Food Chemistry 213 (2016) 602–608

Contents lists available at ScienceDirect

Food Chemistry

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

Effects of NaCl and $CaCl_2$ on physicochemical properties of pregelatinized and granular cold-water swelling corn starches

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ARTICLE INFO

Article history:
Received 11 February 2016
Received in revised form 13 May 2016
Accepted 5 July 2016
Available online 5 July 2016

Keywords:
Corn starch
Granular cold-water-swelling starch
Drum-dried pregelatinized starch
Sodium chloride
Calcium chloride

ABSTRACT

The physicochemical properties of drum dried pregelatinized (PG) and granular cold-water-swelling (GCWS) corn starch pastes were determined in the presence of NaCl and $CaCl_2$ (0, 50, 100, 150 and 200 mM). Light micrographs revealed that NaCl roughened the surface of PG starch particles while $CaCl_2$ did not bring about obvious changes on their morphology. In the case of GCWS starch, there were some wrinkles on the surface of starch granules. NaCl increased the wrinkles but $CaCl_2$ softened the surface of granules. GCWS starch had higher water absorption, cold paste viscosity and textural parameters than PG starch and these parameters were enhanced with addition of $CaCl_2$ while NaCl exhibited an opposite trend for all of these factors. The Freeze-thaw (F-T) stability and turbidity of GCWS were also higher than PG starch. In presence of salts F-T stability and turbidity of both modified starches improved and $CaCl_2$ caused more evident changes.

1. Introduction

Starch is the most important energy reserve of plants which is stored in semi-crystalline granules varying in composition, size and shape based on their botanical sources. It is composed of D-glucose molecules in two forms of amylose and amylopectin. Amylose is a linear molecule in which the glucose units are linked together by α (1→4) linkage. Amylopectin has the same basic structure but about 5% of the glucose units are joined together by α (1→6) linkage (Jobling, 2004). Native starch granules are water insoluble at room temperature due to their complex semi-crystalline structure thus cannot play their role as thickener, gelling agent and water binder. Cold water swelling starches are usually used to overcome these problems in food products that are processed at low temperatures (Eastman, 1987; Majzoobi, Kaveh, Blanchard, & Farahnaky, 2015). Drum drying of starch slurries is a traditional and one of the most common methods in producing these starches but they don't provide a smooth texture and are susceptible to acidic conditions and shear due to the lack of granular structure (Anastasiades, Thanou, Loulis, Stapatoris, & Karapantsios, 2002; Majzoobi, Kaveh, Blanchard, et al., 2015). Thus several methods have been suggested for producing granular cold-water swelling (GCWS) starches. These modified starches provide higher viscosity, smoother texture and are more resistant to processing conditions. GCWS starches are produced by treatments such as aqueous alcohol treatment at high temperature and elevated (Jane, Craig, Seib, & Hoseney, 1986) or atmospheric pressure (Dries, Gomand, Goderis, & Delcour, 2014) polyhydric alcohol treatment at high temperature and atmospheric pressure (Rajaoopalan & Seib, 1992) and alcoholic-alkaline treatment (Chen & Jane, 1994a, 1994b; Li et al., 2014; Majzoobi, Kaveh, Blanchard, et al., 2015). Alcoholic-alkaline treatment is one of the best methods in producing GCWS starches due to its being effective for a variety of starches high efficiency and manufacturing at ambient temperature. In this method sodium hydroxide breaks the intermolecular hydrogen bonds of starch granules, while ethanol inhibits the swelling of granules and maintains their integrity. When ethanol is evaporated, a cavity is formed in the hilum of starch granule and brings about a metastable starch granule with excellent cold water swellability (Han & Lim, 2004; Xin, Wang, & Liu, 2012). PG and GCWS can be used in a wide range

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http://dx.doi.org/10.1016/j.foodchem.2016.07.027
0308-8146/

of food products including pie fillings, puddings, gravies, sauces and soups as thickening agents. These products usually contain components such as salts, sugars, organic acids, etc. which influence the functional properties of these starches. However there are scarce published papers about the effects of food ingredients on functional properties of cold water swelling starches. Majzoobi, Kaveh, Blanchard, et al. (2015), Majzoobi, Kaveh, Farahnaky, and Blanchard (2015) investigated the effects of organic acids on physicochemical properties of PG and GCWS starches and found that acids weakens the structure of both starch pastes however the GCWS starch was more resistant to organic acids due to its granular structure. To the best of our knowledge, there is no report studying the effects of salts on physicochemical properties of these modified starches. Thus, this research was undertaken to investigate the influence of NaCl and $CaCl_2$ on PG or GCWS starches.

2. Materials and methods

2.1. Materials

Native corn starch that contained 9.64% moisture, 0.45% protein, 0.74% fat, 0.17% ash (measured by the approved methods of the AACC, 2000) and 28.30% total amylose as determined according to the iodine method (Morrison & Laignelet, 1983) was supplied by Mahshad Starch Company (Yazd, Iran). Pure ethanol was purchased from Parsian Company (Shiraz, Iran). Analytical grade Sodium chloride (NaCl), calcium chloride ($CaCl_2$), sodium hydroxide (NaOH) and hydrochloric acid (HCl) were obtained from Merck (Darmstadt, Germany).

