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ORIGINAL ARTICLE

Weathering characteristics of bamboo (*Phyllostachys puberscence*) exposed to outdoors for one year

Yoon Soo Kim[1] · **Kwang Ho Lee**[1] · **Jong Sik Kim**[2]

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Abstract The 1–3-year-old bamboo (*Phyllostachys puberscence*) culms were exposed to ambient weathering conditions for 12 months. Changes in color, surface topography, and chemical features of bamboo culms by weathering were investigated. Changes in the surface color of culms increased sharply in the first 3 months weathering and then slowly decreased compared to control culms. Surface checks developed more markedly in the 2- and 3-year-old bamboos than in the 1-year-old ones. The depth of erosion was extended up to 150 µm from the outer surface of culms. Solid-state NMR (nuclear magnetic resonance) and FT-IR (Fourier transform infra-red) spectra showed that the lignin and hemicelluloses of bamboo culms were preferentially affected by natural weathering, while crystalline cellulose remained relatively intact.

Keywords Bamboo · Natural weathering · Surface topography · Lignin · Hemicelluloses

Introduction

Weathering in wood, initiated by ultraviolet (UV) radiation in sunlight, leads to the deterioration of wood surface in parallel with lignin degradation [1, 2]. Recent works demonstrated that not only UV but also visible light possessed sufficient energy to degrade lignin in the wood surface, and structural polysaccharides were also broken-down by photo-oxidation [3, 4]. In addition to chemical alternations, the topography of wood was also affected by weathering; color changes, erosion, and cracks of surface were usually accompanied, resulted in downgrading the aesthetic value as well as the qualities of woods [4]. Diverse meteorological factors, such as rainfall, snow, relative humidity, temperature, and pollutants, also accelerate the weathering of wood. The degraded fragments by weathering were leached by rainfalls, resulting in increased surface roughness. The depth of photo-degradation in wood during weathering varied from 80 to 2500 µm [5, 6].

A lot of information is available on weathering of wood [2–6]. However, the data on bamboo culms by weathering are very uncommon. About 80 % of bamboos in the world are planted in Asia [7] and regarded as one of Asia's important natural resources. High strength, low cost, and fast growing characteristics of bamboo provide great potential as a substitute for wood building materials. Bamboo shares many similarities with woody plants but marked differences in cell wall structures and lignification [8–10]. Due to the absence of vascular cambium, the thickening growth of the culms does not occur in bamboo. The formation of a cell wall in bamboo proceeds in a different way with that in woody plants. Bamboo fiber and parenchyma cell walls are characterized by a polylamellate structure with the alteration of thick and thin layers [11, 12]. The extent of cell wall polylamellation also varies depending on the position of the vascular bundle in the culm and the age of culm [13]. Bamboo cell wall chemistry is also different, showing the presence of *p*-hydroxyphenyl (H) unit in lignin in addition to guaiacyl (G) and syringyl (S) units, whereas G and S units in lignin are the main components in woody plant. A relatively higher amount of ashes than woody plants are also present in bamboo [9].

✉ Yoon Soo Kim
kimys@jnu.ac.kr

[1] Department of Wood Science and Engineering, Chonnam National University, Gwangju 61186, Korea

[2] Department of Forest Products, Swedish University of Agricultural Sciences, Uppsala, Sweden

Anatomical and chemical characteristics of bamboo culms have significant effects on their utilization and durability. In particular, the distribution of tissues and the cell wall chemistry is different between the outer surface and the inner part of culms. Siliceous wax layer on the bamboo outer surface affects the property of interfacial reaction between bamboo and adhesive. Higher percentage of fibers and lower content of cellulose and hemicelluloses are present in the outer surface of bamboo culms. In contrast, the inner culms show higher percentage of vessel and parenchyma cells and lower lignin content than the surface [14]. Although bamboo is known to be liable to attack by molds and blue stain infestation [15, 16], information on durability of bamboo against abiotic agents is limited. Considering that weathering usually occurs to the surface of materials, it would be interesting to explore how weathering affects the surface of bamboo, to expand the potentials of bamboo as a valuable asset for engineered applications. The present work was undertaken to investigate the effect of ambient weathering conditions on the changes in anatomical and chemical characteristics in bamboos.

