Carbohydrate Polymers 180 (2018) 122–127

Contents lists available at ScienceDirect

Carbohydrate Polymers

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

Research Paper

Preparation and characterization of starch nanocrystals combining ball milling with acid hydrolysis

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ARTICLE INFO

Keywords:
Waxy maize starch
Starch nanocrystals
Ball milling
Acid hydrolysis
Relative crystallinity
Yield

ABSTRACT

Waxy maize starch was mechanically treated with a planetary ball mill. X-ray diffraction analysis was employed to determine the optimal ball milling time. After ball milling, the pretreated starch was hydrolyzed with H_2SO_4. The hydrolysates were obtained and their relative crystallinity, morphology, and particle size were estimated by X-ray diffraction analysis, atomic force microscopy, and nanoparticle size analyzer, respectively. The results revealed that it is possible to obtain starch nanocrystals (SNCs) after a combination of ball milling and 3 days of H_2SO_4 hydrolysis with a yield of 19.3 wt% with a shape similar to those acquired by the conventional procedure after 5 days of sulfuric acid hydrolysis, with a yield of 15.8 wt%. Round-edge SNCs with an average diameter of approximately 31 nm were observed. The results revealed that by controlling some parameters, certain mechanical processing methods considered unsuitable could also be applied to the preparation of SNCs.

1. Introduction

As is widely known, starch is second only to cellulose in global natural abundance. Additionally, as a result of its renewability, biodegradability, biocompatibility, and low cost, starch is broadly used in industries such as in food, cosmetics, and pharmaceuticals (Desai, Bera, Singh, & Mondal, 2017; Jong, Dae, & Jong-Yea, 2017; Le Corre & Angellier-Coussy, 2014; Sun, Li, Dai, Ji, & Xiong, 2014). Starch nanocrystals (SNCs) are the preserved crystalline structures arising from the destruction of the amorphous structures of starch grains by acid hydrolysis (Dufresne, Jeanyves Cavaillé, & Helbert, 1996; Herrera, Vasanthan, & Chen, 2017; Putaux, Molina-Boisseau, Momaur, & Dufresne, 2003). SNCs are nanometric particles and have different shapes according to different starch sources and preparation methods. In previous works, SNCs obtained from waxy maize were crystalline nanoplatelets around 5–7 nm thick with a length of 20–40 nm and a width of 15–30 nm (Putaux, Molina-Boisseau, Momaur, & Dufresne, 2003). Nevertheless, other publications have reported different SNC sizes and morphologies (below 40 nm (Jong et al., 2017), 50 nm (Garcia, Ribba, Dufresne, Aranguren, & Goyanes, 2009), 70–100 nm (Namazi & Dadkhah, 2010), and 50–130 nm (Romdhane, Aurousseau, Guillet, & Mauret, 2015) for waxy maize starch with round edges). Initially, applications of highly crystalline nanoscale SNCs derived from different natural starches were mostly as a reinforcing nanophase in nanocomposites (Lin, Huang, & Dufresne, 2012; Pereda, Kissi, & Dufresne, 2014). However, with a large specific surface area, total surface energy, and a highly reactive surface with quantities of hydroxyl groups (Lin, Huang, Chang, Feng, & Yu, 2011), SNCs also have immense potential as drug carriers (Bakrudeen, Sudarvizhi, & Reddy, 2016; Lin, Huang, Chang, Feng, & Yu, 2011), blocking agents (Angellier, Molina-Boisseau, Lebrun, & Dufresne, 2005; Duan, Sun, Wang, & Yang, 2011; Garcia et al., 2009; Garcia, Ribba, Dufresne, Aranguren, & Goyanes, 2011), particle stabilizers (Haaj, Thielemans, Magnin, & Boufi, 2014; Li, Li, Sun, & Yang, 2014), and purifying agents (Alila, Aloulou, Thielemans, & Boufi, 2011; Desai, Bera, Singh, & Mondal, 2017).

