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Chemical treatment and characterization of soybean straw and soybean protein isolate/straw composite films

Milena Martelli-Tosi[a,b,*], Odílio B.G. Assis[c], Natália C. Silva[a], Bruno S. Esposto[a], Maria Alice Martins[c], Delia R. Tapia-Blácido[a]

[a] Departamento de Química, Faculdade de Filosofia, Ciências e Letras de Ribeirão Preto, Universidade de São Paulo, Bandeirantes Avenue 3900, CEP 14040-901, Ribeirão Preto, SP, Brazil
[b] Departamento de Engenharia de Alimentos, Faculdade de Zootecnia e Engenharia de Alimentos, Universidade de São Paulo, Rua Duque de Caxias Norte 225, CEP 13635-900, Pirassununga, SP, Brazil
[c] Embrapa Instrumentação, National Nanotechnology Laboratory for Agriculture, Rua XV de Novembro, 1452, CEP 13561-206, São Carlos, SP, Brazil

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ABSTRACT

This work investigated changes in the chemical composition and structure of soybean straw (SS) treated with alkali (NaOH 5% and 17.5%) and bleached with hydrogen peroxide (H_2O_2) or sodium hypochlorite (NaOCl). Removal of the amorphous constituents increased the degree of crystallinity and the content of cellulose fibers particularly after reaction with high concentrations of alkali. Treatment with NaOH 17.5% contributed to the allomorph transition from cellulose I to II regardless of the bleaching agent, but H_2O_2 as bleaching agent promoted more effective delignification. This work also evaluated the potential use of treated and non-treated SS as reinforcement filler in soy protein isolate film (SPI). Films added with treated SS presented higher mechanical resistance, lower elongation at break, and lower solubility in water. Addition of non-treated SS did not affect the properties of the SPI film significantly. The low solubility and the reasonable water vapor permeability of the composite films make them suitable packaging materials for fresh fruit and vegetables.

1. Introduction

Soybean is a significant agricultural commodity in the Brazilian economy (Milazzo, Spina, Cavallaro, & Bart, 2013). The 2015/2016 harvest placed Brazil as the second largest world producer of soybean (about 30% of the global production) (CONAB, 2015). Unfortunately, grain threshing generates a huge amount of soybean straw. According to Bose and Martins Filho (1984), the soybean/straw ratio statistically varies from 1:1.2 to 1:1.5 t/ha, which means that about 104 to 130 million tons/year of straw originates from the Brazilian soybean harvest alone (FAOSTAT, 2016). The soybean straw consists of stems, leaves, and pods. The average composition of this material includes 35% cellulose, 21% insoluble lignin, 17% hemicelluloses, 11% ash, 1% acid soluble lignin, and remaining constituents such as protein, pectin, and glucuronic acid substitutes (Cabrera et al., 2015; Wan, Zhou, & Li, 2011). Soybean straw is usually disposed as waste through landfilling, incineration, or dumping.

Some studies have suggested that soybean straw could be used as raw material to produce polymer and soluble sugars (Cabrera et al., 2015; Wan et al., 2011; Xu, Wang, Jiang, Yang, & Ji, 2007) or as a natural source to obtain fibers via alkali and acid treatments (Reddy & Yang, 2009).

Various physical, chemical, and enzymatic treatments can enhance the biodegradability and digestibility of soybean straw (Cabrera et al., 2015; Khorvas, Kargar, Yalchi, & Ghorbani, 2010). Application of chemical treatments before enzymatic hydrolysis removes amorphous components like lignin and hemicellulose, thereby increasing the porosity of the material and facilitating further defibrillation and extraction of fibers (Yue et al., 2015). Chemical treatments include reactions with ozone, alkali, acid, peroxide, or other organic solvents (Oh et al., 2015). The pulp industry has traditionally delignified lignocellulose via bleaching with sodium chlorite. However, environmental concerns have led the industry to replace bleaching with sodium chlorite with more environmentally friendly methods such as thermochemical reac-

* Corresponding author at: Departamento de Engenharia de Alimentos, Faculdade de Zootecnia e Engenharia de Alimentos, Universidade de São Paulo, Av. Duque de Caxias Norte 225, CEP 13635-900, Pirassununga, SP, Brazil.
E-mail address: mmartelli@usp.br (M. Martelli-Tosi).

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tions that use oxygen (Kafle et al., 2015) and hydrogen peroxide (Andrade-Mahecha, Pelissari, Tapia-Blácido, & Menegalli, 2015; Zeronian & Inglesby, 1995). According to Khorvash et al. (2010), treatment with H_2O_2 improves the *in vitro* digestibility of soybean straw as compared to $NaClO_2$-based treatments. Depending on the size of the generated soybean fibers, they can serve as reinforcement fillers during formation of biocomposite matrixes.

Biomaterials based on renewable resources, such as proteins and polysaccharides, can be potentially processed into films for food or biomedical applications. In particular, soy protein isolate (SPI), which can be produced by casting (Denavi et al., 2009), extrusion, or injection molding (Calabria et al., 2012; Chan, Lim, Barbut, & Marcone, 2014; Garrido, Peñalba, de la Caba, & Guerrero, 2016), is an attractive sustainable "green polymer" with good film-forming ability. Nevertheless, SPI films have low strength and absorb a high amount of moisture, which limits their applications. Three methods can help to overcome these limitations and to improve the properties of SPI films, namely cross-linking (González, Strumia, & Alvarez Igarzabal, 2011; Xu et al., 2015), blending with a polymer to form a soy-based plastic (Calabria et al., 2012; Kim & Netravali, 2012; Saenghirunwattana, Noomhorm, & Rungsardthong, 2014; Won, Lee, Jin, & Lee, 2015), and addition of reinforcing fillers (Husseinsyah, Yeng, Kassim, Zakaria, & Ismail, 2014; Lodha & Netravali, 2002; Siro & Plackett, 2010).

