

STRUCTURAL, THERMAL AND RHEOLOGICAL PROPERTIES OF NIXTAMALIZED MAIZE MASA OBTAINED FROM VARYING THE CONCENTRATION OF CALCIUM HYDROXIDE AND COOKING TIME

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Abstract

Villa, G. A., R. S. Rosiles; R. R. Villalobos; F. R. González, J. de D. F. Cárdenas and J. A. M. Albores, 2017. Structural, thermal and rheological properties of nixtamalized maize masa obtained from varying the concentration of calcium hydroxide and cooking time. *Bulg. J. Agric. Sci.*, 23 (4): 653–663

In this work, we have evaluated the effect of the concentration of calcium hydroxide (0.1 – 3.9% w/v) and cooking time (15 – 85 min) of maize grain (Pioneer 30G54 and QPM H-374C) on the structural, thermal and rheological characteristics during the nixtamalization process and compared with those without nixtamalization. The X-ray diffraction analysis of both samples of maize grain were shown to be standard type A-pattern, characteristic of most starches of cereal origin with a relative crystallinity of 44.39 – 34.12% and 42.29 – 32.51% for Pioneer and QPM, respectively. The ΔH showed values of 6.22 to 4.93 (J/g) and 5.8 to 4.24 (J/g) for both samples. The results showed that both the yield stress and the flow curves were influenced by the increasing calcium concentration and cooking time. The yield stress in the “masa”, increase sharply (e.g., from 2.51 to 63.10 Pa) and the viscosity significantly ($p < 0.05$) decreased with the increasing of shear rate, due to processing conditions and that the water retention capacity increases with temperature and particle size. SEM micrographics showed that when the concentration of lime increases, agglomerates occurred only in the Pioneer sample; however, this situation is lost when the temperature varies. For QPM sample SEM micrographics showed that the nixtamalization process did not affect the granules with the increasing of calcium hydroxide.

Key word: nixtamalization; X-ray; rheological properties; cooking time

Introduction

Maize (*Zea mays* L.) is the main cereal in the world, with extensive area planted in many countries due to its adaptation and higher productivity and, with uses such as food, feed and industrial (Šeremešić et al., 2016; Shafea and Saffari, 2016), considered as the usual food food for millions of people in Latin America. In México, is consumed as tortillas and others related products from nixtamalized maize grains (Serna-

Saldivar et al., 1998). The nixtamalization process includes a thermo-alkaline treatment, in which maize kernels are cooked and steeped in an oversaturated calcium hydroxide solution (Serna-Saldivar et al., 1993; Gutiérrez et al., 2007; Ruíz-Gutiérrez et al., 2012). After washing and grinding the “nixtamal”, is produced a soft dough, known as “masa” which is used in the production of tortillas. During the alkaline cooking, the OH⁻ ions react and dissolve the pericarp compounds, and is formed a calcium concentration gradient through the

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all structures of maize grain. This promotes physicochemical changes in the germ and endosperm, as such as in the internal anatomical structures of the grain. These changes alter the grain structure and the rheological properties due of heat and mass transference phenomenon (Verma and Prasad, 1999). Rheological properties are sensitive to variations in molecular structure, and are useful in developing structure–function relationships for systems of polysaccharide solutions and intermolecular interactions. The knowledge of rheological behaviour of the food ingredients is important to optimize applicability, stability, sensory properties, storage and processing of foods, stability measurements, and in predicting texture of foods (Kulicke et al., 1996; Abu-Jdayil et al., 2004). The texture of masa is very important during the production of tortillas. Both, in the industrial and the domestic process, the masa should be readily cohesive and adhesive to allow the formation of a sheet and thus, favour its cutting and shaping as round disks or another shape. Studies using the Rapid Visco Analyzer (RVA) have correlated the functionality of nixtamalized maize flour with the produced masa consistency. In addition, have been correlated the particles sizes and polymers with the texture of the masa (Sahai et al., 2001); however, few studies about the rheological characteristics of nixtamalized maize are found in the literature. The objective of this research was to evaluate the effect of the concentration of calcium hydroxide and cooking time of maize grain during the nixtamalization process on the structural, thermal and rheological characteristics of masa obtained from nixtamalized maize flour.

Materials and Methods

Maize variety Pioneer 30G54 (called sample A) and Quality Protein Maize (QPM H-374C) a white dent maize hybrid (called sample B) was harvested on 2012. Instituto Nacional de Investigaciones Forestales Agrícolas y Pecuarias (INIFAP) located in Celaya, Guanajuato, Mexico, provided both materials. The lime (CaOH_2), was food-grade.

Samples preparation

The samples were nixtamalized as described by Arámbula-Villa et al. (2001) and Trejo-Gonzalez et al. (1982), with some modifications. For this, 2 Kg of maize in different lime concentrations (0.1, 1.0, 2.0, 3.0, and 3.9%; w/v) at times (15, 25, 35, 45, 55, 65, 75 and 85 min) were cooked. The cooked grains were steeped in the same cooked liquor (“nejayote”) for 16 h and finally this was discarded. This solution contains some parts of pericarp and other soluble solids from the maize grains, contains most of the lime used in the process. In a nixtamal-stone mill (FUMASA US-25, Mexico) the nixtamalized maize was milled to obtain a masa (dough), a common step in

the traditional nixtamalization process. Through a flash dryer was dehydrated at 240 – 260°C for 3 s to obtain instant maize flour with 12% (w/w) moisture content and the flour was ground in a hammer mill (Pulvex 200, Mexico) and screened in No. 60 sieve (Mont-Inox, Mexico). In addition, a sample of each maize, which does not have the nixtamalized process, was included as control (called C_1 and C_2).

X-Ray diffraction (XRD) and crystallinity

The samples were analysed with a RIGAKU diffractometer, model Dmax2200 (RIGAKU Corp., USA.) working at a voltage of 30 kV, 20 mA, Cu-K radiation, and wavelength of 1.54 Å. The tests were done with the following parameters: angle interval 4– 60° (2 θ), chart speed was 10 mm 2 θ with a running rate of 2 θ min⁻¹ and a measuring time of 5 s. The percent crystallinity was calculated as the ratio of the total area respect to crystalline area between 13° and 26° using a straight-line background (Manful et al., 2008). The following formula was applied:

$$\% \text{Crystallinity} = \frac{\text{total cristalline peak areax} \times 100}{\text{Total area of diffraction pattern 13–32}^\circ} \quad (1)$$

Thermal analysis

The thermal properties were studied using a differential scanning calorimeter (DSC) (Mettler-Toledo model 822a, Switzerland). The calibration was done with Indium (point of fusion of 156.4°C; enthalpy of 6.8 cal/g). The base line was achieved by running a heating program from 25°C to 250°C. The initial (T_o), peak or gelatinization (T_p), final temperature (T_f) and transition enthalpy (ΔH , evaluated by integrating the peak area, corresponding to such transition), were obtained from the tests. About 3.0 μg sample (dry basis) was weighed with a micro balance (Perking-Elmer Corp., Model AD2Z, USA) $\pm$ 0.01 mg of precision, on an aluminium pan. This pan was sealed and could stand for 30 min before running the analysis; as reference, an empty aluminium pan was used. Through a heating program (run three times) over a temperature range from 30 to 110°C and a heating rate of 10°C min⁻¹ with nitrogen flow rate of 50 mL min⁻¹ (Quintanar et al., 2009).

