Effect of microwave treatment on physicochemical properties of maize flour

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Abstract

Relatively little work has been reported about flour changes during microwave irradiation. For this reason, maize flours were treated by microwave radiation at 400W for 0.5, 1, 2 and 4 minutes, and their microstructure and physicochemical characteristics (X-ray diffractometry, differential scanning calorimetry and pasting properties) were analysed. Micrographs showed that maize flour treated by microwave radiation displayed less compacted particles and more swollen starch granules. Treated maize flours displayed higher V-type crystalline structure, indicating amylose-lipid complexes formation. Additionally, onset and peak temperature and gelatinization enthalpy increased when increasing treatment time of samples. Maize flours subjected to mild treatment (0.5 and 1 minute) showed higher peak viscosity and breakdown than native maize flour, and maize samples subjected to severe treatments (2 and 4 minutes) displayed a lower peak viscosity and breakdown, which reflects an increase in shear stability, respect to native maize sample. In general, microwave treatment fostered changes in starch crystallinity and the formation of amylose-lipid complexes affecting the functional properties of flour such as its pasting behaviour and its thermal properties.

Keywords: maize flour; microwave treatment; physicochemical properties; moisture content.

1. Introduction

Maize is the main produced cereal (tonnes) followed by paddy rice and wheat (FAOSTAT 2013). Maize kernels are submitted to different treatment depending on the final product. Grit and meal maize are used in the production of snacks and breakfast cereals, whereas maize flour is mostly used in blends with wheat flours in bakery products. In America, maize is used to make various Latin products like arepas, hallacas, empanadas and pasabocas, but the main consumption is nixtamalized to produce other products such as tortillas, tamales or snacks (Pineda-Gómez et al. 2012). In some of these foods, hydrothermal treated flours (instant flours) are very useful to simplify the production (less time and energy) (Reyes-Moreno et al. 2003; Zeppa et al. 2012).

Physical hydrothermal processes allow modifying the functional properties of the flours for being used in food processing. During hydrothermal treatments, the starch is subjected to high moisture and temperature. Depending on the intensity of the treatment, starch might be gelatinized, broken the structure of granules, increased the swelling power of the granule, and lost the crystallinity (Atwell et al. 1988). Different thermal treatments for producing instant flours have been proposed as drum drying (Anastasiades et al. 2002; Valous et al. 2002), dry heat treatment (Johnson et al. 1980), extrusion (Meshram et al. 2009; Reyes-Moreno et al. 2003) and microwave heating (Martínez-Bustos et al. 2000).

Microwaves are electromagnetic waves in the frequency range of 300–300,000 MHz. Polar molecules absorb microwave energy and orient themselves with respect to the electric field. The rapid change in their orientation generates heat by molecular friction (Sumnu 2001), resulting in a bulk heating throughout the sample and a faster heating rate compared with the conventional heating. There has been a big interest in the industrial application of microwaves to improve conventional processes (Luo et al. 2006). Thus, the effects of microwave treatment on the chemical and physicochemical properties of cereal starches have been reported. Fan et al. (2012) reported that microwave irradiation had no effect on the optical and thermal properties of rice starch during gelatinization respect conventional heating. Lewandowicz et al. (2000) found an increase in gelatinization temperature and a decrease in solubility of microwaved maize and wheat starches. Stevenson et al. (2005) also reported an increase of gelatinization

temperature and decrease of paste viscosity of microwaved maize starch. Anderson and Guraya (2006) and Luo et al. (2006) investigated, respectively, the effect of microwave on rice and maize starches with different proportion of amylose/amylopectin. Rearrangements of the molecular structure during microwave heating produced significant changes in viscosity properties of both waxy and non-waxy starches. Furthermore, Pinkrová et al. (2003) reported that the peak viscosity of rice flour decreased as temperature and microwave power level applied to rice grain increased.

Therefore, the effect of microwave heating has been focused on starches. Nevertheless, flours, as compared to starches, have a higher nutritional value and the extraction process is more economical with a lower environmental impact (Eckhoff and Watson 2009). However, relatively little work has been reported on flour changes during microwave irradiation, solely on wheat (Ashraf et al. 2012). Sun et al. (2014) applied heat moisture treatment to sorghum starch and flour, demonstrating physicochemical differences between both. The treatment had a far greater effect on solubility, swelling power, setback viscosity, enthalpy of gelatinization and crystallinity of flour than that of starch. Consequently, although studies on maize starch have been previously reported (Lewandowicz et al. 2000; Stevenson et al. 2005), it is necessary to study the effect of microwave on maize flours.

