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# Development and characterization of a defatted soy flour-based bio-adhesive crosslinked by 1,2,3,4-butanetetracarboxylic acid

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ABSTRACT

A new, environmentally friendly defatted soy flour-based bio-adhesive was developed by using the cross-linker 1,2,3,4-butanetetracarboxylic acid (BTCA). The reaction between BTCA and defatted soy flour was confirmed by assaying the free amino groups, by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction, and $^{13}C$ nuclear magnetic resonance ($^{13}C$ NMR). Three-ply plywood was fabricated to measure wet shear strength, and the cross-section and thermal behavior of resultant adhesives were characterized in detail. A decrease in the free amino group content, a new ester peak in the FTIR spectra, a weaker resonance at 65.4–76.2 ppm in $^{13}C$ NMR, and a decrease in crystallinity confirmed that BTCA was successfully crosslinked with defatted soy flour. The resulting crosslinked bio-adhesive showed improved wet shear strength (1.36 MPa) and a reduced sol fraction (24.8%). The crosslinked bio-adhesive displayed enhanced thermal stability, and had a more uniform surface based on thermogravimetric analysis and scanning electron microscopy. The results suggest BTCA can be used to prepare high-performance environmentally friendly defatted soy flour-based bio-adhesives.

## 1. Introduction

Formaldehyde-based adhesives are mainly used in the production of wood composites due to their high water resistance [1]. Limitations of these adhesives include their non-renewable nature and the fact that they contain residual toxic components [2], and natural and renewable resources such as soybean protein [3,4], natural tannins and starch [5] are preferable materials for wood adhesives. Defatted soy flour is a natural composite consisting of approximately 50% protein and 40% carbohydrate, which can serve as an alternative to formaldehyde-based adhesives [6,7]. However, low inherent strength and poor water resistance have limited its applications [8].

In general, two major chemical modifications are employed to modify the protein component of defatted soy flour to improve its strength and water resistance for use in defatted soy flour-based bio-adhesives. The first change involves protein denaturation treatment using alkali [9], urea [10] and sodium dodecyl sulphate [3] as denaturing agents to unfold the protein structure and expose the inner functional groups (-$NH_2$, -COOH, -OH, and -SH) to make them available to interact with the wood and thereby improve its strength. However, hydrogen bonds formed between protein functional groups are relatively easily broken in wet conditions [3,11]. In addition, most existing modification strategies are based on proteins, and few studies focusing on carbohydrates have been reported [4,12]. Nevertheless, carbohydrates in defatted soy flour, mainly consisting of polysaccharides with high hydrophilicity, may also reduce the wet shear strength of defatted soy flour-based bio-adhesives.

Another strategy is crosslinking, and aldehydes are the most commonly used crosslinking agent. Reactive groups such as –$NH_2$ and –OH in proteins and –OH in carbohydrates can crosslink with aldehydes to create a three-dimensional network and thereby improve the water resistance of protein- and polysaccharide-based materials [13]. Several researchers have employed glutaraldehyde [14,15] or synthetic resins such as phenol formaldehyde [16] or melamine urea formaldehyde [17] to modify defatted soy flour-based bio-adhesives, and these were shown to be effective crosslinkers. However, these crosslinkers are potentially toxic, hence it is necessary to develop environmentally friendly defatted soy flour-based bio-adhesives using non-toxic crosslinkers.

1,2,3,4-butanetetracarboxylic acid (BTCA) appears to be a very promising non-toxic crosslinking agent that could replace traditional aldehyde crosslinkers [18]. BTCA is capable of crosslinking with the functional groups of defatted soy flour (such as -$NH_2$ and -OH) to form amide or ester linkages that impart water resistance. Reports on improvement of water resistance by the introduction of amide or ester linkages in proteins are limited [19], but some studies have indicated that BTCA can effectively improve the mechanical and barrier properties of polysaccharide-based materials such as cellulose [20], paper

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[21] and cotton [22] by esterification. Thus, it was postulated that the water-resistant properties may also be enhanced by crosslinking proteins and polysaccharides in this manner.

In the present study, BTCA was added to crosslink defatted soy flour in the presence of sodium hypophosphite (SHP) as a catalyst. Reaction between BTCA and defatted soy flour was confirmed through quantification of amine groups and Fourier transform infrared spectroscopy (FTIR). The wet shear strength and sol fraction of the resultant bio-adhesives was investigated to confirm the positive effect of crosslinking, and thermogravimetric analysis (TGA) and scanning electron microscopy (SEM) were employed to verify the improvements in defatted soy flour-based bio-adhesives.

## 2. Experimental

### 2.1. Materials

Defatted soy flour (53% w/w, dry basis) with a moisture content of 8.56%, a crude fat content of 0.97%, and an ash content of 6.20% ground from defatted soy meal was obtained from Shandong Longfeng Soybean Co., Ltd (Shangdong, China). *Pinus massoniana* veneer 300 × 300 mm in size and 1.2–1.3 mm thick with a moisture content of 10–12% (wt) were supplied by Jianyang Luban Wood Industry Co., Ltd. (China). BTCA 99% and SHP 98% were purchased from Maclin (Shanghai, China).