Micro- and nanosized fibers have by far been the most cited reinforcement fillers in the literature (Chan et al., 2014; Chen, Zhang, Peng, & Liao, 2006; Jensen, Lim, Barbut, & Marcone, 2015; Saenghirunwattana et al., 2014; Satyanarayana, Arizaga, & Wypych, 2009; Wang, Cao, & Zhang, 2006; Wei, Fan, Huang, & Chen, 2006). Hydrophobic and electrostatic interactions are the driving forces behind the establishment of a network between fibers and proteins; these interactions improve the mechanical and water resistance properties of composite films (Jensen et al., 2015; Sun, Chen, Liu, Li, & Yu, 2015; Saenghirunwattana et al., 2014; Wang et al., 2006). There are few reports on the characterization and use of chemically treated soybean straw as reinforcing filler in SPI films.

The present study aimed to evaluate (1) how four different sequences of chemical treatment with alkali and bleaching affect the structure and composition of the soybean straw and (2) how the incorporation of treated fibers as reinforcing fillers into soy protein films influences the mechanical and permeability properties of the resulting film.

2. Materials and methods

2.1. Materials

Soybean straw was provided by Embrapa Soja (Londrina, Brazil). The residues were washed with distilled water and dried at 50 °C for 72 h in an oven with forced circulation (Q314M, Quimis, Brazil). The dried samples were then ground in a knife mill SL31 (Solab, Brazil) and sieved through 100-mesh sieves (Tyler series, 150 μm).

Solae® (Brazil) supplied the soy protein isolate (SPI). Glycerol was purchased from Sigma-Aldrich (Saint Louis, USP). Chemicals were obtained from Labsynth (Diadema, Brazil) (NaOH, $NaClO_2$ and H_2O_2) and Dinâmica (Diadema, Brazil) (CH_3COOH and $MgSO_4{\cdot}7H_2O$).

2.2. Chemical treatments of soybean straw

The soybean straw particles underwent four different chemical treatments, including treatment with alkali followed by a bleaching step. The concentrations of alkali and H_2O_2 and the temperature used during the treatments were based on previous results obtained for the treatment of achira fibers (Andrade-Mahecha et al., 2015). The conditions of the bleaching reaction involving $NaClO_2$ were the same as the conditions described by Campos et al. (2013). Fig. 1 summarizes the sequence of these treatments. According to the intensity of the reaction, the treatments were denoted severe or mild as follows:

(i) Severe: NaOH at 5% (T1) or 17.5% (T2) (w/v) at 90 °C for 1 h, repeated twice. The solution was brought to room temperature and rinsed to neutralization. The fibers were then bleached with aqueous 0.7% acetic acid and 3.3% sodium chlorite ($NaClO_2$) solution under agitation at 75 °C for 3 h.
(ii) Mild: NaOH at 5% (T3) or 17.5% (T4) (w/v) at 30 °C for 15 h. After this period, the solution was brought to room temperature and rinsed to neutralization. The resulting fibers were bleached in a mixture of 4% H_2O_2 (w/v) and 2% NaOH (w/v) at 90 °C for 3 h. $MgSO_4.7H_2O$ at 0.3% (w/v) was added as stabilizer. The solution was cooled to room temperature, and the fibers were filtered and washed with distilled water until neutral pH was achieved, followed by rinsing with ethanol and acetone. The final fibers were dried at 50 °C in an oven with air circulation.

2.3. Characterization of soybean straw

2.3.1. Chemical composition

Analysis of the cellulose, holocellulose (cellulose + hemicelluloses), and lignin content in the soybean straw was carried out before and after each treatment. The procedures were performed according to TAPPI T19 om-54 (TAPPI, 1991), TAPPI T 222 om-22 (TAPPI, 1999), and the methodology presented by Sun (2004).

2.3.2. Particle size distribution

The particle size distribution of untreated and chemically treated soybean straw was measured with a Beckman Coulter LS 13320 Laser Diffraction Particle Size Analyzer (Beckman Coulter, Miami, FL, USA). To this end, the powdered samples were sieved through 100-mesh sieves (Tyler series, 150 μm) and dispersed in ethanol under sonication for 5 min. The mean particle size and standard deviation (SD) were calculated by using the Beckman Couter software.

2.3.3. Scanning electron microscopy (SEM)

Soybean straw samples were mounted on aluminum stubs and coated with gold in a Bal-Tec SCD 050 sputtering system (Balzers, Liechtenstein). Images were obtained in a Zeiss EVO 50 (Cambridge, UK) scanning electron microscope at an accelerating voltage of 20 kV.

2.3.4. X-ray diffraction (XRD)

The effect of chemical treatment on the crystallinity of soybean straw was determined in a Shimadzu X-ray Diffractometer XRD-6000 (Shimadzu, Japan) with Cu kα radiation, at 30-kV voltage and 30-mA tube current. The measurements were carried out for 2θ values ranging from 5 to 40°, at a scan rate of 1° min^{-1}. To calculate the crystallinity index (I_{cr}) two different methods were used. One method consisted of estimating $I_{cr(S)}$ according to the Segal, Creely, Martin, and Conrad (1959) relation:

$$I_{cr(S)} = \frac{I_{002} - I_{am}}{I_{002}} x100 \quad (1)$$

where I_{002} is the intensity of the 002 lattice diffraction at 2θ = 22.8° (crystalline contribution), and I_{am} is the intensity of the diffraction at 2θ = 18° considering the amorphous diffraction. The other method uses a curve-fitting process to estimate individual crystalline peaks from the intensity of the diffraction profiles after subtraction of the baseline spectrum. The Origin 9.0 software was