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A preliminary assay of the potential of soy protein isolate and its hydrolysates to provide interfiber bonding enhancements in lignocellulosic furnishes

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ABSTRACT

Soy protein isolate (SPI) was extracted from soy flour and hydrolyzed with hydrochloric acid, sodium hydroxide, and enzyme, separately, to provide a series of hydrolysates. The SPI and its hydrolysis products were later cross-linked with ethylendiaminetetraacetic acid (EDTA) in the presence of sodium hypophosphite (SPH) after which they were complexed to chitosan as part of an on-going general chemical strategy in our laboratories to improve their incorporation into old corrugated container (OCC) matrix and thus increase inter-fiber bonding. Approximately 2% SPI-EDTA-chitosan and hydrolyzed SPI-EDTA-chitosan additives by mass (OCC-based slurry) were thoroughly mixed before generating a sheet for physical testing. The tensile and burst indices of the SPI-EDTA-chitosan additive-treated OCC pulp sheet increased 46.3% and 61.85%, respectively, while the inter fiber bonding of SPI-EDTA-chitosan additive-treated OCC pulp sheet increased 74.86% compared to the control, albeit having a decreased tear strength and roughness, with significantly increased gloss. The additive-treated pulp sheet was characterized by thermogravimetric analysis (TGA), dynamic mechanical analysis (DMA), and ATR to provide evidence for product synthesis.

1. Introduction

Soy protein isolate is a long chain biopolymer consisting of 18 different polar and nonpolar amino acids. Polar amino acids such as cysteine, arginine, lysine, histidine and others can act as effective chemical pivots to crosslink the protein and improve the mechanical, thermal, and physical properties, while reducing water sensitivity and hydrophilicity [1]. Earlier research reported that isolated soy proteins may be cross linked with aldehydes such as formaldehyde, glutaraldehyde (GA), glyoxal, and glyceraldehyde through *Maillard* reactions [2]. Isolated soy proteins cross linked with GA yield biopolymers with enhanced mechanical properties [3]. Chemical modification of pulp fibers within the pulp & paper market is currently a common practice for improving printing quality, surface gloss, surface sizing, and calendaring. In addition, mechanical property improvements tend to be regulated by relatively costly chemical additives such as cationic starch or polyacrylamides. The low cost, commercial availability, and chemical derivatization power of soy protein flour (>50% protein), not surprisingly, is extremely attractive for the development of novel functional soy protein derivatives for paper strength improvements. Typically, starch is used for printing and writing grade papers for surface sizing, i.e., for improving paper surface resistance to uneven penetration and flow of inks/liquid media and acceptable printability [4]. The reclaimed paper market has been mostly focused on attaining improved mechanical strength properties.

Within the reclaimed paper market, the utilization rate of waste old corrugated containers (OCC) (recycled containerboards) in 1963 was 21.1% in the US, while in 2001 it increased to 67% with a recovery rate of nearly 70% [5]. Recently, the American Forest & Paper Association (AF&PA) released a 2011 recovery rate for OCC with a new high of 91.2 percent. Therefore, research in this area is necessary to improve the strength of OCC because waste fibers are typically mechanically inferior to their virgin equivalents. Early work identified several chemical treatments that yielded improvements in the bonding strength of recycled sheets [6,7]. Further innovative studies have shown that fiber surface chemical

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derivatization can prevent strength losses [8,9]. The paper industry is currently using commercial dry strength agents such as cationic starch, polyacrylamide, and glyoxylate polyacrylamide to improve the strength of OCC, but the improvement is still very low relative to virgin pulp [10,11]. In addition, a number of these studies have been conducted with nonrenewable inorganic fillers and petroleum-based matrices for applications that include packaging, a high value sector of the pulp market. Increasing environmental concerns have led to new flexible barrier bio-based packaging materials and the potential uses of renewable resources to offset the use of the inorganic fillers and petroleum-based materials [12].

The present study focuses on the application of an isolated soy protein derivative for improving the mechanical properties of OCC. It will focus on the characterization of the soy protein derivatives and explore their applicability to OCC.

2. Experimental

2.1. Materials

Soy flour was provided by Archer Daniel Midland (ADM, Decatur, IL). The OCC pulp was furnished by Azko Nobel Pulp and Performance Chemicals, Marietta, GA. Commercial dry strength agents such as Glyoxylate-PAM and cationic starch were supplied by Azko Nobel Chemicals, Marietta, GA and Cargill Incorporated, Minneapolis, MN, respectively. Cross linking agents such as ethylenediaminetetraacetic acid (EDTA) and chitosan (Ch) were purchased from Sigma–Aldrich and used as received. Chemicals of reagent grade utilized were sodium hypophosphite, (SHP) CAS registry number 123333-67-5, sodium hydroxide, CAS registry number 1310-73-2, *Alcalase* product No. 126741, and denatured alcohol and acetic acid from Fisher Scientific, Fair Lawn, NJ. Deionized water was used for all experiments that required water as the medium.