Rheological properties

The rheology properties of samples were determined using a stress controlled rheometer (AR1000, TA Instruments, USA), assembled with serrated plate system, 60 mm of diameter, and a solvent trap to minimize moisture loss during test. Samples are left standing (5 min) before conducting rheological measurements such as equilibration time after loading the sample on the sensor system. Temperature control was carried

out with a Peltier Plate system (-40 to 180°C). All tests were run isothermally at 25°C in triplicate. For this, mixtures of each of the samples (5 g) were prepared with distilled water (60 and 52% w/v) to obtain wetted masas of each of the samples. The viscoelastic properties of samples were determined by running amplitude (stress range from 0.1 to 100 Pa, at a frequency of 6.28 rad s⁻¹, to define the linear viscoelastic region) and frequency (0.1-100 rad s⁻¹, at a stress of 3 Pa) sweeps, to determine the storage (G') and loss (G'') moduli (Pa) from each test for every sample. In addition, flow ramp (shear rate 0.1-100 s⁻¹) to estimate shear viscosity and yield point (τ_c) from all samples were made using both the logarithmic mode and linear mode of shear rate ramp. The power law model (Eq. 2) was fitted to the experimental data both from the ascending and from descending segments of the shear cycle:

$$\tau = k\dot{\gamma}^n, \quad (2)$$

where τ (Pa) is the shear stress, $\dot{\gamma}$ is the shear rate (s⁻¹), k (Pa·s ^{n}) is the consistency index, and n is the flow behaviour index (dimensionless).

Scanning electronic microscopy (SEM)

The morphology of the granules from all samples was observed with a Philips XL30 SEM (Philips, Holland) an observed at a voltage of 10 kV. Using SEM, a thin layer of maize flour was mounted on aluminium specimen holder by double-sided tape and micrographs from the surface (magnification 1200 and 1500 X) were taken (Duodu et al., 2002).

Statistical analysis

An experimental design of factorial arrangement was used to evaluating lime solution, cooking time, flour moisture content and type of maize. To analyse the data, the Statistical Analysis System and Duncan's means comparison were used (SAS ver.).

Results and Discussion

X-Ray diffraction patterns and percent crystallinity

The X-Ray diffraction patterns for raw samples (C_1 and C_2) showed a distinctive A-pattern crystal structure (Zobel, 1988), gave identical and superimposable patterns in the 2 θ angular region: 15.1°, 16.4°, 17.5° and 22.6° (Figures 1 and 2). On the other hand, the d -spacings of the identified peaks (5.95, 5.39, 5.2 and 3.9 Å) are agree with Flores-Farías et al. (2002) and Castillo et al. (2009) who indicate that A-type pattern was observed in grain of maize.

Although both samples (A and B) were severely cooked in the laboratory, also showed A-type X-Ray diffraction spectra, and only at 85 min of cooking this pattern was al-

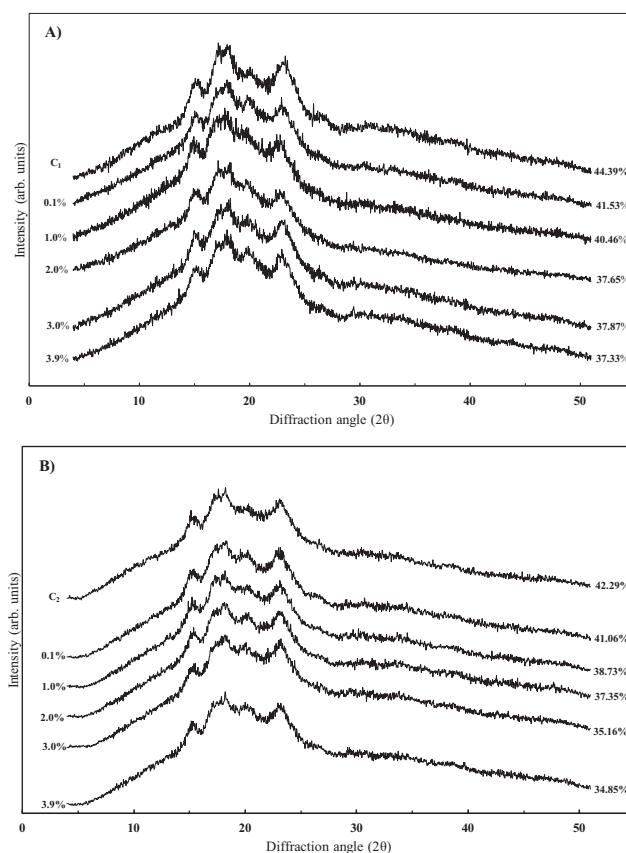


Fig. 1. X-Ray pattern and crystallinity (%) of sample A and B using different Ca(OH)₂ concentrations

most disrupted for both samples, as can be seen observed by the decreased intensity of the X-Ray patterns (Figure 2a y 2b), as the severity of cooking time increased which is manifested in to have low percent crystallinity.

The X-Ray crystal structure for control sample showed very little change between them, mainly for not having had some cooking process. However, Manful et al. (2008) reports that a sample extremely cooks accompany to show low percent crystallinity. This situation was presented in our study when the samples (A and B) were cooked at different times at 65, 75 and 85 min (Figure 2), where the most marked variation in the X-Ray source intensity and the crystallinity were lower with respect control sample C_1 and C_2 . Nevertheless, when the samples were treated with different concentrations of calcium hydroxide, the crystallinity decreased significantly. Also the amorphous state turn around ordered changing shape as the concentration increases, principally from 2.0 to 3.9% for QPM maize. When smaller concentrations were used (0.1 and 1.0%), changes in crystallinity are probably due that the first phase of the endosperm in this class of maize is hard