Materials and methods

Sample preparation and weathering test

One-, two-, and three-year-old bamboo culms (*Phyllostachys puberscence*) obtained from the Bamboo Institute in Damyang County, South Korea were employed for natural weathering test. Bamboo culms were cut 100 × 250 × 15–10 mm (width × length × thickness), dried for 24 h at 105 °C, and then stored in a conditioning room at 20 °C and 65 % relative humidity for 2 weeks before exposure. The outer surface of bamboo culms facing south on the test rack inclined 45°, on the rooftop in the building of Chonnam National University campus, Gwangju (latitude 35.09N, longitude 125.54E), South Korea. Bamboo culms were exposed from March 2011 to March 2012 for a year. The climatic conditions of the test site (Gwangju) during a weathering period are shown in Table 1. Information regarding the meteorological conditions encountered during the exposure trial was obtained from the Korea Meteorological Administration. Five specimens were collected after 3, 6, and 12 months weathering for measurements. Unexposed bamboo culms were served as control.

Table 1 Average climatic condition of test site, Gwangju (2011)

Average temp.	Daily max temp.	Daily min temp.	Avg. relative humidity (%)	Annual sunshine (h/year)	Annual precipitation (mm)
13.7	30.3	−7.7	68.5	2140.9	1300.3

Color measurement

A Minolta colorimeter (Minolta CM-3500d, Japan) was used to quantify color changes of bamboo culms as a result of weathering. Measurements were performed at the upper, middle, and low part of bamboo culms. The diameter of measurement spot was 8 mm in the surface with viewing angle at 45°. Color parameters L^*, a^*, and b^* were calculated using the CIELAB system [17], where L^* is lightness black (0) to white (100), a^* is chromaticity coordinate red (+) to green (–), and b^* is chromaticity coordinate yellow (+) to blue (–). Relative color changes of bamboo culms ΔL^*, Δa^*, and Δb^* were determined between their weathered and initial state (i.e., values of weathered culms minus values of control culms). The total color differences ΔE^* were calculated from the following equation: $\Delta E^* = (\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2})^{1/2}$.

Instrumental analysis

Solid-state NMR (nuclear magnetic resonance) spectra were obtained from Bruker Avance 400 FT-NMR (USA), as described previously [18, 19]. All the ^{13}C CP MAS NMR (cross polarization and magic angle spinning NMR) measurements were performed with a Bruker Avance 400 MHz spectrometer operating at 100.62 MHz at room temperature. About 90 mg of dried bamboo powders were filled in cylindrical rotors made of zirconia (outer diameter 4 mm) with kel-F end caps. All ^{13}C NMR spectra were collected by the ramped CP pulse program [20]. The magic angle spinning speed was 13,000 Hz, acquisition time 10.3 ms, and delay between pulses 5 s with contact times of 1 ms, respectively. For each spectrum, 1000–2000 scans were collected. The chemical shifts in ^{13}C NMR spectra were referenced using the adamantine as an internal standard (38.56 ppm). The ^{1}H radio-frequency field strength was set to give 90° pulse duration around 4.0 μs. NMR data were collected by the Topspin 1.3 software (Bruker Co.), and the regional integration values were obtained using the TopSpin 3.0 software. For FT-IR (Fourier transform infra-red) spectra, about 100 μm thick veneers collected from the bamboo surface were milled and mixed with KBr. FT-IR spectra were obtained from Perkin–Elmer 1800 spectrometer (USA).

Microscopy

For transmission electron microscopy (TEM), small blocks (10 × 10 × 8 mm) cut from control and weathered bamboo culms that were fixed in a mixture of 2 % v/v paraformaldehyde and 2 % v/v glutaraldehyde in 0.05 M cacodylate buffer (pH 7.2). After dehydration using a graded acetone series, blocks were embedded in Spurr's epoxy resin. Transverse ultrathin sections prepared from embedded blocks were observed with a JEM-1400 (Jeol, Japan) after staining with 1 % $KMnO_4$ in 1 % sodium citrate. Transverse thin sections (20 μm thick) prepared using a rotary microtome were also examined with a Zeiss light microscope (LM, German) after staining with 1 % toluidine blue.

To study changes in surface topography, non-embedded small blocks of control and weathered bamboo culms were examined with scanning electron microscope (SEM, Hitachi S-2400, Japan) at 15 kV (8 mm working distance) after sputter-coating with gold. The surface of bamboo culms was also examined using a Zeiss stereo microscope (SM, German).

