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Thermal and rheological properties of masa from nixtamalized corn subjected to a sequential protein extraction

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ABSTRACT

The aim of this work was to study the effect of a sequential extraction of proteins from nixtamalized corn (*Zea mays* L) on the thermal and rheological properties of the resulting dough (masa) from the residual components. Proteins were sequentially extracted from nixtamalized and control corn samples. Masas resulting after each protein fraction extraction were subjected to thermal analysis and rheological tests. The thermogram data suggested that, even though albumins and globulins were in small amount in corn samples cooked with lime, interactions albumins-lime and globulins-lime could probably be taking place and these interactions stabilized the starch crystals. However, zeins and glutelin-like proteins probably interacted with gelatinized starch, weakening its crystal integrity. Rheological characterization showed that all masas, behaved as "weak-gel- like materials", with a predominating elastic behavior ($G' > G''$), over the involved frequency range. The elastic rheological response might be attributed to the formation of a lime-polymerized protein-starch network and G' and G'' were affected by the applied treatments.

1. Introduction

Nixtamalization is a process comprising mainly four steps: a) cooking corn kernels under alkaline conditions until tender; b) steeping the cooked corn in the cooking solution over several hours (from 6 to 14 h); c) washing the corn; d) grinding the steeped corn kernels into a soft non-sticky dough named "masa". During this process, several changes take place: one of the most important is the diffusion of water and calcium ions into the kernel's endosperm (Laria et al., 2007). The gelatinization of starch is another main change that corn kernels undergo during nixtamalization. Changes in starch during nixtamalization have received much attention, considering that it is the main component in corn kernels (Cornejo-Villegas et al., 2013). It has been considered that the changes occurring in starch during nixtamalization are responsible for the textural and sensory properties of masa and its products like tortillas, tortilla chips, corn chips, etc. (Campus-Baypoli et al., 1999).

Starch granules in corn are covered with protein, also known as starch granule-associated proteins (Han et al., 2002; Quintanar-Guzman et al., 2009). A function of starch granule-associated proteins is to maintain gelatinized starch granule structure (Hamaker and Griffin, 1993; Hamaker et al., 1991). A relevant question is how such a small amount of protein could affect the rheology of gelatinized starch pastes.

Proteins are classified according to their solubility into four categories: albumins (soluble in water), globulins (soluble in saline solutions), prolamins (soluble in alcohol) and glutelins (soluble in diluted acid or alkaline). In corn kernels, prolamins are located mainly in the endosperm and are named zeins. Glutelins are in the protein bodies, protein matrix and also in the endosperm. In contrast, proteins in germ are mainly albumins and globulins (Shewry and Halford, 2002).

The nixtamalization process has been studied for over the last four decades, but little work has been done on the effect of the changes occurring in the protein during nixtamalization on masa

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properties (Ortega et al., 1986; Vivas et al., 1987; Rojas-Molina et al., 2008). In a previous work (Quintanar-Guzmán et al., 2011) the effect of lime and cooking temperature on the total protein was studied.

Thus, the objective of this study was to investigate the effect of the sequential extraction of corn proteins after nixtamalization on the thermal and rheological behavior of the resulting masa.

2. Materials and methods

2.1. Material

The commercial corn variety named white dent corn was used. An alkaline treatment was done with commercial lime [calcium hydroxide; purity 88.2% (cal pirámide, Grupo Bertrán, Mexico City) commonly used in the tortilla industry. The rest of the reagents were analytical grade.

2.2. Corn cooking conditions

Lots of 500 g of corn in 1.5 L of deionized water were nixtamalized using 1% (w/w) of calcium hydroxide (lime/weight) of corn. Samples labeled as Ca, were subjected to a thermal alkaline treatment at 90 °C for 20 min up to 35% moisture content, while 500 g of corn named non-nixtamalized corn samples or control (NCa) were cooked in 2.5 L of deionized water 90 °C for 43 min to reach the same mentioned moisture content (Gutierrez et al., 2007).

Both samples of cooked corn (Ca and NCa) were then steeped at room temperature for 14 h, according to the traditional procedure to reach 42% moisture content. After steeping, samples were washed thoroughly with deionized water until the pH of the rinsing water was 7. All washed corn samples were ground by using a commercial coffee grinder, dried overnight at 40 °C, and finally sieved through a 150-μm mesh. Triplicate samples of dried and sieved Ca and NCa were defatted by shaking twice 50 g of flour with 500 mL of hexane (15 min) at room temperature and by removing the supernatant after centrifugation at 12,000 × *g* for 5 min. Samples were dried overnight at 40 °C in order to evaporate residual hexane.

