J Wood Sci (2009) 55:47–52
DOI 10.1007/s10086-008-0994-0

ORIGINAL ARTICLE

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Surface deterioration of moso bamboo (*Phyllostachys pubescens*) induced by exposure to artificial sunlight

Received: April 11, 2008 / Accepted: August 27, 2008 / Published online: November 11, 2008

Abstract The effect of ultraviolet–visible light irradiation on changes in surface chemistry and morphology of moso bamboo (*Phyllostachys pubescens* Mazel) was investigated. Fourier transform infrared (FT-IR) and FT-Raman spectroscopy were used in combination to study chemical changes induced by exposure to artificial sunlight (xenon lamp) for up to 160 h, and the resulting physical changes of cell walls of bamboo surfaces were examined by scanning electron microscopy (SEM). FT-IR results showed that significant changes occurred in the lignin component as indicated by considerable decreases in the intensities of the characteristic aromatic lignin peak at 1512 cm^{-1} and other associated bands. This was accompanied by formation of new carbonyl groups at 1735 cm^{-1}, resulting in photooxidation of bamboo surfaces. The photosensitive nature of bamboo lignin was also demonstrated by FT-Raman analysis, in which obvious decreases in intensities of Raman bands at 1604 and 1630 cm^{-1} mainly derived from lignin and free and esterified *p*-coumaric and ferulic acids were observed. SEM micrographs of the irradiated cross sections of bamboo revealed that significant damage occurred to the fiber walls, whereas the parenchyma cells exhibited slight distortion and some cracks occurred in the cell walls. The structures of cell corners and middle lamellae were nearly intact after irradiation.

Key words Photodegradation · FT-IR · FT-Raman · Lignin · Bamboo

Introduction

Bamboo is an important forest resource growing abundantly in many tropical and subtropical countries, especially in Asia. For example, the largest variety of bamboo resources is in China, with a stock area of over 4.2 million hectares.[1] As a fast-growing lignocellulosic material, bamboo has been widely used as a traditional material for housing construction, furniture manufacture, and household products (e.g., chopsticks, containers, and handicrafts) due to its high strength and surface hardness, easy machinability, and local availability.[2,3] However, in common with other biological materials, bamboo culm is susceptible to environmental degradation without protective treatment. When exposed to the natural elements (e.g., sunlight, air, and water), the surface of bamboo culm appears to undergo complex chemical and physical changes, primarily resulting in disappearance of its attractive fresh color and gloss. Among the weathering factors, solar irradiation contributes most to the degradation process. To overcome this problem and to maintain the economic value of bamboo products, it is necessary to gain an understanding of the mechanism involved in the photodegradation of bamboo.

Many studies have been conducted to investigate the process of photodegradation of wood,[4–6] whereas relevant studies on bamboo are scarcely found in the literature. The photodegradation process involves very complex physical and chemical reactions, which are largely dependent on the surface properties of the woody material considered.[7] Although bamboo has similar chemical constituents to those of wood, they are different in many aspects. For example, the anatomical structure of bamboo is characterized by vascular bundles embedded in the parenchymatous ground tissue without radial tissue like the rays in wood. This disparity in anatomical characteristics makes bamboo and wood quite different in surface structure, roughness, and density. Furthermore, the chemical components of bamboo, particularly hemicellulose and lignin are also quite different from those derived from wood.[8] It has been reported that the hemicellulose structures of bamboo are described as intermediate between those of softwoods and hardwoods, and lignin of bamboo is characterized as a typical Gramineae lignin composed of three phenylpropane units, *p*-coumaryl, coniferyl, and sinapyl alcohols.[9,10] In general, bamboo is different from wood in surface physical

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and chemical characteristics, thereby possibly presenting degradation behavior that is distinct from that of wood.

The objective of the present study was to investigate the chemical and morphological changes of bamboo surface induced by ultraviolet (UV)–visible light irradiation. Moso bamboo (*Phyllostachys pubescens* Mazel) was selected due to its popularity, abundance, and value in China. Several analytical techniques such as Fourier transform infrared (FT-IR) and FT-Raman spectroscopy and scanning electron microscopy (SEM) were applied in combination to gain a better understanding of the photodegradation process occurring in bamboo from different perspectives.