2.2. Production of PG corn starch

Samples were prepared according to the method described by Majzoobi et al. (2011). In brief, suspension of 10%, w/w native corn starch in distilled water was prepared and passed through a double drum dryer (Mathis Machine Corporation, Benton Harbor, Michigan, USA) at a surface temperature of 158 °C, steam pressure of 5 bar, rotation speed of 5 rpm and gap width of 0.4 mm. The pregelatinized starch in the form of a thin film was removed by a blade from the surface of drums and pulverized using a laboratory mill. Afterwards the starch sample was sieved with a 120 mesh number screen to give the average particle size of 125 μm, packed in polyethylene bags and stored at ambient temperature for further experiments.

2.3. Production of GCWS corn starch

GCWS corn starch was produced by the method of Chen and Jane (1994a) with slight modifications. 10 g of native starch powder was added to 70 g of ethanol solution (40% w/w) and mixed with a magnetic stirrer (LABINCO L-81, Amsterdam, The Netherlands) to reach 35 °C and then 50 g of NaOH solution (3 M) was added gradually and mixed for 15 min at 35 °C. Then the sample was filtered and fresh ethanol solution (40%) was added and was neutralized by HCl (3 M in absolute ethanol). The sample was stirred for 1 h and then washed by 60 and 95% ethanol to remove the produced salts. Subsequently the starch suspension was Büchner filtered and dehydrated with absolute ethanol. The modified starch was dried in an oven at 50 °C for 12 h. The dried starch was ground and passed through the screen to give an average particle size of 125 μm and stored at room temperature to be analyzed.

2.4. Preparation of starch pastes

Appropriate amounts of modified starches were weighed and placed in Schott bottle (250 mL) and salt solutions (0, 50, 100, 150 and 200 mM) were added to prepare suspensions with 10% of dry matter (w/w). 0.01% sodium azide as a chemical preservative was also added to them. The samples were stirred using a magnetic stirrer for 15 min at room temperature and then allowed to hydrate for 24 h at an incubator of 22 °C and used for further experiments.

2.5. Microscopic examination

The starch pastes prepared in different solutions as mentioned and were diluted in respective solutions to give a concentration of 1%. A small aliquot of each sample was placed on a glass slide and covered with a coverslip. The prepared slides were observed by an optical microscope (Olympus BX41, Olympus Optical Co., Ltd., Tokyo, Japan) and were photographed with a microscope camera system (Olympus BP12, Olympus Optical Co., Ltd., Tokyo, Japan).

2.6. Water absorption

Since the salts may exist in both pellet and supernatant and bring about complications, the cold water absorption of starch samples was determined volumetrically according to the method developed by Hedayati, Shahidi, Koocheki, Farahnaky, and Majzoobi (2016). 10 mL of each starch paste was poured into a graduated centrifuge tube and centrifuged at 3500*g* for 10 min and the volume of pellet was determined immediately.

Cold-water absorption was measured by the following Equation:

$$\text{Cold water absorption}\,(\%) = \frac{\textit{volume of pellet}}{\textit{volume of starch paste}} \times 100$$

2.7. Cold paste viscosity

The cold paste viscosity of PG and GCWS corn starch samples was determined using a Rapid Visco Analyzer (RVA) (Starch Master2, Perten, Australia) at 25 °C. 28 g of the each starch paste prepared in different salts was straightly weighed in an aluminum canister and run in the RVA with a paddle speed of 160 rpm. The changes in starch paste viscosity over 15 min of experiment were recorded by the instrument.

2.8. Textural properties

Back extrusion test was carried out to evaluate the textural properties of starch pastes by using a texture analyzer (Stable Microsystems, TAXT-2i Texture Analyzer, Surrey, England). 50 g of the starch paste was weighed into a cylindrical glass container with a diameter of 50 mm and left for 2 min at room temperature to relax. The probe was positioned centrally over the container and penetrated to the sample at a pre-test speed of 2 mm/s, test speed of 2 mm/s, post-test speed of 10.0 mm/s, distance of 8.0 mm and trigger force of 5.0 g using a cylindrical aluminum probe with a diameter of 40 mm. Parameters like firmness, consistency, cohesiveness and index of viscosity were calculated from the resulting curves.

2.9. Freeze thaw stability

The Freeze-thaw stability of starch samples was measured by the method of Majzoobi, Kaveh, Farahnaky, et al. (2015) with slight modification. The starch pastes (25 g) were transferred into 50 mL centrifuge tubes and subjected to freeze-thaw cycles. Samples were frozen in a −18 °C freezer for 24 h and then thawed in an incubator at 25 °C for 4 h up to five periods. After each cycle the tubes were centrifuged at 1000*g* for 20 min and the supernatant