2.3. Protein extraction

Proteins were sequentially extracted from nixtamalized corn (Ca) and control corn samples (NCa) according to the methodology described by Rojas-Molina et al. (2008), obtaining five fractions: F1: globulins and saline soluble albumins; F2: water soluble albumins; F3: α-, β-, δ-zeins and zein-like proteins; F4: γ-zeins and glutelin-like proteins and F5: glutelins. Extracted protein fractions were dialyzed against distilled water and then freeze-dried to obtain the protein isolates.

After each protein fraction extraction, 20 g of the remaining sample (residues with no extracted proteins), were dried overnight at 40 °C for thermal analysis and rheological behavior tests. In such conditions, 5 residues were obtained as follows: CaR1 and NCaR1 (after globulin and saline soluble albumin extraction), CaR2 and NCaR2 (previous residue after albumin extraction), CaR3 and NCaR3 (previous residue after α-, β-, δ-zeins and zein-like proteins extraction), CaR4 and NCaR4 (previous residue after γ-zeins and glutelin-like proteins extraction), CaR5 and NCaR5 (previous residue after glutelins extraction) that contained non-extracted proteins and starch.

Crude protein (N × 6.25) of Ca and NCa flours, protein fractions and residues was determined by the Dumas method using an autoanalyzer system FP-528 (LECO Corporation, St Joseph, MI).

2.4. Electrophoresis (SDS-PAGE)

The protein composition of fractions of treated corn kernels was analyzed using SDS-PAGE under reducing (heat and 4% 2-ME) and non-reducing (neither heat nor 2-ME) conditions. Samples of freeze-dried protein extracts from nixtamalized and control samples of approximately 0.20 mg protein were prepared according to the method described by Quintanar-Guzman et al. (2011). SDS-PAGE was done on a vertical gel system Mini-Protean 3 (Bio-Rad Corporation, Hercules, CA) using a 15% acrylamide gel with a 4% stacking gel, at 200 V for approximately 30 min. Gels were stained with Coomassie Brilliant Blue R-250 staining solution (BioRad, Richmond, CA) and then destained with 40% methanol and 10% glacial acetic acid. Standards with molecular mass ranging from 10 to 250 kDa (BioRad, Richmond, CA) were used to determine the molecular masses (Mr) of polypeptide bands of the sample. All gel tests were performed in triplicate.

2.5. Thermal analysis

The peak transition temperatures (Tp) and enthalpies (ΔH) of the samples prior to the protein extraction (Ca, NCa) and also of the residues (R1 to R5) obtained after a sequential protein extraction were determined using a differential scanning calorimeter (DSC, 822e/400, Mettler-Toledo, Columbus, OH). The DSC was calibrated with indium, and data were analyzed using the STARe software. Approximately 100 mg of dried sample were mixed with deionized water to obtain a mixture of 50% moisture content and equilibrated at room temperature for 1 h to ensure complete hydration (Cameron and Wang, 2006). Samples of approximately 8 mg of the equilibrated mixtures were placed in pre-weighed aluminum pans. The pans were hermetically sealed and scanned from 25 to 120 °C at 10 °C/min. All measurements were carried out in triplicate.

2.6. Viscoelastic behavior

The viscoelastic properties of all twelve masa samples prepared from the mentioned residues after protein extraction (Ca, NCa, CaR1, NCaR1, CaR2, NCaR2, CaR3, NCaR3, CaR4, NCaR4, CaR5 and NCaR5) were studied with a stress controlled AR-1000 rheometer (TA Instruments, New Castle, DE), used in feedback on its strain mode, assembled with a parallel plate system (cross-hatched surface) with a diameter of 60 mm and a sample gap of 1 mm. Sample preparation and analyses were done according to methods described by Quintanar-Guzman et al. (2010). Two isothermal tests were undertaken per sample at 25 °C and 60 °C, temperatures commonly used in the tortilla industry. All measurements were done in triplicate. To determine the linear viscoelastic region (LVR), strain amplitude sweeps were run from 0.015 to 3.0% strain, at a frequency of 6.28 rad/s. Once the LVR was determined, frequency sweeps (from 0.628 to 628 rad/s) were run at a constant strain value of 1%. The storage modulus (G') and the loss modulus (G'') were obtained from the tests.

2.7. Statistical analysis

Data were statistically analysed using ANOVA procedures. Where appropriate, means were ranked using the Student-Newman-Keul's test ($P > 0.05$). Data analyses were conducted using the statistical package Statgraphics Plus for Windows ver. 5.1.

3. Results and discussion

3.1. Protein analysis SDS-PAGE

The results of protein distribution of extracts and protein recovery are shown in Table 1. The protein content found in