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Effect of carboxymethylcellulose and xanthan gum on the thermal, functional and rheological properties of dried nixtamalised maize masa

Andrés Aguirre-Cruz, Guadalupe Méndez-Montealvo,
Javier Solorza-Feria*, Luis Arturo Bello-Pérez

Centro de Desarrollo de Productos Bióticos del IPN, Km. 8.5 Carr. Yautepec-Jojutla Col. San Isidro Apartado postal 24 C.P., 62731 Yautepec, Morelos, Mexico

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Abstract

Maize masa was mixed with carboxymethylcellulose (CMC) and xanthan gum at 0.2 and 0.5% (w/w) solids and then freeze-dried for obtaining dried masa (DM) samples which were tested for chemical composition, thermal analysis, water retention capacity (WRC), solubility and rheological properties. The thermal properties of dried masa with hydrocolloids (DM_H), showed a transition temperature higher than DM but lower enthalpies, in an interval between 80.5–81.6 °C and 5.4–11.4 J/g, respectively. Masa samples with hydrocolloids stored for 7 and 14 days, showed similar values of transition temperatures but different enthalpy values, being usually lower than that of the control. The WRC and the solubility of the DM_H, were higher than those of the control. The addition of hydrocolloids to DM increased the viscosity expressed in Brabender Unities. All masa samples behaved as 'weak' viscoelastic gels, with G' (elastic modulus) $>G''$ (viscous modulus), when subjected to a three stages of heating–cooking–cooling kinetics, with an increase in the moduli values as the kinetics progressed. Overall the hydrocolloids addition decreased both moduli values.

Keywords: Dried masa; Nixtamalisation; Carboxymethylcellulose; Xanthan gum; Thermal analysis; Rheology; Zea mays

1. Introduction

Maize (*Zea mays* L.) is probably the oldest cultivated cereal in the American continent, which is also currently grown in Europe, Africa and Asia. This grain plays an important role in the diet of many countries, specially in Mexico (Serna-Saldívar, Gomez, & Rooney, 1990).

The nixtamalisation is a process that consists of cooking maize with lime, then, it is let to rest from 14 to 16 h, later on, it is washed with water to get rid of the excess of lime and finally, the maize is taken to the process of milling for the elaboration of masa, which is used for obtaining specially tortillas, but also products like: chips, cornflour drinks or other snacks and Mexican foods (Serna-Saldívar, Rooney, & Waniska, 1988). The masa obtained from the nixtamalisation is a mélange characterised by a mixture of starch polymers containing starch gelatinised granules, intact starch granules, pieces of endosperm, and some lipids (Gómez, Rooney, Waniska, & Pflugfelder, 1987). The alkali-thermal treatment used in the nixtamalisation, acts on the components of cell walls for converting the hemicellulose into soluble gums (Arámbula, Mauricio, Figueroa, González-Hernández, Ordorica, 1999). This treatment has several functions, such as, to gelatinise the starch, to saponify part of the lipids, and also to solubilise some proteins surrounding the starch granules (Rooney and Suhendro, 1999). Since nixtamalisation typically provides the rheological and texture properties of the masa products, gelatinisation must be carefully controlled because large amounts of gelatinised starch can produce stickiness, which could affect the handling of the masa (Rooney and Suhendro, 1999). In the case of nixtamalised products, e.g. tortillas, immediately after preparation, starch reorganization is carried out, producing crystalline structures, which is known as retrogradation. This phenomenon alters the texture and nutritional characteristics of starchy products.

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* Corresponding author
E-mail address: jsolorza@ipn.mx (
J. Solorza-Feria).

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Since the shelf life of tortillas is short (2–3 days at refrigeration temperature), at the present time, new alternatives to improve and to preserve the quality of tortillas during its storage are being studied and developed. Among these, the use of some additives like the hidrocolloids (e.g. carboxymethyl-cellulose, xanthan, guar, arabic, and locust bean gum), which are water-soluble heteropolysaccharides with high molecular weight, can be mentioned. Hydrocolloids exhibit a variety of functional properties: thickening, gelling, film forming, emulsifying, etc., making them suitable for use in a variety of applications in the food industry (Gurkin, 2002). At low concentrations, (less than 1% (w/w)), the hydrocolloids can be used to improve the quality of tortillas, doing them easier to bend and to roll after their storage (Twillman and White, 1988). However, the addition of hydrocolloids can modify the thermal and rheological properties of masa, which is important during the process of tortilla elaboration. The understanding of these parameters is crucial for equipment design and definition of operation parameters in the tortilla industry.