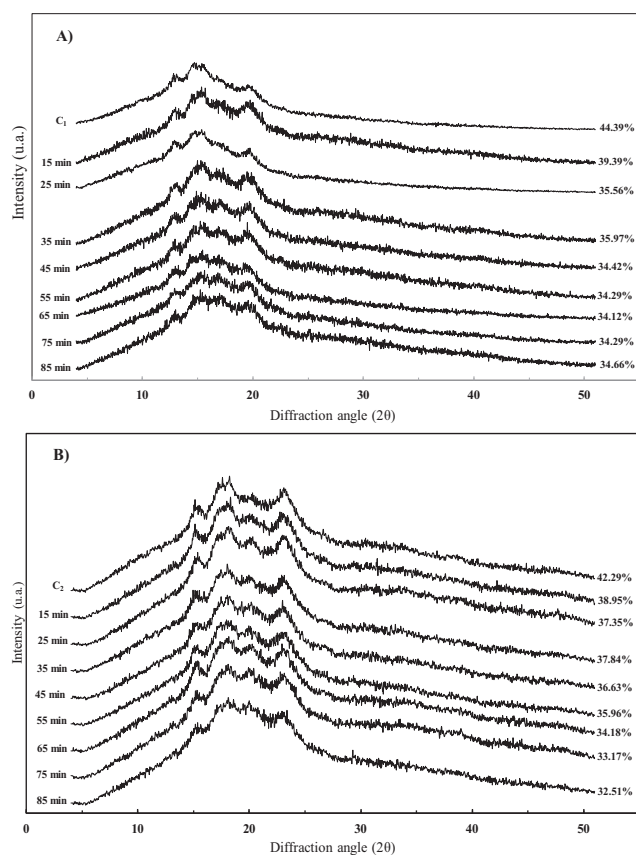


Fig. 2. X-Ray pattern and crystallinity (%) of sample A and B using 2% of $\text{Ca}(\text{OH})_2$ at different cooking time

(Rojas-Molina et al., 2007). Minor changes in percent crystallinity were observed in the variety Pioneer for same condition studied, going from 44.39% for control sample C_1 till 37.33% for sample with 3.9% of concentration of calcium hydroxide. This behaviour agrees with what has been studied by Enrique-

Rodríguez et al. (1995) who described that the calcium introduced into the system, intercede for prevail the starch structure and the process of nixtamalization is not affected.

Thermal analysis

Results of temperature and transition enthalpy (ΔH) for samples A and B with a cooking time of 25 min and to which were varied concentration of calcium hydroxide, are showed in Table 1 and 2. The T_p values for both samples, increased from 68.84 to 71.39°C (sample A) and 69.80 to 72.08°C (sample B) in relation to C_1 (69.32°C) and C_2 (69.93°C).

Sample A with the minor percentage of lime (0.1%) showed a ΔH of 4.93 J/g and crystallinity of 41.53%, values that were lowest in relation to that with 3.9% of lime with ΔH of 5.43 J/g and 37.33% in crystallinity. On the other hand, sample B with 0.1% and 3.9% of lime showed a ΔH of 4.51 and 4.24 J/g, with crystallinity values of 41.06 and 34.85%, respectively. For both samples, the crystallinity values of C_1 (44.39%) and C_2 (42.29%) were higher than nixtamalized samples A and B. This represents a loss of crystallinity for samples A and B and that can be attributed to nixtamalization process and the variations in lime concentration since presumably Ca^{++} modifies the conditions found in the starch components when it penetrates the maize. With different cooking times and only one concentration of calcium hydroxide (2%), the samples A and B showed at 15 min cooking a ΔH value of 4.87 J/g and 5.53 J/g (Table 2); however, when the samples were cooking for 85 min showed a decrease of 34.36 and 23.76% for this parameter in both samples. This situation likewise presented in crystallinity percentage where this pattern varies from 39.39 to 34.66% (sample A), and 38.95 to 32.51% in sample B, with 15 and 85 min of cooking time, respectively.

In accord with Méndez-Montealvo et al. (2005), sample B is a harder material and with content less starch, which imply that ΔH value is lower and is less destroyed their crystallographic

Table 1

Thermal parameters of maize grain Pioneer 30G54 (A) and QPM H-374C (B) using different concentration of calcium hydroxide with time cooking at 25 min

Sample	A			B		
	T_p (°C)	ΔH (J/g)	Crystallinity (%) by XRD	T_p (°C)	ΔH (J/g)	Crystallinity (%) by XDR
C_1, C_2	69.32c	5.38c	44.39	69.93b	4c	42.29
$\text{Ca}(\text{OH})_2$ (%)						
0.1	68.84b	4.93c	41.53	69.80b	4.51bc	41.06
1.0	70.09b	5.44c	40.46	70.13b	5.8a	38.73
2.0	71.08b	4.87c	37.65	69.92b	5.53ab	37.35
3.0	71.39a	6.22a	37.87	70.9ab	5.16b	35.16
3.9	71.37a	5.43bc	37.33	72.08a	4.24bc	34.85

Mean values of three measurements. Same letters after entries within each column indicate that there are no significant differences ($p > 0.05$)

Table 2

Thermal parameters of maize grain Pioneer 30G54 (A) and QPM H-374C (B) at different cooking times using a concentration of calcium hydroxide of 2%

Sample	A			B		
	T_p (°C)	ΔH (J/g)	Crystallinity (%) by XRD	T_p (°C)	ΔH (J/g)	Crystallinity (%) by XRD
C_1, C_2	69.32c	5.38c	44.39	69.93b	4.00b	42.29
Time (min)						
15	65.59d	4.87d	39.39	70.42b	5.53a	38.95
25	77.93a	6.88c	35.56	69.92bc	4.04b	37.35
35	68.48cd	2.46e	35.97	71.42b	3.74bc	37.84
45	70.45c	11.57a	34.42	72.12ab	4.31b	36.63
55	70.4c	11.38a	34.29	71.71b	4.39b	35.96
65	71.79bc	9.83b	34.12	72.23ab	4.25b	34.18
75	73.63b	4.69d	34.29	73.10a	3.4c	33.17
85	65.5d	7.37c	34.66	70.42b	4.46b	32.51

Mean values of three measurements. Same letters after entries within each column indicate that there are no significant differences ($p > 0.05$)

arrangement (Singh et al., 2003). Nevertheless, these changes in enthalpy may be because the samples are not composed only of starch (70%, dry base), since it is a mixture of protein, lipids and minerals (Cruz-Requena et al., 2011). The interaction of Ca^{++} in the nixtamalization process can strengthen the bonds between starch-lipids, protein-starch, starch-protein and calcium with the components already mentioned which entails that the starch can be gelatinized (Quintanar et al., 2011).

Rheological properties

Stress curves versus shear deformation for the control sample and the nixtamalized masa (A and B) using different concentration of calcium hydroxide with time cooking at 25

min, are showed in Figure 3. It can be seen how the control sample C_1 (Figure 3a), exhibited a continuous deformation curve throughout the range of efforts studied.

This behavior is typical of a shear thinning non-Newtonian fluid (Figure 4); while the nixtamalized samples indicate a discontinuous deformation curve with three different flow regions.