Materials and methods

Bamboo specimens

Three 5-year-old moso bamboo (*Phyllostachys pubescens* Mazel) culms with an average height of 7.3 m were obtained from an experimental forest located in Zhejiang Province, China. Internodes from the mid-height of bamboo culms were selected and cut into strips with dimensions of 100 (longitudinal) × 20 (tangential) × 3 mm (radial) to be used as specimens (30 in total), as shown in Fig. 1. The tangential surface of the specimens was used for investigation. In addition, 10 transverse sections of about 5 mm in thickness were also prepared to examine the possible morphological changes on this surface induced by photoirradiation. All the specimens were conditioned at 25°C and 65% relative humidity until an equilibrium moisture content (EMC) of 8%–10% was achieved.

Photoirradiation experiments

The specimens were exposed to artificial sunlight from a xenon lamp at a temperature of 63°C (black panel) and 50% relative humidity in a commercial chamber (X25F, Suga Test Instruments, Japan). The irradiation was interrupted after 5, 20, 80, and 160 h of treatment, respectively. After each exposure period, the irradiated specimens were removed from the chamber for further analysis. Two types of specimens (tangential and transverse sections) were photoirradiated and observed by SEM. In addition, the tangential sections were used for FT-IR and FT-Raman analysis, while the transverse sections were not.

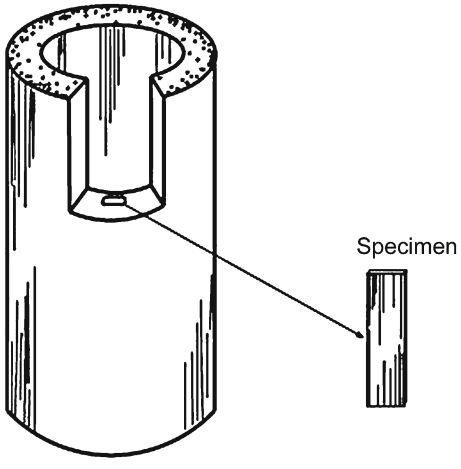

Fig. 1. Sampling from bamboo culm

Measurement of FT-IR spectra

The FT-IR spectra were measured by direct transmittance method using a Nicolet Impact 410 spectrometer (Thermo Nicolet, USA). The powder samples were obtained by removing the top layer of the irradiated surface of the specimens using a sharp razor blade, and then were mixed with KBr in a weight ratio of about 1:100 to form a pellet. Spectra were collected from 400 to 4000 cm^{-1} and 64 scans were recorded for each sample at a resolution of 8 cm^{-1}.

Measurement of FT-Raman spectra

FT-Raman spectra were recorded with a Nicolet Nexus 670 spectrometer (Nicolet, USA) connected to a NXR FT-Raman module (Thermo Fisher Scientific, USA). A high-performance Nd: YVO_4 laser with a wavelength of 1064 nm was used. The Genie germanium detector and integral preamplifier were cooled by liquid nitrogen for all measurements. All the Raman measurement points were located at the center of the irradiated surface of the specimens. For each spectrum, 90 scans were recorded at a resolution of 6 cm^{-1}.

SEM examination

The transverse and tangential surface textures of specimens before and after photoirradiation were examined by a field-emission environment scanning electron microscope (XL30 ESEM-FEG, FEI Company, Netherlands) operated in high vacuum mode with an accelerating voltage of 5 kV. All the specimens were fastened to the mounting stubs using conductive carbon adhesive and were then sputter-coated with a layer of gold prior to examination.

Results and discussion

FT-IR spectroscopic analysis

Chemical changes occurring in bamboo components due to irradiation were characterized with FT-IR spectroscopy. The FT-IR spectrum of untreated bamboo is shown in Fig. 2. It can be observed that bamboo shows basic structure in the FT-IR spectrum that is similar with that of wood species mainly due to the similar chemical constituents present. Thus, the characterization and assignment of IR peaks in bamboo can be done by reference to wood.[6,11,12] There was a strong broad O–H stretching absorption at

