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Properties of microcrystalline cellulose extracted from soybean hulls by reactive extrusion

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ABSTRACT

The objectives of this study were to produce microcrystalline cellulose (MCC) from soybean hulls (SH) employing a simple method based on reactive extrusion, and to characterize the product according its microstructure, morphology, crystallinity and thermal stability. MCC was obtained from SH after a two-step extrusion process; in the first step, the SH was extruded with sodium hydroxide (NaOH), followed by extrusion with sulfuric acid (H_2SO_4) in the second step. The MCC produced from SH by reactive extrusion was composed of short and rod shaped fibers, with a cellulose content of 83.79% and a crystallinity index of 70%. Reactive extrusion is an alternative and effective method for the production of MCC from lignocellulosic residues, and has the advantages of simplicity and was less polluting than conventional methods.

1. Introduction

Recently, increased interest in the conversion of lignocellulosic agro-industrial residues into marketable products without competition with the food supply chain has arisen (Alemdar & Sain, 2008; Cardenas-Toro, Alcazar-Alay, Forster-Carneiro, & Meireles, 2014; Flauzino Neto, Silvério, Dantas, & Pasquini, 2013). Soybean hulls are an important agro-industrial residue in Brazil, represent approximately 8% of the whole seed and are the main byproduct of the soybean processing industry, obtained from the initial processing steps (Gnanasambandam & Proctor, 1999). Soy is one of the principal agricultural products in the world with an annual production of approximately 86.1 million tons in Brazil for the 2014/2015 harvest (CONAB, 2014).

The chemical composition of soybean hull depends on the efficiency of the dehulling process, so the soybean hulls may contain variable amounts of cellulose (29–51%), hemicelluloses (10–25%), lignin (1–4%), pectins (4–8%), proteins (11–15%), and minor extractives (Mielenz, Bardsley, & Wyman, 2009; Rojas, Siqueira, Miranda, Tardioli, & Giordano, 2014; Yoo, Alavi, Vadlani, & Amanor-Boadu, 2011). The low lignin content makes this residue an attractive source for the extraction of cellulose and its derivatives.

Cellulose is the most abundant biopolymer in nature. It is a linear homopolymer of β-(1 → 4)-D-glucopyranose with a high degree of polymerization (DP) between 200 and 12,000 that depends on the origin of the cellulose. Cellobiose is the basic structural unit of cellulose, consisting of two units of 4-O-β-D-glucopyranosyl-β-D-glucopyranose. In nature, the cellulose molecular chains are biosynthesized and self-assembled into microfibrils that comprise crystalline and amorphous domains (Mohamad Haafiz, Eichhorn, Hassan, & Jawaid, 2013; Nishiyama, 2009). A single lignocellulosic fiber is a three dimensional, hygroscopic composite composed mainly of cellulose, hemicelluloses, and lignin with minor amounts of protein, extractives and inorganics (Ibrahim, El-Zawawy, Jütke, Koschella, & Heinze, 2013).

When cellulose from different sources (wood, cotton or lignocellulosic residues) is subjected to acid hydrolysis using diluted mineral acids, the amorphous fractions of the cellulose chains are removed, resulting in MCC (microcrystalline cellulose) or NCC (nanocrystalline cellulose) (Adel, El-Wahab, Ibrahim, & Al-Shemy, 2011; Mohamad Haafiz et al., 2013). There are several different ways of pretreating the lignocellulosic biomass, and the effect of the pretreatment has been described as a disruption of the cell-wall matrix including the connection between cellulose, hemicellulose and lignin, as well as the depolymerization and solubilization of the hemicellulose polymers (Ibrahim et al., 2013).

The conventional process for extracting MCC requires an excessive amount of reagents and causes water pollution, consequently increasing the manufacturing cost because of effluent treatment. Extrusion technology is a high-temperature, short-duration process with the advantage of high versatility and absence of effluents (Harper, 1981). Extrusion processing can provide a unique continuous reactor environment for a combination of thermo-mechanical and chemical treatment

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of the lignocellulosic biomass with higher throughput and solid levels (Lamsal, Yoo, Brijwani, & Alavi, 2010). Thus, this technology could be applied to the extraction of cellulose from lignocellulosic residues, employing a process with a lower moisture content than the conventional methods. In a patent, Hanna, Biby, and Miladinov (2001) reported the use of reactive extrusion for production of MCC from pure cellulose or lignocellulosic residues, however, no other reports in the literature exist for the use of reactive extrusion to obtain microcrystalline cellulose.

MCC has been largely used in food, cosmetic and medical industries as a water-retainer, a suspension stabilizer, a flow characteristics controller in the systems used for final products, and in polymer composites as a reinforcing agent (Ashori & Nourbakhsh, 2010).

The objectives of this study were to produce MCC from soybean hulls employing a simple method based on reactive extrusion, and to characterize the product according its microstructure, morphology, crystallinity and thermal stability.

2. Materials and methods

2.1. Materials

Soybean hulls were kindly provided by SL Alimentos (Mauá da Serra, Paraná, Brazil) and dried (45 °C) and milled to yield particles < 0.30 mm. Insoluble dietary fiber (IDF) were determined according to AACC method (AACC method 32-07). Cellulose was determined by Updegraff's (1969) method and the lignin content by the Technical Association of the Pulp and Paper Industry's (TAPPI T222 om-88, 1999) method. As the IDF fraction in grains is composed of cellulose, hemicelluloses and lignin (Chawla & Patil, 2010; Staffolo, Bevilacqua, Rodríguez, & Albertengo, 2012), hemicelluloses were calculated as IDF minus the cellulose + lignin content.