Results and discussion

The color changes

The total color difference (ΔE^*) of bamboo during weathering increased sharply in the first 3 months and then decreased slowly (Fig. 1a). Feist [2] reported that the appearance of unprotected wood exposed outdoors changed markedly in a few months; thereafter, the wood remained essentially unchanged for years. Differences in color changes between the ages of bamboo were not significant. All the bamboo samples exposed to weathering showed the increase in ΔL^*, indicating that the sample color became lighter (Fig. 1b). This pattern of color changes in bamboo culms under natural weathering differed from that in woods, in which wood became darker and grey with increasing exposure time [2–5]. Different anatomical and chemical characteristics of bamboo from woody plants would be ascribed to the difference in color changes. The value of Δa^* decreased slightly (i.e., negative) during weathering (i.e., less red and more green color than controls) (Fig. 1c). The value of Δb^* increased (i.e., positive) in the first 6 months (i.e., more yellow and less blue than controls), but decreased after 12 month weathering (Fig. 1D).

Microscopic features

Different surface topographies of culms between the ages of bamboos released after 1 year of exposure to natural weathering conditions. Surface cracks occurred more significantly in 2 (Fig. 2c, g)- and 3 (Fig. 2d, h)-year-old bamboo culms than in the 1-year-old culms (Fig. 2b, f), which showed smaller and more uniform in size. These differences would be related to the variations in the surface structure and chemistry of bamboo culms between their ages, probably by different characteristics of siliceous wax layers on the bamboo surface. All the cracks ran parallel to

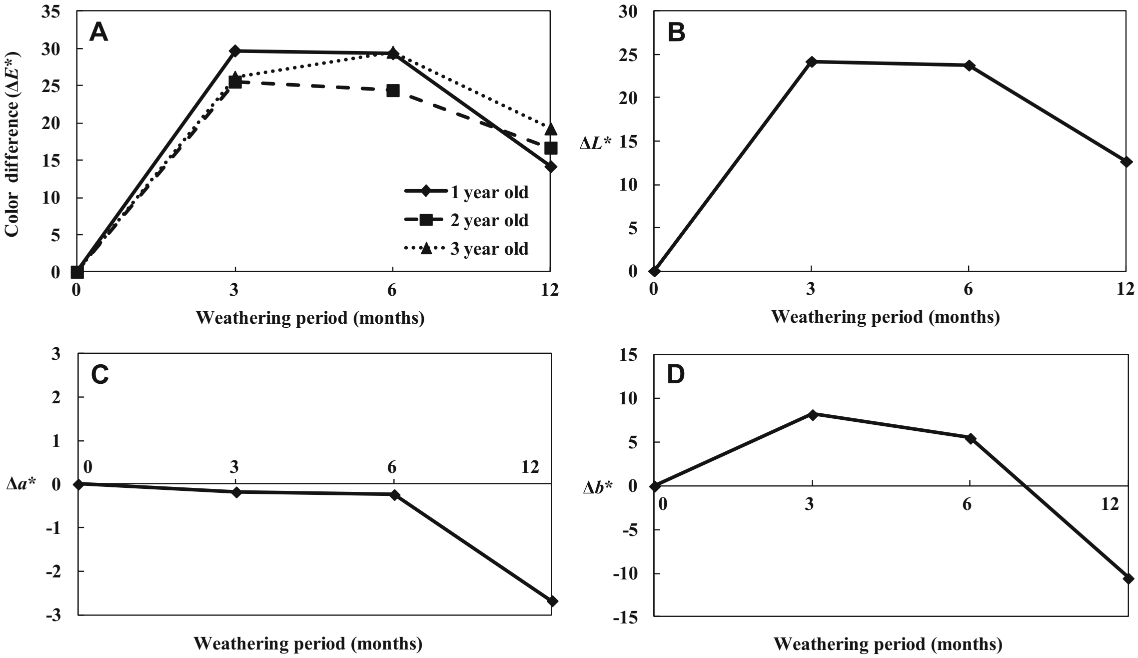

Fig. 1 Total color difference (ΔE^*) of bamboo culms with different ages by weathering (**a**) and changes in color parameters ΔL^* (**b**), Δa^* (**c**), and Δb^*(**d**) of 2-year-old bamboo culms by weathering

