwood samples diminished significantly. The surface of the weathered heat-treated sample was still rich in aromatic and conjugated carbonyl structures, whereas the surface of the reference sample was enriched with cellulose. These results indicated that weathering products of lignin were leached out with water from the reference sample, whereas in the heat-treated wood they were largely unleachable. The structure of the heat-treated

wood was modified and degradation products did not leach out as easily as in the case of the reference sample. The weathering also resulted in a decreased content of amorphous polysaccharides of the reference sample, whereas the changes in the polysaccharide contents between weathered and unweathered heat-treated samples were not as dramatic because the amorphous carbohydrates were already degraded in the heat treatment. The results indicated that heat-treated wood is more resistant to natural weathering than untreated wood. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 2128–2134, 2004

Key words: FTIR; NMR; Raman spectroscopy; heat-treated wood; weathering

INTRODUCTION

Wood, a composite of cellulose, hemicelluloses, lignin, and extractives, is commonly used as engineering and structural material. This is because of its properties such as esthetic appeal, low density, low thermal expansion, and mechanical strength. Heat treatment modifies wood both physically and chemically. Generally known physical changes in heat-treated wood are reduced shrinkage and swelling, better decay resistance, increased thermal insulating capacity, and reduced strength properties.^{1–4} Chemical modifications attributed to heat treatment at high temperatures are decrease in amorphous polysaccharide content, condensation and demethoxylation of lignin, and removal of certain extractives.^{5–7}

Unprotected wood exposed to outdoor conditions undergoes a variety of degradation reactions induced

by diverse factors such as light, moisture, heat, oxygen, and pollutants.^{8–11} The weathering process of wood is primarily a surface phenomenon, although the cracks and checks developing during weathering can be sensitive to fungal attack and lead to more severe destruction of wood. Exposure of wood to UV-light is known to be mainly responsible for the degradation and discoloration of the wood surface in natural weathering. The main UV-light-absorbing component in wood is lignin (20–30%), which is composed of phenylpropane units. In addition, some of the unsaturated wood extractives such as resin acids (2–4%) in softwoods may also participate in light-induced free-radical reactions.⁸ The majority of free radicals are known to be generated in phenolic groups of lignin, which are then easily converted into quinonoid structures. It has also been observed that carbon-carbon bonds adjacent to α -carbonyl groups in lignin are photodissociated by a Norris type I reaction.⁸ Progressive destruction of aromaticity of lignin and formation of carbonyl structures are well-known changes resulting from weathering. It has been reported that the cellulose content of the weathered wood surface increases because of the degradation and solubilization of lignin.⁸ Hon and Chang⁹ suggested that low molecular weight water-soluble phenolic structures with conjugated carbonyl groups were formed from

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lignin. Holmbom et al.¹² and Sjöholm et al.¹³ studied degradation products formed when sheets of spruce groundwood (SGW) and spruce milled wood lignin (MWL), respectively, were exposed to UV-light. Both studies showed that lignin was degraded and vanillin and vanillic acid were the major components formed. Cleavage of α - and β -ether and α - β bonds were the main reactions.

Fourier transform infrared (FTIR), UV resonance Raman (UVR), and solid-state NMR spectroscopies are useful tools for analyzing qualitative changes in wood caused by weathering. FTIR spectroscopy has been applied in numerous studies to characterize weathered wood surfaces.^{9,14–16} UVR spectroscopy has recently been used in the study of lignocellulosics materials.^{17,18} With this technique even trace amounts of aromatic and other unsaturated compounds in polymer blends can be detected because of their resonance enhancement. The UVR spectrum of solid wood shows Raman shifts only attributed to the aromatic lignin without any disturbance from the wood polysaccharides, even though the polysaccharide content of wood fiber cell wall is about 70%. Besides the CPMAS measurements, the dipolar dephasing (DD) technique is suitable for studying photodegradation with solid-state NMR because it suppresses the signals from protonated carbons and thus the aromatic lignin structure can be studied more precisely.^{19,20}

The aim of this study was to clarify how the molecular structure of heat-treated wood is changed in natural weathering. The effects of thermal modification on the chemistry of wood weathering are not well known despite the use of thermally modified wood as exterior construction material, where weather resistance plays an important role. In this work chemical changes caused by weathering were studied with FTIR, UVR, and solid-state NMR spectroscopies.