2.2. Methods

2.2.1. Reactive extrusion

The soybean hulls were subjected to a reactive extrusion process employing four different treatments, according to the reagents employed (Table 1) and, in all cases, the samples were prepared and allowed to stand for 1 h in sealed plastic bags before extrusion. The ESH sample (Table 1) was extruded without any reagent other than water, resulting in a final moisture content of 32% (g/g). The ESH-NaOH and ESH-H_2SO_4 samples (Table 1) were prepared by a single step extrusion process using NaOH and H_2SO_4, respectively; the reagents were dissolved in distilled water and mixed with the soybean hulls, resulting in a final moisture content of 32% (g/g). The MCC (microcrystalline cellulose) sample was obtained from the SH after a two-step extrusion process, in the first step, the SH was extruded with NaOH, followed by extrusion with H_2SO_4 in the second step.

All of the samples were extruded in a single screw extruder (AX Plastics, Diadema, SP, Brazil) with a screw diameter of 1.6 cm and a screw length/diameter ratio (L/D) of 40, with four heating zones and a matrix of 0.8 cm in diameter. The temperature in all zones was 110 °C and the screw speed was 100 rpm. After each extrusion step, all samples were subjected to five consecutive washings with distilled water at 80 °C (1.25 to 2.50 mL of water/g sample), then the samples were dried in a ventilated oven at 40 °C (035 Marconi MA — São Paulo, SP, Brazil) and milled to yield particles from 100 to 180 μm. The effluents obtained after washing the NaOH extruded materials were used to neutralize the effluents obtained after washing the H_2SO_4 extruded materials.

Table 1
Samples subjected to reactive extrusion to obtain MCC.

Sample	NaOH (%-g/g)	H_2SO_4 (%-g/g)	Final moisture (%-db)	Extrusion steps
ESH	–	–	32	1
ESH-NaOH	9.0	–	32	1
ESH-H_2SO_4	–	2	32	1
MCC	9.0	2	32	2

2.2.2. Characterization of MCC

2.2.2.1. Scanning electron microscopy (SEM). The SEM analyses were performed with a FEI Quanta 200 microscope (Oregon, USA). The dried samples were mounted for visualization on bronze stubs using double-sided tape. The surfaces were then coated with a thin gold layer (40–50 nm). All samples were examined using an accelerating voltage of 30 kV. The dimension of the fibers was calculated from SEM micrographs using an image analysis program (ImageJ 1.37v®), and a minimum of 30 measurements were performed for this determination.

2.2.2.2. X-ray diffraction. The crystallinity of each sample was investigated using X-ray diffraction (XRD). The samples were finely powdered (particles < 0.149 mm), and the analysis was performed using a PANalytical X'Pert PRO MPD diffractometer (Netherlands) with copper Kα radiation (λ = 1.5418 Å) under the operational conditions of 40 kV and 30 mA. All of the assays were performed with a ramp rate of 1°/min.

The relative crystallinity index (CI) was calculated using the Segal, Creely, Martin, and Conrad (1959), as follows: $CI\ (\%) = ([(I_{002} - I_{am})]/I_{002}) * 100$, where I_{002} is the intensity of the 002 peak (at approximately $2\theta = 20°–22°$) and I_{am} is the intensity corresponding to the peak at $2\theta = 18°$.

2.2.2.3. Fourier Transform-Infrared Spectroscopy (FT-IR). The pulverized and dried samples were then mixed with potassium bromide and compressed into tablets. The FT-IR analyses were carried out with a Shimadzu FT-IR — 8300 (Japan), which has a spectral resolution of 4 cm^{-1} and a spectral range of 4000–500 cm^{-1}.

2.2.2.4. Thermogravimetric analysis (TGA). Thermogravimetric analysis (TGA 50 — Shimadzu, Japan) was carried out under a nitrogen atmosphere (50 mL min^{-1}), and the samples (approximately 10 mg) were heated from 0 to 600 °C at a heating rate of 10 °C/min. The weight loss (%) was evaluated by measuring the residual weight at 600 °C.

2.2.2.5. Solid state NMR spectroscopy (^{13}C CP MAS NMR). Solid state ^{13}C spectra were recorded on a Bruker (Avance III) instrument operating at 400 MHz. A multinuclear probe (4 mm) and a zirconium oxide rotor were used with a Cross Polarized–Magic Angle Spinning (CP–MAS) unit.

2.2.2.6. Water sorption isotherms. Samples of the materials (0.5 g) were dried for 15 days over anhydrous calcium chloride. The samples were then placed over saturated salt solutions in separate desiccators, each with a specific level of relative humidity (RH) (11, 33, 43, 58, 75 and 90%) and held at 25 °C. Each sample was weighed at regular intervals, and when two consecutive equal measurements had been recorded, it was assumed that the equilibrium weight had been reached. The equilibrium moisture content was calculated as the mass increase of the dried sample at equilibration for each RH. The GAB (Guggenheim–Anderson-de Boer) model was used to fit the data from the sorption isotherms, and the monolayer values were calculated from the equations (Bizot, 1984). The GAB isotherm model can be expressed as follows: $M = m_0 CKa_w/(1 - Ka_w)(1 - Ka_w + CKa_w)$, where M is the equilibrium moisture content at a given water activity (a_w), a_w is RH/100, m_0 is the monolayer value (g water/g solids), and C and K are GAB constants. All tests were conducted in triplicate.