Food Chemistry 207 (2016) 139–147

Contents lists available at ScienceDirect

Food Chemistry

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

Effects of $CaCO_3$ treatment on the morphology, crystallinity, rheology and hydrolysis of gelatinized maize starch dispersions

S. Garcia-Diaz [a], C. Hernandez-Jaimes [b,*], H.B. Escalona-Buendia [a], L.A. Bello-Perez [c], E.J. Vernon-Carter [d], J. Alvarez-Ramirez [d]

[a] Departamento de Biotecnología, Universidad Autónoma Metropolitana-Iztapalapa, Apartado Postal 55-534, Iztapalapa 09340, Mexico
[b] Facultad de Ciencias, Universidad Autónoma del Estado de México, Campus El Cerrillo, Toluca 50200, Mexico
[c] Centro de Desarrollo de Productos Bióticos, Instituto Politécnico Nacional, Yautepec 62731, Mexico
[d] Departamento de Ingeniería de Procesos e Hidráulica, Universidad Autónoma Metropolitana-Iztapalapa, Apartado Postal 55-534, Iztapalapa 09340, Mexico

ARTICLE INFO

Article history:
Received 27 November 2015
Received in revised form 22 February 2016
Accepted 28 March 2016
Available online 30 March 2016

Keywords:
Nixtamalization
Calcium carbonate
Rheology
Crystallinity
Chemical mechanisms

ABSTRACT

Using calcium salts instead of lime allows for an ecological nixtamalization of maize grains, where the negative contamination impact of the traditional lime nixtamalization is reduced. This work assessed the effects of calcium carbonate (0.0–2.0% w/w $CaCO_3$) on the morphology, crystallinity, rheology and hydrolysis of gelatinized maize starch dispersions (GMSD). Microscopy analysis showed that $CaCO_3$ changed the morphology of insoluble remnants (ghosts) and decreased the degree of syneresis. Analysis of particle size distribution showed a slight shift to smaller sizes as the $CaCO_3$ was increased. Also, X-ray patterns indicated that crystallinity achieved a minimum value at $CaCO_3$ concentration in the range of 1% w/w. GMSD with higher $CaCO_3$ concentrations exhibited higher thixotropy area and complex viscoelastic behavior that was frequency dependent. A possible mechanism involved in the starch chain modification by $CaCO_3$ is that starch may act as a weak acid ion exchanger capable of exchanging alcoholic group protons for cations (Ca^{+2}).

1. Introduction

Maize (*Zea mays* L.) is an important worldwide energy source for human consumption. Maize granules are traditionally treated with ash lime ($Ca(OH)_2$) in a process known as nixtamalization. Maize grains are cooked with enough water and lime at atmospheric conditions for 30–60 min. Subsequently, the cooked mixture is steeped down for 12–14 h. Next, maize grains are washed out to remove the excess of lime and finally ground in stone mills resulting in malleable dough that is used for the elaboration of various food products (e.g., flour, tortilla, chips, etc.). Various researchers have investigated the effects of lime on the microstructure, functionality, digestibility and viscoelasticity of maize grains and dough (Fernández-Muñoz et al., 2004; Méndez-Montealvo, García-Suárez, Paredes-López, & Bello-Pérez, 2008; Rodríguez-Martínez et al., 2015; Yahuaca-Juárez et al., 2013). These authors found that besides the functional incorporation of calcium, the traditional nixtamalization caused pericarp degradation, lipid saponification and partial starch gelatinization.

Traditional nixtamalization processing has serious drawbacks: (1) It is inefficient because of the high water consumption; (2) It produces contaminating effluents with a high load (~5–15%) of solid residues (Rosentrater, 2006); and (3) The loss of nutrients (Salazar et al., 2014). It has been proposed that the total or partial substitution of lime by calcium salts may contribute to alleviate these technological problems (Campechano-Carrera et al., 2012). This process termed as ecological nixtamalization is carried out under moderate alkaline conditions (~pH 8), reducing the adverse effects on nutrients and the production of flocculated residues. Further studies showed that the ecological nixtamalization process led to food products (e.g., dough and tortillas) with acceptable sensory and nutritional characteristics, and with cleaner color. It was also found that the ecological nixtamalization with calcium carbonate increased the fiber (Bello-Pérez et al., 2014) and resistant starch (Santiago-Ramos et al., 2015a) contents of tortillas as compared to those obtained by the traditional lime nixtamalization, while both processes induced similar thermal properties (Santiago-Ramos et al., 2015b).

The vast majority of studies of traditional nixtamalization are based on the treatment of the whole maize grain. Only a limited number of reports have focused on the specific effects of lime concentration on maize starch. Bryant and Hamaker (1997) showed

* Corresponding author.
E-mail address: carmenhernandezjaimes@gmail.com (C. Hernandez-Jaimes).

http://dx.doi.org/10.1016/j.foodchem.2016.03.095
0308-8146/

that maize starch gelatinization is affected by lime cooking as starch solubility, water retention capacity and gelatinization temperature were increased by addition of $Ca(OH)_3$ in the range from 0 to 0.40–0.50%, with a peak at 0.20%. Thermogravimetric data has been used to study the thermal degradation of maize starch with and without thermo-alkaline treatment, finding that maize starch treated with lime exhibited the highest activation energy values during the whole thermal degradation process which could be related to the physical cross-linking process between starch constituents and Ca-ions (Pineda-Gómez, Rosales-Rivera, & Rodríguez-García, 2012). Contreras-Jiménez, Gaytán-Martínez, Figueroa-Cárdenas, Avalos-Zúñiga, and Morales-Sánchez (2014) showed that steeping time and calcium hydroxide content had significant effects on water absorption and pH of maize grits. Lobato-Calleros et al. (2015) studied lime concentrations between 0.0 and 2.0%, finding that starch swelling, water retention capacity, and gelatinization exhibited a maximum value at or near 0.2% (w/v) lime concentration.