EXPERIMENTAL

Materials

Wood used for the heat treatment (VTT Building and Transport, Espoo, Finland) was pine (*Pinus sylvestris*) timber. The size of the specimens was 22–25 × 100 × 750 mm (thickness × width × length). The panels were tangentially cut. They were heat-treated at VTT Building and Transport using the process developed by Viitaniemi et al. The temperature of the panels was raised gradually over 2 h to the maximum temperature, and treatment time at the effective temperature (225°C) was 6 h. Heat treatment of the unweathered wood samples studied with solid-state NMR was performed at 230°C (4 h). Weight loss of the pine panels was 10–11.8%.

The panels were weathered vertically heartwood side up on racks in Espoo, Finland for 7 years (1994–

2001). The racks were facing south.^{23,24} Weathered heat-treated and untreated panels (one of each) were selected for spectroscopic analyses. The unweathered sides of the weathered samples were used as reference samples in the FTIR and UVR measurements, whereas unweathered wood samples studied with solid-state NMR were chosen from another test series. Samples for the spectroscopic analysis were taken from the surfaces of the panels. Several parallel spectra from each sample were collected.

FTIR measurements

Infrared measurements were performed with a Bio-Rad FTS 6000 FTIR spectrometer (Bio-Rad, Digilab, MA) fitted with an MTEC 300 photoacoustic cell. Helium was purged for 5 min to the photoacoustic cell before each measurement. The spectra were collected in the rapid-scan mode using a 10-kHz mirror velocity and a spectral resolution of 8 cm⁻¹. Some 400 scans were accumulated before Fourier transformation. All spectra were baseline corrected at 836, 1890, and 3780 cm⁻¹.

UVR measurements

Before the UVR measurements samples (~ 10 mg) scraped from the weathered wood surfaces were mixed with KBr (100 mg) and pressed into pellets. UVR spectra were collected with a Renishaw 1000 Raman spectrometer coupled with Innova 90C FreD frequency doubled argon ion laser and Leica DMLM microscope. Spectra were collected using 15× deep UV objective (OFR). An excitation wavelength of 244 nm was used in all measurements. The detector was a UV-coated CCD and a diffraction grating of 3600 grooves/mm was used. Samples were spinned during the measurements to avoid changes in the sample arising from the focused UV light and to average the spectra. The spectra were recorded in the wavenumber range of 200–2400 cm⁻¹. The spectral resolution was 7 cm⁻¹. All spectra were collected for 150 s.

¹³C CPMAS NMR measurements

Scraped wood samples were placed into the 7-mm NMR rotor and moistened with deionized water to obtain better resolution.^{25,26} ¹³C-NMR measurements were done using a Varian UNITY INOVA 300-MHz NMR spectrometer (Varian Associates, Palo Alto, CA) operating at 75.47 MHz for carbon. The spinning speed was 5000 Hz; contact times were 1 and 2 ms for unweathered and weathered samples, respectively; acquisition time was 20 ms; and delay between pulses was 2 s. For semiquantitative comparison, the chemical shifts were determined in the spectra using cellulose C-1 signal as an internal standard (at 105 ppm)

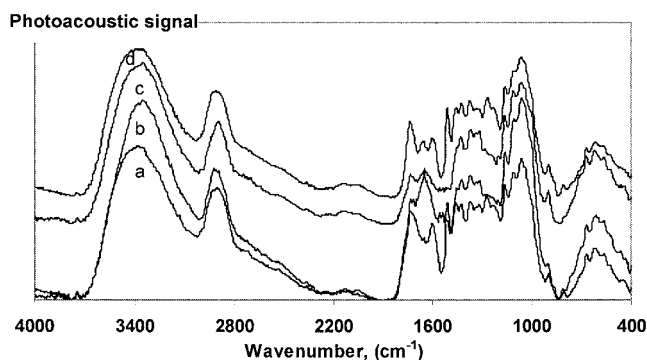


Figure 1 FTIR spectra of (a) unweathered heat-treated (225°C), (b) weathered heat-treated (225°C), (c) weathered reference (kiln-dried), and (d) unweathered reference (kiln-dried) softwood samples.

because the crystalline cellulose is expected to be relatively unaffected during weathering. The dephasing delay, which was inserted between the end of the contact time and the beginning of the data acquisition, was 40 μ s. During this delay the signals from the protonated carbons were allowed to relax.^{27,28} The duration of a single NMR measurement was 24–48 h.

Principal component analysis (PCA)

Principal component analyses were performed with a Simca P-8.0 software. FTIR and UVRR spectral data were baseline corrected and centered before the PCA. The principal component that resulted from the spectral changes attributed to the weathering explained 60–90% of the variation within the data depending on the model.