The aim of the present research was to evaluate the effect of microwave radiation (0.5, 1, 2 and 4 min) to moistened (30%) maize flours on the crystallinity, gelatinization parameters, retrogradation characteristics, hydration and pasting properties.

2. Materials and methods

2.1 Materials

Maize flour was procured from Adpan Europe S.L. (Asturias, Spain), with a moisture content of 11.95%, 7.6 g of proteins and 3 g of lipids per 100 g of sample (Data were provided by the manufacturer).

2.2 Methods

2.2.1 Microwave irradiation of flour samples

Maize flours were heated in a microwave oven Kompernass GMBH, Silver Crest SMW 800 A2 (Bochum, Germany). Previously, flour tempering to 30% moisture content was carried out in a mixer MR-2L Chopin (Villeneuve-la-Garenne, France) for one hour by adding the appropriate amount of water up to 30% moisture content according to the initial moisture of the flour. Then, samples were allowed to stand 24 hours at room temperature in order to equilibrate the moisture content. Microwave oven was preheated to achieve a standard uniform temperature, by heating 200 mL of distilled water for 0.5 min, before each treatment. Samples (100.0 g each) were treated at 400W (intermediate continuous power) in an open cylindrical glass plate (diameter: 150 mm, height: 75 mm) for 0.5, 1, 2 and 4 min. Samples were left into the oven for one additional minute till cooling down and later were adequately homogenized with a glass rod. After microwave treatment, flours were sieved on an automatically Buhler sieving model MLI300B (Uzwil, Switzerland), through a 132 mesh screen, to remove particle clumps. Particle clumps were present in all cases in amounts lower than 10% of the weight of flour. Those clumps were milled using a Perten instruments laboratory mill 3303 (Huddinge, Sweden) and reincorporated to the rest of the flour. Flours were stored in air-tight plastic containers and held at 4°C until further analyses. Two sets of samples were carried out for each treatment. Moisture content of the flour was analyzed in duplicate according to the method 44-16.01 (AACCI, 2012).

2.2.2 Microscopic observations

Flour photomicrographs were taken with Quanta 200FEI (Hillsboro, Oregon, USA) environmental scanning electron microscope (ESEM). Photomicrographs were taken in beam deceleration mode (BDM) at 1.5KeV in high vacuum mode with a backscattered electron detector (BSED).

2.2.3 X-ray diffraction (XRD)

Samples were analyzed using a Bruker D8 Discover A25 (Bruker AXS, Rheinfelden, Germany) equipped with a copper tube operating at 40 kV and 40 mA, producing CuK α radiation of 0.154 nm wavelength. Diffractograms were obtained by scanning from 5° to 40° (2theta) at a rate of 1.2 °/min, a step size of

0.02°, a divergence slit width variable (DS) of 5 mm and a scatter slit width (SS) of 2.92°, and a nickel filter 0.02 to exclude K β radiation.

2.2.4 Differential scanning calorimetry (DSC)

Analyses were performed in a differential scanning calorimeter DSC-7 (Perkin–Elmer, Waltham, MA, USA) as reported Martínez et al. (2014). Thermal transitions of samples for gelatinization were characterized by onset temperature (To), peak temperature (Tp), gelatinization temperature range (Tp-To) as well as the enthalpy of starch gelatinization (ΔH_g) (expressed as mJ/mg of sample). The enthalpy calculations were based on dry-flour weight. All samples were run in triplicate.

2.2.5 Pasting properties

Pasting properties of flours were analyzed using the standard method 61-02.01 (AACCI, 2012), with a Rapid Visco Analyser (RVA-4) controlled by Thermocline software (Newport Scientific Pty. Limited, Warriewood, Australia) for Windows. At least two RVA profiles were obtained for each sample.

2.2.6 Statistical analysis

Simple analyses of variance were used to determine the effects of microwave treatment. Fisher's least significant difference (LSD) test was used to describe means with 95% confidence. Statgraphics Centurion XVI (Statpoint Technologies, Warrenton, USA) was used as statistical analysis software.