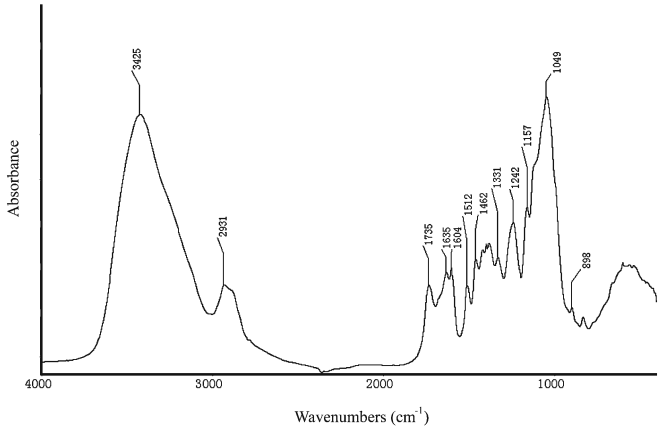

Fig. 2. Fourier transform infrared (FT-IR) spectrum of untreated moso bamboo

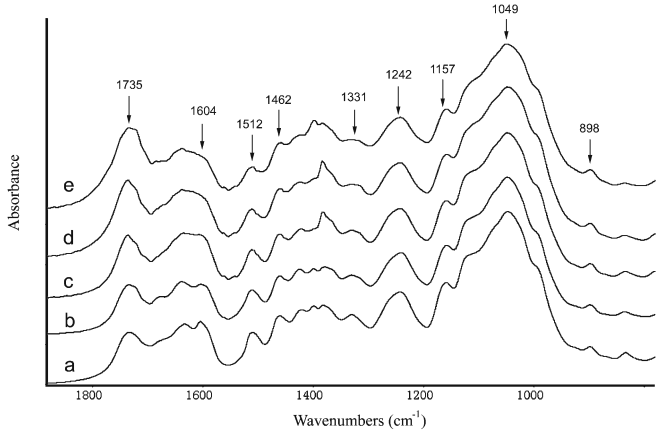

Fig. 3. FT-IR spectra of moso bamboo after various periods of photoirradiation: *a*, 0 h; *b*, 5 h; *c*, 20 h; *d*, 80 h; *e*, 160 h

3425 cm^{-1} and a prominent C–H stretching absorption at 2931 cm^{-1}. The well-defined peaks in the fingerprint region between 800 and 1800 cm^{-1} can provide useful information on various functional groups present in bamboo constituents, such as the peak at 1735 cm^{-1} arising from nonconjugated C=O in xylans (hemicellulose), and peaks at 1512 and 1604 cm^{-1} due to aromatic skeletal vibration in lignin. The bands at 1462, 1331, and 1242 cm^{-1} also had significant contributions from lignin. It has been reported that one of the characteristic IR spectral features of bamboo lignin (HGS type) is the presence of nearly equal absorption intensities at 1270 cm^{-1} (due to the G ring in lignin) and at 1230 cm^{-1} (C–C plus C–O plus C=O stretch).[13] Therefore, the broad 1242 cm^{-1} band in this study may be a result of overlapping between 1270 and 1230 cm^{-1} bands of approximately equal intensity. The peaks at 1157, 1049, and 898 cm^{-1} arose mainly from carbohydrates.

The effect of photoirradiation on the FT-IR spectra of bamboo is shown in Fig. 3. Significant changes can be observed in the IR spectra of bamboo surfaces upon exposure. An obvious decrease in the intensities of absorption peaks associated with lignin at 1604, 1512, 1462, 1331, and 1242 cm^{-1} occurred during the irradiation process, with those at 1604 and 1331 cm^{-1} almost absent after 160 h of exposure (Table 1). This was accompanied by a consecutive increase in the intensity of the carbonyl peak at 1735 cm^{-1}, indicating the photooxidation of bamboo surfaces. The photosensitivity of lignin in wood surfaces due to photoirradiation has been extensively demonstrated.[4–6] Similar to hardwood, bamboo has a lignin content of about 20%–25%,[10] and is also susceptible to photodegradation. However, bamboo may present photodegradation behavior that is different from wood partly due to the high proportion of syringyl units present in bamboo lignin, because it has been demonstrated that the syringyl unit is far less sensitive to the degradation process than the guaiacyl unit.[9,14] Previous studies have shown extensively that both lignin and cellulose components can participate in the photooxidation reactions in wood surfaces, resulting in significant increase in carbonyl absorption.[4,5,14] However, in the present study the carbohydrate peaks at 1157, 1049, and 898 cm^{-1} were not significantly influenced by photoirradiation on bamboo surfaces.

