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Isolation and characterization of nanocrystalline cellulose from corn husk

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ABSTRACT

This study aimed at investigating the influence of the "reaction time" and the "fiber/acid ratio" on the properties of nanocrystalline cellulose isolated from corn husk, which was chosen because it is abundant and so far it has not been extensively investigated as a raw-material option to produce nanocrystalline cellulose. The results showed that corn husk can be used to produce nanocrystalline cellulose and also that reaction time affected the crystallinity index, particle size and thermal stability of the products. Additionally, an interaction between the reaction time and fiber/acid ratio on the crystallinity degree was observed. When dried by a spray-drying technique, the nanocrystalline cellulose aqueous dispersion produced agglomerates of particles with spherical and irregular shapes.

1. Introduction

The needs for materials and processes in accordance with the environmental requirements have motivated many researches for using raw material from renewable sources. Specifically speaking about lignocellulosic materials, it can be cited the extraction of nanofibers, whiskers and nanocrystalline cellulose from lignocellulosic residue for the value-added utilization [1].

The major component of the lignocellulosic materials is the cellulose that is recognized by its chemical and physical properties and also by its biodegradability and renewability characteristics. The isolation of nanocrystalline cellulose is dependent of the cellulosic raw-material used and also the process parameters. There is a vast type of lignocellulosic materials used for isolation of nanocrystalline cellulose, as garlic skin, oil palm, mulberry, sesame and rice husks [2–6]. The isolation process is usually performed in two stages. The first one may consist of successive mechanical and/or chemical treatments to remove complete or partially the non-cellulosic components. The second stage is a chemical treatment, generally acid hydrolysis, which the reaction parameters are acid specie, acid concentration, fiber/acid ratio, time and temperature [7].

Different from the majority of researches, which focus on the evaluation of lignocellulosic sources, and also considering the solid importance of the acid hydrolysis parameters to control and design the nanocrystalline cellulose characteristics, this study aims at investigating the influence of the "reaction time" and "fiber/acid ratio" parameters on the fiber dimension, crystallinity and thermal stability of the nanocrystalline cellulose. As a lignocellulosic source, the corn husk was used because it is an abundant sustainable resource.

2. Materials and methods

Materials: Corn husk (CH) was collected from the local markets. The other reagents were of analytical grades.

Isolation of nanocrystalline cellulose (NC): Mechanical treatment. CH was dried, chopped and milled and classified using a wire Tyler 35mesh.

Isolation of nanocrystalline cellulose (NC): Pretreatment. The milled CH was washed with distilled water (70 °C, 4 h, fiber/liquor ratio: 1:10) to remove soluble substances, and then filtered and dried at 60 °C in an air-circulating oven. The alkali treatment was performed to purify the cellulose by removing lignin and hemicellulose. In this treatment, the CH was treated with an alkali solution (5 wt% NaOH, fiber/liquor ratio: 1:20) at room temperature for 2 h under vigorous mechanical stirring. The bleaching process was performed to obtain α-cellulose. We carried it out by using a solution of H_2O_2 (24%) and NaOH (4%) (H_2O_2/NaOH ratio: 1:1) at 45 °C, for 2 h, with a fiber/solution ratio of 1:20.

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Isolation of nanocrystalline cellulose (NC): Acid hydrolyze. The isolation of NC was investigated by Factorial design 2\widehat2, with centerpoint. The experimental factors were reaction time (30 min and 120 min) and H_2SO_4/fiber ratio (10:1 and 30:1). The other process parameters – acid specie (H_2SO_4), acid concentration (60%w/w) and temperature (45 °C) – were remained constant. To perform the experiments, at about 10 g of blenched cellulose was added in the reaction vessel, containing the H_2SO_4 solution, a stirrer and a thermometer. At the end of the reaction time, the hydrolysis was stopped by adding cold water. The reactional media was discharged and the acid excess was removed by a sequence of centrifugation followed by ultrasonic treatments. Then, we submitted the dispersion to dialysis until the pH reached 6–7 and after that, we dried the NC by using Buchi Mini Spray Dryer B-290.

Characterization: The contents of α-cellulose, hemicellulose and lignin of CH were determined based on the quantitative methods [8]. The fiber dimension was measured by the dynamic light scattering (DLS, Zetasizer Nano S90, Malvern). X-ray diffraction (XRD) spectrum was recorded by a Rigadu Miniflex diffractometer at room temperature from 5° to 40°, using CuKα irradiation (1.54 Å) at 40 kV and 30 mA. The crystallinity index (CrI) was calculated by a deconvolution method using a curve-fitting process (Fityk 0.9.8 software). The thermal stability was determined by a thermogravimetric analysis (TGA, TA Instruments model Q500). About 20 mg of each sample was heated under a nitrogen atmosphere from 25 to 900 °C with rate of 20 °C min^{-1}. Fourier transform infrared (FTIR) spectroscopy was performed using a spectrometer (Perkin-Elmer Spectrum One). Samples were analyzed using attenuated total reflectance mode (ATR) in the range of 600–4000 cm^{-1}. The morphology of NC was investigated using a JEOL JSM-6510LV scanning electron microscope with electron bean acceleration of 10 kV on vacuum mode. The samples were affixed onto metal support stubs using carbon tape and then the samples were coated with gold.