3. Results and Discussion

3.1 Microscopic observations

Fig. 1 shows that microwaved flours (b and c) showed a more disaggregated structure (white arrows) than the native one (black arrow). It was also observed that these flours lose gradually the compact matrix where starch granules were integrated into the protein; instead starch granules showed more naked and slightly swollen structure. This effect increased with the time of treatment. The swelling of the starch granules in treated flours might be due to the modest structural reorganizations (annealing) occurred during microwave treatment owing to the excess of water at temperatures above the glass transition temperature (Biliaderis 2009). In addition, no breakage of the starch granules was observed, indicating

that starch gelatinization was not complete, thus either the temperature or the time of treatment was not enough to produce starch gelatinization.

Luo et al. (2006) also observed changes on starch granule structure when moistened (30%) starch maize were treated 20 min in microwave at 1 W/g. Nevertheless, they observed some breakage, cracks and porous on the surface of the starch granules. Those observations were attributed to possible transfers and internal rearrangements of the particles. Likely, the shorter time, and thus power, employed in the flour treatments of the present study were not sufficient to visibly damage the starch granules.

3.2 X-ray diffraction

The crystalline structures of maize flours were studied using XRD. The diffractograms (Fig. 2) showed that all samples maintained A-type crystallinity, typical of cereal starches, after microwave treatment. Nevertheless, microwave treatment had a strong influence on their crystalline order, increasing the intensity of the peaks and maintaining d-spacing, which agrees with Luo et al. (2006). These findings could indicate a crystalline growth fostered by microwave treatment. Starch granules, being partially crystalline entities, are prone to molecular reorganization (annealing) when held in excess of water at temperatures above the glass transition temperature and below the equilibrium temperature of the crystallites. Softening of the amorphous granular regions enables crystalline growth and/or perfection (Biliaderis 2009). Microwave treatment of maize flours also led to a V-type crystalline peaks formation at 2θ of around 20° (arrow mark). Lopez-Rubio et al. (2008) affirmed that V-type crystalline structure can be originated from single helical amylose, such as amylose-lipid complexes. In a single-helical complex, the linear portion of the starch molecule has its hydrophobic side of the molecule facing the cavity of the helix and interacting with the non-polar moiety of the complexing agent, such as fatty acids (Jane, 2009).

3.3 Differential scanning calorimetry (DSC)

The influence of microwave treatment on thermal properties of maize flours is presented in Table 1. In the range of temperature tested, flours exhibited one endothermic peak, corresponding to amylopectin

gelatinization. Microwave treatment affect the gelatinization temperatures of maize flours since their onset and peak temperatures shifted to higher temperatures. Chiu and Solarek (2009) reported that after hydrothermal treatments the starch gelatinization temperature was higher, the gelatinization endotherm more defined and the energy of gelatinization increased, coinciding with the results of this study. When crystallites perfection is higher, greater gelatinization temperatures are required to melt starch crystallites (Ji et al. 2004). Therefore, the increase of gelatinization temperature observed in moistened treated flours would be in agreement with XRD results. The rise in gelatinization temperatures has also been associated with the formation of amylose-amylose and amylose-lipid complexes within the starch granule (Lewandowicz et al. 2000; Sun et al. 2014). Lewandowicz et al. (2000) also suggested that higher gelatinisation temperature of microwaved starches may indicate an association and a more stable configuration in a granular structure. The present study shows that these associations could be effective after certain time of treatment (1-2 min). Meanwhile, the range of temperature where gelatinization proceeds was narrowed in flours subjected to microwave treatment. Differences observed in Tc-To suggest that microwave irradiation leads to the formation of more stable and homogeneous crystallites. Compared to native maize flour, gelatinization enthalpy increased in microwaved maize flours. This observation is in accordance to Biliaderis (2009), who highlighted a same trend in other hydrothermal treatments carried out in excess of water at temperatures below gelatinization temperature. Conversely, some other researchers reported a significant decrease in the enthalpy when maize starches were subjected to microwave irradiation (Lewandowicz et al. 2000; Luo et al. 2006; Stevenson et al. 2005). These differences could be due to the fact that in these studies, longer microwave treatment of maize starch was applied, between 20-60 min. This excessive treatment could cause the reduction of crystallinity, as a consequence of the partial starch gelatinization (Sun et al. 2014).

3.4 Pasting properties

Pasting profiles of native maize flour and microwaved treated flours are plotted in Fig. 3. Treated samples showed an increase in viscosity during the heating-cooling cycle when very short time of microwave treatments was applied (0.5 min and 1 min). But longer treatment times induced the opposite

effect and a decrease in the viscosity was observed. The decrease of the maximum viscosity was also observed by Pinkrová et al. (2003) when increasing temperature of microwave treatment of rice grain and increasing power output at moisture content of 30%. Luo et al. (2006) related this reduction of peak viscosity with an increment of inter- and intra-molecular hydrogen bonding due to association of starch chains during microwave treatment.