Table 1. Variation of relative intensities of the main absorption peaks in infrared spectra of moso bamboo as a function of irradiation time

Irradiation time (h)	I_{1735}	I_{1604}	I_{1512}	I_{1462}	I_{1331}	I_{1242}	I_{1157}
0	4.94	3.39	3.83	3.11	1.56	7.00	2.89
5	5.41	1.81	3.44	2.48	1.11	6.11	2.56
20	6.31	0.69	3.13	2.31	1.00	5.25	2.19
80	7.80		2.60	2.13	0.80	5.27	2.13
160	8.57		1.86	0.86	0.50	4.79	2.07

Data are given as the ratio of peak heights of infrared peaks against that of carbohydrate reference peak at 898 cm^{-1}. Peak heights were measured using OMNIC software according to the previously published methods[12]

FT-Raman spectroscopic analysis

FT-Raman spectroscopy was used to provide complementary information on photooxidation reactions occurring in bamboo. This technique is suitable for nondestructive analysis and has been extended to many kinds of woody materials.[15–17] The FT-Raman spectrum of untreated moso bamboo is shown in Fig. 4. It has been observed that certain Raman bands show enhanced intensities when aromatic ring conjugation is present.[18] Therefore, the prominent peaks at 1604 and 1630 cm^{-1} are probably derived from lignin, and the free and esterified *p*-coumaric and ferulic acids present in bamboo also contribute considerably to them, as indicated clearly by Takei et al.[17] The intense peak at around 2938 cm^{-1} and the shoulder at 2895 cm^{-1} are assigned to CH and CH_2 stretching.[7,15] By contrast, Raman peaks located in the region between 1000 and 1500 cm^{-1} were generally weak and were often overlapping. Most of these peaks have contributions from both carbohydrates (cellulose and hemicellulose) and lignin.

It can be observed that few bands are prominent in the Raman spectrum of bamboo, and only specific bands (e.g.,

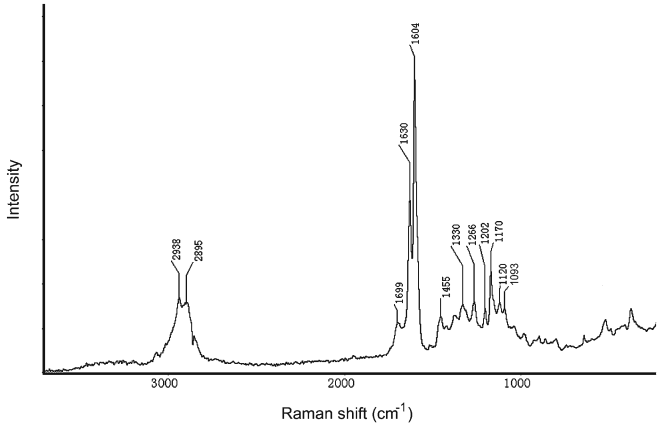

Fig. 4. FT-Raman spectrum of untreated moso bamboo

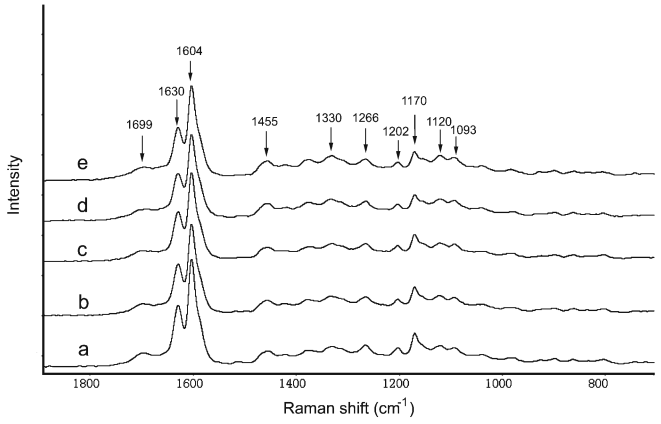

Fig. 5. FT-Raman spectra of moso bamboo after various periods of photoirradiation: *a*, 0 h; *b*, 5 h; *c*, 20 h; *d*, 80 h; *e*, 160 h

