Changes in Chemical Composition and Microstructure of Bamboo after Gamma Ray Irradiation

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Changes in bamboo composition and microstructure following ^{60}Co gamma (γ) ray irradiation were investigated by solid state ^{13}C cross-polarization (CP) magic-angle spinning (MAS) spectroscopic nuclear magnetic resonance spectrometry (NMR) and a field emission scanning electron microscope (FESEM). The results indicated that irradiation doses lower than 100 KGy resulted in the degradation of hemicelluloses *via* scission of molecular chains, but there was also repolymerization and condensation in lignin. Irradiation doses higher than 100 KGy resulted in the degradation of cellulose, hemicelluloses, and lignin by significant oxidation reaction and partial scission of biopolymer chains to yield more small fragments with carbonyl groups.

Keywords: Gamma rays; NMR; Cellulose; Lignin; Composition; Microstructural analysis

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INTRODUCTION

Lignocellulosic biomass is a potential source of renewable energy and green materials. Bamboo stands out from various promising bio-resources for value-added higher performance biomaterials applied in housing construction, furniture manufacture, and household products due to its light weight, exceptional endurance, surface hardness, high strength, easy machinability, and local availability. Bamboo also has the potential for bio-energy production due to its high content of cellulose and hemicelluloses and feasibility for enzymatic hydrolysis at ultra-low enzyme loadings (Scurlock *et al.* 2000; Ray *et al.* 2004; Sathitsuksanoh *et al.* 2010).

Bamboo is composed of cellulose materials reinforced with silica. It is a giant woody perennial evergreen C_4 grass with around 75 genera and about 1250 species, mainly distributed in tropical and subtropical areas such as in Asia, America, and Africa (Jiang 2002; Gratani *et al.* 2008). In spite of its remarkable advantages, *i.e.*, high tensile strength, stiffness, and fast growth, bamboo fiber has so far been utilized only for relatively low-value applications, such as for paper, textiles, and board production. The market demand represents a negligible fraction of current native bamboo production rates (Ray *et al.* 2004). The current phenomena mainly results from the drawbacks of native bamboo in the absence of any chemical or physical pretreatment. In particular, native bamboo is easily attacked by moisture and biological agents, *e.g.*, mold fungi, and this has a negative effect on its long-term durability and dimensional stability (Li *et al.* 2013).

To address such problems, gamma ray (γ-ray) radiation, a type of low-cost environmental-friendly treatment compared to other conventional physical and chemical treatments, was applied herein to modify the chemical structure of bamboo fiber, aiming at the improvement of properties. A previous study indicated that bamboo mold inhibition

can be improved with the treatment of γ-ray irradiation (Sun *et al.* 2011a). However, knowledge of the mechanism of irradiation on bamboo's structure is far from adequate. Chemical structure is a substrate characteristic relevant to the properties of modified bamboo-based products. The monitoring and investigation of the mechanism of modified bamboo could determine the factors related to its durability and corrosion resistance. Such work could further develop an understanding of the mechanisms on a molecular level and characterize the microstructure change caused by γ-ray radiation. A vital component of this is to generate reliable structural models of bamboo with different levels of γ-ray irradiation. These results can then be used in future research, *i.e.*, computational-applied model, to generate new optimized forestry-based products and bamboo material with outstanding properties.

EXPERIMENTAL

Materials

Four-year-old Moso bamboo *P. pubescens* Mazel ex H de Lehaie was harvested in Hangzhou City, Zhejiang province, China. After removing the bamboo inner and outer (epidermal) layers, the bamboo was cut into bamboo strips with dimensions of 30 mm (L) × 20 mm (R) ×5 mm (T).

Methods

Gamma ray radiation

Gamma ray irradiation was carried out on the bamboo strips with a ^{60}Co light source conducted under the control of OMRON PLC (Japan). There were ten bamboo strips for each different radiation dosage, which were ground into a powder using a hammer mill with a size of 0.18 to 0.25 mm after radiation treatment. The different radiation dosages were selected, as shown in Table 1.

Table 1. Bamboo Sample Code with Different Radiation Dose

Sample code	B-0	B-20	B-30	B-40	B-100	B-300	B-500	B-1000
Irradiation dose (KGy)	0	20	30	50	100	300	500	1000

Composition analysis

The composition of bamboo before and after radiation treatment was analyzed in accordance with Chinese Standards, as follows: cold and hot water extractives, GB/T 2677.4 (1993); 1% NaOH extractives, GB/T 2677.5 (1993); cellulose, GB/T 2677.8 (1994); holocellulose, GB/T 2677.10 (1995); and Klason lignin, GB/T 2677.8 (1994).