This type of deformation curve is characteristic of materials with yield stress (τ_c), which indicates that the nixtamalized samples of Pioneer maize (Figure 3a), displayed the formation of a structure that is responsible to induce the τ_c . The low deformation region (10^{-4} to 10^{-2}), is related to the rigidity of the formed structure by the interaction of the $\text{Ca}(\text{OH})_2$ with the components of maize flour. The region of discontinuity is characterized by a

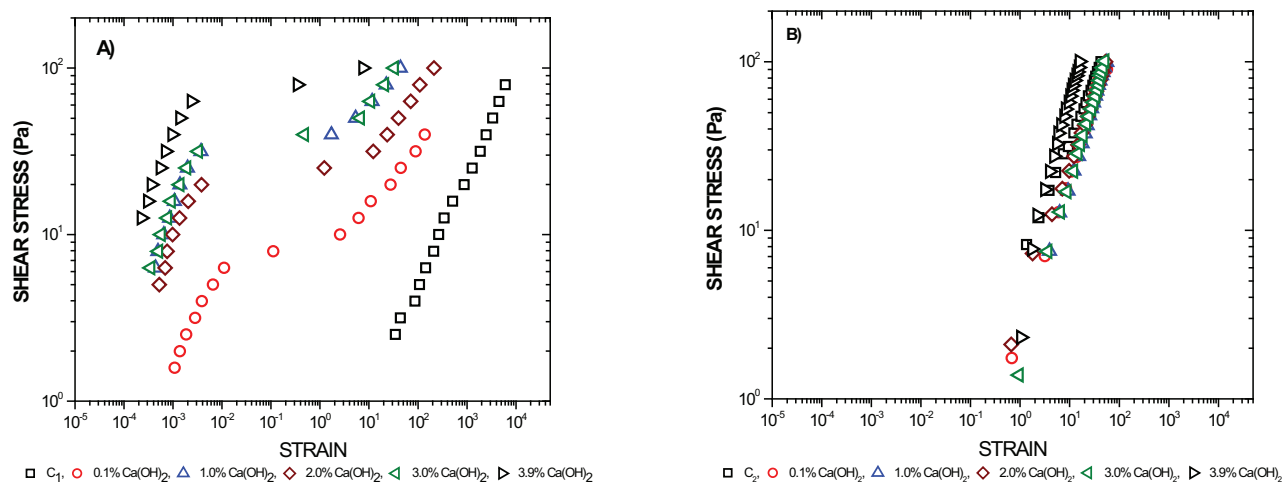


Fig. 3. Shear stress as a function of strain in Pioneer (a) and QPM (b) maize, using different concentrations of $\text{Ca}(\text{OH})_2$ and 25 min of cooking time

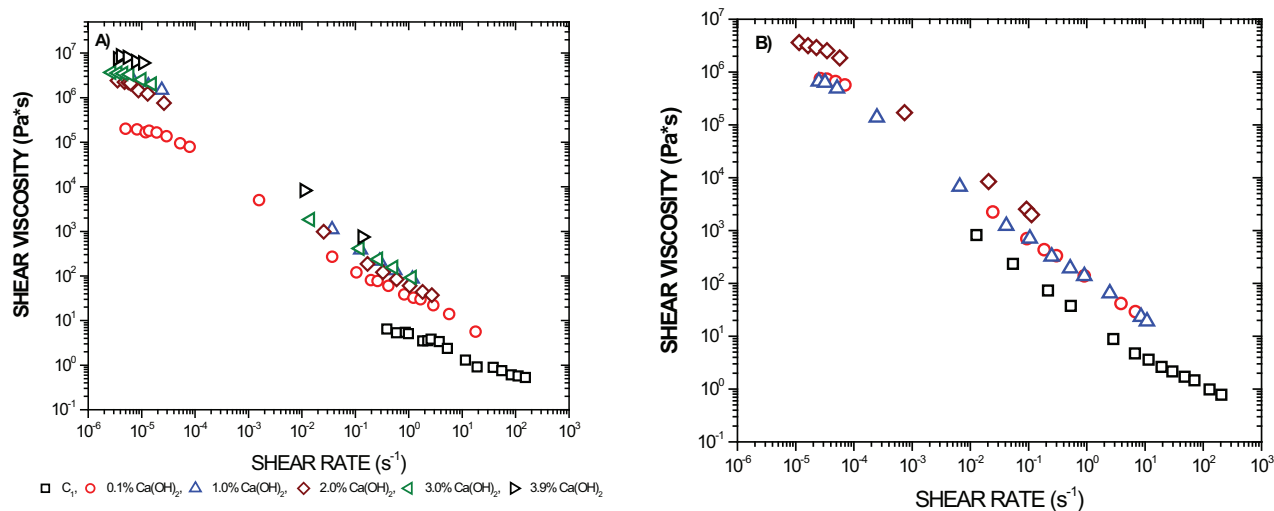


Fig. 4. Experimental flow curves at 25°C for nixtamalized maize flour (Pioneer), with different concentrations of Ca(OH)_2 and that one using a concentration of Ca(OH)_2 of 2% and cooking at different times

sharp leap (10^0 to 10^2) in the deformation of the material which appeared in the low deformation region. This leap is related to the breaking of the formed structure by the interaction of the Ca(OH)_2 with the components of maize flour previously described. Finally come the region of high deformation where the material is already well deformed and flowing in this region. Also, it is observed that as the lime concentration increases in the nixtamalization process, masa showed an increase in yield stress (Figure 3a) as well as in the viscosity (Figure 4). This result suggests that the Ca(OH)_2 , when it penetrates the maize during cooking, changed the conditions of the different constituents of maize grains. On the other hand, in the Figure 3b can be seen that all nixtamalized samples of QPM maize, as well C_2 , displayed continuous deformation curves indicating that these masas have behaviour of a shear thinning non-Newtonian fluid. It is also possible to distinguish that all samples exhibited flow (Figure 3b), but when a shear stress of ~ 100 Pa was reached, occurred a breaking in the masa which caused them to be expelled from the measurement system. With all the above, it can be mentioned that all the nixtamalized masas of Pioneer maize required a greater effort to be subjected to shear deformation, indicating that their masas have a greater firmness in the formed structure by the interaction of the Ca(OH)_2 , which agrees with thermal and RDX analysis of this study. Stress curves versus shear deformation for nixtamalized maize flour (Pioneer, QPM) and control samples at different cooking times using a concentration of calcium hydroxide of 2%, are shown in Figure 5.

This masas evidenced an analogous rheological behaviour which presented the samples treated with different concentration of calcium hydroxide (Figure 3a, b), observing also that just as cooking time increase, masas showed

a greater firmness that manifested with an increase in shear viscosity and yield stress (Table 3 and Figure 4).

This result indicates that the maize cooking time in the presence of Ca(OH)_2 , is an important factor to obtain nixtamalized masas with more firmness. Otherwise, the τ_c values (Table 3 and 4) for masas prepared with nixtamalized maize flour of Pioneer maize, was determined employing a linear regression to the data of the low deformation region of the Figures 3a and 5a. The τ_c values for pioneer maize (Table 3) increased as the Ca(OH)_2 concentration increases, suggesting that this masas exhibited greater firmness with respect to C_1 sample (Rodríguez-Sandoval et al., 2005).