1604 and 1630 cm^{-1}) related to lignin and the abovementioned phenolic acids are strong. This may be advantageous in studying the complex photodegradation process in bamboo because only a few bands are highlighted. The FT-Raman spectra of bamboo surfaces subjected to various periods of photoirradiation are shown in Fig. 5. A comparison of Raman spectra of control and irradiated bamboo surfaces showed some changes due to irradiation, with obvious changes observed at around 1604 and 1630 cm^{-1}. A decrease in the intensities of these two peaks with increasing irradiation time indicated that both lignin and the free and esterified *p*-coumaric and ferulic acids in bamboo constituents were probably degraded during the irradiation process, because the aromatic ring structures present in them are photosensitive to UV light. In addition, the intensities of Raman bands at 1266, 1202, and 1170 cm^{-1} showed a decreasing tendency after 160 h of irradiation, further indicating that the free and esterified *p*-coumaric and ferulic acids were partially degraded by photoirradiation.

In order to better display the degradation process of lignin and the above phenolic acids in bamboo, the ratios of intensities of absorption peaks at 1604 and 1630 cm^{-1} against the cellulose reference peak at 1093 cm^{-1} was calcu-

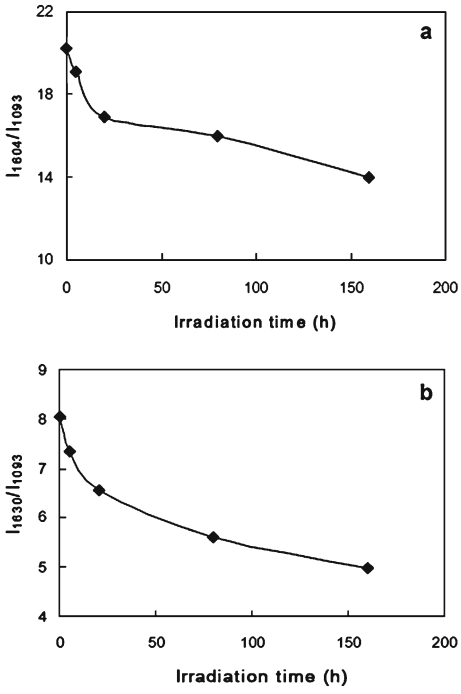

Fig. 6a, b. Relative changes in Raman band intensities at **a** 1604 and **b** 1630 cm^{-1} during photodegradation of moso bamboo

lated according to the previously published methods.[12] The band at 1093 cm^{-1} is used as a reference peak since it is not significantly influenced by irradiation. Figure 6 shows that the ratios of lignin (*p*-coumaric and ferulic acids) to cellulose (I_{1604}/I_{1093} and I_{1630}/I_{1093}) decreased rapidly at the initial exposure of approximately 20 h, above which the rate of change became smaller for longer irradiation time. After 160 h of irradiation, the relative intensities of I_{1604}/I_{1093} and I_{1630}/I_{1093} decreased to 69% and 62% of their initial values, respectively.

In contrast to the FT-IR technique, FT-Raman spectroscopy shows strong Raman scattering of both lignin and the free and esterified *p*-coumaric and ferulic acids due to its sensitivity to aromatic ring-conjugated structures. However, Raman bands at 1630 and 1604 cm^{-1} are overlapped by lignin and these phenolic acids, and their specific contributions are difficult to separate (Fig. 5). Further studies using alkali treatment of bamboo specimens prior to photoirradiation are needed to elucidate the specific contributions of these phenolic acids to photodegradation of bamboo, because these acids are soluble in alkali or are hydrolyzed with alkali.[17]

SEM observation

Photoirradiation-induced chemical changes, especially in the lignin component, may result in physical deterioration of the bamboo surface. SEM was applied to monitor the possible morphological changes of cell walls caused by photoirradiation on bamboo surfaces. The SEM micrographs of the cross section of bamboo specimens before and after