Differential scanning calorimetry has been widely used to characterize the thermal properties of masa and nixtamalised maize flours (Bello-Pérez, Osorio-Díaz, Agama-Acevedo, Solorza-Feria, Toro-Vázquez and Paredes-López, 2003), since it provides information about the order–disorder of molecules within the system.

Rheology contributes to the knowledge of the materials structure. In the food industry, rheological measurements are frequently carried out on raw materials and elaborated products that are very useful for the control of processes (Steffe, 1992). The rheological oscillatory methods provide information about the viscoelasticity of samples, this can be done by varying either the frequency or the amplitude under a controlled stress or strain (Ferry, 1980; Steffe, 1992). The results of the dynamic experiments are represented by parameters such as G' (storage or elastic modulus), G'' (loss modulus) and tan δ (loss tangent), given by the ratio G''/G'.

The objective of this work was to study the effect of carboxymethylcellulose (CMC) and xanthan gum addition on the thermal, rheological and functional properties of dried masa from nixtamalised maize.

2. Material and methods

2.1. Materials

A variety of commercial yellow maize for tortilla production (CML 150 xs CLQ6203) supplied by the INIFAP Iguala Guerrero, Mexico, was used.

Xanthan gum was supplied by Colloides Naturales of Mexico (México, D.F.). Sodium carboxymethylcellulose (CMC) was purchased from AMTEX Mexico (México, D.F.).

All reagents used were of analytical grade of the brands Roche, Sigma, Merck and Fermont (México, D.F).

2.2. Methods

For preparation of masas, maize was nixtamalised to obtain the samples (Rendón-Villalobos, Bello-Pérez, Osorio-Diaz, Tovar, & Paredes-López, 2002), which were then mixed with the hydrocolloids (CMC and xanthan gum) at two concentrations (0.2 and 0.5% w/w) recommended for tortilla production. Later on, they were freeze-dried and ground to obtain a flour and the corresponding analyses were made to the dried masa (DM), this with the idea of obtaining a homogeneous sample and facilitate the experimental tests. The samples of dried masa with no hydrocolloid addition (control), were compared with those with hydrocolloid (DM_H) addition.

2.2.1. Proximal analysis

Moisture content, lipids, protein and ash were obtained from DM samples according to the AACC (2000), methods 44-16, 30.25, 46.13 and 08-01, respectively.

2.2.2. Quantification of the amylose

The amylose content was determined to DM samples following the colorimetric technique of Gilbert and Spragg (1964). About 1.5 mg of DM was weighed and transferred to a 50-ml volumetric flask. Then, 0.5 ml of a solution NaOH 1 N was added and the mixture simmered during 3 min in a boiling water bath. It was then cooled down and neutralized with 0.5 ml of HCl 1 N and 0.07 g of potassium bitartrate was added and diluted with distilled water until obtaining an approximate volume of 45 ml. Once the bitartrate was dissolved, 0.5 ml of a solution of iodine (2 mg/ml of iodine and 20 mg/ml of KI) was added and the volume completed with distilled water to 50 ml. The solution was mixed, then it was allowed to rest during 20 min at room temperature and the absorbance was measured at 680 nm in a Genesys 5 spectrophotometer (Spectronic Instruments, USA). A standard curve was prepared using mixtures of commercial amylose and amylopectin from maize. The amylose content in the dried masas was quantified by interpolation of the absorbance values in the standard curve.

2.2.3. Thermal analysis

The thermal properties of the maize dried masas were studied using a differential scanning calorimeter (DSC, TA Instruments, 2010, New Castle, USA), previously calibrated with indium.

The gelatinization of the samples was evaluated by the method proposed by Paredes-López, Bello-Pérez, & López (1994). About 2 mg sample (dry basis) was weighed on an aluminum pan, 7 μL of deionised water was added. The pan was sealed tightly and then it was allowed to stand for 1 h before carrying out the analysis. An empty aluminum pan was used as reference. The sample was subjected to a heating program over a range of temperature from 30 to 140 °C and a heating rate of 10 °C/min. The gelatinization or peak temperature (T_p) and the transition enthalpy (ΔH), were obtained directly from the analysis of the software TA Instruments OS/2 version 2.1.

To determine the retrogradation temperature and retrogradation enthalpy, gelatinized samples as mentioned above were stored for 7 and 14 days at 4 °C. After completion of the storage time, the pans were allowed to stand for 1 h at room temperature and then analyzed in the DSC, using the same conditions described previously.

