# Characterization and Application of Bamboo (*Sinocalamus affinis*) Lignophenols in Lignophenols-Pulp Sheet Composites

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Bamboo (*Sinocalamus affinis*) lignophenols (Lps), synthesized using a phase separation system, were used as a natural plasticizing additive to complex with pulp (short fiber and fluffy short fiber) sheets. The structural features of Lps were analyzed by gel permeation chromatography (GPC), Fourier transform infrared (FT-IR) spectroscopy, and proton-nuclear magnetic resonance ($^1$H-NMR). The pulp sheet absorptivity of Lps, as well as the physical properties of complex sheets, were discussed. Results showed that when the concentration of bamboo Lps solution was 10 g/L, the absorption amount of Lps in the sheets made up of short pulp fibers (12%) was slightly higher than that of sheets made of fluffy short pulp fibers (10%), while physical properties, such as tightness, tensile strength, elongation, bursting, and tearing, were improved obviously after the addition of Lps. More obvious improvement in the physical strength was found in sheets made up of fluffy short pulp fibers. Results indicated that the amount of absorbed Lps was of the same importance as the properties of the pulp fibers. It is necessary to adjust the properties of both the Lps and sheets to get the best mechanical strength for the pulp sheets.

*Keywords: Bamboo; Lignophenols; Pulp sheets; Mechanical properties*

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## INTRODUCTION

There are more than 300 different kinds of bamboo resources in China. The production and reserves of bamboo in China rank first in the world (Bystriakova *et al*. 2003). Bamboo, which has the highest content of lignin among non-wood resources and the most similar chemical structure to hardwoods, is one of the most important herbaceous forest products (Ren and Funaoka 2007). In addition to the utilization of bamboo pulp, the use of bamboo lignin also has an important social significance.

Lignin, an amorphous, aromatic network polymer, can work as an adhesive to strengthen the physical properties of particleboards and other wood products. However, the amount of condensation structures in industrial lignin is high, and the corresponding amount of active functional groups is relatively low, which leads to limitations in its performance when used as an adhesive or plasticizer (Mancera *et al.* 2011). In this study, a phase-separation system (a two-step process), developed at Mie University in Japan, is used to convert the native lignin into lignophenols (Lps). Subsequently, the Lps are used to complex with an array of paper sheets made up of different fiber pulps. The influence

that the regulation of pore distribution had on the adsorption capacity of Lps, using different paper sheets, was investigated by the changes in the sheet composite properties.

## EXPERIMENTAL

### Materials

Bamboo (*Sinocalamus affinis)* was collected from the Jiang Xi Province in China. The chemical composition of the bamboo meal was 1.32% ash, 26.43% lignin, 17.26% xylose, and 46.87% cellulose at 8.12% moisture content. The bamboo was chopped into small samples, then ground using a Wiley mill. The fraction that passed through a 60-mesh screen of the Wiley mill was extracted using acetone for 48 h, after which the solvent was completely evaporated. The extractive-free bamboo meal was used as the raw material, through the phase separation system, to synthesize Lps.

Short fibers (SF; bleached eucalyptus pulp) and fluffy short fibers (FSF; bleached Eucalyptus pulp ground by a HD-WSJ-50B mill (Hongda Sanitary Products Inc. Company, China) were obtained from UPM-Kymmene Corporation (Changshu Mill, China). Both were used as raw materials to make the sheets.

### Methods

*Synthesis of lignophenols*

A total of 100 g of extractive-free bamboo meal was dissolved for 24 h in acetone with 3 mol/$C_9$ of *p*-cresol, after which the solvent was completely evaporated. Sulfuric acid (72%; 4mL/g meal) was added to the mixture and vigorously stirred for 1 h, after which the mixture was dispersed into excess water. The precipitates were washed by using distilled water until the pH of precipitates became 7. Lps with impurities were dried *via* freeze drying and subsequently ground into uniform powders. Then, Lps with impurities were completely dissolved in acetone, and, using a filtration method, the carbohydrates were separated. Finally, a transparent lignophenol-acetone solution was obtained. The concentration of the solution was determined controlling the volume of acetone solvent, after which a part of the fraction was added dropwise to an excess of ethyl ether and stirred. The precipitated lignin derivatives were collected after they had dried. The refined lignophenol powders were used to characterize the Lps.