The viscoelastic properties of nixtamalized sample A and B, including control (C_1 y C_2), were evaluated by oscilla-

Table 3
Results obtained from mathematical modelling of rheogram data of nixtamalized maize flour (Pioneer maize) using different concentration of calcium hydroxide with time cooking at 25 min

Ca(OH)_2 (%)	τ_c	n	K	γ	R^2
0	np	0.608a	3.773		0.9878
0.1	2.51d	0.532ab	44.072	0.027	0.9913
0.5	32.62a	0.285b	111.952	0.0011	0.9959
1.0	15.85bd	0.296b	96.21	0.0019	0.9713
2.0	19.95b	0.399b	67.54	0.0013	0.9723
3.0	19.95b	0.289b	87.74	0.0018	0.9813
3.5	19.95b	0.236b	91.98	0.004	0.9698
3.9	25.12ab	0.068c	108.53	0.0011	0.8610

Same letters after entries within each column indicate that there are no significant differences ($p > 0.05$). τ_c : yield stress (Pa); n : flow behaviour index; K : consistency index; γ : deformation; R^2 : coefficient of determination

Table 4

Results obtained from mathematical modelling of rheogram data of nixtamalized maize flour (Pioneer maize) at different cooking times using a concentration of calcium hydroxide of 2%

Time (min)	τ_c	n	K	δ	R^2
0	Np	0.608a	3.773		0.9878
15	31.6b	0.369b	88.83	0.0014	0.973
25	19.95c	0.399b	67.54	0.0013	0.9723
35	63.10a	0.058c	130.41	0.0014	0.796

Same letters after entries within each column indicate that there are no significant differences ($p > 0.05$). τ_c : yield stress (Pa); n : flow behaviour index; K : consistency index; γ : deformation; R^2 : coefficient of determination

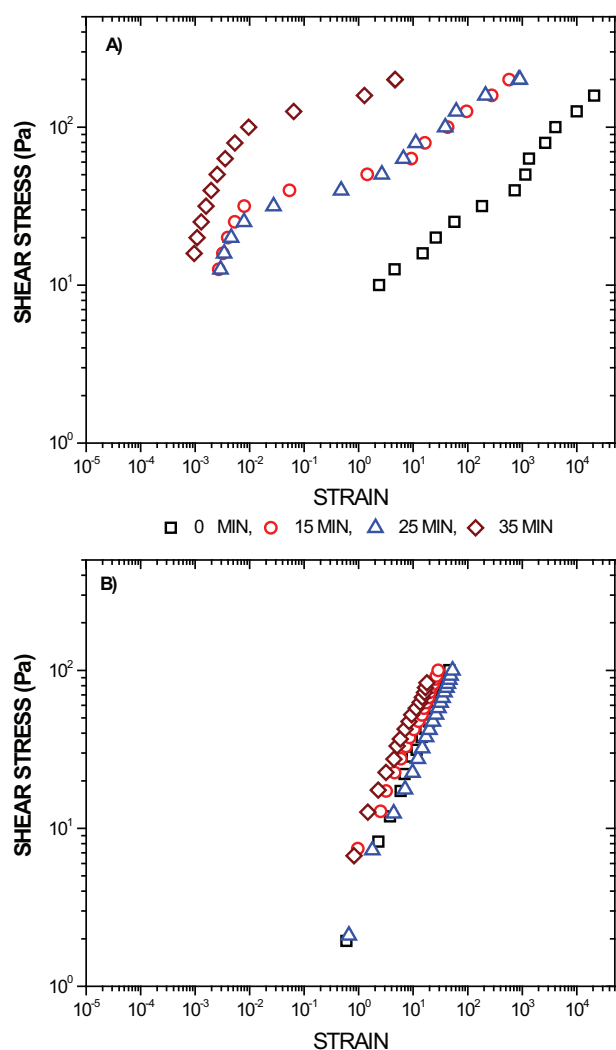


Fig. 5. Shear stress as a function of strain in Pioneer (a) and QPM (b) maize using a concentration of $\text{Ca}(\text{OH})_2$ of 2% and cooking at different times

tory experimental measurements, and the results are shown in Figure 6. The storage and loss modulus (G' and G'') are independent of angular frequency, in addition there is predominance of the storage modulus ($G' > G''$) over the entire temperature range, indicating that masas displayed a behaviour of a viscoelastic material.

This behaviour establishes that both masas have a stable structure to mould tortillas (Tabilo-Munizaga and Barbosa-Cánovas, 2005; Quintanar et al., 2011). Figure 7 shows the viscoelastic properties of nixtamalized masa sample (A, B, and C₁, C₂), at different different cooking times using a concentration of calcium hydroxide of 2%. A similar behavior is observed such as that already described in Figure 6 where the predominant behavior is $G' > G''$, typical of a viscoelastic material.

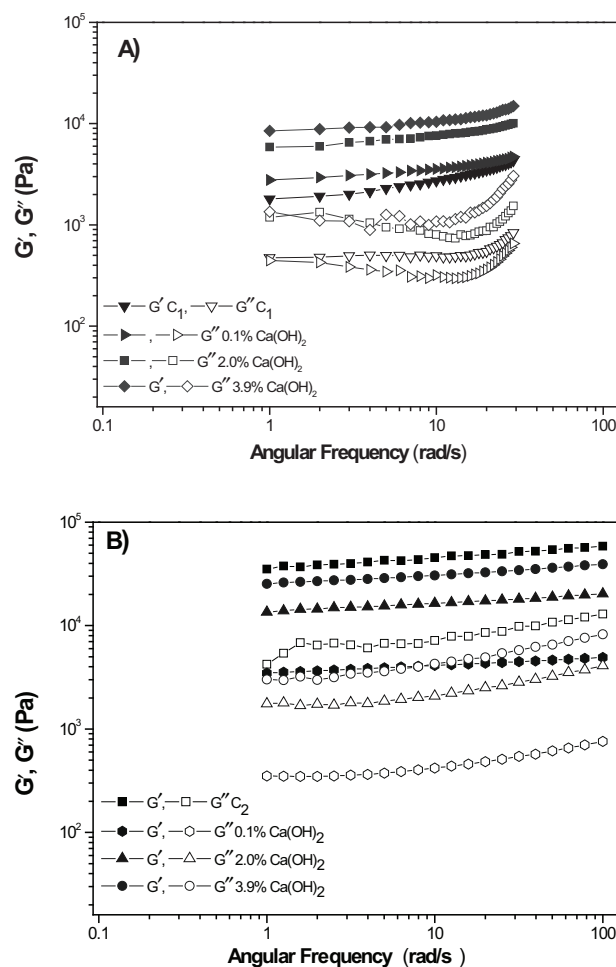


Fig. 6. Variation of G' and G'' with angular frequency for nixtamalized flours with different $\text{Ca}(\text{OH})_2$ concentrations. Closed symbols represent G' ; open symbols represent G'' . a) = Pioneer and, b) = QPM sample

