

## Thermo characteristics of steam-exploded bamboo (*Phyllostachys pubescens*) lignin

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**Abstract** Bamboo (*Phyllostachys pubescens*) internode was subjected to steam explosion treatment to produce an excellent fiber for binderless boards. Lignin was isolated from extract-free bamboo meal with Björkman's procedure and steam-exploded pulp. The self binding-mechanism was discussed by scanning electron microscopy (SEM), thermo-gravimetry (TG), differential scanning calorimetry (DSC) and analytical ozonation. It is well-known that steam explosion treatment liberates lignin from the cell wall to the fiber surface, which is the most important component relevant to binderless board production. Results of TG and DSC analyses showed that steam-exploded bamboo pulp started mass loss at lower temperature compared to bamboo internode meal. The thermal softening temperature of lignin prepared from steam-exploded pulp was much lower than that of lignin prepared from extract-free bamboo meal. This suggests that intermonomer linkages of lignin, especially  $\beta$ -aryl-ether linkage which is the major intermonomer linkage of lignin, were cleaved during steam explosion treatment resulting in low molecular weight phenolic compounds. The cleavage of  $\beta$ -aryl-ether intermonomer linkage of lignin was also confirmed by ozonation analysis.

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## Introduction

Bamboo (*Phyllostachys pubescens*) is an important non-wood forest resource in southeast China. It is considered as one of the important resources in wood industry to replace woody resources due to its fast growth, easy propagation, and short renovation.

Steam explosion is a physicochemical treatment of plant materials that involves an instant discharge of materials under high-pressure steam in a sealed container. The process was invented by Mason in 1926 as an alternative to chemimechanical and chemithermomechanical pulping processes (Mason 1926). Asplund (1953) applied the process to fiberboard production. He refined wood chips at elevated temperature and pressure to produce coarse and dark colored fibers for board manufacturing presenting an excellent process to produce binderless board. This was recognized not only as a very effective process to produce pulps, but also to separate plant cell wall components with low energy consumption, and it was noted as an ideal process for total utilization of lignocellulose with low emission of wastes. One of the most important findings is that the lignin portion can easily exude from the cell wall to the fiber surface during steam explosion treatment. Exuding of lignin is hardly observed in thermomechanical (TMP) and ground (GP) pulping processes (Tanahashi et al. 1983). Lignin of oil palm frond can be easily exuded from the cell wall to the fiber surface during steam explosion treatment, and binderless boards produced from steam-exploded pulp satisfied the requirement of Japan Industrial Standard (JIS A 5905 1994) (Suzuki et al. 1998; Laemsak and Okuma 2000).

The thermoplastic property of lignin is an important factor to promote the thermal adhesion of the fiberboard pulps from which the board is formed by hot pressing. Baldwin and Goring (1968) elucidated some of the practices in fiberboard technology by investigating thermoplastic and adhesive behaviors of fiberboard pulps from steam-exploded wood. They concluded that moisture of lignin and hemicelluloses not only softens but also develops adhesive properties at relatively low temperatures. Takamura (1968) also reported that the softening of lignin and hemicelluloses is markedly dependent on the water content. Sakata and Senju (1975) showed that a combined use of the plasticizer and water brought about the most effective plasticizing for the lignins. The in situ plasticization of lignin improves the final mechanical properties (Bouajila et al. 2005). Softening and steam plasticizing of lignin have been recognized for some time in various processes of the formation of board and dimensional stabilization of solid wood.

The chemical characteristics of steam-exploded bamboo pulp are reported in a previous paper (Shao et al. 2008). Lignins were isolated from extract-free bamboo internode meal, meal of binderless board prepared from steam-exploded pulp and steam-exploded pulp using Björkman's method. In this paper, thermoplastic property of steam-exploded bamboo lignin was investigated in view of binderless board production by scanning electron microscopy (SEM), thermo-gravimetry (TG) and differential scanning calorimetry (DSC). In addition, structural modification of lignin during steam-explosion was elucidated by analytical ozonation.

## Experimental

### Materials

*Phyllostachys pubescens* Mazel ex Houzeau de Lehaie (Moso Bamboo) (5 years old) was harvested at Tanashi Experimental Station (35.7N 137.7E) of the University Forest of the University of Tokyo, Japan. Internode of bamboo was chopped to chips by a chisel (5 cm length and 2–3 cm width).