2.1. Extraction of the soy protein isolate

Soy flour was carefully added into acidified water so that solution pH was within the isoelectric range of the soy protein (pH 4.0–4.8) and that only the soluble fraction of the soy flour dissolved. The resulting mixture was centrifuged to separate the protein-rich precipitate from the supernatant to give a high quality concentrate soy protein [13].

2.2. Hydrolysis of the soy protein isolate

For hydrolysis of soy protein isolate, three different routes were followed: acid, alkali, and enzymatic treatments. Approximately 1 g of soy protein isolate was added into 50 ml of 1 N HCl or NaOH solution and heated at 70 °C for 3 h. The suspension was centrifuged at 5300 rpm for 15 min. to concentrate the hydrolyzed soy protein isolate and remove the excess aqueous acid or alkali. The resultant precipitate was rinsed and re-centrifuged until constant neutral pH [14]. The enzymatic hydrolysis was carried out with Alcalase as follows: soy protein isolate was dissolved in water at 50 °C for 10 min. When the protein solution temperature reached 50 °C, the Alcalase (2.4U/g) was added. The soy protein isolate and enzyme ratio was 1:0.002. pH of solution was maintained at 7 by adding 1 N NaOH during the first 15 min. of reaction, while at the end of reaction, pH was adjusted to 4.5 using 1 N HCl. The mixture was cooled, adjusted to pH 7.0, and heated at 95 °C for 15 min. to inactivate the enzyme. The enzymatic hydrolyzed soy protein isolate was centrifuged, rinsed, and re-centrifuged until constant neutral pH [15]. The mixture was freeze-dried and stored.

2.3. Chemical modifications of soy protein isolate (SPI) and hydrolyzed soy protein isolate

Into 15 mL of 1 N sodium hydroxide solution in a 50 ml Petri Dish, 5 g of EDTA and 1 g of SHP were dissolved. Soy protein isolate or hydrolyzed soy protein isolate (5 g) was added to the solution and manually mixed with a glass rod. The mixture was placed in an oven at 130 °C for 3 h. Reaction products were washed with water and filtered several times to remove unreacted materials. The product obtained was a modified soy protein isolate that was air dried at 50 °C in an oven overnight [16]. The proposed reaction scheme is shown in Fig. 1.

2.4. Polyelectrolyte complexation

Chitosan (Ch, 1 g) was dissolved into 50 ml of 1.5% acetic acid solution. Modified soy protein isolate (1 g) was dissolved with 50 ml water and added to a 50 ml chitosan solution in a 250 ml round bottom flask. The reaction mixture was stirred at 70 °C for 90 min [17]. The proposed reaction scheme is shown in Fig. 2.

2.5. Preparation of OCC pulp sheet

The sheet was prepared according to TAPPI Standard Method T 205 using a 600 ml pulp slurry (1.8 g oven dried OCC pulp) in a sheet molder machine. The pulp slurry was diluted with 10 L of DI water in a sheet molder to produce a uniform sheet. The sheet was conditioned and cured at 105 °C for 1.0 h [17].

3. Testing methods

3.1. Determination of carboxyl content

A known amount of soy protein isolate derivative was dissolved in 0.1 N NaOH and hydrolyzed for one hour. The excess amount of NaOH was determined by titration with 0.1 N HCl using phenolphthalein as an indicator [18] while the carboxyl content in milliequivalents (meq.) per 100 g was calculated as follows:

$$\text{Carboxyl Content } (meq) = \frac{(V_2 - V_1) \times N \times 10}{W} \quad (1)$$

N = Normality of HCl
V_2 = Volume of HCl without sample
V_1 = Volume of HCl with sample
W = Weight of Sample.

3.2. Gloss testing

The gloss of OCC pulp hand sheet was tested with a GLOSSMETER according to TAPPI T 480 test method.

3.3. Roughness testing

The roughness of OCC pulp hand sheet was tested with an L & W roughness tester according to TAPPI T 538 test method.

3.4. Tensile strength

The tensile of OCC pulp hand sheet strength was tested with an ALWETRON TH1 tester according to TAPPI T 220 test method.

3.5. Burst strength

The burst strength of OCC pulp hand sheet was tested with a MULLEN tester according to TAPPI T810 test method.