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Viscoelastic behaviour of masa from corn flours obtained by nixtamalization with different calcium sources

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ABSTRACT

The viscoelastic characteristics of nixtamalized corn masa were assessed by the dynamic oscillatory test. Masa samples were prepared with flours obtained by nixtamalization with different calcium sources: $Ca(OH)_2$ (traditional), wood ashes (classic), $CaCO_3$ (ecological), $CaSO_4$ (ecological), $CaCl_2$ (ecological), and $Ca(C_2H_5COO)_2$ (ecological). A sample cooking without calcium source was used as control. Storage (G′) and loss (G″) moduli were higher in masa from traditional and classic processes indicating a more elastic and viscous masa. Masa of flours from $CaCl_2$ and $Ca(C_2H_5COO)_2$ had the lowest values of G′ and G″. Viscoelastic properties were explained in terms of the degree of starch gelatinization, the hydrolysis of pericarp and fibre content, the calcium-starch and calcium-zein interactions, as well as the presence of amylose-lipid complexes. Nixtamalization with $Ca(OH)_2$ and wood ashes gave the best viscoelastic characteristics of masa.

1. Introduction

Nixtamalized corn flours are used to prepare a large variety of food products, such as tortillas or tamales, which are widely consumed worldwide. Flours are obtained by cooking corn grains, at temperatures higher than 80 °C, for 25–60 min in water solutions, using a calcium compound, usually calcium hydroxide $Ca(OH)_2$ (traditional nixtamalization). Nevertheless, other calcium sources can be used, such as wood ashes (Santiago-Ramos, Figueroa-Cárdenas, Véles-Medina, & Mariscal-Moreno, 2017), calcium carbonate $CaCO_3$, calcium chloride $CaCl_2$, calcium sulfate $CaSO_4$, calcium acetate $Ca(CH_3\ COO)_2$, calcium propionate $Ca(C_2\ H_5\ COO)_2$, or calcium lactate $Ca(CH_3CHOHCOO)_2$ (Figueroa Cárdenas, Rodríguez Chong, & Véles Medina, 2011). After cooking, the nixtamal (cooked grains) is steeped in the cooking solution for 1–16 h, rinsed, and finally milled to obtain masa, which is dried to obtain nixtamalized corn flour (Santiago-Ramos et al., 2017).

In all stages of the process, the main components of corn undergo several changes. During cooking and steeping, in the traditional nixtamalization, the pericarp is hydrolyzed mostly into arabinoxylans; the starch of the endosperm undergoes a partial gelatinization and annealing simultaneously; some lipids are saponified, and the proteins are solubilized and polymerized (Quintanar Guzmán, Jaramillo Flores, Solorza Feria, Méndez Montealvo, & Wang, 2011). Another important change is the calcium absorption, which occurs due to saponification of fatty acids, neutralization of the acidic groups of hemicelluloses (mainly uronic acids), and the interaction between Ca ions and amylose or amylopectin chains in the form of an alkoxide and among them through the formation of Ca bridges (Gonzalez, Reguera, Figueroa, & Sánchez-Sinencio, 2005). The subsequent milling of nixtamal increases the starch gelatinization and allows a better interaction among all components, mainly between lipids and starch, to form amylose-lipid complexes (Santiago-Ramos et al., 2017). The extent of these changes produces a masa with different viscoelastic behaviour.

In corn starch-based systems, (Qiu et al., 2015) reported that the inclusion of arabinoxylans (corn fibre gum) increased the apparent viscosity, storage modulus (G′), and loss modulus (G″) suggesting chain entanglements between arabinoxylans and amylose or short-chain amylopectin molecules. In corn masa, rheological studies have shown that it has a pseudoplastic behaviour with storage modulus (G′) higher than loss modulus (G″), which depends on the $Ca(OH)_2$ concentration, suggesting the formation of cross-links between calcium and amylose or amylopectin chains of the gelatinized starch granules (Contreras-Jiménez et al., 2017; Mondragón, Mendoza-Martínez, Bello-Pérez, & Peña, 2006). Quintanar Guzmán et al. (2011) reported that calcium-protein interactions, as well as protein polymerization also had a strong influence on corn gel strength by enhancing its elastic character. The

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formation of amylose-lipid complexes has been reported to decrease the starch gel consistency (G′), because of the lower availability of amylose to develop a stronger gel network (Mondragón et al., 2006; Vázquez-Carrillo, Santiago-Ramos, Gaytán-Martínez, Morales-Sánchez, & Guerrero-Herrera, 2015).

Cooking and steeping of corn, using a calcium source other than $Ca(OH)_2$, has different effects on corn components. Corn pericarp and aleurone, which contain mainly hemicellulose, cellulose, and proteins, are retained during the different steps in the process when using $CaSO_4$, $CaCO_3$, $CaCl_2$ or $Ca(CH_3COO)_2$ (Campechano Carrera et al., 2012). Santiago-Ramos et al. (2015) reported that starch annealing and gelatinization depend on the dissociation of each salt in water and the ability of anions to penetrate into the starch granule and break hydrogen bonds.

All those changes affect the rheological properties of masa; however, to our knowledge, no studies have explored these properties in masa from nixtamalized flours other than those obtained by the traditional nixtamalization. Therefore, the objective of this work was to study the effect of nixtamalization with different calcium sources on the thermal and viscoelastic properties of masa.