Pasting temperatures of maize flour increased as longer treatments were applied, similarly to what was observed with gelatinization temperatures in the DSC analysis, indicating that flour might have greater difficulty to absorb water and start swelling. Higher crystallinity and rigidity of the starch granules impede water absorption; in fact, the increased crystallinity promotes a delay in the gelatinization onset, since water is principally absorbed by amorphous regions (Sun et al. 2014). Hence, this rise in the pasting temperature agrees with the major crystallinity found in XRD analysis of treated flours. Moreover, Jane et al. (1999) reported the association between higher pasting temperature and the formation of amylose-lipid complexes, which in fact were envisaged in the XRD analysis of moistened treated flour. In consequence, microwave treatment of flours in the presence of sufficient water induced the formation of amylose-lipid complexes besides an increase in crystallinity, which led to a delay in the gelatinization and pasting temperature. Moreover, other components of maize flour, such as proteins could have interacted with starch after microwave treatment increasing the pasting temperature and retarding gelatinization. In fact, Sun et al. (2014) studying heat moisture treatment found a higher pasting temperature of sorghum flour as compared to starch, which they attributed to protein effect.

The breakdown viscosity also decreased with longer microwave treatment of flours, which reflects an increase in shear stability of microwave heat-treated flour (Anderson and Guraya 2006; Sun et al. 2014). The increasing stability may be due to the formation of amylose-lipid complexes (Rumroytum et al. 2014) as a result of the stiffer starch granules and the presence of rigid non-fragmented swollen granules. The tendency observed in setback is the one seen for the peak viscosity, resulting in a more elevated final viscosity at the two shorter times. The reduction of final viscosity would be due to the formation of amylose-lipid complexes, because amylose chains would not be any more available for recrystallization.

4. Conclusion

Microwave treatments in which flours have enough water content are likely to modify the crystallinity of their starch granules, promoting a swelling and amylose-lipid complexes formation, without causing starch gelatinization. Furthermore, shear stability of these flours is improved while setback is cut down. Therefore, microwave treatment could be used to obtain modified maize flours more suitable for some food applications.

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Tables

Table 1. DSC characteristics of native and microwave treated flours.

Type	Time of treatment (min)	T _o (°C)	T _p (°C)	T _c (°C)	T _p - T _o (°C)	ΔH _{db} (J/g)
Native	0	66.6 a ±1.4	74.0 a ±0.6	77.3 a ±5.2	7.4 c ±0.9	2.819 a ±0.778
Treated	0.5	67.3 a ±2.1	73.2 a ±0.5	78.3 a ±0.5	5.9 bc ±1.6	5.391 c ±0.222
	1	70.5 b ±1.4	74.2 a ±0.5	78.4 a ±0.4	3.8 a ±0.9	4.132 b ±0.927
	2	70.1 b ±1.0	75.6 b ±0.9	80.6 a ±1.0	5.5 b ±0.1	4.014 b ±0.575
	4	69.6 b ±1.2	75.2 b ±0.4	80.4 a ±0.5	5.5 b ±0.8	5.645 c ±0.148

Values followed by the same letter in each column are not significantly different ($P < 0.05$). To, gelatinization onset; Tp, peak temperature; Tc, conclusion temperature, Tp-To, gelatinization range, ΔH_{db}, enthalpy, expressed as dry basis.

Figure captions

Fig. 1 – Environmental scanning electron microscope of maize flours. a, native; b, treated-0,5 min; c, treated-4 min. White and black arrows show disaggregated and aggregated structures, respectively.

Fig. 2 – X-ray diffraction patterns of microwaved flour samples as compared to native one. Arrow mark shows V-type structures. DSC patterns of the different times of treatment of flour (Native, 0.5, 1, 2 and 4 min) appear in vertical axis.

Fig. 3 – Pasting characteristics of maize flours. Viscosity profiles for Native (—) and microwave treated samples for 0.5 min (———), 1 min (———), 2 min (— —) and 4 min (- - -) are represented in vertical axis. Temperature profile is represented by

292 **Fig. 1**

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299 **Fig. 2**

301 **Fig. 3**