2.2.4. Viscoamylographic test

To determine the viscosity (BU) profile of dried nixtamalised maize masa, the technique proposed by the AACC (2000), was used. Maize dried masa dispersions with 10% (w/v) of total solids were prepared; 100 ml of dispersion (sample) were transferred to the bowl of a microviscoamylograph (Brabender OHG, Duisburg, Germany). The equipment was programmed to run a heating–cooking–cooling cycle that began at 30 °C and then increased to 95 °C, staying at this temperature for 10 min, then cooled down to 40 °C and maintained at this temperature for another 10 min. A heating and cooling rate of 2.5 °C/min was used throughout the cycle with a speed of agitation of 125 rpm.

2.2.5. Water retention capacity (WRC) and solubility

The WRC and the solubility were determined with the method proposed by Tecante and Doublier (1999), that consisted in preparing suspensions of DM and DM_H with 10% (w/v) of total solids on a dry basis. A kinetics of heating–cooking–cooling was followed using the microviscoamylograph bowl as heating devise, starting at room temperature with a constant heating rate of 1.5 °C/min, until 95 °C, maintaining the sample isothermal for 10 min, and then cooling down to 40 °C at the same rate (1.5 °C/min), maintaining this temperature for 10 min as well. Samples (500 μL) were taken by triplicate along the kinetics, using tubes with deionised water, in such a way that the final concentration was of 0.5% (w/v) of solids. The 1st sample was taken starting at 30 °C (beginning of the heating stage), then at 50, 70, 80 and 95 °C (beginning of the cooking stage), another sample was taken at the end of the cooking stage (95 °C), and at the end of the cooling stage and beginning of the isothermal stage (40 °C) and the last one, at the end of the isothermal stage (40 °C).

The slurries were centrifuged at 2200 rpm for 15 min. The supernatant was decanted, and the volume was measured; aliquots were used to estimate the total carbohydrates (Dubois, Gilles, Hamilton, Robers, & Smith, 1956). The precipitate was used to measure the moisture content (24 h at 100 °C) and thus to determine the solubility. The WRC of the samples was calculated from the centrifuged residual and the dry residual.

2.2.6. Dynamic viscoelastic method

Masa dispersions with 10% (w/v) of total solids were prepared using distilled water. Their viscoelastic properties were measured running oscillatory tests in a TA Instruments Rheometer, model AR 1000, New Castle (USA) using a parallel plates system, with a diameter of 60 mm, a gap of 200 μm, and either a heating or cooling rate of 2.5 °C/min. To determine the linear viscoelastic region (LVR), strain amplitude sweeps were run from 0.1 to 3% in the 1st stage (25 °C) and from 0.1 to 5% in the 2nd (90 °C) and 3rd stage (25 °C), of a heating (25–95 °C, stage 1)–cooking (95 °C, 10 min, stage 2)–cooling (95–25 °C, stage 3) kinetics, all tests were run at a frequency value of 1 Hz. Once the LVR was found, the machine was programmed for running frequency sweeps (0.1–10 Hz) for which a constant strain value of 0.3% was used in the 1st and 2nd stage and of 0.5% in the 3rd stage of the kinetics. The storage modulus (G'), loss modulus (G'') and loss tangent ($\tan \delta$) were evaluated from each test.

2.2.7. Statistical analysis

To determine statistical differences on the gelatinization parameters (T_p and ΔH) and retrogradation (7 and 14 days of storage) of dried masa samples, due to the addition of hydrocolloids (gums) and their concentration, two-way analysis of variance (ANOVA) was applied. The same method was used for the WRC and solubility data. To find out statistical differences among the rheological data (viscoamylography and dynamic tests) as affected by temperature and gum concentration, one way ANOVA was applied.

In all cases, the significance level was of 5% ($\alpha = 0.05$), and the statistical package used was Sigma-Stat, version 2.1 (Fox, Shotton, & Ulrich, 1995). When significant differences were found, the test of multiple comparison of Tukey was applied (Walpole, Myes, & Myes, 1991).