### Steam explosion of chips of bamboo stem

The chips of bamboo internode (200 g) were subjected to a steam explosion digester (2 l volume stainless steel reactor, Nittokoatsu Co. Ltd., Tsukuba, Japan). The sample was steam exploded at 2.0 MPa and 210°C for 5 min. Steam-exploded pulp was collected together with black liquor, and air-dried at room temperature.

### Preparation of binderless board of steam exploded pulp

The steam exploded pulp adjusted to a moisture content of 12% by air-drying was heat-pressed by one step breathing time (40 s) method at 150°C to prepare medium density binderless boards.

### Lignin extraction

Bamboo internode chip was ground by a Wiley mill to pass 420 µm sieves. The ground sample was extracted with ethanol-benzene (1:2, v/v) for 6 h using a Soxhlet extractor. The extract free sample was air-dried, then dried in a vacuum oven overnight at 40°C, and finely ground with a vibratory ball mill VS-2 (Irie Shokai Co. Ltd., Tokyo, Japan) for 72 h with cooling by tap water flow. Dispersing solvent was not used during milling (Koshijima et al. 1972). Björkman lignin was extracted with dioxane-water (9:1, v/v) from the finely ground sample and purified according to the procedure of Björkman (Björkman 1956), referred to as EFBL. In addition, lignin was extracted from air-dried steam-exploded pulp and purified as above (referred to as SEBL). The yields of purified lignins isolated from the finely ground sample (EFBL) and the air-dried steam-exploded pulp (SEBL) were 16.4 and 23.5% (wt% of lignin), respectively. Lignin contents of the extract-free bamboo sample, steam-exploded pulp and binderless board made by the steam-exploded pulp were determined by Klason procedure (Tappi Standard T 222om-88).

### Microscopy

The steam-exploded pulp was extracted with dioxane-water (9:1, v/v) until the color of dioxane-water solvent was clear. The original steam-exploded fibers and the fiber after extractions were observed using a SUPERSCAN SS-550 scanning electron microscope (Shimadzu, Japan) operating at 20 kV, after sputter coating with gold-palladium.

## Thermal analysis

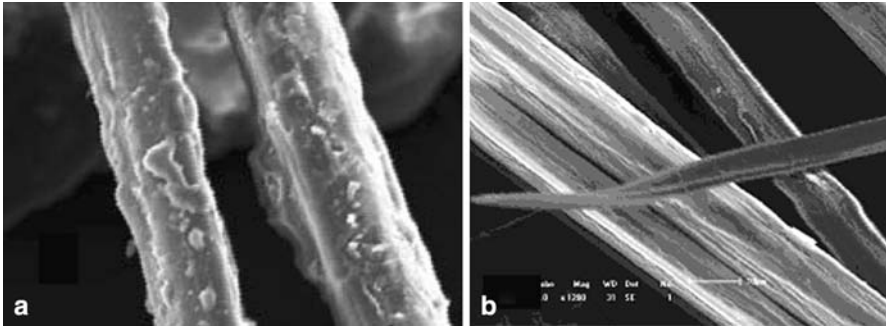
Differential scanning calorimetry (DSC) and thermo-gravimetry (TG) analyses were performed with a Netzsch STA 409 PC Luxx (Burker, Germany) in nitrogen atmosphere (25 mL min<sup>-1</sup>) at a temperature range of 20–350°C with a heating rate of 20°C min<sup>-1</sup>.