RESULTS AND DISCUSSION

Surfaces of the weathered wood samples became gray and checks and cracks appeared during weathering. The surface of the heat-treated specimen was altered more extensively than that of the reference specimen.

FTIR spectroscopy

FTIR spectra of the weathered and unweathered samples are clearly distinguished from each other (Fig. 1). The loading line plot of the first principal component of the reference and weathered reference samples shows more distinctly the spectral changes attributed to the weathering process. Negative bands in Figure 2 characterize the weathered reference sample and positive bands, the unweathered reference sample. Positive bands at 1593, 1508, 1269, 1226, 871, and 813 cm^{-1} result from the softwood guaiacyl lignin.²⁹ Their presence in the loading line plot indicates degradation of guaiacyl lignin during the weathering. The band at

1650 cm^{-1} is related to C=O stretching of the aromatic structures. The band at 1743 cm^{-1} originates from the C=O stretching vibration of the acetyl groups of galactoglucomannan,³⁰ which is a sign of the cleavage of acetyl groups during the weathering. Evans et al.³¹ showed that the intensity of a band at 1728 cm^{-1} decreased and hemicelluloses became partly soluble in hot water as a result of weathering of radiata pine veneers. Sudiyani et al.³² reported a decrease in hemicellulose content of softwood during natural weathering. A slight loss of certain carbohydrate structures of UV-irradiated SGW pulp was observed by Kimura et al.³³ Owen and coworkers¹⁴ detected a decrease in the carbonyl absorption band at 1750 cm^{-1} of softwoods after 300 h of weathering with UV light in conjunction with water. Negative bands in Figure 2 originate from the new chemical structures formed on the surface of the weathered reference wood. The bands at 1635 and 1555 cm^{-1} are attributed to C=O stretching of conjugated carbonyl groups and C=C stretching of ring structures, respectively.³⁴ The band at 1797 cm^{-1} could be attributable to the unsaturated ester structures such as aromatic esters and/or lactones. The band at 898 cm^{-1} , characteristic for C1–H group vibration of cellulose and hemicelluloses, shows that surface content of polysaccharides is increased during the weathering process. Other typical bands for carbohydrates could be at 1003 and 1115 cm^{-1} , attributed to the O–H association and/or C–O stretching vibrations.³⁵ These bands probably overlap with vibrations of the structures generated during the weathering.

Modification of guaiacyl lignin is also observed from the loadings of the PCA model of the heat-treated wood samples (Fig. 3). Positive bands in the loadings in Figure 3 characterize structures formed in the heat-treated wood during the weathering process. Bands at 3179 and 3090 cm^{-1} are related to the alkene C–H stretching and the bands at 1651 and 1543 cm^{-1}

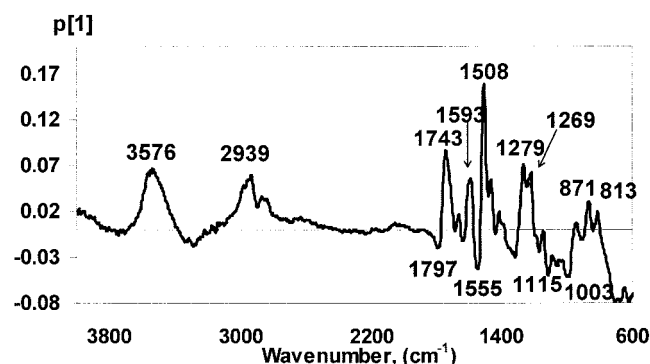


Figure 2 Loading line plot of the first principal component of the FTIR spectral data of the weathered and unweathered reference softwood samples. Positive and negative bands characterize unweathered reference and weathered reference samples, respectively.

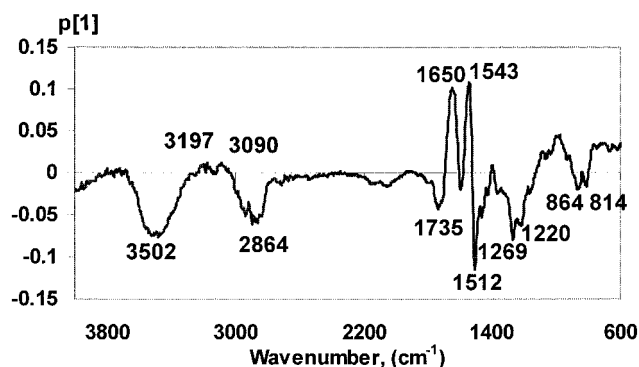


Figure 3 Loading line plot of the first principal component of the FTIR spectral data of the weathered and unweathered heat-treated (225°C) softwood samples. Positive and negative bands characterize weathered heat-treated and unweathered heat-treated samples, respectively.

