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Extraction and process analysis of high aspect ratio cellulose nanocrystals from corn (Zea mays) agricultural residue

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ABSTRACT

Cellulose nanocrystals (CNCs) have long been an interest of researchers because of their exceptional mechanical properties as well as being sourced from natural, inexpensive, and renewable materials. In this work, maize CNCs (m-CNC) were obtained from maize (*Zea mays*) husk, which is an agricultural residue. This material is a common waste product from agricultural production in different parts of the world, and of potential value if CNCs with advantageous properties are extracted from them. Maize husk is a major agricultural waste in the United States and is used for erosion prevention or to produce insulating materials, paper, and other chemicals. Dried materials were alkali treated, bleached, and hydrolyzed to CNCs using sulfuric acid. The extracted CNCs were found to have a length of 940 ± 70 nm and width of 6 ± 2 nm, high aspect ratio of approximately 157, and increase the Young's modulus of natural rubber composites from 0.89 ± 0.15 MPa to 1.98 ± 0.73 MPa with the addition of 2 wt% m-CNCs. Other characterization techniques employed in this study are dynamic light scattering (DLS), conductometry, thermal gravimetric analysis (TGA), x-ray diffraction (XRD), and optical transmittance. Maize husks provided high aspect ratio cellulose Iβ CNCs, similar to tunicate CNCs, but with much lower processing required. Therefore, m-CNCs are more cost effective as shown by an economic evaluation. This study could provide assistance for producing CNC from one of the world's largest supply of agricultural waste.

1. Introduction

In 2013, the worldwide output of maize (*Zea mays*) was approximately 1 trillion tons as reported by the Food and Agricultural Organization of the United Nations, with the United States producing 350 million tons of that in 2013 (Faostat, 2015). The maize plant is comprised of the stalk, leaf, cob, and husk. The cob, which is the edible part of the plant, is 20% of the plant's mass and the remaining parts are agricultural waste. The husk of the maize plant is 10% of the plant's mass (Myers, 2017). For the 640 million tons of corn produced, a significant 45 million tons are maize husks (Pordesimo et al., 2005).

The husk of the maize is commonly thought of as a residue of maize harvesting, and is commonly used to prevent erosion (Padgitt, 2000) or to produce insulting materials, paper, and other chemicals (Gogerty, 1996). Work has been done to obtain fibers from maize husk for textile applications (Reddy and Yang, 2005). The use of maize husk as a source for nanocellulose crystals would provide a natural resource that is renewable, low cost, and a large source worldwide for cellulosic material, not just in the United States. By using an agricultural reside the environmental impact would be lessened and would conserve land by extracting cellulose from a food source.

The composition of the maize husk has been extensively characterized (Arroya Rosas, 2008; Duguid et al., 2009; Prado-Martínez et al., 2012) as well as the crystallinity, chemical composition, and some mechanical properties (Arroya Rosas, 2008; Reddy and Yang, 2005). Prado-Martínez, reported the following percentages of hemicellulose, α-cellulose, lignin, and ash in maize husk, respectively, 78.86, 43.14, 23, and 0.761(Prado-Martínez et al., 2012). For the chemical composition, Duguid and colleagues have stated that the maize husk contains 44.71% carbon, 0.35% nitrogen, and other trace amounts of phosphorous, potassium, calcium, magnesium, zinc, copper, manganese, and iron using National Renewable Energy Laboratory (NREL) protocols (Duguid et al., 2009).

Arroyo Rosas has studied the crystallinity, chemical composition,

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and the mechanical properties of maize husk nanofibers as a nanofiller in thermoplastic starch based composites. The crystallinity was reported to be 55.1% for nonhomogenized nanofibrils and 60.4% for homogenized samples using XRD, with Iα = 33.54% and Iβ = 66.54%, Iα = 19.96% and Iβ = 80.04%, for nonhomogenized and homogenized, respectively, measured by FTIR. The Young's Modulus of nanofibril based thermoplastic starch composites increased as the percentage of nanofibril increased from 15 GPa with 0% fibril to 40, 60, 100, 120 GPa for 3, 5, 10,20%, respectively (Arroya Rosas, 2008). While Reddy has reported that the crystallinity was approximately 48–50%, and had a crystal size of 3.2 nm (Reddy and Yang, 2005).

There have been previous studies conducted extracting nanocellulose crystals from other parts of the maize plant, such as the straw, which includes the husk (Reddy and Yang, 2005; Rehman et al., 2013), and the cob (Silvério et al., 2013). The maize straw includes any agricultural products that remain in the field following harvest including leaves, stalks, and husks (Hall, 2007).

The purpose of this study was to present a protocol for extract cellulose nanocrystals (m-CNCs) from a common agricultural waste, maize husk. CNCs were produced by acid hydrolysis following an alkali and bleaching treatment in order to isolate the cellulose from the other chemical compounds such as hemicelluloses and lignin. Acid hydrolysis degraded the amorphous component of the cellulose, while retaining the crystalline part, which conforms the CNCs. The composition, morphology, thermal stability, crystallinity, and mechanical properties were measured to see if there is potential to use CNCs derived from maize husk for applications in material science.

