Food Chemistry 241 (2018) 380–386

Contents lists available at ScienceDirect

Food Chemistry

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

Effect of high pressure on rheological and thermal properties of quinoa and maize starches

Guantian Li, Fan Zhu*

School of Chemical Sciences, University of Auckland, Private Bag 92019, Auckland 1142, New Zealand

ARTICLE INFO

Keywords:
Rheology
Gelatinization
Retrogradation
High hydrostatic pressure
Small granule starch
Non-thermal processing

ABSTRACT

Quinoa starch has small granules with relatively low gelatinization temperatures and amylose content. High hydrostatic pressure (HHP) is a non-thermal technique for food processing. In this study, effects of HHP up to 600 MPa on physical properties of quinoa starch were studied and compared with those of a normal maize starch. Both starches gelatinized at 500 and 600 MPa. The pressure of 600 MPa completely gelatinized quinoa starch as revealed by thermal analysis. Dynamic rheological analysis showed that HHP improved the gel stability of both starches during cooling. HHP had little effects on amylopectin recrystallization and gel textural properties of starch. Overall, quinoa starch was more susceptible to HHP than maize starch. The effects of HHP on some rheological properties such as frequency dependence were different between these two types of starches. The differences could be attributed to the different composition, granular and chemical structures of starch, and the presence of granule remnants.

1. Introduction

Quinoa (*Chenopodium quinoa* Willd.) is an Andes-originated pseudocereal and has recently gained much attention for its attractive nutritional value (Wang & Zhu, 2016). Quinoa seeds have been processed into a range of food products (Wang & Zhu, 2016). Starch is the major component of quinoa seed, which accounts for more than 50% of the dry weight. Recent studies showed that quinoa starch could be used as an ingredient for food and non-food applications such as in structuring Pickering emulsions and for controlled release (Wang & Zhu, 2016). Quinoa starch has small granules (~2 μm) and a low amylose content (e.g., ~7%) (Abugoch, 2009; Li, Wang, & Zhu, 2016; Li & Zhu, 2017a). The amylopectin of quinoa starch has a high proportion of short chains and a high amount of fingerprint A-chains (A_{fp}) (Li & Zhu, 2017a). The presence of super-long chains in quinoa amylopectin was suggested by conducting the size-exclusion chromatography of debranched amylopectin (Tang, Watanabe, & Mitsunaga, 2002). The quinoa amylose is more branched than amyloses of other starches (Abugoch, 2009; Tang et al., 2002). These structural features of quinoa starch result in several distinct properties such as low gelatinization temperatures, low gel strength, and high enzyme susceptibility (Li et al., 2016). The functional properties of quinoa starch suggest that it may be used as a novel starch resource for food and other applications. Modifications of quinoa starch can expand the range of its functionalities for different uses.

High hydrostatic pressure (HHP) treatment is a non-thermal food processing technique, and can be used for starch modifications (Yang, Chaib, Gu, & Hemar, 2017). Starch can be gelatinized under HHP. HHP-induced gelatinization of starch is similar to heat-induced gelatinization in many ways with some notable differences (Kim, Kim, & Baik, 2012). HHP-induced gelatinization could much better preserve the granular structure of starch as compared to the traditional heating process (Kim et al., 2012; Yang et al., 2017). HHP decreased the amylose leaching with increasing pressure. Instead of leaching to the liquid phase, amylose may form complexes with lipids or interact with the outer branch chains of amylopectin, which reduces the granule swelling during HHP treatment (Kim et al., 2012; Vallons, Ryan, & Arendt, 2014). HHP-induced starch gelatinization is affected by the experimental conditions such as the level of pressure, holding time and temperature during the experiment (Yang et al., 2017). The concentration, chemical composition, and structure of starch also have significant effects on the outcomes of this process (Kim et al., 2012). For example, A-type starch tends to be more sensitive to HHP than B-type and C-type starches due to the differences in the granular structure (Kim et al., 2012; Vallons et al., 2014). Oh, Pinder, Hemar, Anema, and Wong (2008) classified starches into three categories according to their behaviors under HHP. They included waxy starch which is fully gelatinized at high pressure (e.g., > 400 MPa), normal starch which is partially gelatinized at high pressure, and pressure-resistant starch such as high amylose starch which normally does not gelatinize at pressure below 600 MPa. Therefore, the outcomes of HHP heavily depend on the