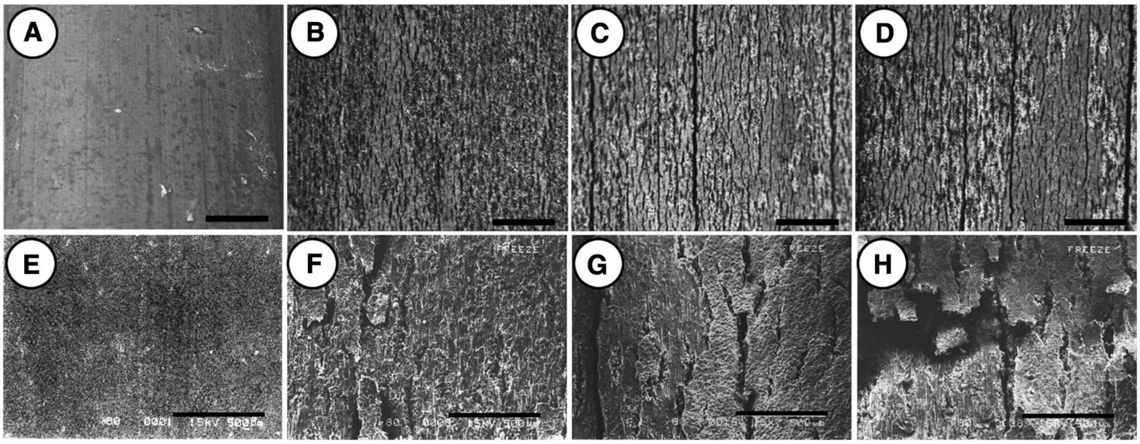

Fig. 2 Occurrence of surface cracks and erosion after 12 months weathering. **a–d** SM micrographs (×10) showing the surface of control (**a**) and weathered 1 (**b**)-, 2 (**c**)-, and 3 (**d**)-year-old bamboo culms. **e–h** SEM micrographs corresponding to **a–d**, respectively. *Bars* 1000 µm (**a–d**), 500 µm (**e–h**)

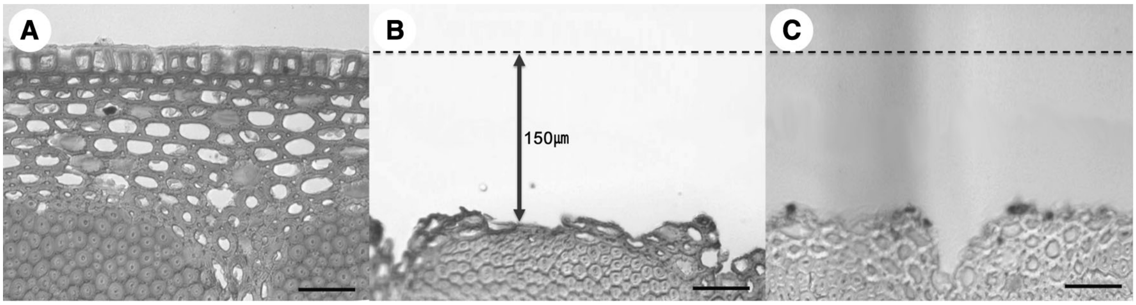

Fig. 3 Cross sections of 3-year-old bamboo culms after 12 months weathering (LM micrographs). **a** Control culm. **b**, **c** Weathered culms. Note that the degradation of ground tissues was extended to the boundary of vascular bundles. *Bars* 50 µm

the fiber axis of bamboo culms. Surface cracks were overall extended to the 8–10th cells from the surface toward the boundary of vascular bundles in transverse sections (Fig. 3c). Most parenchyma cells in the ground tissues were severely affected (Fig. 3b, c). The extent and degree of erosion did not show any great difference from the age of bamboo culms (Fig. 4), although the formation of V-shaped cracks was greater in the 2- and 3-year-old bamboos than 1-year-old ones (Fig. 2). The erosion was extended to the 5–8th cells (about 100–150 µm) from the surface of bamboo culms (Fig. 3b).