2. Materials and methods

2.1. Materials

Commercial white corn of intermediate endosperm hardness (flotation index 46) (Santiago-Ramos et al., 2017), with 11.6% moisture, 82.4% starch, 10.5% crude protein, 4.3% crude fat, 1.3% ash, and 20.3% amylose, was purchased from Central de Abastos (Queretaro, Mexico), and used for preparation of nixtamalized flours. The calcium hydroxide $Ca(OH)_2$, calcium carbonate $CaCO_3$, calcium sulfate $CaSO_4$, calcium chloride $CaCl_2$, and calcium propionate $Ca(C_2\,H_5\,COO)_2$ were of 97–99% purity and food grade (Alquimia Mexicana, Mexico City, Mexico). Ashes of oak tree (*Quercus* spp.) were obtained in Oaxaca City, Mexico. Mineral composition of ashes was: Ca (19.9 ± 0.28%), Mg (2.26 ± 0.13%), P (1.26 ± 0.03%), K (0.63 ± 0.01%), Fe (0.63 ± 0.03%), Na (0.59 ± 0.01%), and Zn (0.17 ± 0.00%). An X-ray diffraction analysis showed that Ca in ashes was found mainly as calcite $CaCO_3$.

2.2. Preparation of nixtamalized corn flours

2.2.1. Classic nixtamalization process

One kg of corn was cooked for 35 min at 94 °C with 2 L of water containing 1.0% (w/w) of wood ashes, then the cooked grains (nixtamal) were removed from the heat and allowed to steep/soak in the cooking solution to reach room temperature (25 ± 2 °C) after 16 h. The nixtamal was then separated from the cooking solution and washed to eliminate excess ashes (Mariscal Moreno et al., 2015).

2.2.2. Traditional nixtamalization process

Corn (1 kg) was cooked for 35 min at 94 °C with 2 L of water containing 1.0% (w/w) $Ca(OH)_2$. Nixtamal was steeped and washed in the same way as in the Classic nixtamalization process (Santiago-Ramos et al., 2015).

2.2.3. Ecological nixtamalization process

The procedure was similar to the process described for Classic and Traditional nixtamalization processes, but selected specific solutions of 1.0% of calcium carbonate $CaCO_3$, calcium sulfate $CaSO_4$, calcium chloride $CaCl_2$, or calcium propionate $Ca(C_2H_5COO)_2$ were used for cooking as patented by Figueroa Cárdenas et al. (2011).

The washed nixtamal from each specific nixtamalization process was ground in a stone mill (M100, Fumasa, Queretaro, Mexico) to obtain fresh masa. The masa was dried in a flash dryer (Cinvestav, Queretaro, Mexico) at 260 °C passing it four times, for 4 s each time. The resulting flour was ground in a Pulvex grinder (Maquinaria Pulvex S.A. de C.V., Mexico City, Mexico) and sifted through a U.S. 60 mesh (0.5 mm). The dried nixtamalized flour was packed into polyethylene bags and stored at 25 °C until used. This procedure was repeated for each calcium source. A treatment with no calcium source added was included as control.

2.3. Thermal analysis

A sample (100 g) of raw corn grain was ground and sieved through a U.S. 60 mesh (0.5 mm). Thermal analyses were conducted in flours from raw and nixtamalized corn with a differential scanning calorimeter (DSC1 model 821, Mettler Toledo, Greifensee, Switzerland) previously calibrated with indium, according to the method reported by Santiago-Ramos et al. (2017). Four mg of raw corn flour or nixtamalized corn flour were weighed in an aluminium pan, and deionized water was added to reach 60% moisture content. The pan was sealed, and it was allowed to stand for 1 h before performing the analysis. An empty aluminium pan was used as a reference. The sample was subjected to a heating programme over a range of temperatures from 30 to 130 °C and a heating rate of 10 °C/min. Each endotherm was characterized by the onset (To), peak (Tp), and final (Tf) transition temperatures, as well as the enthalpy change (ΔH). Each sample was run in triplicate.

The degree of gelatinization (DG) was calculated with the following equation, based on the equation reported by Baks, Ngene, van Soest, Janssen, and Boom (2007):

$$DG = 1 - \frac{\Delta Hgel_{HN}}{\Delta Hgel_{NS}} \tag{1}$$

where $\Delta Hgel_{HN}$ is the starch gelatinization enthalpy of the nixtamalized corn flour and $\Delta Hgel_{NS}$ is the starch gelatinization enthalpy of the raw corn flour.

2.4. X-ray diffraction

Diffractograms were obtained, following the method reported by Santiago-Ramos, de Figueroa-Cárdenas, Véles-Medina, & Salazar (2018). All samples were previously equilibrated to 7.0 ± 0.2% moisture content by allowing them to stand (5 g of each flour) at 30 °C for 48 h. Then 1 g of sample was placed on a glass surface and scanned from 5 to 50° on the 2θ scale with an X-ray diffractometer (DMAX-2100, Rigaku, Tokyo, Japan), which operates at 30 kV and 16 mA with a CuKα radiation of λ = 1.5405.

2.5. FT-IR analysis

Infrared absorption spectra of flours from raw and cooked corn were recorded by Fourier transform infrared spectroscopy (FT-IR) with a Spectrum GX spectrometer (Perkin Elmer, MA, USA) with a diffuse reflectance accessory (Pike Technology model). The fine powder sample was mixed with dry potassium bromide (KBr) at a ratio of 4:98 (w/w). Spectral data within the range of 400–4000 cm^{-1} were collected in 24 scans at a resolution of 4 cm^{-1} against a background spectrum recorded from the KBr at 25 °C (Santiago-Ramos et al., 2018).

2.6. Calcium content

Calcium content, in flours from raw, control and nixtamalized corn, was determined by Inductively coupled plasma spectroscopy (ICP) according to the method 40-75.01 (AACC International., 2017). Results were reported as mg/100 g of dry sample; therefore, the moisture content was determined according to the AACCI Approved Method 44-15.02 (AACC International, 2017).