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Effect of lime concentration on gelatinized maize starch dispersions properties

C. Lobato-Calleros [a], C. Hernandez-Jaimes [a,*], G. Chavez-Esquivel [b], M. Meraz [c], E. Sosa [d], V.H. Lara [e], J. Alvarez-Ramirez [b], E.J. Vernon-Carter [b]

[a] *Departamento de Preparatoria Agrícola, Universidad Autónoma Chapingo, Km 38.5 Carretera México-Texcoco, Texcoco 56230, Mexico*
[b] *Departamento de Ingeniería de Procesos e Hidráulica, Universidad Autónoma Metropolitana-Iztapalapa, Apartado Postal 55-534, Iztapalapa 09340, Mexico*
[c] *Departamento de Biotecnología, Universidad Autónoma Metropolitana-Iztapalapa, Apartado Postal 55-534, Iztapalapa 09340, Mexico*
[d] *Instituto Mexicano del Petróleo, Programa de Investigación en Integridad de Ductos, Lázaro Cárdenas No. 152, Col. San Bartolo Atepehuacan, México, D. F. 07730, Mexico*
[e] *Departamento de Quimica, Universidad Autónoma Metropolitana-Iztapalapa, Apartado Postal 55-534, Iztapalapa 09340, Mexico*

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ABSTRACT

Maize starch was lime-cooked at 92 °C with 0.0–0.40% w/w $Ca(OH)_2$. Optical micrographs showed that lime disrupted the integrity of insoluble remnants (ghosts) and increased the degree of syneresis of the gelatinized starch dispersions (GSD). The particle size distribution was monomodal, shifting to smaller sizes and narrower distributions with increasing lime concentration. X-ray patterns and FTIR spectra showed that crystallinity decreased to a minimum at lime concentration of 0.20% w/w. Lime-treated GSD exhibited thixotropic and viscoelastic behaviour. In the linear viscoelastic region the storage modulus was higher than the loss modulus, but a crossover between these moduli occurred in the non-linear viscoelastic region. The viscoelastic properties decreased with increased lime concentration. The electrochemical properties suggested that the amylopectin-rich remnants and the released amylose contained in the continuous matrix was firstly attacked by calcium ions at low lime levels (<0.20% w/w), disrupting the starch gel microstructure.

1. Introduction

Lime (i.e., $Ca(OH)_2$) cooking is widely used for enhancing the properties of products made from maize grains. Different studies have shown that lime cooking improves the nutritional quality of maize by increasing the availability of lysine in the glutelin fraction of the protein (Robles, Murray, & Paredes-Lopez, 1988). In fact, lime cooking results in denaturation of the maize protein, particularly the glutelins, making them more readily digestible (Bressani & Scrimshaw, 1958). After lime cooking, maize kernels are milled for forming a paste (aka, masa) that is mostly used for fabricating different foodstuffs, such as tortilla, thin porridges, additives, etc.

It has been shown that lime cooking increases calcium bioavailability by making calcium ions chemically linked to starch molecules via deprotonation of primary hydroxyl of the glucose rings (Stylianopoulos, Serna-Saldívar, & Arteaga-MacKinney, 2002; Trejo-González, Feria-Morales, & Wild-Altamirano, 1982). X-ray diffraction analysis indicated that during lime cooking, crystallinity of maize starch was reduced with certain recovery during steeping and cooling due to recrystallization processes (Gomez, Lee, McDonough, Waniska, & Rooney, 1992). Further X-ray diffraction studies suggested the presence of V-type crystalline structures, which has been related to the formation of amylose complexes with lipids (Mondragón et al., 2004). Maize starch gelatinization was also affected by lime cooking as water retention capacity, starch solubility and gelatinization temperature were increased by addition of lime at levels between 0% and 0.40–0.50%, peaking at 0.20% (Bryant & Hamaker, 1997). The viscoelastic behaviour of starch gels after lime-heat treatment was affected by the calcium interactions with starch (Mondragón, Mendoza-Martínez, Bello-Pérez, & Peña, 2006; Méndez-Montealvo, García-Suárez, Paredes-López, & Bello-Pérez, 2008). Processing variables, such as cooking time and lime concentration, had significant effects in moisture content, pH and colour of maize pastes (Sefa-Dedeh, Cornelius, Sakyi-Dawson, & Afoakwa, 2004). Overall, lime cooking produces important chemical and physical changes in the components of the maize kernels, with important effects on the rheological, textural and structural characteristics of food products (e.g., masa, tortilla, etc.).

Traditionally, lime cooking is performed by combining dent maize and lime-water solution (about 1% w/v) and cooking at

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* Corresponding author. Tel./fax: +52 55 58044650.
E-mail address: carmenhernandezjaimes@gmail.com (C. Hernandez-Jaimes).

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boiling temperature for 30 min and steeping for 16 h. The degradation of pericarp, the loss of soluble proteins (e.g., albumin and globulin of low molecular weight contained in the germ) and the partial gelatinization of starch are observed effects of alkali cooking. Since maize kernels are compact structures, the extent of the alkali treatment is strongly dominated by the diffusion of calcium ions into the grain complex structure. At common boiling temperatures (about 90–100 °C), starch contained within the maize kernel undergoes partial gelatinization, easing the transport and binding of calcium ions. Studies have suggested that the variation in calcium content is a result of a simultaneous kinetic diffusion process taking place in the pericarp, endosperm, and germ (Fernández-Muñoz, Zelaya-Angel, Cruz-Orea, & Sánchez-Sinencio, 2001). Also, the incorporation of calcium does not proceed at the same rate for all grains and can occur abruptly with significant kernel damage (Zazueta et al., 2002). Differences in calcium content between damaged and undamaged kernels were also detected (Fernández-Muñoz et al., 2004).