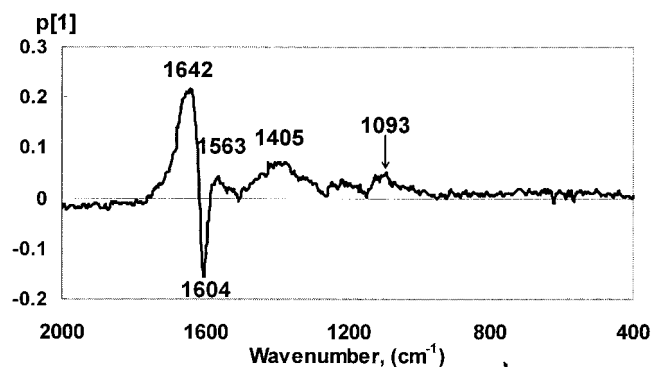


Figure 4 Loading line plot of the second principal component of the UV resonance Raman spectral data of the weathered and unweathered reference softwood samples. Positive and negative bands characterize weathered reference and unweathered reference samples, respectively.

originate from aromatic carbonyl and unsaturated cyclic structures, respectively. These bands are more intense than the corresponding structures in the weathered reference wood. Bands in the loadings of the reference sample indicate that only a tiny amount of unsaturated structures accumulated on the surface after weathering, which probably results from the fact that the degradation products of lignin are leached out and the surface content of polysaccharides is increased. It is known from earlier studies of artificial weathering that UV-light in conjunction with water has a greater effect on the chemistry of wood surfaces than UV-light alone because of the leaching out of degradation products.³⁶ Weathering causes changes on the surface of heat-treated wood but leaching does not occur to great extent. It is known from earlier studies that lignin in the heat-treated wood is crosslinked.^{6,37} Thus, the modified structure of lignin in heat-treated wood could partly inhibit UV-light-induced free-radical reactions and formation of low molecular weight degradation products such as quinones. Another reason can be higher-dimensional stability of the heat-treated wood that diminishes the effect of moisture content variation attributed to the outdoor weather conditions.

UVRR spectroscopy

Characteristic bands for weathered reference and unweathered reference wood are seen in the loading line plot of the second principal component (Fig. 4). Positive and negative bands are associated with the structures of the weathered wood and its reference, respectively. The bands at 1642 and 1563 cm^{-1} result from the unsaturated structures. The band at 1093 cm^{-1} originates from cellulose.¹⁷ In addition, other cellulose bands are probably overlapped by the new structures formed as a result of weathering in the region of about

1300–1500 cm^{-1} . The UVRR spectrum of untreated solid wood shows no bands characteristic for polysaccharides because the signals from lignin are strongly resonance enhanced.¹⁸ Thus, it is obvious that lignin on the surface of the weathered reference wood is degraded and almost completely leached out while the cellulose content is increased. The loading line plot of the first principal component of the weathered heat-treated wood and unweathered heat-treated wood (Fig. 5) reveals that the guaiacyl structure is degraded in the weathering. Characteristic vibrations for softwood guaiacyl lignin are seen at 1608, 1495, 1273, and 1153 cm^{-1} .¹⁸ Weathered heat-treated wood consists of the conjugated carbonyl compounds that show an intensity maximum at 1653 cm^{-1} .

¹³C CPMAS NMR spectroscopy

¹³C CPMAS NMR spectra of the weathered wood sample heat-treated at 225°C and of its reference sam-

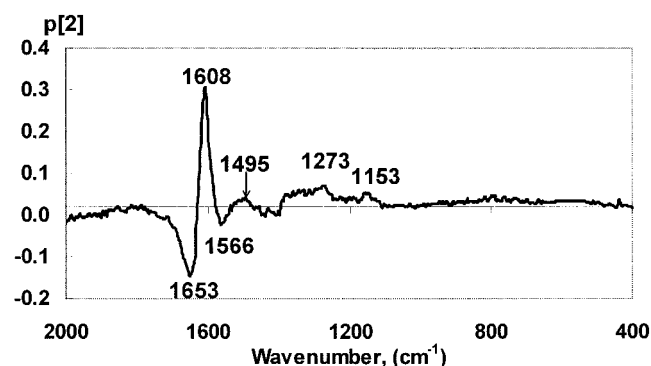


Figure 5 Loading line plot of the first principal component of the UV resonance Raman spectral data of the weathered and unweathered heat-treated softwood samples. Positive and negative bands characterize unweathered heat-treated and weathered heat-treated samples, respectively.

