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 ($p < 0.05$).

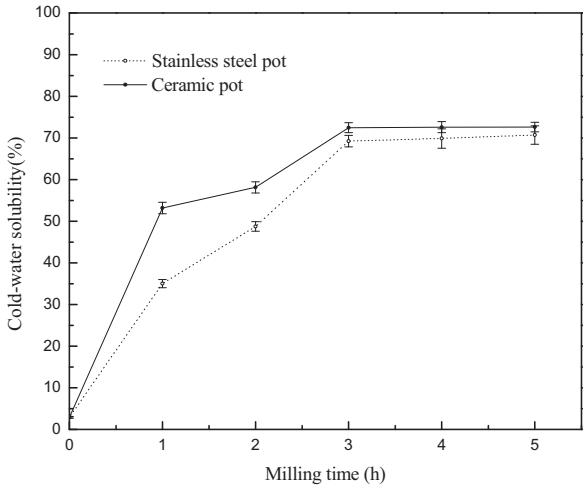

Fig. 1. The effect of ball-milling time on the cold water solubility of maize starch.

distortions that corresponds to an overall enlargement of the particle size, as seen in our results during the ball-milling process.

3.2. Cold-water solubility of maize starch

The effect of ball-milling time of maize starch in either a ceramic or stainless steel pot on CWS is shown in Fig. 1. Results showed that the longer the milling time, the greater the CWS. Interestingly, the CWS of maize starch increased quickly through the first 3 h of milling but then slowed thereafter. This result is likely due to the fact that the ball becomes ensconced by the maize starch as the ball-milling time increases thus decreasing the crushing power of the ball as time increases. The observed increase in CWS of maize starch results in a greater viscosity, a smoother texture, and increases the processing tolerance as compared to the traditional pregelatinized maize starch.

The types of pot used in the milling process did not significantly affect 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%) ($p < 0.05$). This observed increase in CWS of the maize starch as the milling time increased is consistent with previous models showing that mechanical agitation is capable of degrading the crystalline regions of the starch thus allowing a greater entry of water into the interior of the starch granule. The low CWS of untreated maize starch can be attributed to it having a more rigid structure and greater amylose content [5,10].

3.3. X-ray diffractometry of maize starch with differing CWS

We next investigated the X-ray diffraction spectra of maize starch milled in ceramic and stainless steel pots with various CWS (30%, 45%, 60%, and 75%) (Fig. 2). The spectrum of the untreated starch sample shows two peaks at 18θ and 22θ, presumably reflecting the crystalline and amorphism regions in the starch. As the CWS of the starch increases the regions of amorphism become larger and larger at the expense of the crystalline regions, causing the diffraction pattern to decrease. This result shows that maize starch treated by ball-milling has been converted largely into a non-crystalline state. Consequently, the diffraction spectrum shows a broad, featureless peak typical of amorphism, indicating that during the ball-milling treatment the crystalline molecular structure of maize starch is destroyed and converted largely into a non-crystalline (amorphous) state. Of importance to this study, however, starch in a non-crystalline state has a higher CWS. Taken together, these results indicate that the ball-milling treatment of maize starch improves its physicochemical properties thus increasing its possible industrial applications because the market actually prefers starches with less extensive crystalline regions. This ability of ball-milling to convert starch to the non-crystalline state is greater than that observed through heat–moisture treatment [14], radiation degradation [15], microwave degradation [16], and ultrasonic degradation [17]. Although the current work only reflects the basic characterizations of the crystal structure following ball-milling, based on a previous paper we were able to infer that this method induces the starch to change the spatial arrangement disorder of its amylopectin and amylose thus leading to the destruction of its crystalline areas and promoting the amorphous areas in each granule [8].

