Food Research International 50 (2013) 121–128

Contents lists available at SciVerse ScienceDirect

Food Research International

journal homepage: www.elsevier.com/locate/foodres

Morphological, crystalline, thermal and physicochemical properties of cellulose nanocrystals obtained from sweet potato residue

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ARTICLE INFO

Article history:
Received 26 June 2012
Accepted 10 October 2012

Keywords:
Cellulose nanocrystals
Morphology
Crystalline
Thermal
Physicochemical

ABSTRACT

Sweet potato residue (SPR), a by-product of sweet potato starch industry, was used as starting material to prepare cellulose nanocrystals. The method of sulfuric acid hydrolysis accompanied with ultrasonication and homogenization was used to prepare cellulose nanocrystals. The morphological, crystalline, thermal, and physicochemical properties of the cellulose nanocrystals were studied. SEM and TEM images showed spherical or elliptic granules of cellulose nanocrystals with sizes ranged from 20 to 40 nm. XRD analysis indicated that the cellulose nanocrystals retained the cellulose I crystalline structure, with a crystallinity of approximately 72.53%. TGA curves showed that the decomposition temperature of nanocrystals was decreased. These results showed that cellulose nanocrystals were successfully obtained from SPR and might be potentially applied in various fields, such as pharmaceutical and food additives, bio-nanocomposites, packaging, etc.

1. Introduction

Cellulose is one of the most important and abundant biopolymers in nature, which is a linear syndiotatic homopolymer of β-$(1\rightarrow4)$-glycosidic bond linked *D*-anhydroglucopyranose (Kim, Yun, & Ounaies, 2006). It is widely used because of its characteristics, such as availability, biocompatibility, biological degradability, and sustainability. Cellulose is generally known to be fibrillar, crystalline (Saxena & Brown, 2005) and exhibits its unique structural hierarchy of different biological origin. The cellulose fibrils play an important role in contributing to the high strength of plant cell walls (Zuluaga et al., 2009). They are composed of nanofibrils with a diameter that ranges from 2 to 20 nm, and a length of more than a few micrometers. These nanometer-sized single crystals of cellulose, which are commonly referred to as nanofibrils, whiskers or nanocrystals (Eichhorn et al., 2010; Siró & Plackett, 2010), can be obtained from various sources such as natural fibers (Abe, Iwamoto, & Yano, 2007; de Morais Teixeira et al., 2010); agro-industrial by-products (Alemdar & Sain, 2008; Chen, Liu, Chang, Cao, & Anderson, 2009; Rosa et al., 2010), and sea animals (Samir, Alloin, & Dufresne, 2005). These agro-industrial by-products, such as unripe coconut husk, wheat straw, soy hulls, pea hull fiber and cassava bagasse, were regarded as raw material to extract cellulose nanocrystals since they are basically constituted of cellulose fibers and some other component. Because these agro-industrial by-products are basically constituted of cellulose fibers and some other component, all of them are investigated as raw material to extract cellulose nanocrystals.

The extraction of cellulose whiskers from renewable sources has gained more attention in recent years due to their exceptional physicochemical and mechanical properties, large specific surface area, low cost and environmental benefits (Medeiros, Mattoso, Bernardes-Filho, Wood, & Orts, 2008). Cellulose nanocrystals were widely used as reinforced nanocomposites, foams, aerogels (Svagan, Samir, & Berglund, 2008), optically transparent functional materials (Nogi, Iwamoto, Nakagaito, & Yano, 2009) and oxygen-barrier layers (Fukuzumi, Saito, Kumamoto, & Isogai, 2009). Some applications of cellulose nanocrystals had been reported, such as fabrication of polymethylmethacrylate/cellulose nanocrystal composites (Cao, Dong, & Li, 2007) and reinforcement components in polyethylene nanocomposites (de Menezes, Siqueira, Curvelo, & Dufresne, 2009; Roohani et al., 2008).