Design of experiment (DOE): We performed the design analysis using the software Statistica 8. The analysis of variance (ANOVA) was performed using 95% of confidence level.

3. Results and discussion

Corn husk characterization: The chemical composition results showed that corn husk is a residue with low lignin content (7.9 ± 2.0%) and similar amounts of hemicellulose (37.5 ± 2.8%) and α-cellulose (35.3 ± 3.2%). As expected, the CrI (23.5 ± 2.5%) was lower than α-cellulose content in CH.

Nanocrystalline cellulose characterization: Besides the crystalline region, cellulose also has bundles of amorphous regions where the chains are randomly oriented in a spaghetti-like arrangement leading to a lower density in these domains [6,8]. Table 1 shows the CrI values for all experiments where we can observe a crystallinity interval from 81% to 92%, which is typical for nanocrystalline cellulose materials (CrI between 54% and 88%) [1]. Additionally, Fig. 1 illustrates the (a) X-ray diffractograms from Exp. 01 to Exp. 04 and (b) the response surface of CrI.

According to the DOE analysis, there is an interaction between *reaction time* and *H_2SO_4/fiber ratio* (*P*-value: 0.006). Furthermore, the *reaction time* (*P*-value: 0.018) had influence on the CrI. The cellulose acid hydrolysis is a process that involves the protonation of glycosidic oxygen by H+, followed by the break of the β-1,4-glycosidic bonds of the polymer by the water addition. Knowing that this process occurs preferably in the amorphous region of the cellulose; it is expected that the longer the extension of the hydrolyze reaction is; the higher the CrI will be too. Since we observed that the CrI practically stabilizes when the reaction time is higher than ~80 min and H_2SO_4/fiber ratio is higher than ~25 mL (Fig. 1b), it suggests that the hydrolysis reaction reached its end. Additionally, from the

Table 1
Experimental conditions used, crystallinity index and thermal properties of the reactions products.

Exp.	Experimental conditions		Crystallinity index %		Thermal properties		
	Reaction time (min)	H_2SO_4/fiber (mL/g)	Experimental value	Predict limits	Tonset (°C)	TMax (°C)	Residue (%)
01	30	10/1	81	81 ± 2	260	276	18
02	120	10/1	92	92 ± 2	195	230	14
03	30	30/1	89	89 ± 2	213	249	21
04	120	30/1	87	87 ± 2	187	223	14
05–08	75	20/1	87.3 ± 1.4	87 ± 2	193 ± 8	227 ± 8	20.5 ± 1.7

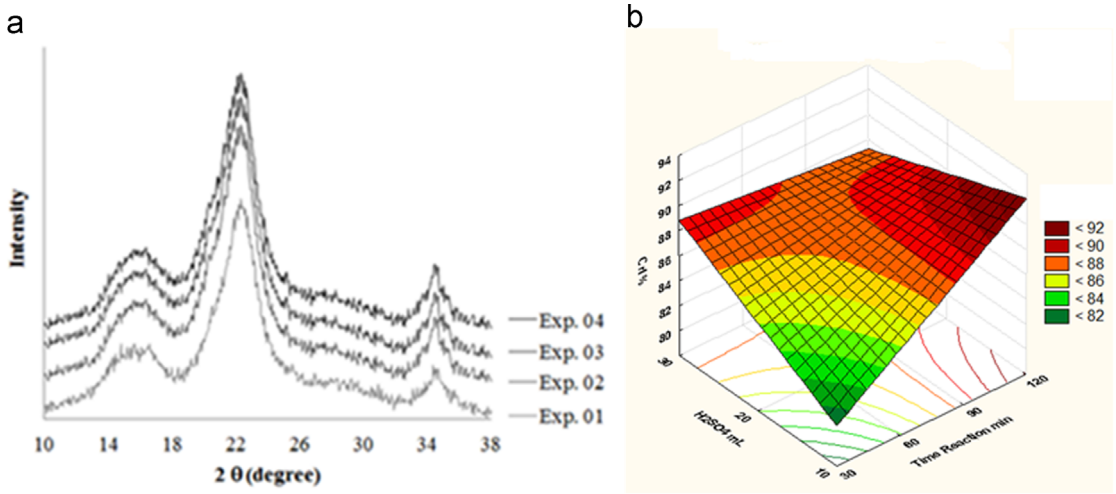

Fig. 1. (a) X-ray difratogramas of NC produced from Exp. 01 to Exp. 04 and (b) response surface of CrI.