Solid CP/MAS ^{13}C-NMR analysis

The pre-wet nuclear magnetic resonance (NMR) samples were prepared with ground bamboo powder packed into a cylindrical ceramic magic angle spinning (MAS) rotor. Repetitive steps of packing the sample into the rotor were performed to fully compress and load the maximum amount of sample. Solid-state NMR measurements were carried out on a Bruker AV300 nuclear magnetic resonance instrument (Bruker BioSpin International AG; Sweden) operating at a resonance frequency of 75.5 MHz with a 4-mm

MAS probehead at a 5-kHz spinning speed with a 5.0-s recycle delay, 4000 to 8000 scans, and a 3.0-μs (90°) proton pulse width.

FESEM micrograph analysis

The surface morphologies of bamboo before and after radiation were examined with an FEI XL30 ESEM-FEG field emission scanning electron microscope (XL30, ESEM-FEG, FEI, USA) operating at an accelerating voltage of 7.0 kV in the high-vacuum mode. All the specimens were mounted on aluminum stubs using conductive carbon adhesive and sputter-coated with a layer of gold prior to examination.

RESULTS AND DISCUSSION

Composition Analysis

The carbohydrate and Klason lignin values for the various γ-ray irradiation doses described in Table 1 are reported in Fig. 1 for untreated and irradiated bamboo. Gamma ray radiation significantly altered and decreased the holocellulose content, which suggests the degradation of hemicellulose and/or cellulose. An irradiation dose lower than 100 KGy increased the cellulose and lignin content in varying amounts, and a dose higher than 100 KGy decreased both the cellulose and lignin contents. This data, in conjunction with holocellulose changes, indicates irradiation doses less than 100 KGy can favor the depolymerization and degradation of hemicellulose and partial polymerization of cellulose and lignin. In contrast, irradiation doses higher than 100 KGy can result in the degradation of carbohydrate and lignin biopolymers (Yang *et al.* 2010).

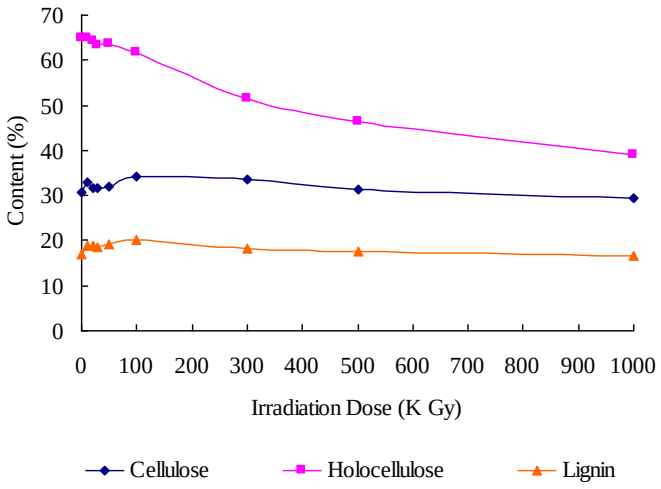

Fig. 1. Changes in the components of Moso bamboo with various irradiation doses

The water and 1% NaOH extractives following gamma irradiation are presented in Fig. 2. Gamma ray irradiation increased the soluble components in cold water, hot water, and 1% NaOH, which indicates that bamboo released more mono-saccharides, low-molecular weight polysaccharides, inorganic salts, wax, pigment, resin, tannin, amino acids, and small amounts of hemicellulose and lignin after γ-ray irradiation (Suzuki and Itoh 2001; Zehui *et al.* 2006), which can be the result of radiation-caused degradation and depolymerization of hemicellulose and lignin.