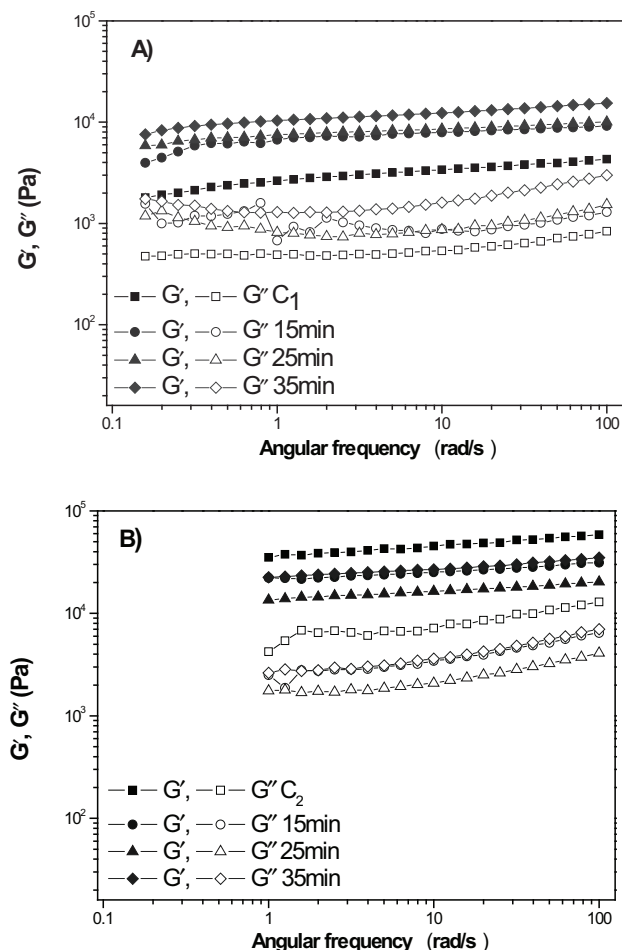


Fig. 7. Variation of G' and G'' with angular frequency for nixtamalized flours using 2% of $\text{Ca}(\text{OH})_2$ at different cooking time. Closed symbols represent G' ; open symbols represent G'' .

a) = Pioneer and, b) = QPM sample

The results obtained in the present work are comparable with what was observed in masas of wheat flour added with minerals, and those on the rheological properties of extruded nixtamalized corn masa, where $G' > G''$ (Salvador et al., 2006; Mariotti et al., 2009; Contreras-Jiménez et al., 2017). Firmness behaviors shown by both samples can be correlated with crystallinity, temperature and enthalpy of gelatinization previously discussed.

Scanning electron microscopic

Microscopy revealed that, in both samples is observed mainly granules with polyhedral shapes (Figure 8); how-

ever, the sample A has some granules get attached by adhering themselves (Figure 8a, b, c, d), as the concentration of calcium hydroxide increases. In contrast, for sample B it shows that the nixtamalization process did not affect the granules with the increases of calcium hydroxide (Figure 8e, f, g).

The effect of lime induces destruction and granular swelling in dry masa flour because of calcium-starch interaction (Quintanar et al., 2011; Robles et al., 1988). When the samples A and B were cooking at different times using a 2% of lime, agglomerated granules can be observed (Figure 9), being more marked this behavior

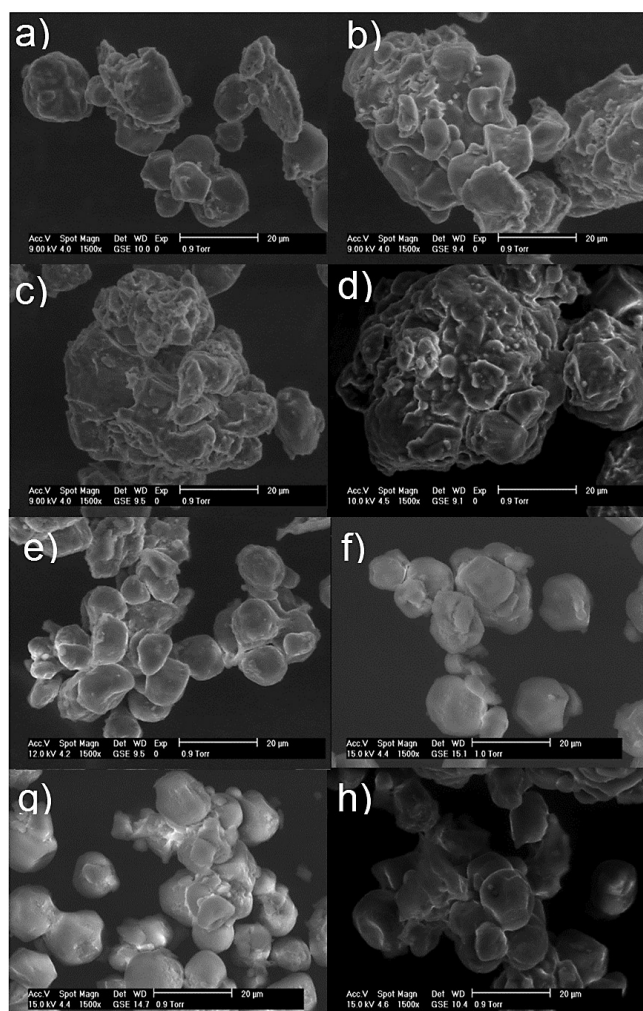


Fig. 8. SEM micrographs of nixtamalized maize flour with different concentrations of $\text{Ca}(\text{OH})_2$: Pioneer maize = a) control, b) 0.1%, c) 2.0%, d) 3.9% and QPM maize = e) control, f) 0.1%, g) 2.0%, h) 3.9%

at 65 min. Heating causes the starch granules to swell and become deformed by losing their polyhedral shapes (Maizeejo-Villegas et al., 2013; Quintanar et al., 2011). In the absence of nixtamalization process did not were observed agglomerated granules in control samples (Figure 9a, e). Scanning electron microscopic images show evidences that when the conditions of nixtamalization (lime concentrations, time cooking and maize variety) has been changed, the material becomes more rigid (Pineda-Gómez et al., 2012) as could be observed in the thermal and rheological properties described in this study.