Several methods have been used to obtain highly purified nanocrystals from cellulosic materials. These methods include chemical method, which was mainly carried out by acid hydrolysis (Bondeson, Mathew, & Oksman, 2006; Elazzouzi-hafraoui et al., 2008) and enzyme-assisted hydrolysis (Henriksson, Henriksson, Berglund, & Lindström, 2007; Pääkkö et al., 2007), mechanical treatments, such as high-pressure homogenizing (Li et al., 2009; Nakagaito & Yano, 2008); grinding (Abe & Yano, 2010; Nogi et al., 2009) and ultrasonication (Wang & Cheng, 2009), as well as a combination of two or several of the aforementioned methods. All these methods lead to different types of nanocrystal materials, depending on the cellulose raw material and its pretreatment, and more importantly, depending on the disintegration process itself.

Sulfuric acid hydrolysis is a well-known process which is used to prepare cellulose nanofibers, because the method is able to disintegrate amorphous regions, introduce negative charges to nanopartical surfaces

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Abbreviations: SPR, sweet potato residue; SEM, scanning electron microscopy; TEM, transmission electron microscopy; XRD, X-ray diffraction; TGA, thermogravimetric analysis; OHC, oil holding capacity; WC, welling capacity; WHC, water holding capacity.

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http://dx.doi.org/10.1016/j.foodres.2012.10.013

(Beck-Candanedo, Roman, & Gray, 2005), and form stable nanocrystal suspensions. Ultrasonic technique has been also successfully used to isolate cellulose nanocrystals in recent years. Ultrasonication is the application of sound energy to physical and chemical systems. Ultrasound energy is transferred to cellulose chains through a process called cavitation, which refers to the formation, growth, and violent collapse of cavities in water (Filson & Dawson-andoh, 2009). Then, the ultrasonic impact can gradually disintegrate the micron-sized cellulose fibers into nanocrystals. High-pressure homogenizing can further decentralize and reduce the size of the cellulose nanocrystals. The homogenization of cells after fibrillation induces the total disruption of the cells and the release of cellulose nanocrystals in the medium. After homogenizing, the cellulose whisker suspension did neither precipitate nor flocculate, and exhibited the rheological property of pseudo plasticity (Bendahou, Kaddami, & Dufresne, 2010).

Sweet potato is a root crop largely grown in different countries such as China. It is a starch-rich material, containing proteins, lipids, fibers and sugars (Waramboi, Dennien, Gidley, & Sopade, 2011). The industrial exploitation of sweet potato starch involves the elimination of soluble sugars and the separation of most fibers resulting in a purified starch and a solid residue called sweet potato residue (SPR).

The SPR is mainly composed of residual starch and cellulose fibers (Bailey, Ramakrishna, & Kirchhof, 2009). After removing the residual starch, the content of cellulose fibers is about 75 wt.%. However, mass utilization of SPR has not been carried out yet. Most of them are wasted for agro-wastes or animal feed. The objective of this work was to investigate the preparation of cellulose nanocrystals from SPR by the method of sulfuric acid hydrolysis accompanied with ultrasonication and homogenization. Their morphological, crystalline, thermal and physicochemical properties were also investigated.

2. Materials and methods

2.1. Material

The SPR was acquired from Company Limited of Sichuan Guangyou Shuye (Sichuan, China). It was washed by distilled water at room temperature to remove some starch and impurities in the residue. After pretreatment, the residue was dried at 80 °C for 8 h and smashed. Then the residue was hydrolyzed by 0.6% (m/v) α-amylase (10 mL/g) at 60 °C for 45 min with the ultrasonic processor (power 105 W) to remove the starch. Next, the samples were treated in 7% (m/v) sodium hydroxide at 70 °C for 90 min and centrifuged at 4500 rpm for 10 min in order to leach hemicellulose and pectin. After that, the residual product was washed thoroughly with deionized water and bleached by 3% (v/v) hydrogen peroxide for 2 h at 70 °C, to remove the lignin residues (Fang, Sun, & Tomkinson, 2000). The bleached fibers were centrifuged (4500 rpm, 10 min) and washed repeatedly by distilled water and subsequently dried by oven (60 °C, 8 h), that was the raw cellulose. All chemicals used are of analytical grade.