Actual utilization of SNCs obtained by the conventional acid hydrolysis method are limited because the traditional preparation method is time consuming and results in low yield (5% waxy maize starch suspension with 2.2 N HCl for 6 weeks in 36 °C with 0.5% yield (Putaux, Molina-Boisseau, Momaur, & Dufresne, 2003), 14.69% waxy maize starch suspension with 3.16 M H_2SO_4 for 5 days in 40 °C with 15.7 wt% yield (Angellier, Choisnard, Molina-Boisseau, Ozil, & Dufresne, 2004). More recently, many scientists have been devoted to improving SNC preparation methods. LeCorre, Vahanian, Dufresne, and Bras (2012) developed an enzymatic pretreatment of starch to reduce the acid hydrolysis duration. In comparison with the routine kinetics of hydrolysis for preparing SNCs, preprocessed starch was hydrolyzed much more quickly. The regular final yield was reached in 45 h (LeCorre et al., 2012). Using ultrasound-assisted hydrolysis methods, SNCs have been prepared in reduced time or with enhanced yield. Kim et al. prepared SNCs with high yield (78%) and crystallinity by 4 °C hydrolysis for 6 days followed by ultrasonication (Kim, Lee, Kim, Lim, & Lim, 2012). Amini and Razavi treated corn starch with ultrasound and sulfuric acid hydrolysis simultaneously. This method produced nanocrystals within 45 min with particle sizes smaller than 100 nm and up

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http://dx.doi.org/10.1016/j.carbpol.2017.10.015
Received 27 July 2017; Received in revised form 30 September 2017; Accepted 3 October 2017
Available online 05 October 2017
0144-8617/

to 21.6% yield (Jiranuntakul et al., 2013). However, these recently proposed methods are costly or rely on customized apparatuses for large-scale production.

Acid hydrolysis consists of two stages: the first stage is a fast step due to hydrolysis of the amorphous regions; the second stage is a slow step due to hydrolysis of the crystalline regions (Kim et al., 2012). Atomic force microscopy (AFM) and transmission electron microscopy (TEM) images revealed that the surfaces of most starch granules were rough and consisted of a few small pores (Huang et al., 2014; Jiranuntakul et al., 2013). In the initial stage of hydrolysis, before the hydrogen ions diffuse to the internal starch granules from the surface pores, the outer surface is attacked primarily. As a result, the hydrolysis rate is limited in the first stage. In addition, according to previous research, SNCs were generated after only one day of sulfuric acid hydrolysis and those early-stage SNCs were slowly hydrolyzed thereafter (LeCorre, Bras, & Dufresne, 2011). The yield of SNCs was reduced in this process. Therefore, we need to develop a method to simultaneously damage the granule structures and protect the crystallinity.

Ball milling is a cost-efficient and environmentally friendly physical processing method that has been proven capable of changing starch properties (Li, Niu, Zhang, Zhao, Xiong, & Xie, 2017; Lin, Qin, Hong, & Li, 2016). However, most of the published works focused on the influences of ball milling on starch physicochemical properties (Huang, Xie, Chen, Lu, & Tong, 2008). Meanwhile, the ball milling time was quite long (several to dozens of hours), bringing about loss of starch crystallinity. To the best of our knowledge, there is no published work concerning the preparation of starch nanocrystals by combining ball milling with acid hydrolysis.

The objective of present study was to prepare SNCs with higher yield in less time. In this paper, we report the application of ball milling to damage the starch granule structures. Raw waxy maize starch was mechanically treated with a planetary ball mill. The basic principle of ball milling was to protect the crystalline structures from damage. Afterward, the pretreated starch was hydrolyzed by sulfuric acid.

2. Materials and methods

2.1. Materials

Waxy maize starch was purchased from Shangdong Fuyang Biotechnology Co., Ltd. (Shangdong, China). The waxy maize starch contained 0.25% protein, 0.11% ash, and 13.5% moisture, with amylopectin content 95%. All other chemicals and reagents were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China), and were of analytical grade unless stated otherwise.

2.2. Ball milling of waxy maize starch

To equably mix the starch and acquire ball-milled starch with uniform granularity distribution and degree of fragmentation, wet ball milling was adopted (anhydrous ethanol served as the solvent) (Zhang, Ding, Ndeurumi, Wang, & Feng, 2015).