*Acetylation of lignophenols*

A 20-mg Lps sample in a 20-mL vial was acetylated with 1 mL of a pyridine-acetic anhydride (1:1, v/v) solution at ambient temperature for 24 h. Then, it was added dropwise to an excess amount of cold water with vigorous stirring and the precipitated acetylated Lps were collected by centrifugation, washed with cold water, and freeze-dried (Wen *et al.* 2013).

*Structural analysis of lignophenols*

Gel permeation chromatography (GPC) of lignophenols was carried out on a PL-GPC50 plus Integrated GPC System (Varian Inc. Company, USA), equipped with a Waters 2410 RID detector. Sepax Mono-GPC columns (100 Å, 300 Å, 500 Å, 10 mm ID×300 mm) were connected, and tetrahydrofunan (THF) was used as an eluent (flow rate: 1.0 mL/min). Calibration for the weight-average molecular weight ($M_w$), number-average molecular weight ($M_n$), and polydispersity ($M_w/M_n$) was performed using

standard polystyrene beads. The original Lps and acetylated Lps were separately used as raw materials for the proton-nuclear magnetic resonance ($^1$H-NMR) analysis, using a mixture of deuterated pyridine and deuterated chloroform (v:v=1:3) as the solvent. Additionally, *p*-nitrobenzaldehyde was used as an internal standard. The $^1$H-NMR analyses of lignocresols were performed using a Bruker ADVANCE III FT-NMR 600 System (Germany). The amounts of combined cresols were calculated based on the signal intensity of cresolic methyl protons (1.6 to 2.4 ppm) against aromatic protons (7.8 to 8.4 ppm) of the internal standard (*p*-nitrobenzaldehyde) in an $^1$H-NMR spectra. The hydroxyl group contents were determined from a comparison of the original and acetylated proton signals, using the $^1$H-NMR spectra of acetylated Lps (Funaoka and Fukatsu 1996). Fourier transform infrared (FT-IR) spectra were obtained with a Bruker VERTEX 80 spectrometer, using KBr discs, which contained 1% finely ground samples. The spectra were recorded in the range of 400 to 4000 $cm^{-1}$, with a resolution of 4 $cm^{-1}$, over 32 scans.

*Property analysis of pulp fibers*

The degree of polymerization (DP) was determined according to the methods of the relevant Chinese national standard (GB/T1548-1989 (1989)). The properties of pulp fibers were obtained using a Metso FiberLab (Metso Corporation, Finland) in the UPM-Kymmene Corporation Asian R&D Center. The pore size and pore size distributions of the two pulp fibers were measured according to the BET method described in Nilsson *et al.* (2006), using an automatic specific surface area and porosity analyzer (ASAP2020, Micromeritics Inc., USA).

*Paper making and compositing process*

Short fibers and fluffy short fibers were defibered and screened to uniform size, then used separately to manufacture sheets; both fibers had the density of 80 $g/m^2$ under the same process conditions. The two sheet types were separately soaked in a lignophenol-acetone solution (10 g/L) for 12 h, after which the solvent was evaporated, leaving lignophenol-sheet composites.

*Mechanical testing of sheets*

The porosity of the sheets was measured by the method reported by Qi *et al.* (2008). The physical properties of sheets, both untreated and treated with Lps, such as tightness, tensile strength, elongation, bursting, and tearing, were tested using the methods of relevant standards (Tensile strength, elongation ISO 1924-2: 1994; Bursting ISO 2758: 2001; Tearing ISO 1974: 1990; Folding Strength ISO 5656: 1993; Tightness ISO 438: 1994.)

## RESULTS AND DISCUSSION

### Lignophenol Properties

Crude bamboo lignophenols (bamboo Lps with impurities), collected from the two-step process of phase-separation, had a moisture content of 6.92%. The yield of the refining Lps, collected from the acetone-soluble fraction after the crude bamboo Lps were immersed into the acetone solvent, was 16.84%. The Lps had a pink hue and quickly dissolved in polar organic solvents such as ethanol, acetone, and tetrahydrofuran (Nagamatsu and Funaoka 2003). The weight-average molecular weight of the bamboo