For a given lime concentration in the water solution, an important question is the extent of chemical attachment of calcium into the starch molecular structure. This question is relevant since high concentrations of free-calcium increase the risk of formation of calcium-based calculus (Vargas et al., 2012). Using dielectric determinations for maize dough, it was estimated that the $Ca(OH)_2$ threshold concentration for alkaline cooking is about 1%, above which most calcium ions move freely within the dough bulk (Vargas et al., 2012). However, since most studies on maize alkali cooking have been based on maize kernels, the determination of the mechanisms underlying starch transformation by calcium ions can be masked by diffusion effects (Gutiérrez et al., 2007).

Diverse results have been reported in the open literature about the physicochemical effects of lime treatment on maize grain kernels. However, there is a lack of detailed studies about the effects of lime treatment on maize starch, where the concurrent lipid–protein–starch effects observed for complete maize grains are deleted. Some works dealing with alkali treatment with NaOH of maize starch can provide some insights regarding the effects of lime treatment. For instance, Han and Lim (2004) showed that with sodium hydroxide treatment the majority of –OH groups in the anhydrous glucose units were ionised at high pH (12.5), so agglomeration of starch chains and paste retrogradation could be retarded. However, other research studies indicated that molecular degradation was accelerated by alkali (Wang & Zopf, 1989). It has been also reported that sago starches treated with NaOH experienced a significant increase in amylose content, but decreases in intrinsic viscosity and peak viscosity values, compared to those exhibited by the native starches (Kaur, Fazilah, & Karim, 2011).

Motivated by the need of an accurate characterisation of the physical and chemical effects of lime treatment concentration, and by considering that maize kernels are mostly composed by starch, the aim of this work was to study the lime cooking of gelatinized maize starch dispersions (GDS) at different $Ca(OH)_2$ concentrations. To this end, the morphological, particle size distribution, crystallinity, rheological, and electric properties were evaluated. By doing this, the diffusion limitations to calcium ion chemical attachment are minimised, and a more accurate picture of the chemical effects of calcium ion on starch molecules can be gained.

2. Materials and methods

2.1. Materials

Native maize starch was obtained from Gluten y Almidones Industriales (Mexico City, Mexico). $Ca(OH)_2$ (98%) was obtained from Spectrum Chemical Mfg. Corp. (New Brunswick, NJ, USA), and I_2 (98%) was obtained from J.T. Baker (Mexico City, Mexico). Deionised water was used in all experiments.

2.2. Lime treatment

Gelatinized starch dispersions (GSD) were prepared by putting maize starch (7% w/w) in lime water solutions prepared at different concentrations (0.0%, 0.05%, 0.10%, 0.15%, 0.20%, 0.25%, 0.30%, 0.35% and 0.40% w/w). The dispersions were gently stirred and heated at 92 °C (boiling temperature in Mexico City) for 20 min to allow interaction between calcium and starch granules, and also the complete gelatinization of the starch granules. The starch dispersions were then cooled down to room temperature and kept in sealed containers. For reducing the adverse effects caused by starch retrogradation, all analysis runs were carried out within the first 15 min after the GSD attained room temperature.

2.3. Optical microscopy

For optical microscopy tests, GSD were stained 15 min at room temperature by mixing 1.0 mL of the sample 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 samples were observed with an optical microscope (Olympus BX45, Olympus Optical Co., Tokyo, Japan) coupled to an image analyser system (digital Olympus camera C3030 and Image Pro-Plus version 4.5 software, Media Cybernetics, Inc., Rockville, MD, USA). Selected micrographs at 100× are presented.

2.4. Particle size distribution

The hydraulic particle size after lime cooking was estimated by taking 0.25 mL of the sample, adding 0.5 mL of distilled water, and homogenising by gently stirring. The particle size distribution was determined by laser diffraction using a Mastersizer 2000 (Malvern Instruments Ltd., Malvern, Worcestershire, UK), with the help of a Hydro wet disperser unit. The obscuration was in the interval of 5–10%. The Fraunhofer approximation was used for calculation of the size distribution and the corresponding volume moment mean diameter ($d_{4,3}$).

2.5. Syneresis

An estimate of gel syneresis as a function of the $Ca(OH)_2$ concentration was obtained by draining the leached water of the GSD after 24 h at room temperature (about 20 °C). For 1 mL of the cooked starch gel, the syneresis ratio (SR) was taken as the leached water relative to the cooked starch with 0.0% lime concentration. That is, under the same sample weight, the SR is given by

$$SR = \frac{W}{W_0}$$

where W and W_0 are the water amounts leached by the lime-cooked and the uncooked starch gel, respectively.

2.6. X-ray diffraction (XRD)

XRD patterns were measured at room temperature. A Siemens D-5000 diffractometer (Karlsruhe, Germany) using Cu Kα radiation ($\lambda = 1.543$) and a secondary beam graphite monochromator was operated at 40 kV and 30 mA. Intensities were measured in the 10–60° 2θ range with a 0.03° step size and measuring time of 1.0 s per point. Crystallinity was measured according to the Hermans–Weidinger method. Diffractograms were smoothed