Biotechnology Reports 3 (2014) 54–59

Contents lists available at ScienceDirect

Biotechnology Reports

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

Effect of ball-milling on the physicochemical properties of maize starch

Shenghua He [a], Yibing Qin [b], Elfalleh Walid [c], Lin Li [a], Jie Cui [a], Ying Ma [a,*]

[a] School of Food Science and Engineering, Harbin Institute of Technology, Harbin 150090, China
[b] Shanghai Entry-Exit Inspections and Quarantine Bureau, Shanghai 200135, China
[c] Institut des Régions Arides de Médenine, Laboratoire d'Aridoculture et Cultures Oasiennes, 4119, Tunisia

ARTICLE INFO

Article history:
Received 17 March 2014
Received in revised form 12 June 2014
Accepted 16 June 2014
Available online 20 June 2014

Keywords:
Ball-milling
Maize starch
Physicochemical properties

ABSTRACT

The effect of ball-milling on physicochemical properties of maize starch was evaluated. Results found that the cold water solubility (CWS) of maize starch was positively correlated with the time of milling up to 3 h. There was no significant influence of using a ceramic pot versus a stainless steel pot on CWS. However, following 5 h of ball-milling CWS increased quite dramatically in the ceramic pot (72.6%) and in the stainless steel pot (70.7%), as compared to the untreated maize starches (2.9%). In addition, as CWS increased, the regions of amorphism enlarged at the expense of the crystalline regions, resulting in a change from the native starch state (oval with a smooth surface) to having more of a rough, abrasive surface. Finally, the transparency of the starch increased as CWS increased and that the syneresis of freeze–thawed ball-milled maize starch also increased with an increase in the number of freeze–thaw cycles.

1. Introduction

Maize starch is one of the most valuable ingredients in the production of food, comprising more than 80% of the starch market worldwide [1]. However, their application is actually limited due to their poor functional physicochemical properties that result in a lack of cold water solubility (CWS) and low viscosity. These physicochemical properties of maize starch are affected by its structure, such as the relative crystallinity, ratio of amylose to amylopectin, surface morphology, and granular particle diameter [2–4]. Proper processing of starches is required to alter their structural status. Conventional treatments involve heating the starches in slurry. However, this method causes gelatinization, which seriously influences their application due to the resultant starches becoming grainy and poor tasting. Therefore, novel techniques for preparing granular cold water soluble starches is thought to be one of the best ways for expanding the industrial application of modified starches. To date, several technologies have been developed for producing cold water soluble (CWS) starches that retain their granular integrity, such as heating starches in aqueous, high temperature and pressure conditions, and alcoholic–alkaline treatments [5–7], each exhibiting variable levels of efficacy.

Ball-milling refers to the use of friction, collision, impingement, shear, or other mechanical actions to modify the structure and properties of starch granules [8]. Treatment of starch using ball-milling is low cost and environmental friendly. As a physical method of modification, ball-milling has been used to effectively decrease the relative crystallinity and increase the solubility and digestibility of starch. However, there is currently no published information available on the effect of ball-milling on the physicochemical properties of maize starch. Therefore, the objective of this study was to investigate the effect of processing maize starch with ball-milling treatment on the CWS, crystal structure, granule shape, transparency, and freeze–thaw stability of maize starch. These studies provide a theoretical basis for the industrial production of granular CWS starch.

2. Materials and methods

2.1. Raw materials

Native maize starch was obtained from the Huanglong Food Industry (Changchun Province, China); the amylose content of the maize starch was 27.9%.

2.2. Ball-milling methodology

For these experiments, we used a QM-DK low temperature planetary ball-mill (Nanda, Nanjing, China) equipped with an insulation cover and an air cooling machine that used R22 as a cryogen. The weight ratio of starch to balls (Φ10 mm:Φ20 mm = 2:1) in the ceramic (500 mL) and stainless steel pots (500 mL) were 15:1 and 20:1 (w:w), respectively. Each container was filled to approximately one third of their capacity. During

* Corresponding author. Tel.: +86 451 86282903; fax: +86 451 86282906.
E-mail address: maying@hit.edu.cn (Y. Ma).

http://dx.doi.org/10.1016/j.btre.2014.06.004

milling, the balls were rotated horizontally at a constant milling speed of 500 rpm for up to 5 h. The ball-milling rotational direction was changed every 30 min. The ball-milling process was carried out at 5–10 °C and the temperature was maintained by the air cooling system to prevent overheating of the starch samples. After the treatment, the samples were sealed in a bag for analysis.