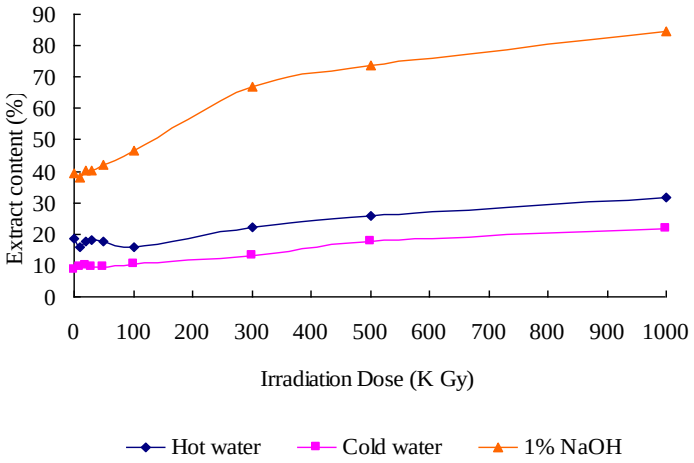

Fig. 2. Extraction changes of Moso bamboo at various irradiation conditions

NMR Results

Nuclear magnetic resonance spectroscopy is a useful tool for examining the structural chemistry of natural organic matter. Selected NMR spectra with normalized relative area values for bamboo after various γ-ray irradiation doses as shown in Fig. 3 are reported in Table 2 (Johnson *et al.* 2005). The NMR spectrum bamboo peak at 105 ppm, primarily due to the presence of cellulose C_1, specifically the CH_2 of cellulose, was used for spectrum normalization. The decrease in the cellulose and hemicellulose region (60 to 94 ppm and 0 to 45 ppm) caused by γ-ray irradiation supports the carbohydrate analysis. Under higher irradiation doses of 100, 500, and 1000 KGy the decrease in the lignin region (144 to 165 ppm) and increase in the methoxyl group proportion (45 to 60) indicate the degradation and scission of lignin side chains, followed by some condensation reaction to yield small fragments, which may be due to γ-ray radiation-induced radical reactions (Sun *et al.* 2009) and is therefore consistent with the 1% NaOH extraction results. In contrast, the relative increase in lignin proportion of the B-50 sample suggests that the repolymerization reaction is the most important mechanism influencing the relatively higher yield of lignin under lower irradiation doses. Moreover, the increase in the carbonyl and amide carbon region (165 to 190 ppm) in B-100, B-500, and B-1000 indicates an oxidation reaction in bamboo biopolymer cellulose and hemicellulose due to higher irradiation doses. In low doses up to 50 KGy, the efficient chain scissions are the main mechanisms that provide a high number of carbonyl groups. This is in good agreement with the water and 1% NaOH extraction results and is consistent with a previous study (Henniges *et al.* 2012).

Table 2. CP/MAS ^{13}C- NMR Assignment and Relative Area of Bamboo under Different Irradiation Conditions

Chemical Shift (ppm)	Assignment	Normalized relative peak area				
		B-0	B-50	B-100	B-500	B-1000
0 to 45	Alkyl C	0.18	0.20	0.18	0.18	0.2
45 to 60	Methoxyl C	0.3	0.37	0.46	0.42	0.43
60 to 94	O-alkyl C	5.24	5.16	4.67	5.09	5.03
94 to 110	Di-O-alkyl C cellulose C1	1.0	1.0	1.0	1.0	1.0
110 to 144	Aryl and unsaturated C	0.03	0.03	0.02	0.03	0.02
144 to 165	O-aryl C	0.29	0.3	0.24	0.28	0.28
165 to 190	Carbonyl and amide C	0.16	0.17	0.16	0.18	0.21