* Corresponding author.
E-mail address: fzhu5@yahoo.com (F. Zhu).

http://dx.doi.org/10.1016/j.foodchem.2017.08.088
Received 7 May 2017; Received in revised form 3 August 2017; Accepted 27 August 2017
Available online 30 August 2017
0308-8146/

type, source, and amylose content of starches.

In recent years, studies of the impact of HHP were conducted on starches from a range of sources (Kim et al., 2012; Liu, Hu, & Shen, 2010; Vallons et al., 2014; Yang et al., 2017). Quinoa starch, as a novel source of starch, remains to be treated by HHP. This study reports the effect of HHP up to 600 MPa on physicochemical properties of quinoa starch. Normal maize starch, as one of the mostly used commercial starches, was employed as a reference for comparison. The results of this study may provide a basis to better utilize quinoa starch for novel applications and also to develop quinoa as a sustainable crop. A large number of nomenclatures were used and a table of their abbreviations was presented (Supplementary Table 1).

2. Materials and methods

2.1. Materials

Quinoa seeds (brand: Fresh Produce Be Fresh Quinoa; country of origin: Peru; seed color: white) were purchased from Countdown supermarket, New Zealand. Quinoa starch (200 g) was isolated by a procedure of a previous report (Li et al., 2016). Normal maize starch (Melogel) (Ingredion ANZ Pty Ltd., Auckland, New Zealand) was used as a reference. The amylose contents of quinoa and maize starches were 10.9 and 25.8%, respectively, according to a concanavalin A precipitation-based method (Gibson, Solah, & McCleary, 1997).

2.2. HHP treatment

HHP treatments were carried out in a laboratory-scale high-pressure unit (QFP 2L-700, Avure Technologies Inc, Middletown, US). Quinoa starch was mixed with water to a concentration of 10% (w/v) and sealed in a plastic bag by a vacuum sealer. Before sealing, gas inside the bag was carefully removed. Each bag was shaken several times before HHP treatment to prevent sedimentation. Starches were treated at 100 MPa to 600 MPa at room temperature. The duration of HHP treatment was 5 min according to a previous report which showed that treatments for 5 min and 1 h gave rather similar results (Katopo, Song, & Jane, 2002). After HHP treatment, starch samples were immediately stored in a freezer (−80 °C) and lyophilized on the next day. The freezing and lyophilization process may minimize the retrogradation of the gelatinized starches (Blaszczak, Valverde, & Fornal, 2005; Kim et al., 2012). The untreated starches were also subjected to freezing and lyophilization for comparative purpose.

2.3. Morphology

The morphology of starch samples were analyzed by scanning electron microscopy (SEM) (Hitachi S-3400N, Tokyo, Japan). The accelerating voltage was 3–5 kV and the working distance was between 4500 and 7000 μm.

2.4. Particle size distribution

Particle size distribution of starch was estimated by a particle size analyzer (Mastersizer 2000, Malvern Instruments Ltd, Malvern, UK). Starch was suspended in water to a concentration of 1%, which was shaken overnight on a shaker. The starch suspension was added to the Hydro 2000SM (AWM2002) dispersion unit and was kept stirring at 2,100 rpm for 2 h before measurement. The dispersant refractive index and particle absorption index were 1.33 and 0, respectively. The mass moment mean diameter or De Brouckere mean diameter (D [4, 3]), surface area moment mean diameter or Sauter mean diameter (D [3, 2]), and number median diameter (d [n, 0.5]) were recorded. The Span and Uniformity were also calculated as indicators of deviation from the median of number-based size distribution. The plotted results were transformed into number-, volume-, and surface-based distribution.