After ambient weathering, parenchyma cells exposed by surface erosion showed frequently the separation of middle lamellae, indicating the degradation of lignin (Fig. 5a). The numerous fungal spores were also present on the outer surface as well as on the eroded regions (arrows in Fig. 5a–d). The most dominant fungi grown on wood surface exposed outdoors without ground contact were identified as molds and staining fungi, such as *Trichoderma* sp and *Epicoccum* sp. [21, 22]. TEM examinations also showed the degradation of middle lamellae of parenchyma cells by ambient weathering (Fig. 5d). Parenchyma cells showed frequently delamellation of cell walls, whereas fibers adjacent to parenchyma cells in vascular bundles revealed relatively intact cell wall structure after 12 months weathering (Fig. 5e). Degradation of middle lamellae and delamellation of secondary cell walls were also observed frequently in the wood cells exposed to natural weathering [23]. Consequently, results demonstrate that bamboo lignin is the initial target of degradation in the course of weathering similar to weathering in wood.

Chemical characteristics

FT-IR spectra were almost identical regardless of bamboo age (Fig. 6). The bands assigned to lignin-related structures (1460, 1510, and 1600 cm^{-1}) were reduced. A spectrum assigned to total carbohydrates (1160 cm^{-1}) was also decreased, indicating the degradation of carbohydrate. Using solid-state NMR combined with 2-year-old bamboo culms, changes in chemistry by weathering were further advanced (Fig. 7). Since the FT-IR spectra were almost

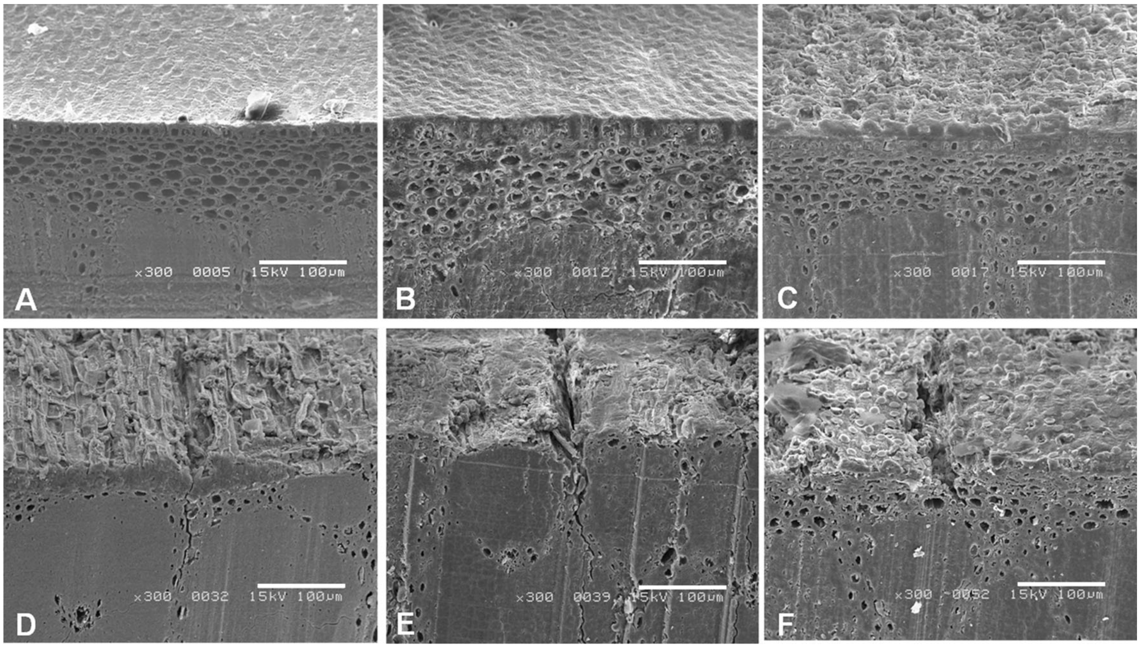

Fig. 4 Surface topography of bamboo culms after 12 months weathering (SEM micrographs). **a–c** Control of 1-, 2-, 3-year-old bamboo culms, respectively. **d–f** Weathered culms corresponding to **a–c**, respectively