2.3. Laser diffraction analysis

The particle size distribution of the starch samples was determined using a Malvern Mastersizer S (Malvern Instruments, Ltd., UK) laser scattering analyzer at room temperature, as described by Edwards et al. with a few minor modifications [9]. Briefly, ethyl alcohol was used instead of water as the dispersing reagent (refractive index = 1.36). We then computed D(v, 0.1), D(v, 0.5) and D(v, 0.9) from each distribution, each representing the particle diameter including the cumulative volume of the particles (10%, 50% and 90%, respectively). The size dispersion was evaluated using the dispersion index, referred to as the span, by the following Eq. (1):

$$\text{Span} = \frac{D(v,0.9) - D(v,0.1)}{D(v,0.5)} \quad (1)$$

2.4. Determination of cold water solubility

Cold water solubility (CWS) of the maize starch was determined according to Singh with minor modifications [10]. Briefly, 2 g (dry weight basis) sample was dissolved in 100 mL deionized water. The solution was heated to a constant temperature (30 °C or 40 °C) for 20 min with continuous stirring in order to avoid agglomeration, centrifuged at 3000 × *g* for 20 min, and then the supernatant was removed and dried at room temperature. The resulting residue was placed in a drying oven at 110 °C until we obtained a constant weight. The CWS was calculated by the following Eq. (2):

$$\text{CWS}\% = \frac{\text{Grams of solid in supernatant} \times 4}{\text{Grams of sample}} \times 100 \quad (2)$$

2.5. X-ray diffraction analysis

X-ray diffraction (XRD) analyses of test samples were performed using a Rigaku D/max-2500 V diffractometer (Rigaku, Tokyo, Japan) under the following conditions: X-ray tube – Cu Kα (Ni filter), 40 kV, 30 mA, 1°/1° divergence slit/scattering slit, and a 0.3 mm receiving slit. The relative intensity was recorded at a scattering angle range (2θ) of 4–37° with a scintillation counter at a scanning speed of 0.02°/min. The smoothened resultant diffractograms by 15 points using the Origin 7.5 software (Originlab Corporation, Northampton, USA) and then finally calculated the relative crystallinity.

2.6. Scanning electron microscope

The dried maize starch samples were mounted on circular aluminum stubs with double-sided adhesive tape, coated with 12 nm gold film, and then examined and photographed in an S-5400N scanning electron microscope (Hitachi Ltd., Tokyo, Japan) at an accelerating potential of 15 kV.

2.7. Transparency

We measured the transparency of the native and milled starched as previously described [11]. Briefly, aqueous suspensions (1%) of the samples were heated in a water bath at 85 °C for 20 min with constant stirring and then cooled for 1 h at room temperature. The transparency was determined by measuring the translucence of the particles at 650 nm against a water blank with a 721-Spectrophotometer (Precise Scientific Instrument Co., Ltd., Shanghai, China).

2.8. Syneresis of freeze–thawed samples

The stability of the maize starch following freeze–thaw was determined according to the Srichuwong method [12] with minor modifications. Briefly, approximately 5 g (dry weight basis) of each sample was dissolved in deionized water (100 mL), creating a 5% starch dispersion. Heating and cooling were performed as follows: heating from 50 to 95 °C at 6 °C/min (after an equilibration time of 1 min at 50 °C), a holding period at 95 °C for 5 min, cooling from 95 to 50 °C at 6 °C/min, and a holding phase at 50 °C for 2 min. The constant rotating speed of the paddle was maintained at 160 rpm. The resulting gel was allowed to cool at room temperature for 15 min, and the gel (5 ± 0.5 g) was transferred to a 25 mL centrifugal tube, stored at −18 °C for 21 h, and then thawed at 30 °C for 3 h in a water bath incubator. This freeze–thaw cycle (FTC) was repeated up to five times. Finally, the tubes were centrifuged at 8000 × *g* for 10 min and the released free water was carefully weighed.

2.9. Statistical analysis

All experiments were conducted in triplicate and the data were analyzed using SPSS Program Version 16.0. For each data set, we performed an analysis of variance (ANOVA) followed by the least significant difference test (LSD-test). The level of significance used was 95%. In all cases, a value of $p < 0.05$ was considered significant.

3. Results and discussion

3.1. Particle size and distribution

Following 5 h of milling, we first determined the particle size (diameter; 10%, 50%, and 90% of the cumulative particle volume) and span (the width of the volume distribution) for each maize starch sample (Table 1). Results revealed that the span of the ball-milled maize starch granules (processed in both the ceramic and stainless steel pot) increased significantly above that of the relatively narrow and uniform size distribution found in the untreated maize starch granules ($p < 0.05$).

This increase in size can be explained by the fact that the effect of the ball-milling treatment process can be broadly divided into both grinding and mechanical activation processes. During the milling process, the grinding and mechanical mechanisms are in a dynamic equilibrium that depends on the granule size throughout the tough–brittle transition [13]. During mechanical activation, starch granules are broken into smaller particle sizes that clump together into lumps or adhere to the surface of larger granules. During this process, starch granules are transformed from “brittle” to “tough” leading to an increase in size and causing structure

Table 1
Size characteristics of starch granules treated with ball-milling for 5 h.

	D(v, 0.1)/μm	D(v, 0.5)/μm	D(v, 0.9)/μm	Span
Ceramic pot	10.7 ± 0.1b	42.5 ± 0.3b	135.3 ± 1.9b	2.9 ± 0.2b
Stainless steel pot	17.2 ± 0.8c	58.3 ± 0.5c	240.2 ± 8.3c	3.8 ± 0.4c
Native maize starch	7.7 ± 0.1a	16.1 ± 0.1a	32.1 ± 0.1a	1.5 ± 0.1a

D(v, 0.1) and D(v, 0.9) represent the particle diameters with cumulative particle volumes of 10% and 90%, respectively; D(v, 0.5), median diameter.
Span: size dispersion index.
Values followed by the same letter within a column do not differ significantly ($p < 0.05$).