Lps synthesized by the two-step process was 2884 ($M_w/M_n$=1.55) after GPC testing. The content of phenolic hydroxyl group and amount of combined cresols in bamboo Lps were calculated to be 1.2 mol/$C_9$ and 0.8 mol/$C_9$, respectively, by using $^1$H-NMR spectra. It was concluded from these facts that, through the phase-separation system, the molecular weight of lignin decreased (Ohmae *et al.* 2004). Furthermore, the amount of active functional groups on the surface increased after grafting the *p*-cresol to lignin structural units (Aoyagi and Funaoka 2004; Funaoka 1998). The FT-IR spectra of bamboo Lps had the typical absorption of lignin at 1325, 1270, 1220, 1130, and 1040 cm$^{-1}$, which are the vibrations that belong to the syringyl groups and guaiacyl groups, respectively. Also, the tested Lps had a result of 815 cm$^{-1}$ from combined cresols. This data made no major difference in the characterization of bamboo Lps synthesized by phase separation system (one step method), which is in accordance with what was reported in the literature (Ren and Funaoka 2007).

## Comparison of Pulp fibers Properties

Figure 1 shows the similar length and width distributions of SF and FSF. The detailed data are shown in Table 1. As described before, the two pulp fibers were collected from the same eucalyptus hardwood (*Eucalyptus globulus*). The data (Fig. 1 and Table 1) indicated that the average length, average width, average roughness, the amount of fibers, and the average degree of polymerization of fibers were similar. However, the specific surface area and the total pore volume of FSF was larger than that of SF, and the pore diameter of FSF was smaller than SF, which indicates that there was a difference in the number of pores between the FSF and SF.

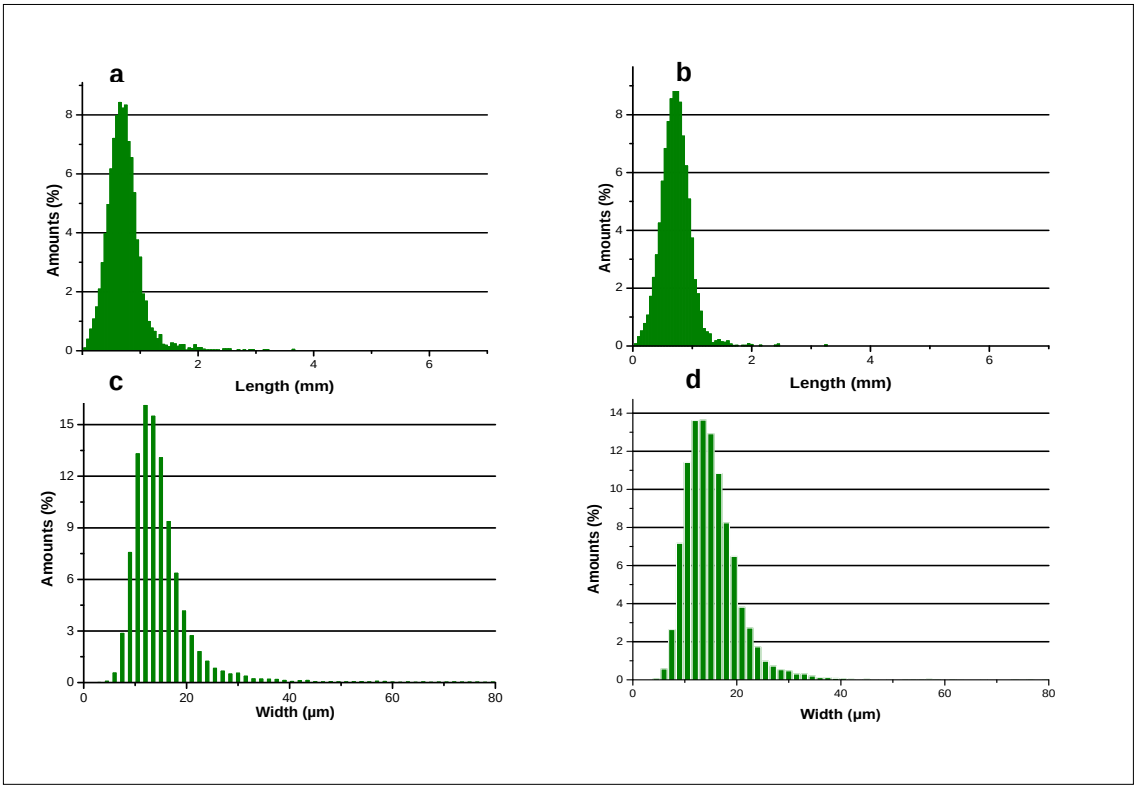


**Fig. 1.** The length and width distribution of SF and FSF. (a) the length distribution of SF, (b) the length distribution of FSF, (c) the width distribution of SF, and (d) the width distribution of FSF