3.4. Surface morphology of soluble and insoluble starch granules

The surface morphology of the cold soluble and insoluble starch granules treated with ball-milling in either ceramic or stainless steel pots are presented in Figs. 3 and 4. The untreated maize starch granules were either oval or polyhedral and had uniform surfaces and smooth yet slightly porous surfaces. These results are similar to previous reports on native maize starch [18]. After 5 h of ball-milling, the starch granules were subjected to various forces (such as compression, impact, shear, and attrition) to cause a further physical breakdown of the granules and produce a range of fractions. Results revealed that the surface of the starch granules across the range of fractions lost their smoothness and became rough with some debris. Among them, highly hydrated gel-forming and low molecular weight soluble fractions are known to be more likely attacked more rapidly by α-amylase as compared to

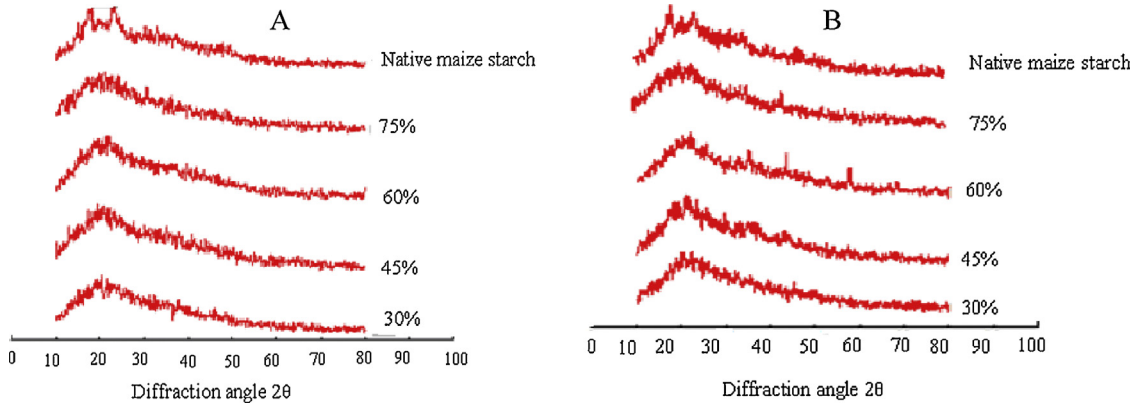

Fig. 2. X-ray diffractometry of maize starch with different cold-water solubility in (A) ceramic pots and (B) stainless steel pots.