## Ozonation

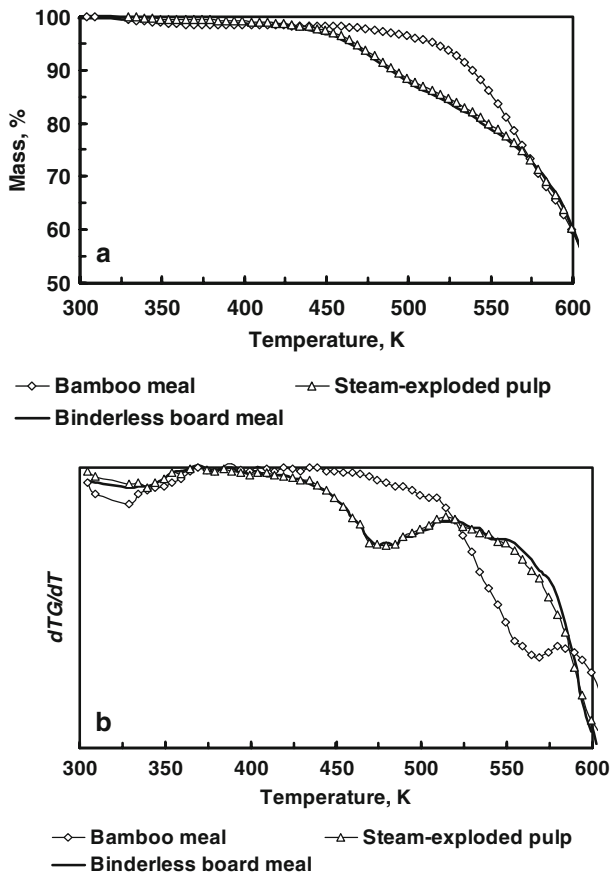
Ozonation analysis to discuss intermonomer linkages was carried out according to the scheme of Akiyama et al. (2002) for the extract-free and steam-exploded sample. The ozonation products were trimethylsilylated with hexamethyldisilazane and trimethylchlorosilane in dimethylsulfoxide for 30 min at 60°C. The trimethylsilylated derivatives were analyzed by a Shimadzu GC-17A Gas chromatograph (Shimadzu, Japan) using NB1 capillary column (25 m × 0.25 mm id) equipped with FID. Both injector and detector temperatures were 280°C. The column temperature was kept at 120°C for 5 min, and then programmed at 4°C min<sup>-1</sup> to 170°C followed by 10°C min<sup>-1</sup> to 280°C. Erythritol was used as an internal standard.

## Results and discussion

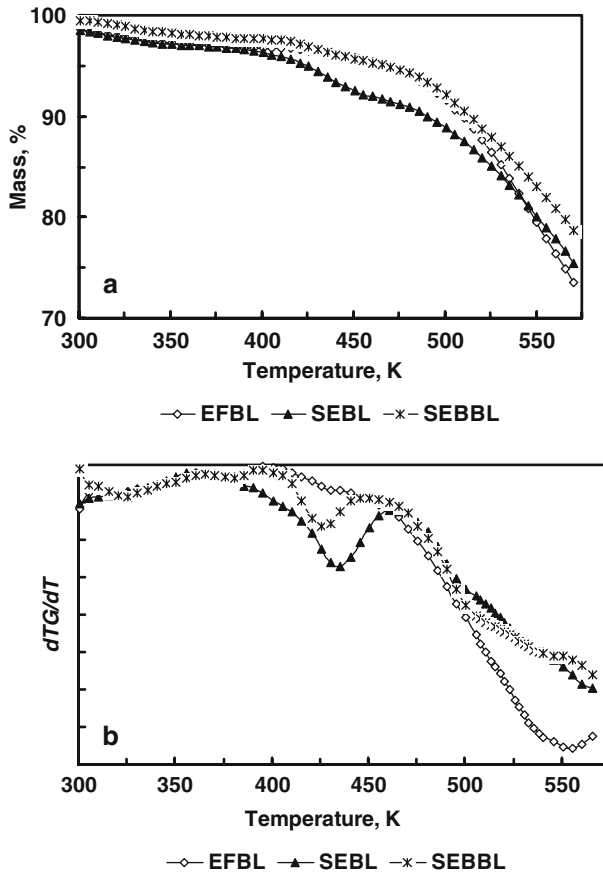
Steam explosion is a physicochemical treatment of plant materials that involves an instant discharge of materials under high-pressure steam in a sealed container. By scanning electron microscopy it was observed that the surface of steam-exploded fibers was rough and covered with particles, while the surface of steam-exploded fibers extracted with dioxane-water (9:1, v/v) was significantly smooth (Fig. 1a, b), suggesting that those particles are lignin liberated from cell wall by steam-explosion treatment. The suggestion was supported by the higher yield of purified lignin isolated from the air-dried steam-exploded bamboo pulp (SEBL), which was directly extracted with dioxane-water (9:1, v/v) without vibratory ball milling, compared to lignin isolated from finely ground extract-free bamboo internode sample by Björkman's procedure (EFBL). The yields of SEBL and EFBL were 23.5 and 16.4% (wt% of lignin), respectively. This result was in accordance with Suzuki et al. (1998), who reported that those materials covering the surface of pulp fiber during steam explosion were lignin, and were easily extracted with dioxane-water. It is known that the architecture of plant cell walls can be crushed by vibratory ball milling and near native lignin can be isolated by extraction with neutral solvent, which is effectively utilized for lignin structural investigations. The higher yield of lignin from SEBL than of EFBL suggests that the steam-explosion process is very effective to produce pulps and also to separate plant cell wall components with low energy consumption. Tanahashi et al. (1983) concluded that the brown colored oily substances detected both inside and outside of exploded wood pulp fibers were lignin, originating from both middle lamellae and secondary walls liberated from cell wall polysaccharides during steam explosion. Production of these substances is