**Table 1.** Basic Fiber Properties of SF and FSF (Average ± Standard Deviation)

| Sample | Average Length (mm) | Average Width (μm) | Average Roughness (mg/m) | Amount (pcs/mg) | Average DP | BET Surface Area ($m^2/g$) | Pore Volume ($cm^3/g$) | Pore diameter (nm) |
|---|---|---|---|---|---|---|---|---|
| SF | 0.75±2.20 | 14.40±43.52 | 0.08±0.006 | 22050 | 1050±39.54 | 15.58 | 0.01 | 4.02 |
| FSF | 0.75±2.20 | 14.40±43.52 | 0.07±0.007 | 22074 | 1032±37.90 | 28.24 | 0.02 | 3.07 |

## Sheet Physical Properties

Comparisons of physical properties for the two types of sheets (treated and untreated with Lps) are shown in Fig. 2. The tightness, tensile index, elongation, tearing index, and folding index properties of sheets made up of SF were better than those of sheets made up of FSF. This was due to the larger combined areas and the better stress distribution that can be provided by long fibers. Furthermore, the longer fibers typically have more connection points with each other.

The physical properties of the sheets with Lps were obviously improved compared to sheets without Lps, as shown in Fig. 2. The results showed that when the concentration of bamboo Lps solution was 10 g/L, the absorption amount of Lps in sheets made up of SF (12%) was slightly higher than that of sheets made up of FSF (10%). Although the absorbed doses of FSF are slightly lower than SF, the porosity of sheets composed of FSF was more than that of sheets made up of SF, as shown in Table 2. Furthermore, the tensile index, tightness, and elongation of sheets made up of FSF exhibited better improvement than sheets made up of SF (after being treated with Lps), as shown in Table 3. The porosity, pore volume, and the specific surface area were changed during the fiber fluffing process, which led to an altered distribution of Lps in the fibers with different properties. This phenomenon is similar to native lignin in plants working as an adhesive to form a supramolecular system with cellulose and hemicellulose, which enhances the mechanical strength of the plant (Chapple *et al.* 2007). The results in this study hint that a new type of binderless fiberboard (recyclable and freely formed) could be developed using pulp fibers and Lps.

**Table 2.** Porosity of Sheets Made Up of SF and FSF

| Sample | Porosity (Ɛ) |
|---|---|
| SF | 0.68 |
| FSF | 0.80 |

**Table 3.** Ratio of Sheets Untreated and Treated with Lps

| Sample | Tightness | Tensile index | Elongation | Tear index | Burst index |
|---|---|---|---|---|---|
| SF | 0.94 | 1.58 | 1.69 | 1.56 | 1.69 |
| FSF | 1.06 | 1.83 | 2.32 | 1.46 | 0.96 |

Paper sheets composed of FSF exhibited better physical property improvement in comparison to sheets treated with SF and Lps. This resulted from the FSF fiber

interaction (thought to be fairly weak), which is directly related to how fluffy the FSF sheets were in comparison to the SF sheets, at the same density (80 g/m$^2$). Meanwhile, Lps have comparatively smaller molecular weight, higher contents of active functional groups, and better solubility in common organic solvents (Funaoka and Fukatsu 1996; Ren and Funaoka 2007; Funaoka 2013). The tightness, intensity of sheets, and the interaction among fibers were clearly increased after treatment with Lps because of the physical interactions between the active functional groups of Lps and the hydroxyls on the surface of the pulp fibers. This study demonstrated that Lps have considerable application prospects in lignophenol-pulp sheet composites.