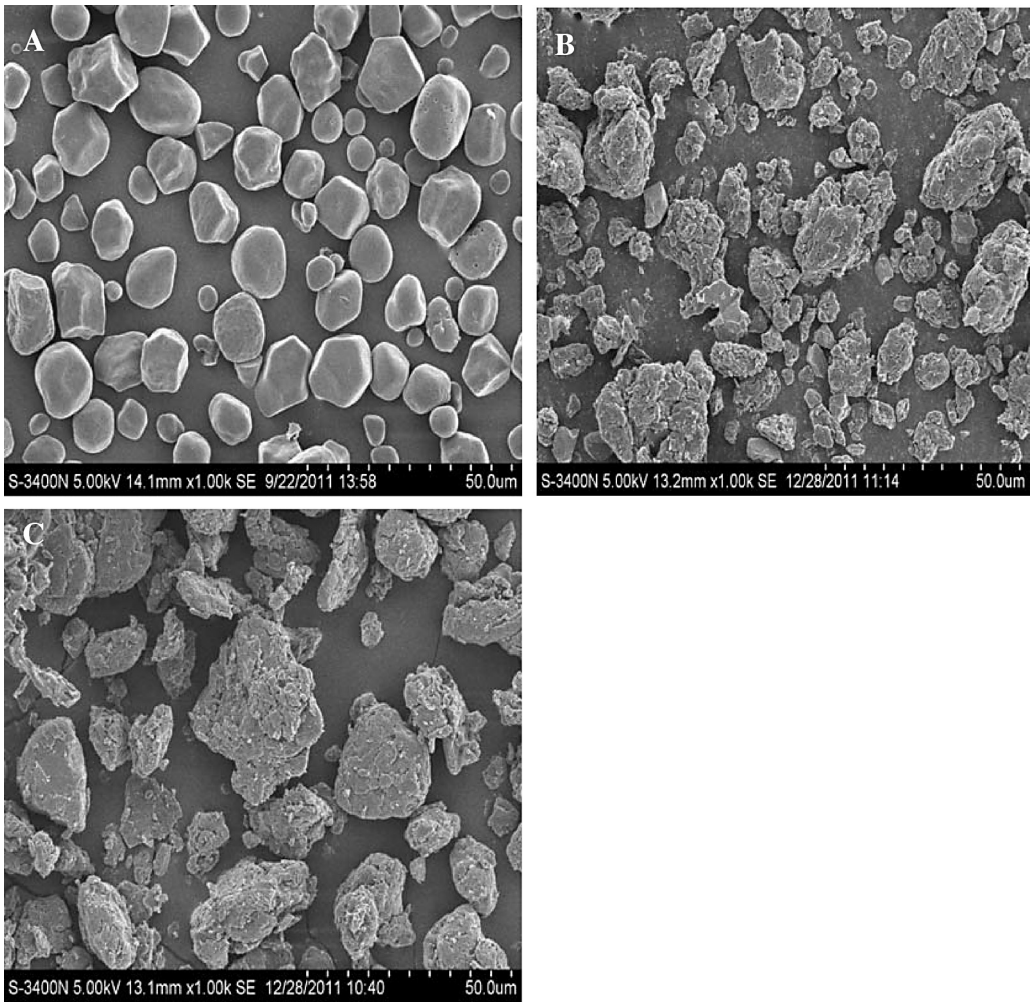

Fig. 3. Representative scanning electron micrographs of (A) untreated maize starch, (B) maize starch treated by ball-milling in ceramic pots, and (C) maize starch treated by ball-milling in stainless steel pots.

intact granules. Consequently, ball-milling significantly not only increased the CWS but also damaged the physical properties of the starch (Figs. 1 and 3). Clear fissures and grooves were observed on the surface of a large number of starch granules and a few fragments peeled off from the outer layer of the starch granules imparting excessive roughness on their surfaces. These phenomena are similar to that reported by Dhital et al. [19] who also proposed that fissures on the granule surface facilitate enzymatic diffusion and increase susceptibility to amylolysis. In addition, they hypothesized that these fragments would have more surface area per unit mass and would thus be expected to be more rapidly hydrolyzed than intact granules due to the enzymes having an easier access to the inside of the native granules via pores and channels. The current results also found that the ball-milling operation increased the enzymatic availability within the granule fractions. Moreover, the starch granules were broken into smaller particle sizes and clumped together either into lumps or adhering to the surface of the larger granules. All the above variations indicate that significant changes occur in the internal structure of the granule during the milling process. Finally, the results also reveal that the integrity and granule periphery remained intact even after 5 h of ball-milling time, indicating the stability of the starches process by this method.

The surface morphology of cold insoluble native starch granules is similar to the surface morphology of cold soluble native starch granules, showing an oval or polyhedral shape with a uniform surface. Following 5 h of ball-milling treatment, the surface of the insoluble starch granules milled in both ceramic and stainless steel pots showed compact aggregates with more angular shapes; some insoluble starch granules had smooth surfaces and lost particle morphology. However, cold insoluble starch granules retained their crystalline amorphism and the hydrophobic hydroxyl groups were not exposed. These insoluble starch granules are likely caused by friction, collision, impingement, shear or other mechanical actions that make starch granules polymerize together and prevent the water from entering into the interior of the starch granule.

3.5. Transparency

The transparency of the ball-milled maize starch indicates that transparency increases as the CWS also increases in both types of pots investigated (Fig. 5). These results are likely due to the destruction of the crystalline structure as the polycrystalline structure converts into more of an amorphous form. The importance of these results is related to its applicability in creating packaging film whose material properties depend on the flexibility of the molecular chain. Since both the granular and crystalline structures of the maize starch were mostly destroyed by ball-milling the water can enter into the interior of the starch granule and ultimately leads to an increase the possible use of these transparent starches in producing packaging film.