3. Results and discussion

3.1. Proximal analysis

The results obtained for the chemical composition of masa were as follows, for protein 8.6 ± 0.041%, lipid 4.7 ± 0.016%, ash 1.8 ± 0.004% and moisture 9.7 ± 0.016%. In other study, masa presented a lower protein content (6.7%) (Campus-Baypoli, Rosas-Burgos, Torres-Chávez, Ramirez-Wong, & Serna-Saldivar, 1999), but other authors (Bello-Pérez et al., 2003) found a similar protein value (8.2%) than that determined in this study. Lipid content presented a similar pattern to protein values, because Campus-Baypoli, Rosas-Burgos, Torres-Chávez, Ramirez-Wong, & Serna-Saldivar (1999) reported a lower value (3.7%) and Bello-Pérez et al. (2003) reported a higher value (5.7%) than that determined in this study. However, ash content was similar to that reported by Campus-Baypoli, Rosas-Burgos, Torres-Chávez, Ramirez-Wong, & Serna-Saldivar (1999) and higher than that (1.6%) determined by Bello-Pérez et al. (2003). The values of chemical composition can be due to maize variety and the conditions used in the nixtamalisation process, as calcium hydroxide concentration, cooking and steeping time. These parameters are important for obtaining a masa and thereafter nixtamalised products with better sensorial and functional characteristics.

3.2. Amylose content

The dried masa presented an amylose content of 10± 0.9%. This value is because masa has other constituents as protein, lipids, etc. and only between 50 and 60% is starch, because in normal maize starch, amylose content ranged between 25 and 30%. Besides, during the nixtamalisation process, partial gelatinization of starch granules is produced and lixiviation of amylose is carried during cooking and steeping of the maize grain, reducing the amylose content in the masa. Singh, Singh, Sharma, & Saxena (2003), reported an amylose content for maize of 9%, a slightly lower value than the one found in this investigation, although in their work, nixtamalisation was not carried out. The amylose content can vary depending on the botanical source, affecting the thermal and rheological properties (Moore, TuschHoff, Hastings, & Schanefelt, 1984).

3.3. Thermal analysis

The thermal properties of the dried masa samples are presented in Fig. 1. In all cases a single endothermic transition (gelatinization) was observed, the thermograms were well defined, probably because of a homogeneous granule structure of the starches present in the masa. The addition of hydrocolloids caused a significant increase ($\alpha=0.05$) of the T_p (gelatinization temperature) compared with that of the control sample (Fig. 1a, Table 1), this was probably the result of the interaction starch-hydrocolloid, that produced a more stable structure, needing a higher temperature for disorganization (Christianson, Hodge, Osborne, & Detroit, 1981). The presence of either hydrocolloid (both negatively charged gums) in the masa, causes the union of the protons (H^+) of water and also

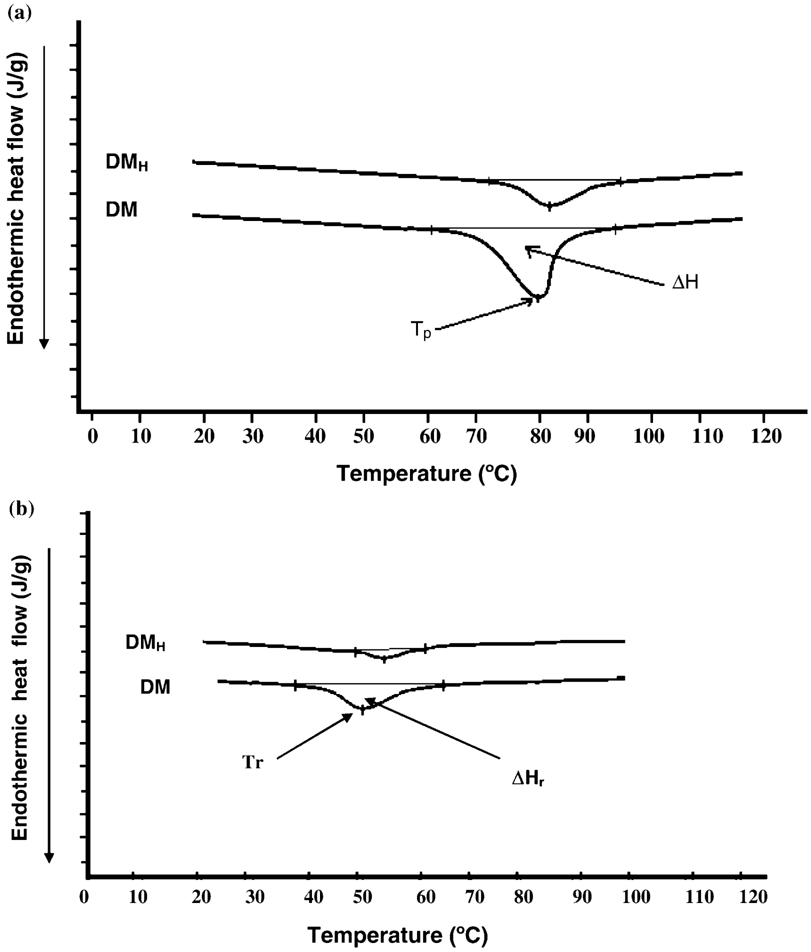

Fig. 1. Typical thermograms of dried nixtamalized maize masa with 10% (w/v) of total solids, control (DM) and with hydrocolloid addition (DM_H): (a) gelatinization, (b) retrogradation.