2.2. Preparation of cellulose nanocrystals

Cellulose nanocrystals were obtained from cellulose fibers in SPR. In order to prepare the cellulose nanocrystals, the raw cellulose was micronized to pass through a 180-mesh screen, and the micropowder of cellulose was set as microcrystalline cellulose. The microcrystalline cellulose was dispersed in 65% (w/w) sulfuric acid solution (10 mL/g) into a flask (Rosa et al., 2010), and then placed in an ultrasonic equipment (Numerical control ultrasonic cleaning processor KQ 3200DB, Kunshang City, China). Hydrolysis was performed at 55 °C with the ultrasonic power of 120 W for 120 min. To avoid the increase in the temperature of solution, ice was put in the reactor during the process of sonication. Suspensions were diluted five-fold to stop the hydrolysis reaction. The suspension was centrifuged at 11,000 rpm for 15 min to separate the nanocrystals in the suspension. The nanocrystals were washed with distilled water and centrifuged at 11,000 rpm for 15 min. The process was repeated three times. Then, the suspension was submitted to neutralizing with 2% (m/v) sodium hydroxide until the pH of the suspension reached a constant value of 7.0. To further decentralize and reduce the size of the cellulose nanocrystals (Bai, Holbery, & Li, 2009), the suspension of cellulose nanocrystals was processed through a high-pressure homogenizer(GYB60-6s, Shanghai City, China) with a pair of Z-shaped interaction chambers under an operating pressure of 300 MPa (Lee, Chun, Kang, & Park, 2009). After that, the suspension became more settled and colloid, and was collected for further characterization. The concentration of suspension was about 0.5 wt.%.

2.3. Chemical composition measurement

The chemical composition of raw cellulose, microcrystalline cellulose and cellulose nanocrystals was measured according to the standard of the Technical Association of Pulp and Paper Industry (TAPPI). The holocellulose (cellulose + hemicelluloses) content was determined according to the method described in TAPPI T19m-54. The α-cellulose content of the fibers was determined by further NaOH treatment of the fibers to remove the hemicelluloses. The difference between the values of holocellulose and α-cellulose gives the hemicellulose content of the fibers. Lignin content was analyzed by reaction with sulfuric acid using the standard method recommended in TAPPI-T222 om-88. A minimum of three samples from each material was tested, and the averaged values were obtained.

2.4. Morphological properties of cellulose nanocrystals by SEM and TEM

2.4.1. Scanning electron microscopy (SEM)

The suspensions of the cellulose fibers were subjected to freeze-drying. The obtained powders were coated with gold using a vacuum sputter coater and being photographed with S-3000N and S-4800N scanning electron microscope (Hitachi, Japan).

2.4.2. Transmission electron microscopy (TEM)

Drops of diluted (0.001 w/w%) cellulose nanocrystal suspensions were placed on a glow-discharged carbon-coated TEM copper grid. The excess liquid was absorbed by a piece of filter paper. After the specimen has been completely dried, it was introduced into the electron microscope. The sample was viewed using an H-7500 transmission electron microscopy (Hitachi, Japan) at an acceleration voltage of 75 kV.

2.5. X-ray diffraction analysis

The X-ray diffraction (XRD) patterns were obtained for the samples with an X-ray diffractometer (XD-3, Beijing PGENERAL Company, China) using Ni-filtered Cu $K\alpha$ radiation ($\lambda = 1.5406$ Å) at 36 kV and 20 mA. Scattered radiation was detected in the range of $2\theta = 10$–35°, and the proportional counter detector was set to collect data at a scan rate of 1°/min with increments of 0.01° for 2θ values. The crystallinity index (C_I) was calculated from the heights of the 200 peak (I_{002}, $2\theta = 22.6°$) and the intensity minimum between the 200 and 110 peaks (I_{am}, $2\theta = 18°$) using the Segal method (Seagal, Creely, Martin, & Conrad, 1959) (Eq. (1)). I_{002} represents both crystalline and amorphous material, whereas I_{am} represents the amorphous material.

$$C_I(\%) = \left(1 - \frac{I_{am}}{I_{002}}\right) \times 100 \tag{1}$$

2.6. Thermal stability

The thermal stabilities of samples were characterized using simultaneous thermal analyzer (Q600, New Castle, USA) filled with a