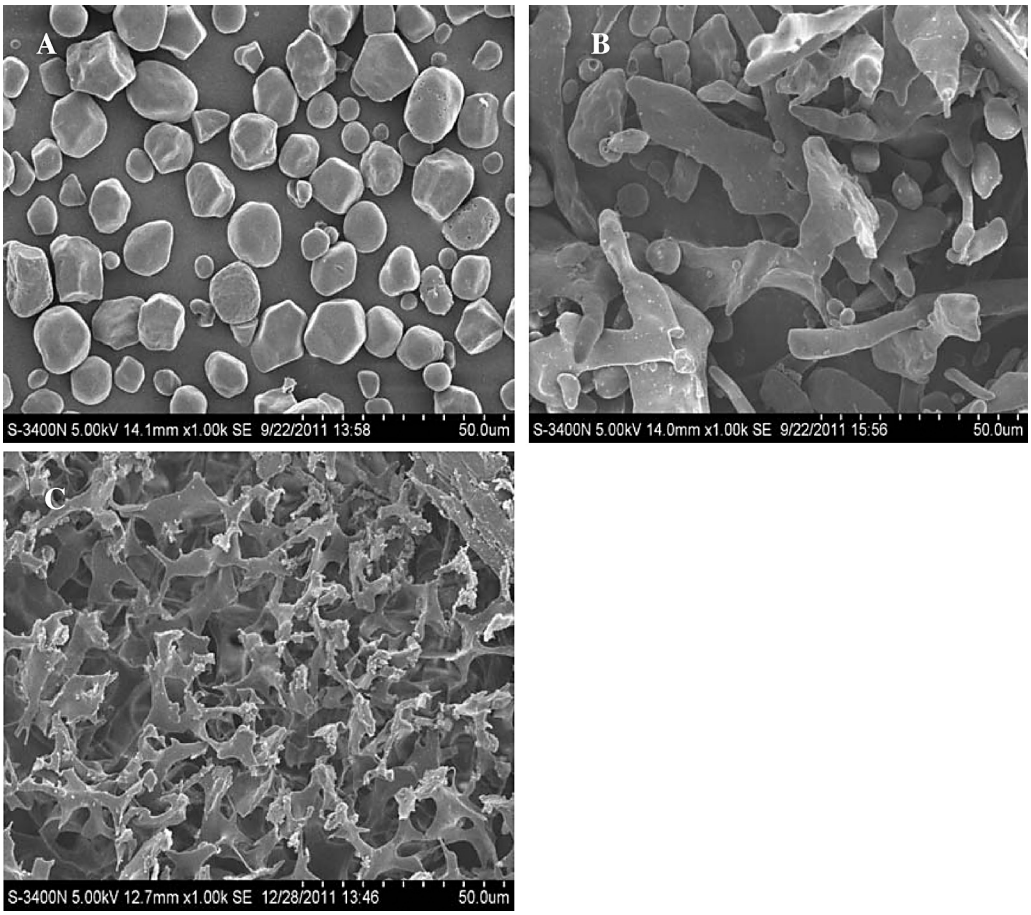

Fig. 4. Representative scanning electron micrographs of cold-water insoluble (A) untreated maize starch, (B) maize starch treated by ball-milling in ceramic pots, and (C) maize starch treated by ball-milling in stainless steel pots.

Of note, when the CWS is above 60%, the transparency of the starch milled in stainless steel pots is significantly higher than in the ceramic pot (Fig. 6). This result may be related to the density, mass, and/or motion state of each ball and also in relation to the interaction of the ball and the wall of the pot. Since, the density and mass of the stainless steel balls are higher than that of the ceramic balls, the damage to the maize granules treated with stainless steel balls is more severe. As such, the amount of amorphous starch granules produced by ball-milling in stainless steel pots is higher than in ceramic pots.

