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Changes in the thermal and structural properties of maize starch during nixtamalization and tortilla-making processes as affected by grain hardness

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ABSTRACT

The objective of this work was to evaluate the changes in the thermal and structural properties of maize starch during nixtamalization and the tortilla-making process and their relationship with grain hardness. Three maize types with varying hardness (hard, intermediate, soft) were processed by three nixtamalization processes (classic, traditional and ecological). Starch from the three maize types showed an A-type pattern and two endotherms corresponding to gelatinization and melting of the Type I amylose-lipid complexes. After cooking and steeping, in intermediate and soft grains the partial gelatinization and the annealing affected the starch properties and promoted the formation of amylose-lipid complexes. These effects were not observe in hard grains. The increase in melting enthalpy and the intensity of the peak $2\theta \sim 20^\circ$ from nixtamal to tortillas demonstrated the formation of amylose-lipid complexes. A third endotherm above 114 °C in some treatments of nixtamal and tortilla starch demonstrated the transformation of some amylose-lipid complexes in a most ordered structures (Type II complexes). The V-type polymorph structure found in native starch, nixtamal, and tortilla corresponds to a coexistence of Type I and Type II complexes. Formation of amylose-lipid complexes in tortillas had a partial effect on decreasing starch retrogradation ($r = -0.47$, $P < 0.05$).

1. Introduction

Maize (*Zea mays* L.) is the basis for the preparation of a large variety of nixtamalized corn products worldwide. Several nixtamalization processes can be used for the preparation of these products, mainly tortillas, at industrial and domestic levels, including the Classic (CNP), Traditional (TNP) and Ecological (ENP) processes (Mariscal Moreno et al., 2015). In each process, grains are boiled for 25–60 min in water solutions with different sources of calcium, wood ashes in CNP, lime [$Ca(OH)_2$] in TNP, or calcium salts [$CaCl_2$, $CaSO_4$, $CaCO_3$, $Ca(C_2H_5COO)_2$] in ENP (Figueroa Cárdenas et al., 2011; Mariscal Moreno et al., 2015). After cooking, the nixtamal (cooked grains) is steeped in the cooking solutions for 1–16 h, rinsed, and finally milled to obtain masa. Masa is used directly to prepare tortillas or can be dried to obtain nixtamalized maize flour (Santiago-Ramos et al., 2015a).

Several types of maize varying in hardness can be used to make

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Abbreviations: AACCI, American Association of Cereal Chemists International; CNP, Classic Nixtamalization Process; DSC, Differencial Scanning Calorimetry; ENP, Ecological Nixtamalization Process; ESEM, environmental scanning electron microscope; FI, flotation index; FE, floury endosperm; ΔH_{gel}, gelatinization enthalpy; ΔH_{RS3}, enthalpy of melting of recrystallized amylopectin; ΔH_{RS5I}, melting enthalpy of the amylose-lipid complexes Type I; ΔH_{RS5II}, melting enthalpy of the amylose-lipid complexes Type II; Tf_{gel}, final gelatinization temperature; Tf_{RS3}, final temperature of melting of recrystallized amylopectin; Tf_{RS5I}, final temperature of melting of the amylose-lipid complexes Type I; TNP, Traditional Nixtamalization Process; To_{gel}, Onset gelatinization temperature; To_{RS3}, Onset temperature of melting of recrystallized amylopectin; To_{RS5I}, onset temperature of melting of the amylose-lipid complexes Type I; Tp_{gel}, peak gelatinization temperature; Tp_{RS3}, peak temperature of melting of recrystallized amylopectin; Tp_{RS5I}, peak temperature of melting of the amylose-lipid complexes Type I; Tp_{RS5II}, peak temperature of melting of the amylose-lipid complexes Type II; VE, vitreous endosperm.

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tortillas. Grain hardness is influenced by the presence of two types of endosperm: floury (soft) or vitreous (hard), which depend on the size, morphology and compaction grade of starch granules and the protein matrix that surrounds them (Narváez-González et al., 2006b). The starch properties of each type of endosperm are distinct, and in each stage of the nixtamalization and tortilla-making process, this component undergoes several changes that influence the functional properties of nixtamal, masa, nixtamalized flours and tortillas (Santiago-Ramos et al., 2015a).

Annealing is one of the phenomenon that occurs during nixtamalization, mainly during nixtamal steeping. Figueroa et al. (2013) and Santiago-Ramos et al. (2015b) reported and increase in starch gelatinization temperatures in TNP and ENP; however, it is unclear how the grain hardness or endosperm type influences this effect.