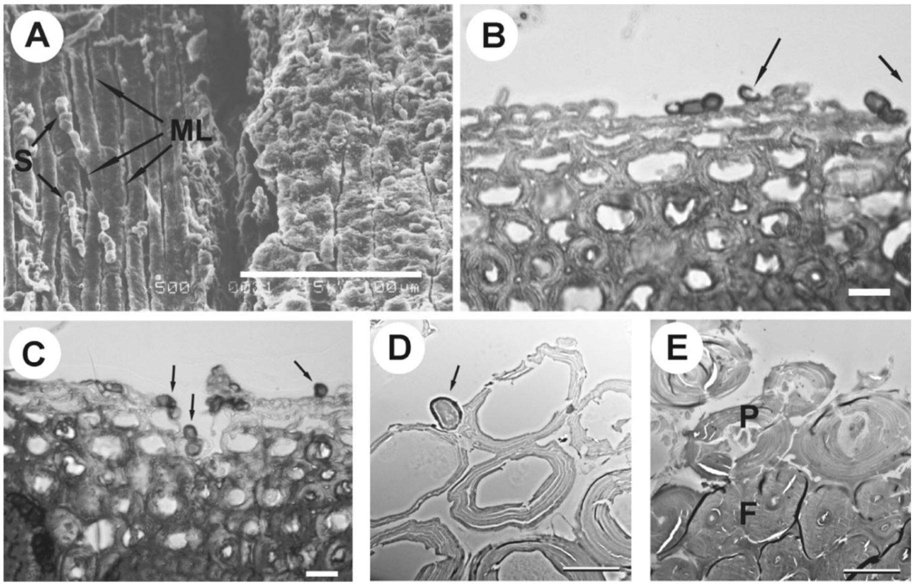

Fig. 5 Separation of middle lamellae and growth of fungal spores on weathered bamboo culms. **a** SEM micrograph showing the presence of spores (*S*) in the eroded surface and the split of middle lamellae (*ML*) of parenchyma cells. **b–c** LM micrographs showing the spores (*arrows*) on the outer surface (**b**) and in the eroded regions at early stages of weathering (**c**). **d**, **e** TEM micrographs showing severe degradation of middle lamellae and delamellation of parenchyma cells. Note the presence of fungal spore (*arrow* in **d**) and the relatively intact fibers (*F*) in comparison with parenchyma cells (*P*). *Bars* 100 µm (**a**), 20 µm (**b**, **c**), 5 µm (**d**), 10 µm (**e**)

identical regardless of bamboo age, it has been assumed that the changes in 2-year-old bamboo culms can represent changes in 1- and 3-year-old bamboo culms. The most significant changes in NMR spectra were disappearances and/or decreased signal intensities specific to the aromatic carbons of lignin (105–155 ppm), indicating the preferential degradation of lignin by weathering. The intensity of the signals assigned to the S lignin (153 and 148 ppm) and the methoxyl groups (56 ppm) was also decreased, reflecting that comparatively lower condensation lignin would be susceptible toward weathering. The intensity of the signals in the 33 ppm spectral region

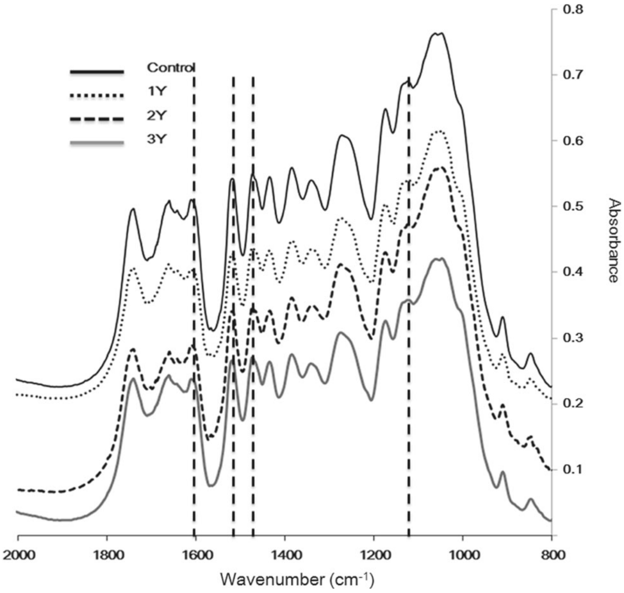

Fig. 6 FT-IR spectra of bamboo culms with different ages after12 -months weathering. 1-, 2-, and 3-year-old indicate 1-, 2-, 3-year-old bamboo culms, respectively