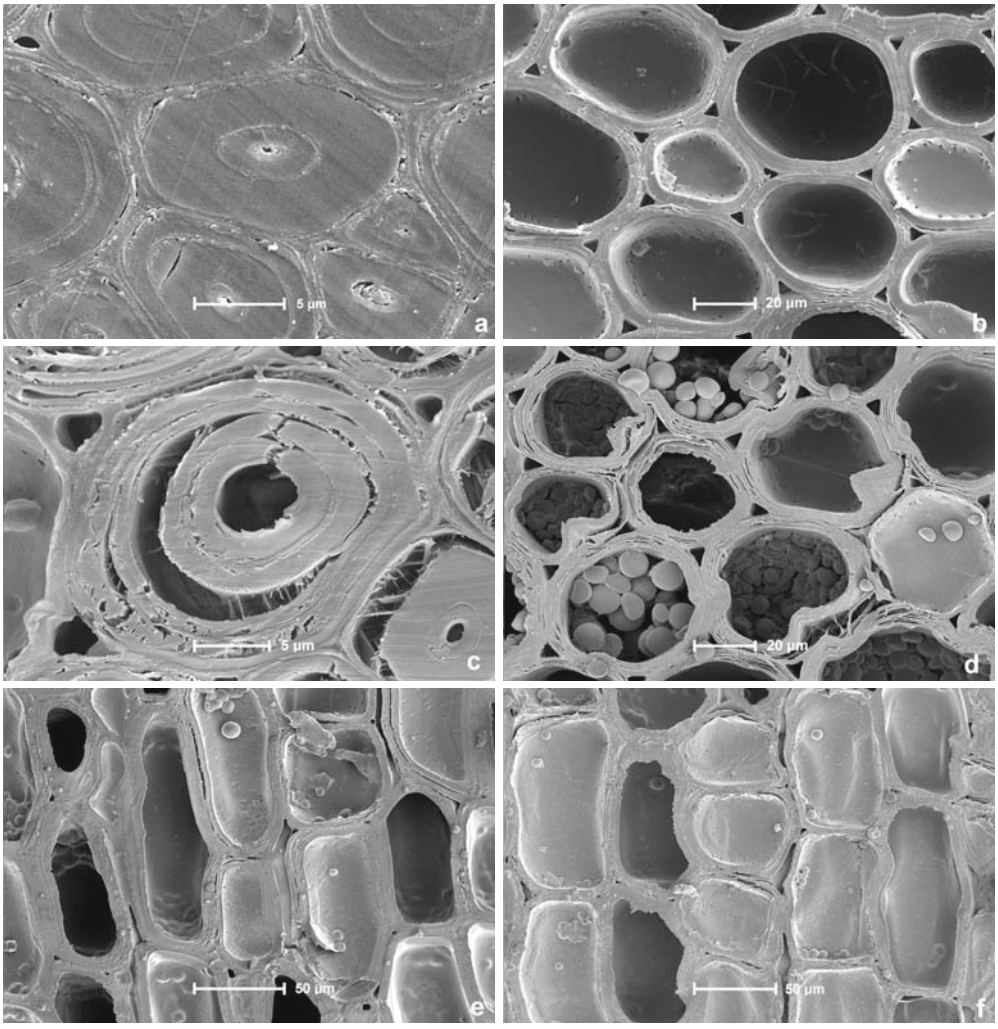

Fig. 7a–f. Scanning electron microscopy (SEM) micrographs of cross sections of bamboo specimens: **a** untreated thick fiber cells; **b** untreated parenchyma cells; **c** fiber cells exposed to ultraviolet (UV)–visible light for 160 h, showing considerable cracks occurring within the secondary walls of fiber cells; **d** parenchyma cells exposed to UV–visible light for 160 h, showing distortion and cracks occurring in the cell walls; **e** untreated parenchyma cells at tangential section; **f** parenchyma cells at tangential section exposed to UV–visible light for 160 h, showing no significant changes in wall structure