3.6. Syneresis of freeze–thawed maize starch following ball-milling

The freeze–thaw stability of a product is one of the most desirable quality of modified starches for their use as clean-label ingredients in frozen food products [12]. The freeze–thaw stability

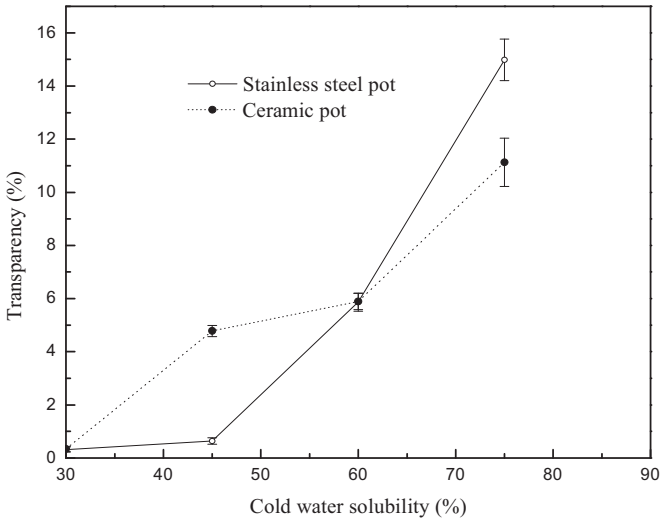

Fig. 5. The transparency of maize starch with increasing cold-water solubility.

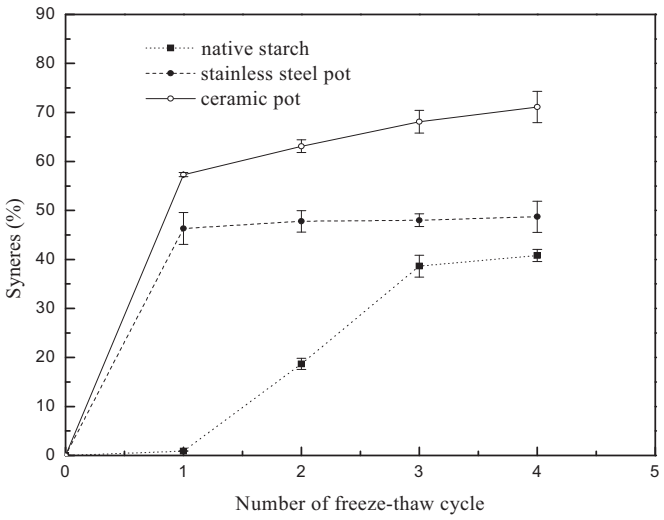

Fig. 6. Syneresis of ball-milled maize starch following freeze–thaw.

of a starch gel is expressed by syneresis, which can be determined following anywhere between zero and four freeze–thaw cycles (FTC). In the current paper, we found the degree of syneresis of starch gel prepared by ball-milling in ceramic pots to be significantly increased after the 1st FTC, as compared to stainless steel pots. Very little syneresis was observed in untreated maize starch, but these small levels of syneresis did increase with the number of FTC. These results are likely due to the modification of the structure and properties of starch granules after sever ball-milling, resulting in a loss of the shorter range crystalline order and double helix content, depolymerization of amylase, and a breakdown of the amylopection in the damaged maize starch granules. These changes in the structure of maize starch can also be observed in the surface morphology of starch granules by SEM (Fig. 3). All these phenomena are results of a decrease in the enthalpy and temperature of gelatinized starch thus leading to an increase in the release of the free water from the maize starch.

4. Conclusions

In this study, we investigated the effect of ball-milling on the physicochemical properties of maize starch and found that this methodology significantly increases the cold water solubility of processed starches. Moreover, ball-milling alters the surface morphology of starch granules as compared to native maize starch, increasing their overall surface area and texture. In addition, we found that ball-milling not only increases the transparency of maize starch as the cold water solubility increases, but also results in an increase of the freeze–thaw syneresis as the number of freeze–thaw cycles increase. Taken together, we conclude by stating that ball-milling is a viable and efficient means for manufacturing high quality maize starch for industrial use and food production.

Conflict of interest

The authors declare that there are no conflicts of interest.

Acknowledgements

The author would like to thank the National Key Technology Research and Development Program of the Ministry of Science and Technology of China. This work was also supported by the Fundamental Research Funds for the Central Universities (Grant No. HIT.NSRIF.2014094), the National Nature Science Foundation of China (Grant No. 31071571) and the China Postdoctoral Science Foundation Grant (2012M520756) from the Chinese Postdoctoral Science Foundation Commission.