### 2.2. Preparation of defatted soy flour-based bio-adhesives

A defatted soy flour-based bio-adhesive was prepared as follows: 20 g dried defatted soy flour and 80 g distilled water were placed into a three-necked flask and stirred at 35°C for 40 min. The defatted soy flour slurry was then adjusted with sodium hydroxide solution (30%) to pH 11.0 for 30 min then adjusted to pH 5.0 with hydrochloric acid solution. Different amounts of BTCA and 0.6 g SHP were then slowly added into the defatted soy flour slurry with continuous stirring for 30 min then cooled to room temperature. In the control experiment, the bio-adhesive was prepared following the above process but without adding BTCA.

### 2.3. Plywood preparation

Three-layer plywood samples were made under the following conditions: 140 g/m$^2$ of the adhesive was spread onto each veneer layer under static pressures of 1.2 MPa at 160 °C for 3.6 min. After hot pressing, plywood samples were stored under ambient conditions for at least 24 h before the shear strength was tested.

### 2.4. Assay of free amino groups

The modified ninhydrin method was used as described by Eslah et al. [23]. Ninhydrin (2 g) was dissolved in distilled water (100 ml) under a stream of nitrogen gas to prepare ninhydrin solution. Ninhydrin solution (1 ml) was added to 0.1% (wt) aqueous sample solution heated in a boiling water bath for 5 min and immediately cooled in an ice bath. The absorbance (580 nm) of samples was measured with an Agilent 8453 spectrophotometer (USA).

### 2.5. FTIR spectroscopy

The cured defatted soy flour-based bio-adhesive samples were overflowed from the plywood during the pressing process. The cured samples were fully milled with potassium bromide and compressed for FTIR analysis on a Nicolet 380 FTIR (USA). Each sample was scanned 32 times over a region of 400–4000 cm$^{-1}$ at a resolution of 4 cm$^{-1}$. Spectral data were subsequently processed using OPUS 5.5 software. All spectra were baseline corrected and min-max normalized.

### 2.6. $^{13}C$ NMR analysis

Solid state $^{13}C$ CP/MAS NMR spectra were recorded on an AVANCE III 400WB spectrometer(Bruker, Switzerland) operating at a carbon frequency of 100 MHz. The contact time, acquired time and repetition time were of 2 ms, 0.03 s and 5 s, respectively. The spectral width was 500 ppm, with 3072 data points, and the number of scans 2880. Chemical shifts were calibrated based on the carbonyl carbon resonance of glycine at 176.2 ppm.

### 2.7. XRD analysis

XRD was performed on a XRD diffractometer (Rigaku Ultima IV) using a cobalt source. The diffraction data were collected from 2 values of 5° to 60°.

### 2.8. Wet shear strength test

The wet shear strength of adhesive samples was determined according to Chinese National Standards GB/T 9846-2015. Ten plywood specimens (100 mm × 25 mm) were soaked in water at 63 °C for 3 h, then dried at room temperature for 10 min. The wet shear strength was tested using a MTS tensile testing machine (USA) at a crosshead speed of 10 mm/min. All measurements were performed 10 times, and the average wet shear strength was calculated.

### 2.9. Sol-gel test

A sol-gel test was performed according to our previous work [4]. After storage at 25 ± 1 °C and 70% relative humidity for 24 h, 1.50 g ($m_1$) of defatted soy flour based bio-adhesive samples and 150.0 g distilled water were placed into a glass bottle and heated in a boiling water bath for 3 h. The contents of the bottle were washed and filtered using a filter paper with an average pore size of 3 μm. The solid residue was dried in an oven at 103 °C until the weight ($m_2$) remained constant. The sol fraction of bio-adhesive was calculated using the following equation:

$$\text{Sol fraction} = \frac{(m_1 - m_2)}{m_1} \times 100\%$$

All measurements were performed three times, and average values were used for analysis.

### 2.10. TGA analysis

Native defatted soy flour-based bio-adhesive (DSB), controls, and BTCA-modified bio-adhesive (BMB) were freeze-dried, and the thermal stability was analyzed using a NETZSCH STA449F3 Thermogravimeter (Germany). Samples were heated from 25 to 450 °C at a rate of 10 °C/min under a nitrogen gas flow at 20 ml/min.

### 2.11. SEM analysis

The surfaces of cured defatted soy flour-based bio-adhesive samples and the fractured surfaces of wood specimens after shear strength testing were coated with gold under vacuum, and all specimens were observed using a Hitachi SU8010 scanning electron microscope (Japan) under a vacuum of 1.48 × 10$^{-6}$ mbar.

## 3. Results and discussion

### 3.1. Mechanism

The defatted soy flour used in this study had a protein content of 54.0 wt% and a carbohydrate content of 36.4 wt%. Lysine, histidine and arginine amino acids in defatted soy flour contain amino groups,