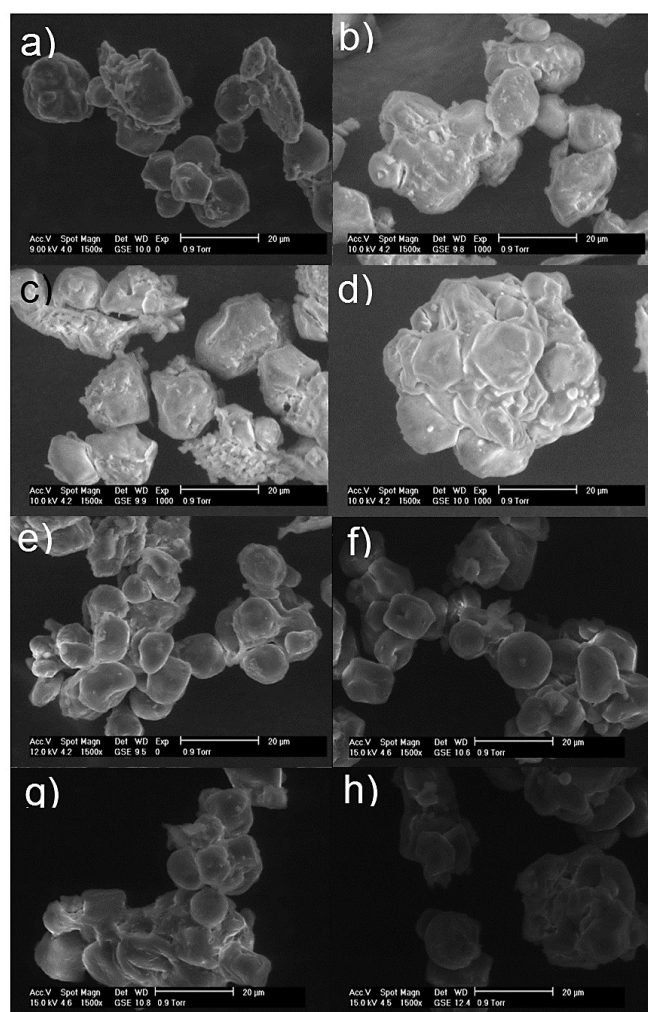


Fig. 9. SEM micrographs of nixtamalized maize flour using 2% of $\text{Ca}(\text{OH})_2$ with different cooking times. Pioneer maize= a) control, b) 15 min, c) 35 min, d) 65 min and QPM maize = e) control, f) 15 min, g) 35 min, h) 65 min

Conclusions

Notwithstanding both maize samples (Pioneer 30G54 and QPM H-374C) were cooked with $\text{Ca}(\text{OH})_2$, remains A-type X-Ray diffraction spectra even if it was accompanied by loss in its structure, showing low percent crystallinity. The $\text{Ca}(\text{OH})_2$ addition on the nixtamalization process, causes an increase in temperature and enthalpy of gelatinization in a dependent concentration, although QPM H-374C sample exhibited the lowest values and their crystallographic arrangement was less destroyed. The control samples showed a typical behavior of a shear thinning non-Newtonian fluid in comparison of the nixtamalized samples that display a discontinuous deformation curve, characteristic of materials with yield stress, evidencing that the nixtamalized samples of Pioneer 30G54 maize, displayed the formation of a structure that is responsible to induce the yield stress. In another way, there is predominance of the storage modulus ($G' > G''$) over the frequency range applied, indicating that masas displayed a behaviour of a viscoelastic material and that both masas have a stable structure to mould tortillas. SEM micrographics showed that as the concentration of calcium hydroxide increases some granules for Pioneer maize get attached by adhering themselves, contrary situation was observed in QPM maize when the nixtamalization process did not affected the granules.

Acknowledgments

The authors are grateful to CONACyT, Centro de Investigación y de Estudios Avanzados del IPN (CINVESTAV-IPN), Centro de Desarrollo de Productos Bióticos (CEPRO-BI-IPN) and Sistema para la Gestión Integral de Apoyo para el Personal Docente (SAD-IPN).

References

- Abu-Jdayil, B., H. Mohameed and A. Eassa, 2004. Rheology of starch-milk-sugar systems: effect of heating temperature. *Carbohydrate Polymers*, **55** (3): 307-314.
- Arámbula, V. G., A. L. Barrón, H. J. González, E. Moreno and B. Luna, 2001. Efecto del cocimiento y reposo del grano de maíz (*Zea mays* L.) nixtamalizado, sobre las características fisicoquímicas, reológicas, estructurales y texturales del grano, masa y tortilla de maíz. *Archivos Latinoamericanos de Nutrición*, **51**(2):187-194.
- Castillo, V. K. C., M. L. A. Ochoa, C. J. D. Figueroa, L. E. Delgado, I. J. A. Gallegos and C. J. Morales, 2009. Efecto de la concentración de hidróxido de calcio y tiempo de cocción del grano de maíz (*Zea mays* L.) nixtamalizado, sobre las características fisicoquímicas reológicas del nixtamal. *Archivos Latinoamericanos de Nutrición*, **59** (4): 425-432.

