Industrial Crops & Products 126 (2018) 31–37

Contents lists available at ScienceDirect

Industrial Crops & Products

journal homepage: www.elsevier.com/locate/indcrop

Blending cottonseed meal products with different protein contents for cost-effective wood adhesive performances

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ARTICLE INFO

Keywords:
Adhesive
Cottonseed
Maple
Protein
Rheology
Temperature

ABSTRACT

Water washed cottonseed meal (WCSM) is an excellent bio-adhesive resource because of its cost-effective extraction process and environmentally friendly performance. To evaluate the effects of protein content on the adhesive performance of cottonseed meal-based adhesives, we reconstituted cottonseed meal products with protein contents ranged from 34.9% to 94.8% by blending different amounts of WCSM, cottonseed protein isolate (CSPI), and residues after protein extraction (CSIR). Their physicochemical properties and three types of adhesive strengths (dry, wet, and soaked) were measured with press temperatures at 100, 150 and 170 °C. The morphological and rheological data showed that the low-protein-content adhesives with a high amount of residual cotton hull and fiber possessed poor spreadability and adhesive strength. Molecular and thermal analysis suggested that protein ratio had a stronger influence than press temperature to thermal property and adhesive strength. With these data, multiple linear regression models were established, providing analytical tools to predict the bonding strength affected by protein content and press temperature in cottonseed meal-based adhesives. On the other hand, the blends with 65–70% of protein content demonstrated the bonding performance and flowability comparable to highest protein product CSPI (94.8% protein) within the acceptable standard deviations. Thus, these observations and data could be helpful in set-up of industrial standard requirements and quality control for protein content in cost-effective adhesive-grade WCSM products.

1. Introduction

Bio-based environmentally friendly products receive a good global response due to an increase of public concern associated with human health risk and environmental issues. Varieties of natural resources have been studied in order to develop eco-friendly and sustainable products (He, 2017; Jiang et al., 2018; Petrič, 2018). In addition, an increase in energy demand is contradictory to a decrease in petroleum supply. Therefore, the bio-based wood adhesive products become excellent candidates to replace the petrochemicals and petroleum-based wood glue agents (He, 2017).

The global adhesive market for wood application is predicted to be $6.18 billion by 2025 (Grand View Research Inc., 2017b). Petroleum and formaldehyde-based adhesives play an important role in the wood adhesive market due to their good adhesive performance (Pizzi and Mittal, 2011). In the forest products industries, formaldehyde-based adhesives account for more than 70% of the wood adhesives. Especially, urea-formaldehyde (UF) resins are the most important type of adhesive resins for the production of wood based panels, and approximately 5–6 million Mg are produced per annum worldwide (Dunky, 1998; Liu et al., 2018). However, the United States Environment Protection Agency (EPA) proposed strict regulations for formaldehyde emission standards for wood composite products so as to reduce the carcinogenic risk in humans (EPA, E.P.A., 2017). Therefore, there is a great opportunity for bio-based adhesives in the wood adhesive market (He, 2017). Soy protein-based products have a small market portion (Grand View Research Inc., 2017a). Many scientists are still continuously improving soy protein adhesive properties (Li et al., 2004; Liu et al., 2015; Luo et al., 2015; Pradyawong et al., 2017). On the other hand, researchers have also explored other plant-protein sources such as canola (Bandara et al., 2017; Wang et al., 2014), camellia (Zhu et al., 2017), peanut (Li et al., 2015), sorghum protein (Li et al., 2011), sesame (Wei et al., 2017), and wheat (Lagel et al., 2015) in order to enlarge the protein-based adhesives market share. Similarly,

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https://doi.org/10.1016/j.indcrop.2018.09.052
Received 4 May 2018; Received in revised form 24 September 2018; Accepted 27 September 2018
0926-6690/ Published by Elsevier B.V.

lots of work have been done on cottonseed protein-based adhesives, showing their great potential in serving as environment-friendly wood glues (Cheng et al., 2016).

Plant seed protein isolates are typically extracted from plant seed meals (flours) so that these isolates are much more expensive than the meals. Thus, there are studies on use plant seed meals as wood adhesives with or without modification (e. g., Luo et al., 2016; Wang et al., 2018). However, the meal products generally showed poor adhesive performance, compared to the corresponding protein isolates (Frihart and Lorenz, 2013). By comparison of the wood adhesive performance of a series of soy flours, protein concentrates and isolates, Lorenz et al. (2015) reported that the carbohydrate interference is only part of the poor performance of meal products, while both the level and the nature of the protein played larger roles. In our previous studies (He and Chapital, 2015; He et al., 2014), we found that, while the raw cottonseed meal shows poor adhesive performance, water washing significantly improve the water resistance of cottonseed meal. In other words, the novel product washed cottonseed meal (WCSM) is cheaper and more environmentally friendly in preparation than cottonseed protein isolate (CSPI).