2.5. Swelling power (SP) and water solubility index (WSI)

SP and WSI of starch at 55, 65, 75, 85, and 95 °C were estimated, following the method of a previous work (Li et al., 2016).

2.6. Thermal properties

Differential scanning calorimeter (DSC) (Q1000 Series, TA Instruments, New Castle, USA) was used to analyze thermal properties of starch. Starch (~3 mg) was accurately weighed in an aluminum pan before adding water (3 times in weight to starch). The aluminum pan was sealed and allowed to equilibrate at room temperature for 1 h. The temperature range was 25–90 °C and the heating rate was 10 °C/min. After measurement, sample was stored at 4 °C for two weeks before retrogradation analysis using the same DSC settings. The retrogradation measured by DSC in this study is mostly due to the amylopectin recrystallization. Onset (T_o), peak (T_p), conclusion (T_c) temperatures, and enthalpy change (ΔH) were recorded.

2.7. Rheological properties

2.7.1. Steady flow

The steady flow experiment followed a previous report with some modifications (Zhu, Bertoft, & Li, 2016). Briefly, starch suspension (1 mL, 5%, w/v) was prepared in Eppendorf tube by vortexing. The suspension was heated in a water bath (90 °C) with intermittent mixing for 30 min. The paste was transferred to bottom plate of an Anton Paar rheometer (Physica MCR 301, Anton Paar GmbH, Graz, Austria). A parallel plate geometry (PP25) was used in the steady flow experiment and the gap size was 1 mm. The paste was kept at 25 °C for 5 min before shearing from 0.1 to 1000 s^{-1} and then from 1000 to 0.1 s^{-1}. The relationships between shear stress and shear rate were described by Herschel-Bulkley (Eq. (1)) equation:

$$\tau = K_0 + K\cdot(\dot{\gamma})^n \quad (1)$$

Where τ is shear stress (Pa), $\dot{\gamma}$ is shear rate (s^{-1}), n is flow behavior index (dimensionless), K is consistency coefficient ($Pa\cdot s^n$), and K_o is yield stress (Pa). The goodness of fitting was estimated by R^2 (coefficient of determination).

2.7.2. Dynamic oscillation

The procedure followed a previous report with some modifications (Zhu et al., 2016). Starch sample was mixed with water to a concentration of 16.7% (w/w) in an Eppendorf tube. The suspension was stirred for 5 min before loading on the bottom plate of the rheometer. A programmed cycle of heating and cooling was used to estimate the dynamic oscillation properties of starch. The sample was heated to 90 °C before cooling to 25 °C at 2 °C/min. The strain and frequency were 2% and 1 Hz, respectively. The edge of sample was covered by a thin layer of oil to prevent evaporation. After temperature sweep, starch gel was allowed to stand at 25 °C for 5 min before subjecting to frequency sweep test. The frequency was increased from 0.1 to 40 Hz before decreasing to 0.1 Hz with temperature and strain holding constant. Storage modulus (G'), loss modulus (G''), and loss tangent (tan $\delta = G''/G'$) were estimated. G' was fitted into the following equation:

$$\log G' = k_{G'} \times \log\omega \quad (2)$$

2.7.3. Pasting

An Anton Paar MCR 301 rheometer (Anton Paar GmbH, Ostfildern, Austria) with a starch cell was used to determine the pasting properties of starch. The procedure was according to a previous description (Li et al., 2016). The pasting parameters were pasting temperature (PT), peak viscosity (PV), peak time (P_{time}), peak temperature (PKT), hot paste viscosity (HPV), and cold paste viscosity (CPV). Other derived parameters were breakdown (BD = PV − HPV), setback