**Fig. 1** Scanning electron micrograms of (a) steam-exploded pulp of bamboo and (b) steam-exploded pulp extracted with dioxane-water (9:1, v/v)



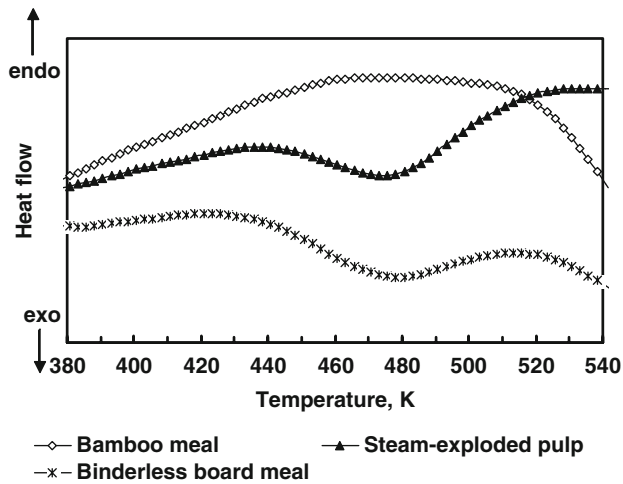
**Fig. 2** TG curves (a) and their differential curves (b) of extract-free bamboo meal, steam-exploded pulp of bamboo and binderless board meal prepared by steam-exploded pulp of bamboo



**Fig. 3** TG curves (a) and their differential curves (b) of isolated lignins from extract-free bamboo (EFBL), steam-exploded pulp of bamboo (SEBL) and binderless board made by steam-exploded pulp (SEBBL)

expected as one of the important characteristics of the steam explosion process, because those phenomena were hardly detected in thermomechanical pulp (TMP) and ground pulping (GP) processes.

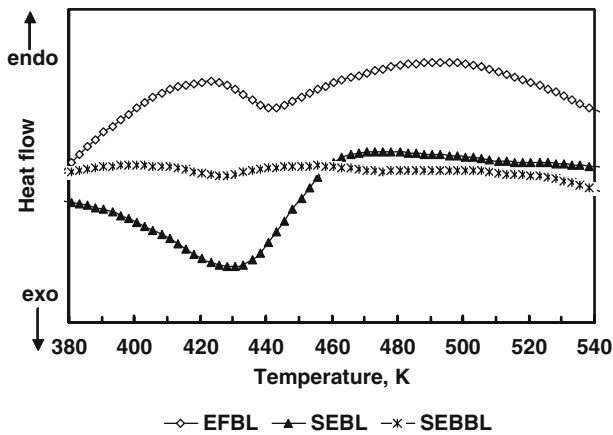
Thermal weight loss of the extract-free bamboo internode meal started at about 473 K and it occurred in one step. Both the steam-exploded pulp and the meal of binderless board made by steam-exploded pulp started sharp weight loss at 437 K and the curve characterized two steps (Fig. 2a, b). The rate of weight loss reached a maximum at 573 K and weight loss was almost 25% at the temperature. Such weight loss is mainly due to the thermal decomposition involving discharge of  $\text{CO}_2$ ,  $\text{CO}$ , and  $\text{H}_2\text{O}$  (Jiang et al. 2007). Lignins from EFBL and SEBL started thermal weight losses at 403 and 383 K (Fig. 3a, b), which were lower than that of the extract-free bamboo internode meal and steam-exploded bamboo pulp (Fig. 2a, b), respectively. Thermal weight losses within the temperature range of 383–513 K were 7.5 and 8.9% (based on lignin) for EFBL and SEBL, respectively.



**Fig. 4** DSC curves of extract-free bamboo meal, steam-exploded pulp of bamboo and binderless board meal prepared by steam-exploded pulp of bamboo