Thus, the scale-up experiment was carried out recently and the results indicated that the procedure applied in WCSM laboratory-scale is practical in pilot-scale production (He et al., 2016). Accordingly, the pilot-scale produced WCSM has been characterized and its adhesive properties have been evaluated with several preparation conditions (He et al., 2017, 2018; He and Chiozza, 2017; Li et al., 2017). Compared to the laboratory-scale produced material, the pilot-scale produced WCSM contained lower protein content, but higher fiber content apparently due to the high, but variable batch by batch, fiber/carbohydrate content in the mill-produced raw material (i.e., defatted cottonseed meal) (He et al., 2016). However, unlike the soy products (O'Dell et al., 2013; Lorenz et al., 2015), it is unclear how the protein concentrations in WCSM products affect the adhesive performance of WCSM. Thus, in this work, we reconstituted cottonseed meal products with different protein contents by blending different amounts of WCSM, CSPI, and residues after protein extraction (CSIR), characterized their physicochemical properties, and measured their adhesive performances. The objectives of this work were to increase the understanding on the relevant bonding mechanism and relationship of cottonseed products with protein contents, and the range or ratio of protein percentage in WCSM required for cost-effective adhesive performance. The eventual goal was to provide critical data on protein contents required for adhesive-grade WCSM products for industrial standard setup and quality control.

2. Materials and methods

2.1. Materials

Maple wood veneer (1.59 mm thick) was purchased from Certainly Wood, Inc. (East Aurora, NY, USA) and was precut to 5 × 12 cm (width × length) panels. The wood density was 0.79 g cm^{-3}. The moisture content of the wood under the conditioning environment was 9.45% dry basis. Hydrochloric acid was purchased from Fisher Scientific (Fair Lawn, NJ, USA).

The raw material, mill-grade defatted cotton meal, was provided by Cotton Inc., Cary, SC, USA. The three products used in this work, WCSM, CSIR and CSPI, were isolated previously in a pilot scale from the raw material (He et al., 2016). The percentage of total protein of CSIR, WCSM, and CSPI were 34.9, 46.3 and 94.8, respectively. The morphological characteristics were captured by Samsung Galaxy S7 (Samsung, Korea). The macro lens (Model CamRah iPhone Camera Macro Lens, CamRah, Texas, US) were equipped for close up observation.

2.2. Preparation of adhesive slurries

The adhesive slurries with different protein contents were formulated by blending WCSM, CSIR and CSPI according to the ratios presented in Table 1. Then these cottonseed mixtures were blended with distilled water to reach the total solid content of 12% (w/w). The pH of the slurries was adjusted to 4.5 using 3 M HCl and stirred at 300 rpm at room temperature for 2 h.

Table 1
The blending ratios of adhesives with different protein contents. The protein content of washed cottonseed meal (WCSM), protein isolate (CSPI), and extraction residues (CSIR) are given in the parenthesis following the product. The blend labels are designed associating with the percentages of total protein content in each adhesive blend.

Samples	CSIR (34.9%)	WCSM (46.3%)	CSPI (94.8%)
B34.9	1	–	–
B40.5	0.5	0.5	–
B46.3	–	1	–
B55.1	0.67	–	0.33
B62.5	–	0.67	0.33
B64.9	0.5	–	0.5
B70.6	–	0.5	0.5
B82.7	–	0.33	0.75
B94.8	–	–	1

2.3. Sodium dodecyl sulfate polyacrylamide gel electrophoresis (SDS-PAGE)

The sodium dodecyl sulfate-polyacrylamide electrophoresis (SDS-PAGE) of selected adhesives B34.9, 46.3 and 94.8 was performed on 12% separation gel and 4% stacking gel in a discontinuous buffer system (Qi et al., 2017; Qi and Sun, 2011). Adhesive slurries B34.9, 46.3 and 94.8 were dried at 100, 150 and 170 °C on a hot plate, separately. The dried samples were ground, mixed with deionized water (40 mg ml^{-1}) and sonicated at room temperature for 6 h. The supernatants were mixed with loading buffer containing 2.1% SDS, 26.3% glycerol, 0.01% bromophenol blue and 5% mercaptoethanol at pH 6.8 at the ratio of 1:1, and were boiled for 5 min. SDS-PAGE was carried out under reducing condition. The molecular weight size marker (10–250 kDa) (Precision Plus ProteinTM Standards, Dual color, BIO-RAD, CA, USA) was loaded on the first lane. A total of 10 μl of the mixtures were loaded onto each lane. Electrophoresis was conducted under 150 V and 40 mA for 60 min. The gel was stained with 0.25% Coomassie brilliant blue R- 250 and destained in a de-staining solution containing 30% acetic acid, 30% methanol, and 40% distilled deionized water. The bands intensity was analyzed by ImageJ (http://rsbweb.nih.gov/ji/).

2.4. Rheological measurement

The apparent viscosity of approximately 180 μl of the fresh adhesive slurries from section 2.2 was measured by the Bohlin CVOR 150 rheometer (Malvern Instruments, Southborough, MA, USA). The gap between the plate and the 20 mm-diameter parallel plate head was set to 500 μm. The apparent viscosity curves were recorded at the shear rate range of 0.01–100 s^{-1}. Silicone oil was applied to the samples to prevent water evaporation.

2.5. Differential scanning calorimetry (DSC) and Fourier Transform Infrared Analysis (FTIR)

The thermal property of adhesives was measured with a DSC Q200 V24.4 instrument (TA Instruments, New Castle, DE, USA). The DSC was calibrated by indium and zinc before using. The dried powder (7–10 mg) from the SDS-PAGE experiment was weighed in a hermetic aluminum pan. The powder was heated at the increasing temperature from 25 °C to 250 °C, at a heating rate of 10 °C min^{-1}. The test was operated under nitrogen atmosphere with a gas flow rate of 50 ml