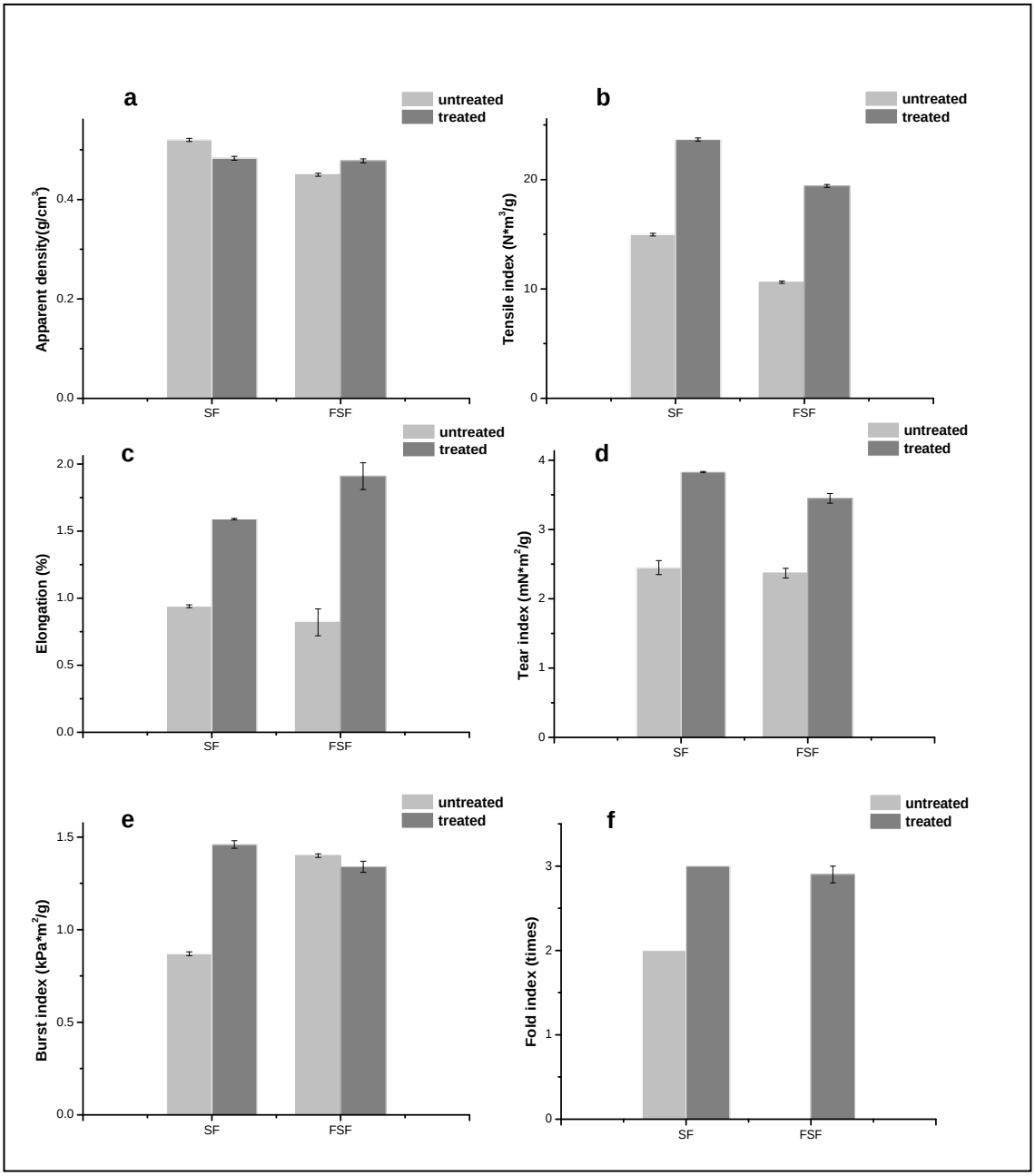


**Fig. 2.** Comparison of sheet physical properties: (a) tightness, (b) tensile index, (c) elongation, (d) tear index, (e) burst index, and (f) fold index

## CONCLUSIONS

1. The physical properties, such as apparent density, tensile strength, elongation, bursting, and tearing, are obviously improved by adding bamboo lignophenols (Lps) into two kinds of paper sheets. It is possible for lignophenols to act as a natural plasticizer when added to the fiber composites. However, the detailed functional mechanism between the Lps and pulp fibers needs to be further investigated.
2. The absorption amount of Lps for sheets composed of fluffy short fibers obtained by milling (FSF) was slightly lower than that of sheets made of SF under the same experimental conditions. However, more obvious improvements regarding the physical strength were found for sheets made of FSF, which indicates that fiber morphology has an important influence on the adsorption form and effect of Lps.
3. The influence of different pore distribution and specific surface area of fiber, as well as the concentration of Lps solutions on the physical properties of pulp fiber molds with different thicknesses would be an interesting study for developing a new type of composite material.

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