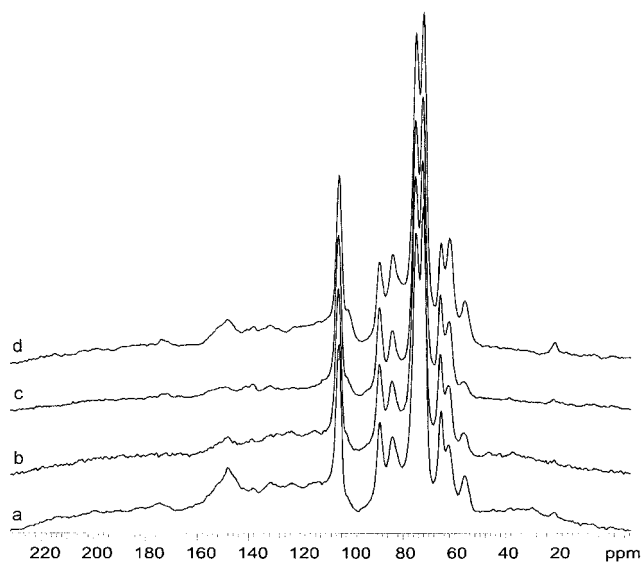


Figure 6 ^{13}C CPMAS NMR spectra of the (a) unweathered heat-treated, (b) weathered heat-treated, (c) weathered reference, and (d) unweathered reference softwood samples.

ple are shown in Figure 6(b) and (c), respectively. The spectra of the unweathered wood sample heat treated at 230°C [Fig. 6(a)] and of its reference sample [Fig. 6(d)] are also shown for comparison. The signal assignments of the ^{13}C CPMAS spectra are shown in Table I. The lignin content decreases in weathering as seen in Figure 6; that is, the relative intensity of the aromatic area (110–156 ppm) is diminished in spectrum b and especially in spectrum c compared to spectra a and d, respectively. The aromatic C-3,4 band at 149 ppm and aromatic C-1 band at 134 ppm are broadened and their relative intensities are highly diminished in proportion to the carbohydrate fraction. Demethoxylation is also observed in spectra b and especially spectrum c as a relative intensity decrease of the methoxyl signal at 56 ppm. Some structural changes of the carbohydrate components are also observed. The relative intensity of the C-1 signal at 102 ppm attributed to hemicelluloses is diminished in spectrum c compared to spectrum d, indicating depolymerization of hemicellulosic carbohydrates. This signal is almost absent from spectra a and b because thermal modification deteriorates hemicelluloses.⁶ The signals of methyl (22 ppm) and carboxylic (173 ppm) carbons of acetyl groups attached to hemicelluloses are weaker in spectra b and c, which indicates that deacetylation occurred during weathering. Even though these changes are small in the spectra they are still detectable. The relative intensity of the amorphous cellulose C-4 signal (84 ppm) is decreased compared to the relative intensity of the C-4 signal of crystalline cellulose (89 ppm) in spectrum c compared to that in spectrum d. The relative intensity of the amorphous cellulose C-6 signal (63 ppm) also becomes

weaker compared to the relative intensity of the crystalline cellulose C-6 signal (66 ppm). These changes suggest degradation of less-ordered cellulose and hemicelluloses whose signals overlap with those of cellulose. However, lignin signals overlap amorphous cellulose signals in this area and the depreciation of the lignin content during the exposure partly affects the decrease of the amorphous cellulose C-4 and C-6 signals. These spectral regions are similar in spectra a and b because thermal modification itself decomposes amorphous cellulose.⁶

The dipolar dephasing (DD) spectra of the weathered samples were measured to examine lignin structure more accurately. DD spectra of the weathered wood sample heat-treated at 225°C and of its reference sample are shown in Figure 7(b) and (a), respectively. Despite the long measuring times, the resolution remains poor in the spectra. Some rough conclusions may be made nonetheless. Using the dephasing delay of $40\ \mu\text{s}$, the signals of the crystalline cellulose are still shown in the spectra. The cellulose C-1 signal is used as an internal standard (at 105 ppm) because the crystalline cellulose is expected to be relatively unaffected during weathering. The large band at 149 ppm can be resolved into three signals at 153, 149, and 146 ppm. The main signal at 149 ppm has been assigned to C-3 of etherified and nonetherified structures. A shoulder at 153 ppm is assigned to etherified C-4 structures and the shoulder at 146 ppm is assigned to nonetherified C-4 structures. The band at 134 ppm is assigned to C-1 of etherified and nonetherified structures and the small shoulder at 132 ppm is assigned to C-5 condensed structures. The relative intensities of both of these bands are highly diminished in spectrum a, in-