It is apparent that calcium hydroxide affects the maize starch supra-molecular structure along two ways: (1) calcium ions are linked to starch chains to form cross-linked structures that enhance water retention and viscoelasticity (Lobato-Calleros et al., 2015), and (2) hydroxyl ions brake down ramified amylopectin molecules, improving both calcium-ion diffusion and viscoelasticity of the treated maize starch gels (Bryant & Hamaker, 1997). An interesting question is whether starch treatment with calcium salts can produce similar results as those obtained with calcium hydroxide. Findings in this line should provide valuable insights regarding the potential of ecological nixtamalization for obtaining corn flour with the malleability and functionality obtained via the traditional nixtamalization process. Although knowledge has been gained about the effects of calcium salts on the supra-molecular structure of maize starch, the issue requires more specific clarifications. In this regard, the aim of this work was to study the effects of calcium carbonate on the morphology, crystallinity, rheology and hydrolysis of gelatinized maize starch dispersions, and to contrast these results with those reported for $Ca(OH)_2$ treatment of maize starch granules.

2. Materials and methods

2.1. Materials

Native maize starch (Nr. S-4126, moisture content <15%, pH 4.8–5.8, amylose content 26.7%) was purchased from Sigma-Aldrich (St. Louis, MO, USA). Calcium carbonate ($CaCO_3$) reagent grade was obtained from J.T. Baker (Xalostoc, Mexico). Deionized water was used for all solutions and experimental runs.

2.2. Calcium carbonate treatment

Maize starch (5% w/w) was dispersed in calcium carbonate solutions at different concentrations (0.0%, 0.25%, 0.5%, 1.0% and 2.0% w/w). The dispersions were heated at 92 °C under gently stirring for 25 min for allowing a close interaction between starch chains and calcium ions, and for achieving complete gelatinization of starch granules. In all cases, the pH of the starch dispersion was monitored (Mettler delta340, Columbus, USA). The gelatinized maize starch dispersions (GMSD) were then cooled down to achieve room temperature. The dispersions were coded as $GMSD_x$, where the subindex indicates the $CaCO_3$ concentration used. A fraction of the GMSD samples was used for analysis (optical microscopy, particle size and rheology) within 15 min of their preparation in order to minimize possible adverse effects caused by starch retrogradation. A second fraction of the GMSD samples was air-dried at 30 °C for 24 h for analysis requiring dry samples (SEM, swelling volume, solubility, XRD and thermal properties).

2.3. Size-exclusion chromatography (SEC)

The effect of the $CaCO_3$ treatment on the molecular size distributions of corn starch was assessed with High Performance Size Exclusion Chromatography (HPSEC) (Shimadzu, Tokyo, Japan). For 10 mL of samples at room temperature, 1 mL of 1.0 M $NaNO_3$ was added and subsequently the sample was passed through an 8.0 μm filter. The filtrate was injected into the HPSEC system, which consisted of a LC-10AT pump, RID-10A refractive index detector SIL-10A automatic injector and three Ultrahydrogel columns (linear, two 120) in series connection. 0.1 M $NaNO_3$ was used as mobile phase at flow-rate of 0.3 mL/min. The temperature of the columns and the RI detector was set respectively at 55 °C and 80 °C.

2.4. Optical microscopy

The GMSD (1 mL) were mixed with 1.0 mL of iodine and potassium iodide solution (0.3 g of iodine and 7.5 g of potassium iodide in 500 mL of 50% glycerol). The microstructure of the GMSD was assessed with an optical microscope (Olympus BX45, Tokyo, Japan) that was coupled to an image analyzer system (digital Olympus camera C3030 and Image Pro-Plus 4.5 software, Media Cybernetics, Inc., Rockville, MD, USA). Selected micrographs at 100 × were used for illustration purposes.

2.5. SEM microscopy

Scanning electron microscopy (SEM) was performed on the GMSD samples to explore the surface microstructure features. To this end, dried GMSD samples were coated with a thin layer of gold in a Fine Coat Ion Sputter JFC 1100 (Jeol Ltd., Akishima, Japan). A high vacuum JEOL Scanning Electron Microscope JMS-6360LY (Jeol Ltd., Akishima, Japan), at 20 kV, was used to record each sample at magnification of 2000×. Representative SEM micrographs were presented to illustrate the surface features.

2.6. Particle size

The volume fraction-length mean diameter ($d_{\phi L}$) of the GMSD was estimated by means of laser diffraction method by using a Mastersizer 2000 (Malvern Instruments Ltd., Malvern, Worcestershire, UK). A Hydro wet was used as disperser unit. In all cases, samples of GMSD (0.25 mL) were mixed with 0.5 mL of distilled water, and the obtained mixture was homogenized under gently stirring conditions. An obscuration of 5–10% was considered for all measurements.

2.7. Syneresis

Syneresis was determined after 24 h of the GMSD preparation. To this end, GMSD samples (14 g) were placed in calibrated test-tubes and subsequently centrifuged at 222*g* for 3 min at room temperature (~20 °C). The clear supernatant was poured off and weighed. The results were expressed as a syneresis %, obtained as follows: (leached out water weight from the GMSD aged 24 h/initial water weight content in GMSD) × 100.

2.8. Contact angle

The sessile drop method is an optical angle approach that is commonly considered to estimate wetting properties of solid surfaces. To this end, the testing surfaces were obtained by pouring