Lignin is a thermoplastic amorphous polymer, i.e., lignin undergoes what is known as a glass transition. When lignin softens, it becomes tacky and exhibits auto-adhesion, and the significance of lignin softening in the production of fiberboard is expected to be particularly important (Goring 1971). The glass transition temperature of bamboo powder is at 538 K, higher than that for cellulose at about 503 K (Li et al. 2006). Dry cellulose softens at 503–523 K because of its crystalline nature, and this softening temperature did not fall a lot by the presence of moisture. Hemicelluloses and lignin soften at 433–473 K, but unlike cellulose, the softening temperatures of these amorphous components undergo a marked fall with moisture content (Baldwin and Goring 1968). Both the steam-exploded pulp and the steam-exploded binderless board meal presented the glass transition temperature around 448 K (Fig. 4). The glass transition temperatures of hemicelluloses and lignin were markedly lowered after steam-explosion treatment. The low glass transition temperature of the steam-exploded pulp indicates cellulose, hemicelluloses and lignin being separated by steam-explosion treatment. The glass transition temperature of lignin ranges from 400 to 466 K depending on their source and method of isolation (Goring 1971). The SEBL showed glass transition temperature at 409 K, which was much lower than that of the bamboo internode meal at about 435 K, suggesting that lignin was depolymerized during steam-explosion treatment. It is well known that glass transition temperature of dioxane lignin drops with the decrease of its molecular weight (Goring 1971). The glass transition temperature of SEBL was lower than the board press temperature at 423 K, which is expected to contribute to the adhesive behavior of the fiberboard.

On the DSC curves, EFBL and SEBL showed the maximum endothermic peaks at 442 and 429 K, and the endothermic energies were 10.6 and 84.7 J g<sup>-1</sup>, respectively (Fig. 5). The lower maximum endothermic peak and the higher endothermic energy of SEBL indicate that the lower molecular weight of SEBL



**Fig. 5** DSC curves of isolated lignins from extract-free bamboo (EFBL), steam-exploded pulp of bamboo (SEBL) and binderless board made by steam-exploded pulp (SEBBL)

compares to EFBL due to the cleavage of ester bond between lignin and *p*-coumaric acid during steam explosion treatment in addition to the cleavage of  $\beta$ -aryl-ether intermonomer linkage ( $\beta$ -*O*-4 linkage) of lignin. This suggestion was supported by the results of the lower *p*-hydroxybenzaldehyde in products of alkaline nitrobenzene oxidation and higher value of phenolic hydroxyl group of the steam-exploded pulp, which indicates that *p*-coumaric acid esterified to lignin side chain was cleaved by steam-explosion treatment and release of free phenolic hydroxyl groups (Shao et al. 2008).

The cleavage of  $\beta$ -aryl-ether intermonomer linkage ( $\beta$ -*O*-4 linkage) of lignin was confirmed by ozonation analysis. Marchessault et al. (1982) reported that  $\beta$ -*O*-4 linkage was significantly cleaved during steam-explosion process. The  $\beta$ -*O*-4 linkage is a major intermonomer linkage in lignin, and the *erythro* form of the  $\beta$ -*O*-4 linkages predominates in angiosperms (Akiyama et al. 2005; Matsumoto et al. 1993). By analytical ozonation, erythronic and threonic acids are obtained from *erythro* and *threo* forms of  $\beta$ -*O*-4 structure, respectively (Akiyama et al. 2005; Matsumoto et al. 1993). The total yields of erythronic and threonic acids range from 220 to 370 mmol (200 g lignin)<sup>-1</sup> for various woody angiosperm lignins (Akiyama et al. 2005).

**Table 1** Analytical ozonation products of EFBL and SEBL (mmol·(200 g lignin)<sup>-1</sup>)

	EFBL	SEBL
E	71	56
T	50	43
Total	121	99
E/(E + T)	0.59	0.57

EFBL: Lignin from extract-free bamboo internode with Björkman's procedure

SEBL: Lignin from steam-exploded bamboo pulp extracted with 90% dioxane (v/v) and purified with Björkman's procedure

*E* erythronic acid, *T* threonic acid



The total yield of erythronic and threonic acid in ozonation products of EFBL was 121 mmol (200 g lignin)<sup>-1</sup> which was higher than the values of SEBL (Table 1). This result clearly suggested significant cleavage of  $\beta$ -O-4 intermonomer linkages during steam explosion treatment. The cleavage of  $\beta$ -aryl-ether intermonomer linkages was also confirmed by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy (Suzuki et al. 1998; Shao et al. 2008).

## Conclusion

1. Lignin liberated from cell wall by steam-explosion treatment accumulated on the surface of the steam exploded pulp to give surface roughness.
2. The glass transition temperature of SEBL was at 409 K, which was significantly lower than that of EFBL, suggesting that lignins were depolymerized during steam-explosion treatment. They are expected to contribute to the adhesive behavior for the formation of binderless boards.
3. The intermonomer linkage of lignin and ester bond between lignin and *p*-coumaric acid was cleaved by steam-explosion treatment resulting in low molecular weight lignin rich in phenolic hydroxyl end groups.

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