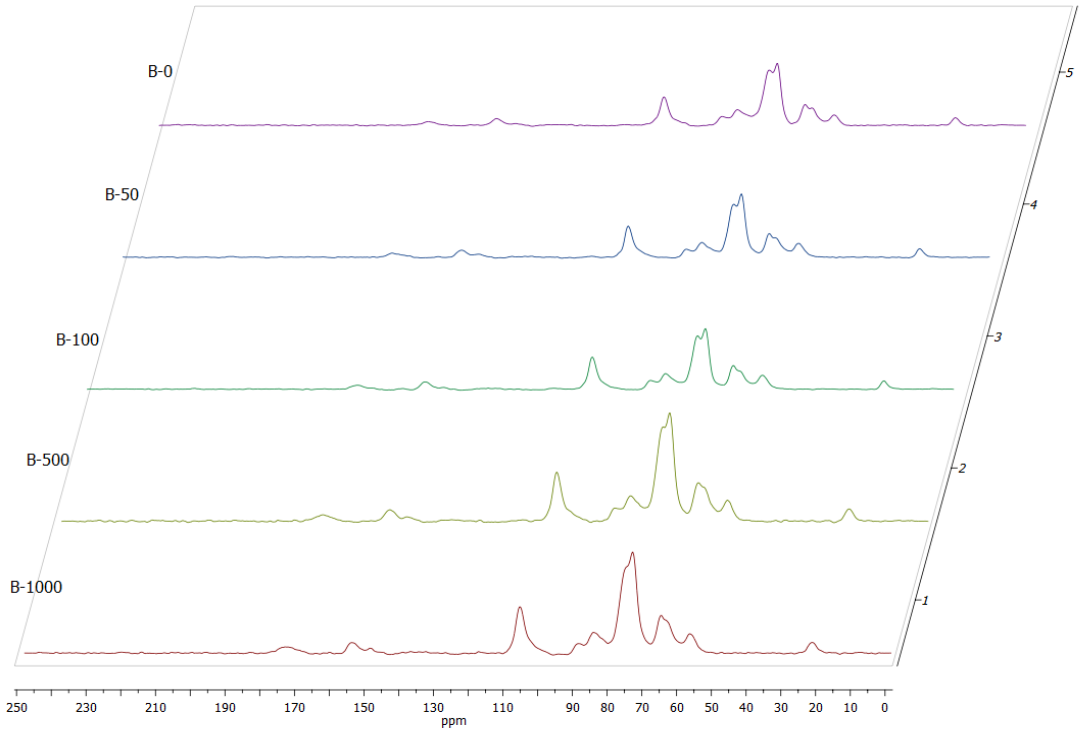

Fig. 3. Selected ^{13}C NMR spectra of bamboo before and after γ-ray irradiation

FESEM Analysis

A field-emission SEM was used to monitor the possible morphological changes in cell walls caused by γ-ray irradiation. FESEM micrographs of the cross-section of bamboo specimens before and after irradiation are shown in Fig. 4. Irradiation-induced chemical changes, especially in the hemicelluloses and lignin components, resulted in physical deterioration of the bamboo microstructure.

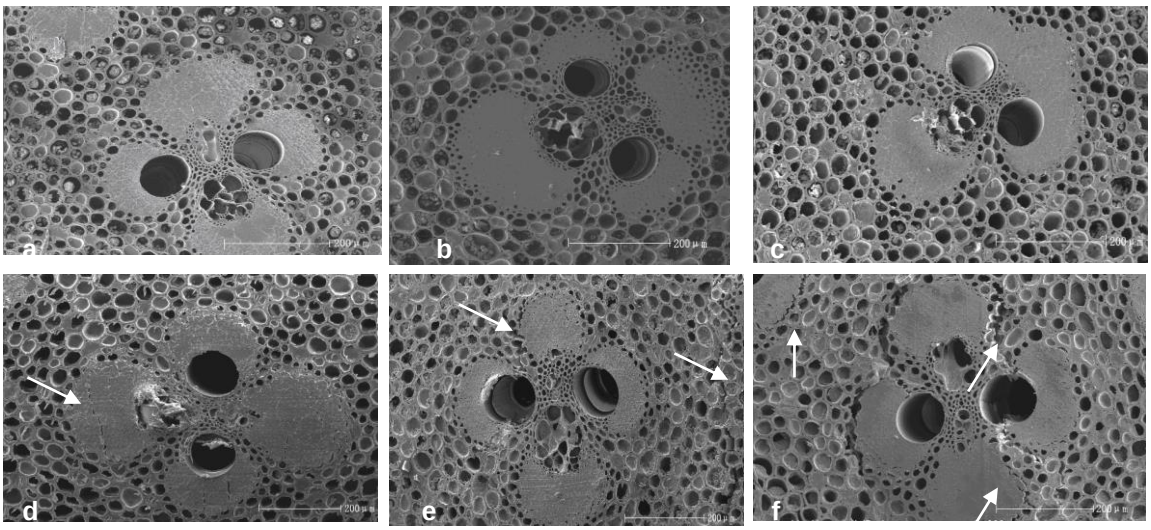

Fig. 4. The FESEM micrographs of cross section bamboo with various irradiation conditions. (a) B-0, (b) B-50, (c) B-100, (d) B-300, (e) B-500, and (f) B-1000

In the cross-section, the thick fiber cells of different shapes and sizes were densely packed within the vascular bundles. Irradiation at 300 KGy caused some cracking of the cell wall, and irradiation doses higher than 300 KGy resulted in the significant collapse of the fiber cell wall, which may be closely associated with the lignin distribution and hemicellulose degradation. This can occur predominantly at the interlayers of the bamboo fiber walls, with the structures of cell corners and middle lamellae remaining intact (Wang and Ren 2009). Lignin can act as a physical barrier, encapsulating and confining cellulose. In the absence or reduction of an intact hemicellulose and lignin matrix at irradiation doses lower than 100 KGy, cellulose crystallites have an increased propensity to expand through cellulose annealing and conversion of amorphous to crystalline cellulose, thereby resulting in higher crystallinity. In contrast, at irradiation doses higher than 300 KGy, cellulose degradation to include the decrease in the cellulose crystalline region can result in a decrease in bamboo crystallinity (Sun *et al.* 2011b).

CONCLUSIONS

1. The key chemical composition and microstructure features related to bamboo, specifically cellulose, holocellulose, and lignin contents, were studied. Gamma ray irradiation altered the bamboo chemical components and structure.
2. There was degradation of hemicellulose as the irradiation dose was increased to 1000 KGy. Cellulose and lignin increased initially at irradiation doses lower than 100 KGy and decreased to level-off with more carbonyl and methoxyl groups at irradiation doses higher than 100 KGy, suggesting initial repolymerization and later degradation reaction in the two biopolymers to yield small fragments readily soluble in water and 1% NaOH.
3. The correlation between these measured chemical and structural features and γ-ray radiation made in this study can be optimized by the choice of radiation and irradiation conditions in the future for high-value added bamboo-based materials.

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