TABLE I
Signal Assignments for ^{13}C CPMAS NMR Spectra of Pine

Chemical shift (ppm)	Assignment ^a
168–180	–CO
153	aromatic C-4e
149	aromatic C-3e, C-3f
146	aromatic C-4f
134	aromatic C-1
125	aromatic C-5s
114	aromatic C-5
105	C-1 of cellulose
102	C-1 of hemicelluloses
89	C-4 of crystalline cellulose
84	C-4 of amorphous cellulose
76	C-2 of cellulose
73	C-3, C-5 of cellulose
66	C-6 of crystalline cellulose
63	C-6 of amorphous cellulose
56	–OCH ₃
30–35	aliphatic carbons (–CH ₂ –)
22	–CH ₃ C=O

^a e, etherified; f, free; s, substituted.

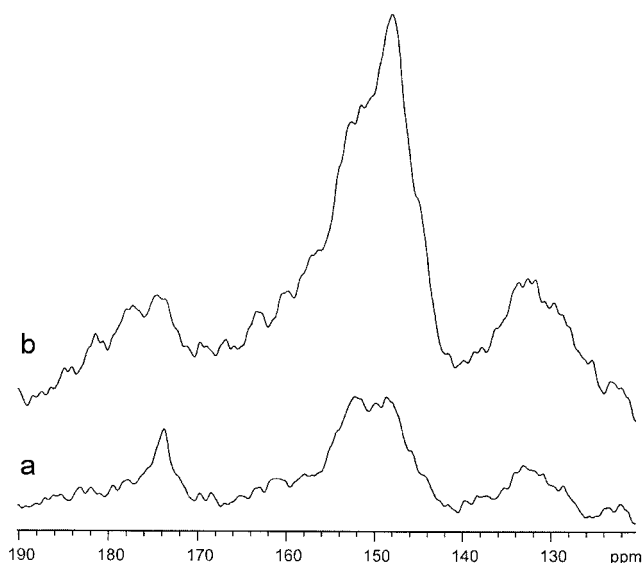


Figure 7 Dipolar dephasing NMR spectra of the (a) weathered reference and (b) weathered heat-treated (225°C) wood samples.

dicating severe degradation of lignin guaiacyl structures. The shoulder at about 132 ppm is more intense in spectrum b because heat treatment increases the amount of condensed lignin structures.⁶ The increase of the condensed structures might be one reason for the better weather resistance of heat-treated wood as discussed earlier. The shape of the carbonyl signal at 173 ppm is different in spectra a and b. New carbonyl structures formed in weathering are still shown in the spectrum of heat-treated wood [Fig. 7(b)], whereas they are absent from the reference spectrum [Fig. 7(a)].

CONCLUSIONS

Spectroscopic results revealed that the lignin content of the weathered heat-treated and especially weathered reference softwood samples diminished significantly. FTIR, UVRR, and NMR results showed that the surface of the weathered heat-treated sample was still enriched with aromatic and conjugated carbonyl compounds, whereas the surface of the reference sample was rich in cellulose. These results indicated that degradation products of lignin of the reference sample were leached out with water (humidity, dew, rain, and snow). The structure of the heat-treated wood was altered so that the degradation products did not leach out as easily as in the case of the reference sample. The reason for this can be the condensed structure of lignin of the thermally modified wood that could partly inhibit UV-light-induced free-radical reactions. In addition, the lower equilibrium moisture content of the heat-treated wood attributed to the lower hemicellulose content could diminish leaching out of the degradation products. Depolymerization and deacetyla-

tion of hemicellulosic carbohydrates of the weathered reference sample were observed with NMR and FTIR spectroscopies. In addition, the amount of less-ordered cellulose decreased. Changes in the content of amorphous polysaccharides between weathered and unweathered heat-treated samples were not dramatic because hemicelluloses and amorphous cellulose are already degraded in the thermal-modification process. Results indicated that heat-treated wood is more resistant to natural weathering than reference wood.

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