References

[1] S. Jobling, Improving starch for food and industrial applications, Curr. Opin. Plant Biol. 7 (2004) 210–218.
[2] Y. Wandee, C. Puttanlek, V. Rungsardthong, S. Puncha-arnon, D. Uttapap, Effects of gelatinization and gel storage conditions on the formation of canna resistant starch, Food Bioprocess Technol. 5 (2012) 2665–2673.
[3] K.S. Sandhu, N. Singh, Some properties of corn starches II: physicochemical, gelatinization, retrogradation, pasting and gel textural properties, Food Chem. 101 (2007) 1499–1507.
[4] N. Singh, N. Inouchi, K. Nishinari, Structural, thermal and viscoelastic characteristics of starches separated from normal, sugary and waxy maize, Food Hydrocolloid 20 (2006) 923–935.
[5] J. Chen, J. Jane, Preparation of granular cold-water soluble starches by alcoholic–alkaline treatment, Cereal Chem. 71 (1994) 618–622.
[6] J.E. Eastman, C.O. Moore, Cold-water-soluble granular starch for gelled food compositions, U.S. Patent 4, 465 (1984) 702.
[7] S. Rajagopalan, P.A. Seib, Granular cold-water-soluble starches prepared at atmospheric pressure, J. Cereal Sci. 16 (1992) 13–28.
[8] Z.Q. Huang, X.L. Xie, Y. Chen, J.P. Lu, Z.F. Tong, Ball-milling treatment effect on physicochemical properties and features for cassava and maize starches, C. R. Chim. 11 (2008) 73–79.
[9] M.A. Edwards, B.G. Osborne, R.J. Henry, Effect of endosperm starch granule size distribution on milling yield in hard wheat, J. Cereal Sci. 48 (2008) 180–192.
[10] J. Singh, N. Singh, Studies on the morphological and rheological properties of granular cold water soluble corn and potato starches, Food Hydrocolloid 17 (2003) 63–72.
[11] C. Perera, R. Hoover, Influence of hydroxypropylation on retrogradation properties of native, defatted and heat–moisture treated potato starches, Food Chem. 64 (1999) 361–375.
[12] S. Srichuwong, N. Isono, H. Jiang, T. Mishima, M. Hisamatsu, Freeze–thaw stability of starches from different botanical sources: correlation with structural features, Carbohydr. Polym. 87 (2012) 1275–1279.
[13] P. Pourghahramani, E. Forssberg, Comparative study of microstructural characteristics and stored energy of mechanically activated hematite in different grinding environments, Int. J. Miner. Process. 79 (2006) 120–139.
[14] A. Gunaratne, R. Hoover, Effect of heat–moisture treatment on the structure and physicochemical properties of tuber and root starches, Carbohydr. Polym. 49 (2002) 425–437.
[15] A.C. Bertolini, C. Mestres, P. Colonna, J. Raffi, Free radical formation in UV- and gamma-irradiated cassava starch, Carbohydr. Polym. 44 (2001) 269–271.
[16] G. Lewandowicz, T. Jankowski, J. Fornal, Effect of microwave radiation on physical–chemical properties and structure of cereal starch, Carbohydr. Polym. 42 (2000) 193–199.
[17] C. Renata, R. Bozena, L. Salah, U. Piotr, M. Janusz Rosizk, Degradation of chitosan and starch by 360-kHz ultrasound, Carbohydr. Polym. 60 (2005) 175–184.
[18] S.L. Amaya-Llano, F. Martinez-Bustos, A.L.M. Alegria, J.D. Zazueta-Morales, Comparative studies on some physico-chemical, thermal, morphological, and pasting properties of acid-thinned jicama and maize starches, Food Bioprocess Technol. 4 (2011) 48–60.
[19] S. Dhital, A.K. Shrestha, B.M. Flanagan, J. Hasjim, M.J. Gidley, Cryo-milling of starch granules leads to differential effects on molecular size and conformation, Carbohydr. Polym. 84 (2011) 1133–1140.