- Contreras-Jiménez, B., M. Gaytán-Martínez, E. Morales-Sánchez, J. D. Figueroa-Cardenas, R. Pless, E. González-Jasso, G. Méndez-Moltealvo and G. Velázquez. 2017. Effects of tempering time, $\text{Ca}(\text{OH})_2$ concentration, and particle size on the rheological properties of extruded corn flour. *Cereal Chemistry*, **94** (2): 230-236.
- Cruz-Requena, M., R. Rodríguez-Herrera, C. N. Aguilar-González, J. Espinoza-Velázquez, M. Gaytán-Martínez and J. D. Figueroa-Cárdenas, 2011. Alkaline cooking quality of polyembryonic and non-polyembryonic maize populations. *Advance Journal of Food Science Technology*, **3** (4): 259-268.
- Duodu, K. G., A. Nunes, I. Delgadillo, M. L. Parker, E. N. C. P. S. Mills, O. S. Belton and J. R. N. Taylor, 2002. Effect of grain structure and cooking on sorghum and maize in vitro protein digestibility. *Journal of Cereal Science*, **35** (2): 161-174.
- Enrique-Rodríguez, M., J. Martín-Yanez, A. Cruz-Orea, J. J. Alvarado-Gil, O. Zelaya-Angel, F. Sánchez-Sinencio, H. Vargas, J. D. Figueroa, F. Martínez-Bustos, J. L. Martínez-Montes, J. González-Hernández and L. C. Miranda, 1995. The influence of slaked lime content on the processing conditions of cooked maize tortillas: changes of thermal, structural and rheological properties. *Z. Lebensm Unters Forsch*, **201** (3): 236-240.
- Flores-Farías, R., F. Martínez-Bustos, Y. Salinas-Moreno and E. Ríos, 2002. Caracterización de harinas comerciales de maíz nixtamalizado. *Agrociencia*, **36** (5): 557-567.
- Gutiérrez, E., I. Rojas-Molina, J. L. Pons-Hernández, H. Guzmán, B. Aguas-Ángel, J. Arenas, P. Fernández, A. Palacios-Fonseca and M. E. Rodríguez, 2007. Study of calcium ion diffusion in nixtamalized quality protein maize as a function of cooking temperature. *Cereal Chemistry*, **84** (2): 186-194.
- Kulicke, W. M., A. H. Kull, W. Kull, J. Engelharth and J. B. Pannek, 1996. Characterization of aqueous carboxymethyl cellulose solutions in terms of their molecular structure and its influence on rheological behaviour. *Polymer*, **37** (13): 2723-2731.
- Maizeejo-Villegas, M. A., E. Gutiérrez-Cortez, I. Rojas-Molina, A. Real-López, M. L. Zambrano-Zaragoza, V. Martínez-Vega and M. E. Rodríguez-García, 2013. Physicochemical, morphological, and pasting properties of nixtamalized flours from quality protein maize and its particle distribution. *LWT – Food Science and Technology*, **53** (1): 81-87.
- Manful, J. T., C. C. Grimm, J. Gayin and R. D. Coker, 2008. Effect of variable parboiling on crystallinity of rice samples. *Cereal Chemistry*, **85** (1): 95-95.
- Mariotti, M., M. Lucisano, M. A. Pagani and K. W. Perry, 2009. The role of maize starch, amaranth flour, pea isolate, and psyllium flour on the rheological properties and the ultrastructure of gluten-free doughs. *Food Research International*, **42** (8): 963-975.
- Méndez-Montealvo, G., J. Solorza-Feria, M. Velázquez del Valle, N. Gómez-Montiel, O. Paredes-López and L. A. Bello-Pérez, 2005. Composición química y caracterización calorimétrica de híbridos y variedades de maíz cultivadas en México. *Agrociencia*, **39** (3): 267-274.
- Pineda-Gómez, P., A. A. Acosta-Osorio, D. F. Coral, A. Rosales-Rivera, L. A. Sánchez-Echeverri, I. Rojas-Molina and M. E. Rodríguez-García, 2012. Physicochemical characterization of traditional and commercial instant maize flours prepared with threshed white maize. *CyTA-Journal of Food*, **10** (4): 287-295.
- Quintanar-Guzmán, A., M. A. Jaramillo-Flores, R. Mora Escobedo, L. Chel-Guerrero and J. Solorza-Feria, 2009. Changes on the structure, consistency, physicochemical and viscoelastic properties of maize (*Zea mays* sp.) under different nixtamalization conditions. *Carbohydrate Polymers*, **78** (4): 908-916.
- Quintanar-Guzmán, A., M. E. Jaramillo-Flores, J. Solorza-Feria, M. G. Méndez-Montealvo and Y. Wang, 2011. Rheological and thermal properties of masa as related to changes in maize protein during nixtamalization. *Journal of Cereal Science*, **53** (1): 139-147.
- Robles, R. R., E. D. Murray and O. Paredes-López, 1988. Physicochemical changes of maize starch during the lime-heat treatment for tortilla making. *International Journal of Food Science and Technology*, **23** (1): 91-98.
- Rodríguez-Sandoval, E., A. Fernández-Quintero and A. Ayala-Aponte, 2005. Modelos reológicos aplicados a masas de trigo y maíz. *Revista de Ingeniería e Investigación*, **25** (2): 87-93.
- Rojas-Molina, I., E. Gutiérrez-Cortez, A. Palacios-Fonseca, L. Baños, J. L. Pons-Hernández, S. H. Guzmán-Maldonado, P. Pineda-Gómez and M. E. Rodríguez, 2007. Study of structural and thermal changes in endosperm of quality protein maize during traditional nixtamalization process. *Cereal Chemistry*, **84** (4): 304-312.
- Ruiz-Gutiérrez, M. G., A. Quintero-Ramos, C. O. Meléndez-Pizarro, R. Talamás-Abbud, J. Barnard, R. Márquez-Meléndez and D. Lardizábal-Gutiérrez, 2012. Nixtamalization in two steps with different calcium salts and the relationship with chemical, texture and thermal properties in masa and tortilla. *Journal of Food Process Engineering*, **35** (5): 772-783.
- Sahai, D., M. O. Buendia and D. S. Jackson, 2001. Analytical techniques for understanding nixtamalized maize flour: Particle size and functionality relationships in a masa flour sample. *Cereal Chemistry*, **78** (1): 14-18.
- Salvador, A., T. Sanz and S. M. Fiszman, 2006. Dynamic rheological characteristics of wheat flour-water doughs. Effect of NaCl, sucrose and yeast. *Food Hydrocolloids*, **20** (6): 780-786.
- Shafea, L. and M. Saffari, 2016. Evaluation of grain filling rate and path analysis in different combinations of nitrogen and zinc in maize. *Bulgarian Journal of Agricultural Science*, **22** (1): 60-64.
- Šeremešić, S., Lj. Nikolić, D. Milošev, M. Živanov, Ž. Dolijanović and M. Vasiljević, 2016. The possibility of maize gluten application for weed control in maize and soybean. *Bulgarian Journal of Agricultural Science*, **22** (1): 52-59.

- Serna-Saldívar, S. O., R. Canett, J. Vargas, M. González, S. Bedolla and C. Medina, 1988. Effect of soybean and sesame addition on the nutritional value of maize and decorticated sorghum tortillas produced by extrusion cooking. *Cereal Chemistry*, **65** (1): 44-48.
- Serna-Saldívar, S. O., M. H. Gómez, H. D. Almeida-Domínguez, A. Islas-Rubio and W. Rooney, 1993. A method to evaluate the lime-cooking properties of maize (*Zea mays*). *Cereal Chemistry*, **70** (6): 762-764.
- Singh, N., J. Singh, L. Kaur, S. N. Sodhi and B. S. Gill, 2003. Morphological, thermal and rheological properties of starches from different botanical sources. *Food Chemistry*, **81** (2): 219-231.
- Tabilo-Munizaga, G., and G. V. Barbosa-Cánovas, 2005. Rheology for the food industry. *Journal of food Engineering*, **67** (1-2): 147-156.
- Trejo-González, A., A. Feria-Morales and C. Wild-Altamirano, 1982. The role of lime in the alkaline treatment of maize for tortilla production. Modifications of proteins: Food, nutritional and pharmacological aspects. In: R. E. Feeney and J. R. Whitaker (Eds.), *Advances in Chemistry, American Chemical Society*, Washington, DC, pp. 245-263.
- Verma, R. C, and S. Prasad, 1999. Kinetics of absorption of water by maize grains. *Journal of Food Engineering*, **39** (4): 395-400.
- Zobel, H. F., 1988. Starch crystal transformations and their industrial importance. *Starch/Stärke*, **40** (1): 1-7.

Received May, 13, 2017; accepted for printing June, 7, 2017