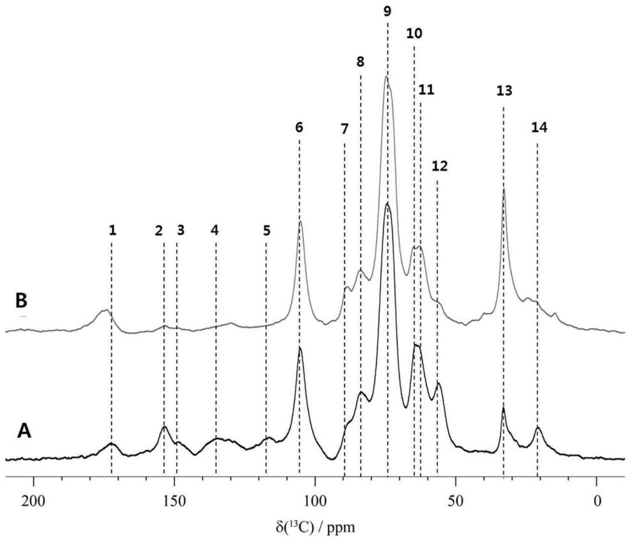

Fig. 7 ^{13}C solid-state NMR spectra of 2-year-old bamboo culms. **a** Control. **b** After 12 months weathering. Vertical scales adjusted so that the tallest peak is the same height in each of the two spectra. Resonance numbers assigned to chemical shift refer to Table 2

Table 2 Resonance assignment of solid-state NMR of wood and grass. Excerpted from [27, 28]

Resonance number	Chemical shift (ppm)	Assignment
1	173	Acetyl groups in hemicelluloses
2	153	S3, S5 lignin
3	148	S3, S5, G1, G4
4	135	Etherified S and G
5	116	C3, C5 in *p*-hydroxyphenyl
6	105	C1 carbohydrate
7	89	C4 crystalline cellulose
8	84	C4 amorphous cellulose
9	75	Cellulose
10	65	C6 crystalline cellulose
11	62	Xylan
12	56	Methoxyl in lignin
13	33	Aliphatic carbons (=extractives)
14	21	Acetyl groups in hemicelluloses

S syringyl lignin, *G* guaiacyl lignin

suggests either the accumulation of saturated alkyl structures in the altered lignin [24] or non-extractable lipid materials. Some changes in the carbohydrate fraction were also revealed. The relative intensity of the signals assigned to hemicelluloses (21 ppm) and carboxylic carbons (173 ppm) was diminished in the weathered samples, indicating the degradation of hemicelluloses during weathering. In contrast, signals assigned to crystalline cellulose (89 ppm) were not changed, showing that crystalline cellulose was relatively resistant against weathering. The degradation of hemicelluloses suggests that lignin-hemicelluloses matrix in bamboo cell walls would be preferentially destroyed by weathering. Ma et al. [25] demonstrated that lignin-bound xylan was much more easily removed than the xylan tightly bound to the surface of cellulose microfibrils during the hydrothermal treatment of poplar. It can be assumed that lignin decomposition accompanies the loss of hemicelluloses during exposure to ambient weathering conditions. An increase in the crystallinity index of cellulose during weathering would be resulted from the reduction of the amorphous fractions of wood cellulose and, consequently, to the enrichment of the relative crystallinity content [26].

NMR and FT-IR spectra exhibit clearly weathering affects mainly lignin and hemicelluloses, whereas cellulose is relatively less affected, reflecting the lignin-carbohydrate complexes was hit by weathering. Overall changes in the chemistry of bamboo culms affected by weathering were similar to those in wood weathering in terms of preferential degradation of lignin to cellulose [1, 2, 4, 23, 26, 27].

Conclusions

After 1 year of exposure to ambient weathering conditions, the color of outer surface of bamboo culms became lighter. Changes in the surface topography varied with the age of bamboo culms. Numerous checks developed in the 2- and

3-year-old bamboo, whereas the 1-year-old bamboo showed little. Cracks extended from surface to almost to the vascular bundles. In contrast to crack formation, the depth of surface erosion was not so different from the age of bamboo culms. Regardless of bamboo age, changes in chemistry of culms by weathering were similar. Syringyl-type lignin and hemicelluloses were greatly affected, whereas crystalline cellulose was relatively intact.

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