Another important change that is not well understood is the formation and presence of amylose-lipid complexes. Some authors have reported the formation of these complexes in TNP during cooking and steeping and have suggested some influence on the starch properties of nixtamal (Mondragón et al., 2004a, 2004b, 2006) and tortillas (Flores-Morales et al., 2012; Santiago-Ramos et al., 2015a). Recently, González-Amaro et al. (2015), Mariscal Moreno et al. (2015), and Santiago-Ramos et al. (2015a, b) suggested that amylose-lipid complexes are formed during CNP and ENP.

Osorio-Díaz et al. (2011) reported that tortillas prepared with hard maize (vitreous endosperm) had a more rigid texture and lower available starch content than tortillas made with soft maize. They attributed these results to a higher retrogradation rate.

As mentioned above, no studies have reported the influence of the tortilla-making process and grain hardness on changes occurring to the starch or how these changes can affect the properties of tortillas.

The objective of this work was to study the changes in the thermal and structural properties of maize starch during the nixtamalization and tortilla-making process and their relationship with grain hardness.

2. Materials and methods

2.1. Materials

Commercial hard, intermediate and soft endosperm maize samples were obtained from a market in Queretaro, Mexico. The calcium hydroxide $Ca(OH)_2$ and calcium chloride $CaCl_2$ were 97–99% purity and food grade (Alquimia Mexicana, México, D. F.). Ashes were of oak tree (*Quercus* spp.).

2.2. Grain hardness

Grain hardness and endosperm types were classified based using two tests: flotation index (FI) and puncture test. FI was evaluated by placing 100 grains in a beaker containing 300 mL of $NaNO_3$ solution (1.250 g/mL). The mixture was stirred and left standing for 1 min. The number of floating kernels indicated the kernel hardness by the flotation index according to the norm NMX-FF-034/1-SCFI-2002 (Secretaría de Economía, 2002), and the test was performed in duplicate. When FI was 0–12, maize was classified as very hard; a FI of 38–62 was considered intermediate hardness, and a FI of 88–100 was classified as very soft.

In the puncture test, kernel hardness in Newtons (N) was measured using a TA-XT2 texture analyzer (Texture Technologies Corporation, Stable Micro Sys-tems; Surrey, England) equipped with a 30° conical probe. Ten kernels of each type of maize were punctured at the opposite side of the germ in the central part of the endosperm with a velocity of 2 mm/s and a penetration depth of 2 mm (Narváez-González et al., 2006b).

2.3. Content of floury and vitreous endosperm

Ten grains were soaked in boiled water for 5 min and were hand-dissected. Pedicel, pericarp and germ kernel fractions were removed, and portions of endosperm differing in texture were separated into floury (soft) and vitreous (hard) fractions (Narváez-González et al., 2006a).

2.4. Pericarp thickness

Two samples of each grain type were prepared by cutting the grain with a razor blade at the median longitudinal section of the grain perpendicular to the face and mounted onto the aluminum stubs for observation. An environmental scanning electron microscope (ESEM; Philips model XL30) with a beam of 20 kV (50 mA) and a gaseous secondary electron (GSE) detector was used to evaluate the pericarp thickness. The images were taken at 2500X, 1 torr with a spot size of 4.6 (Figueroa et al., 2013).

2.5. Chemical analyses

Amylose content in raw maize starch was quantified using the Megazime kit (Megazyme International, Ireland), which is a modification of a Con A method developed by Yun and Matheson (1990). The total starch content in raw maize starch was determined with the Megazyme kit (Megazyme International, Ireland) based on the AACCI Approved Method 76–13.01.

2.6. Nixtamalization processes and tortilla preparation

Tortillas were prepared from each type of maize with the following three nixtamalization processes: classic, traditional and ecological. The cooking time of each type of maize was assigned based on FI; hard maize was cooked for 45 min, intermediate for 35 min, and soft for 25 min (Secretaría de Economía, 2002).

2.6.1. Classic nixtamalization process

One kg of maize was cooked at 90 °C with 2 L of water containing 1.0% (w/w) of wood ashes, and the cooked grains (nixtamal) were removed from the heat and steeped for 16 h to reach room temperature. The nixtamal was then separated from the cooking solution and washed to eliminate excess ashes.

2.6.2. Traditional nixtamalization process

Maize (1 kg) was cooked at 90 °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 CNP (Santiago-Ramos et al., 2015a).

2.6.3. Ecological nixtamalization process

The procedure was similar to the process described for CNP and TNP, but a solution of 1.0% calcium chloride was used for cooking (Figueroa Cárdenas et al., 2011).

A sample of 100 g of nixtamal was taken at the end of washing in each treatment and dried at 40 °C for 24 h. The nixtamal was then ground and sifted through a U.S. 60 mesh (0.5 mm). The dried nixtamal flour was packed into bags and stored in a cold room at 4 °C until analysis.

The rest of the nixtamal 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). The resulting flour was ground in a Pulvex grinder (Maquinaria Pulvex S.A. de C.V., Mexico City, Mexico) with a hammer head and was sifted