irradiation are shown in Fig. 7. In the cross section, the thick fiber cells of different shapes and sizes were densely packed within the vascular bundles (Fig. 7a), and the parenchyma cells surrounding the vascular bundles showed regular triangle-shaped void spaces in the cell corners. Considerable numbers of starch granules were present in some cell lumens (Fig. 7b, d), which were also observed by Liese.[19] After 160 h of irradiation, significant damage to cell wall structures can be observed. Intense cracks occurred in an approximately concentric pattern within the secondary walls of fiber cells, showing a tendency of fiber wall lamellae separating from each other (Fig. 7c). This interesting damage pattern of cell walls may be closely associated with the peculiar ultrastructure of fiber walls in bamboo. As previously reported, the fiber wall of bamboo is characterized by a polylamellate wall structure with alternating broad and narrow layers of differing microfibrillar orientation.[19] In addition, the degree of lignification varies considerably across the wall, with a higher lignin content in the narrow layers.[19,20] Owing to the higher lignin content present in the narrow layers of the fiber wall, the photodegradation may occur preferentially in this area, leading to intense concentric cracks formed within the secondary wall. The micrographic observations also support the conclusion that lignin is the most photosensitive component in bamboo, as deduced from the chemical analysis (FT-IR and FT-Raman spectroscopy).

In contrast, the parenchyma cell walls underwent no such intense structural changes as fiber walls did after 160 h of irradiation, with only slight distortion of the cell walls and some cracks occurring within the cell walls (Fig. 7d). The lesser damage to parenchyma cell walls indicates that this tissue is less influenced by photoirradiation than the thick fibers, which may be attributed to the lower degree of lignification in parenchyma cells.

The photodegradation of some wood species by UV light irradiation has shown that the cell corners and the compound middle lamellae degrade preferentially due to the higher lignin content present in these areas of cell walls.[21–23] However, such phenomena were not observed in our study of bamboo. Alternatively, the degradation of bamboo occurred predominantly at the interlayers of fiber walls, with the structures of cell corners and middle lamellae being kept nearly intact. On the tangential section, however, no

obvious damage to the bamboo structure was observed (Fig. 7e, f). These disparities in photodegradation between bamboo and wood may be attributed to their differences in the ultrastructure and chemical composition of cell walls. In the present study, 160 h of irradiation may not be sufficient to initiate the deterioration of cell corners and middle lamellae as well as pit structures in bamboo, which is nevertheless frequently observed during photodegradation of wood. Thus, longer exposure time is needed in future studies.

Conclusions

This study investigated the chemical and morphological changes in bamboo surfaces induced by UV–visible light irradiation for up to 160 h. FT-IR spectroscopy results showed that photoirradiation modified the chemical structure of bamboo surfaces. Significant changes occurred in the lignin component as indicated by considerable decrease in the intensities of the characteristic aromatic lignin peaks at 1512 cm^{-1} and other associated bands. This was accompanied by formation of new carbonyl groups at 1735 cm^{-1}, resulting in photooxidation of bamboo surfaces. The photosensitive nature of bamboo lignin was also demonstrated by FT-Raman analysis, in which obvious decreases in intensities of Raman bands at 1604 and 1630 cm^{-1} mainly derived from lignin and free and esterified *p*-coumaric and ferulic acids were observed. Furthermore, the decreases in the intensities at 1604 and 1630 cm^{-1} were not uniform during the irradiation process, with the most of the changes occurring at the initial exposure of about 20 h. FT-IR and FT-Raman techniques can provide complementary information on chemical and structural changes in bamboo constituents during photodegradation.

On the other hand, SEM micrographs of the irradiated cross sections of bamboo showed significant damage occurring in the fiber walls. Intense cracks occurred in an approximately concentric pattern within the secondary wall of fiber cells, showing a tendency of fiber wall lamellae separating from each other. The parenchyma cells, in contrast, exhibited slight distortion of the cell walls and some cracks occurred within the cell walls. The structures of cell corners and middle lamellae were nearly intact after irradiation.

Acknowledgments This study was funded by the subproject of the National Science and Technology Support Program of China (no. 2006BAD19B04) and the National Natural Science Foundation of China (no. 30730076). The authors thank Mr. H. P. Yan and Mr. C. S. Li from our institute, and Mr. G. L. Tian and Mr. H. T. Chen from the International Center for Bamboo and Rattan, Beijing, China, for their helpful advice and technical support in carrying out the experiments.

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