The ball milling treatment was carried out with a QM-3SP4 ball mill (Nanjing University Instrument Plant, Jiangsu, China). Waxy maize starch (10 g, dry basis) was placed in a 50-mL mill pot, and 30 mL anhydrous ethanol was added to disperse the starch. The operation was performed at a rolling speed of 300 rpm for 15, 30, 45, 60, 75, and 90 min. The ball-milled starch was filtered and dried at 40 °C until a constant weight was reached.

2.3. Acid hydrolysis of ball-milled starch

Acid hydrolysis was implemented according to the method of the previous study with minor modification (Angellier et al., 2004; Wei et al., 2016). Ball-milled starch (100 g, dry basis) with different ball milling times and raw waxy maize starch (100 g, dry basis) were mixed with 1000 mL of 3.16 M of sulfuric acid solution, respectively, and placed at 40 °C for 5 days under constant stirring at 200 rpm. Every day, three 50-ml suspensions were taken from each set of experiments and washed in distilled water by successive centrifugations until a constant pH of the supernatant was obtained. The precipitated starch hydrolysates were then freeze-dried. The yield of hydrolysis was calculated as the percent ratio of the hydrolysate solids based on the initial starch solids.

2.4. Particle size distribution and zeta potential measurement

Particle size distribution and zeta potential measurement of samples were performed at 20 °C using a Zetasizer Nano ZS90 (Malvern Instruments Ltd, Britain) after 3 min homogenization using a Scientz-IID (Ningbo Scientz Biotechnology Co., Ltd., Ningbo, China). The pH of suspensions was approximately neutral. A value of 1.35 was regarded as the refractive index and the data were the means of at least three replicates.

2.5. Degree of relative crystallinity

X-ray diffraction (XRD) of different samples was measured using an X'Pert PRO (PANalytical B.V., Netherlands) operating at divergence slit, generator voltage, and tube current of 0.38 mm, 40 kV, and 40 mA, respectively. The measurement was performed in the diffraction angle range of 5–40° at a step length of 0.02. Relative crystallinity was calculated based on the two-phase method proposed by Lopez-Rubio, Flanagan, Gilbert, and Gidley (2008).

2.6. Morphology

Scanning electron microscopy (SEM) was implemented using a Hitachi SU-8010 (Hitachi, Japan) at an accelerating voltage of 30 kV. A drop of the suspension (0.01%) was deposited onto copper grids coated with carbon support film, and then dried at room temperature. Before observation, the samples to be tested were coated with gold.

Atomic force microscopy (AFM) was performed using a Bruker Dimension Icon (Bruker, Germany) with tapping mode. A drop of starch hydrolysates (0.01%) was spread onto a mica substrate and dried at room temperature overnight. NanoScope Analysis was used for offline data analysis.

2.7. Statistical analyses

Experimental results were performed using ORIGIN 9.0 (OriginLab Inc., Massachusetts, USA). Data were presented as means ± standard deviations ($P < 0.05$).

3. Results and discussion

3.1. Ball milling treatment

Fig. 1 presents the X-ray diffraction (XRD) patterns of pretreated starch with different ball milling times (0, 15, 30, 45, 60, 75, 90 min) after smoothing. Ball milling-15 represents that the raw starch was subjected to a ball mill treatment for 15 min and other annotations are similar. The relative crystallinity (RC) of starch samples in relation to ball milling times is illustrated as Fig. 2. As it can be seen in Fig. 1, for all the samples including raw starch and ball-milled starch, there are two weak peaks at 10° and 11.5°, a strong peak at 15°, double strong peaks at 17° and 18°, and a strong peak at 23.5°, assigned with typical peaks of A-type crystalline (Wang & Zhang, 2008). However, when the relative crystallinity (Fig. 2) was calculated using the XRD patterns from Fig. 1, the differences were revealed. With an increase of ball milling time, relative crystallinity of samples decreased gradually. It is worth noting that before the ball milling time reached 30 min, the