2. Methods and materials

2.1. Materials

Dried maize (*Zea mays*) husk was purchased from Industria Agricola Carredana S.A. de C.V. (Ciudad de Mexico, Mexico). Sodium chlorite ($NaClO_2$) and hydrochloric acid (HCl) was purchased from Sigma-Aldrich France Ltd. (Lyon, France). Sodium hydroxide (NaOH) was purchased from Carl Roth GmbH + Co. KG (Rheinhäfen Karlsruhe, Germany). Ethanol (C_2H_6O) and sulfuric acid (H_2SO_4) was purchased from Chimie Plus (Denicé, France). Reagent grade for analysis Toulene was purchased from Panreac Química (Barcelona, Spain). Cellulose nanocrystals (w-CNCs) were purchased from University of Maine Process Development Center (Orono, Maine, USA). The w-CNCs were extracted from wood pulp using sulfuric acid hydrolysis. All materials were used without any modification. Natural rubber (NR) latex was provided by Centrotrade Deutschland GmbH (Eschborn, Germany) with a solid content of ≈60 wt% and with spherical particles with an average diameter of 300 nm.

2.2. Methods

2.2.1. Bleaching of maize husks

Dried maize husk was milled following TAPPI standard T257 cm-85 (TAPPI, 1985) using a Retsch 2000 (Haan, Germany) with a 4 mm sieve. The dried, milled maize husk was placed in 2% NaOH solution, with a 1:20 solid to liquid ratio, overnight at ambient conditions to remove hemicelluloses and ash. The husk particles were removed by filtration and washed with deionized H_2O until the affluent was clear and had a pH ≈ 7. The washed fiber was placed in a three-neck flask, and per 10 g of dry mass of fiber, 110 mL of DI H_2O, 110 mL of acetic buffer solution, 110 mL of 1.7% $NaClO_2$ solution was added to create a suspension of liquid and fibers and heated at 80 °C for 2 h under continuous stirring. The pulp was filtered and washed with DI H_2O until a neutral pH was achieved.

2.2.2. Acid hydrolysis for maize cellulose nanocrystal (m-CNC) production

The bleached maize husk fibers were suspended in 34.4 mL of DI H_2O and 72.1 g of concentrated sulfuric acid, per 10 g of dried fiber mass, was added dropwise to the suspension under stirring at 15 °C. The suspension was heated to 45 °C once the sulfuric acid was added and stirred for 45 min. The hydrolysis was stopped with the addition of DI H_2O ice cubes added to the suspension. The suspension was centrifuged and washed until a pH of 4.5 was obtained. A neural pH was achieved by dialysis in DI H_2O with the water changed daily. The suspension was sonicated for 5 min (50% discontinuous, 50% power) and filtered through 1 μm nylon mesh following dialysis. The filtrate was stored in the refrigerator and 3 drops of chloroform was added to prevent denaturation.

2.2.3. Determination of extractives, acid insoluble lignin, holocellulose, hemicellulose and cellulose content

Extractives were determined according to TAPPI standard T207 cm-97 (TAPPI, 1993b), using ethanol-toluene as the extraction media. The extractives removed from lignocellulosic matter mainly consist of low molecular weight carbohydrates, salts, waxes, fats, resins, and non-volatile hydrocarbons. To determine this, 4.0 ± 0.1 g of milled maize husk was placed in a previously tarred extraction thimble and placed in a Soxhlet system. 150 mL of 2:1 ethanol-toulene was used to extract for 6–8 h under reflux. The extraction thimble was then dried at 105 ± 3 °C for 24 h. Following cooling, the thimble was weighed. The now extractives-free sample was placed in a desiccator for further analysis.

Acid insoluble lignin content was determined using TAPPI standard T222 om-98 (TAPPI, 1998). 1.0 ± 0.1 g of moisture and extractive free sample was mixed with 15 mL 72% sulfuric acid and kept at 20 °C for 1 h. Followed by the addition of 575 mL of DI H_2O was added and kept under reflux for 4 h. The insoluble fraction was filtered and washed until pH ≈ 7. The sample was dried for 24 h at 105 °C and was weighed.

Holocellulose content was determined using a protocol established by Wise et al. (Wise et al., 1946). 2.5 g of extractive free sample was mixed with 80 mL hot water and kept at 70 °C. 0.5 mL glacial acetic acid and 2.6 mL of 25% $NaClO_2$ were added each hour for 6–8 h.

Cellulose and hemicellulose determination was determined by adding 2 g of a moisture free holocellulose sample to 10 mL of 17.5% NaOH. 5 mL of 17.5% NaOH were added every 5 min until a final volume of 25 mL was achieved. Following 30 min, 33 mL of DI H_2O was added and stirred for 1 h. The recovered fraction as washed and filtered with 100 mL 8.3% NaOH and then twice with DI H_2O. 15 mL of 10% acetic acid was added and washed until pH ≈7. The dried sample was weighed (Rowell, 1983).

Ash content was determined following TAPPI T211 om-93, which is based on the mass of the material following combustion at 525 °C for 3 h (TAPPI, 1993a).

2.2.4. Preparation of nanocomposite films

Nanocomposite films were prepared following the protocol of Mariano and colleagues (Mariano et al., 2016). Suspensions of m-CNC and w-CNC were sonicated for 5 min. CNCs were added to a suspension of 5 g of natural rubber latex (NR) with varying amounts (0.1, 0.5, 1, 2 wt%). These amounts correspond to below the percolation threshold of the m-CNCs (0.1 wt%), at the percolation threshold (0.5 wt%), and above (1, 2 wt%) (Mariano et al., 2014). The suspensions of NR latex and CNCs were agitated for 6 h to increase homogeneity, followed by casting on aluminum plates at 30 °C for 24 h. The dried nanocomposites were conditioned for 4 days at 25 °C, 50% RH before mechanical testing (Tables 1–3).

2.3. Characterization of CNCs

2.3.1. Conductometric titration

The sulfate content of hydrolyzed m-CNCs was determined by conductometric titration. Samples of m-CNC (10 mg) were added to