Table 1
Temperature and enthalpy of gelatinization and of retrogradation of dried nixtamalized maize masa at 7 and 14 storage days, measured by differential scanning calorimetry (average of three repetitions ± standard error)

Sample	T_P	ΔH	T_r7	ΔH_r7	T_r14	ΔH_r 14
Control	80.5 ± 0.32^{a}	11.4 ± 0.42^{a}	50.5 ± 0.23^{aA}	6 ± 0.50^{aA}	54 ± 0.25^{aB}	7 ± 0.34^{aA}
CMC 0.2%	81.2 ± 0.43^{b}	10.3 ± 0.39^{b}	53.8 ± 0.17^{bB}	5 ± 0.38^{bB}	54 ± 0.28^{aB}	5.5 ± 0.43^{bB}
CMC 0.5%	81.5 ± 0.28^{b}	9.8 ± 0.45^{c}	53.8 ± 0.22^{bB}	4.6 ± 0.41^{bC}	54.6 ± 0.32^{aB}	4.8 ± 0.38^{cC}
Xanthan 0.2%	81.4 ± 0.19^{b}	8.2 ± 0.32^{d}	53.9 ± 0.25^{bB}	3.7 ± 0.35^{cD}	54.2 ± 0.17^{aB}	3.7 ± 0.35^{dD}
Xanthan 0.5%	81.6 ± 0.32^{b}	5.4 ± 0.38^{e}	54 ± 0.31^{bB}	2 ± 0.37^{dE}	55 ± 0.22^{aC}	2.6 ± 0.32^{eE}

T_P (Temperature of gelatinization) and T_r (temperature of retrogradation) in °C, ΔH in J/g of dried masa. Same letters inside each column indicate that the data are not significantly different ($\alpha=0.05$). Same capital letters (used to compare independently T_r and ΔH_r, retrogradation enthalpy, at two storage times) inside each row indicate that the data are not significantly different ($\alpha=0.05$).

the linkage of the amylose chains with this hydrocolloid, which in consequence, promotes certain inhibition in the gelatinization of the DM_H, causing an increase of its T_p (Rojas, Rosell, & Barber, 1999).

However, statistical differences were not shown in T_p values among the samples with hydrocolloid addition; suggesting that neither the concentration nor the hydrocolloid type affected this parameter, possibly because although a similar hydrocolloid–masa interaction is taking place, the gum addition at the two concentrations used (0.2 and 0.5%), was not enough to detect differences in the T_p among the masa samples.

With respect to the gelatinization enthalpies (Table 1), significant differences ($\alpha=0.05$) were observed, among the samples studied. The values of ΔH decreased as the "hydrocolloid concentration increased". This could be because a higher hydrocolloid–starch interaction retain more water molecules, causing a higher mobility during the heating, increasing the kinetic energy and decreasing the enthalpy value (Slade and Levine, 1991; Gimeno, Moraru, & Kokini, 2004). The enthalpy values in J/g starch were 15.2 for the control, 13.7 for CMC 0.2%, 13.0 for CMC 0.5%, 10.9 for Xanthan 0.2% and 7.2 for Xanthan 0.5%, showing the same trend as for the dried masas, with significant differences ($\alpha=0.05$) among the samples, due to starch being in highest proportion in the dried masa (75%) and is also the main component that interacts with the hydrocolloids. Similar values on a starch content basis have been found by other researchers (Yuan, Thompson, & Boyer, 1993).

The effect of the hydrocolloid concentration was more pronounced with xanthan gum (negatively charged polymer composed of a 1–4 linked β-D-glucose backbone substituted with a trisaccharide side chain, bearing two mannoses and one glucuronic acid at every second residue) treated masas, than those with CMC (linear anionic polymer produced by treating cellulose with aqueous sodium hydroxide, followed by an esterification reaction) treated samples, suggesting that the hydrocolloid chemical structure and its conformation in solution, play an important role in this pattern (Gimeno, Moraru, & Kokini, 2004).

The thermograms of the retrogradation process are shown in Fig. 1b, they are less defined than those of the gelatinization stage, but presenting the same trend of the hydrocolloids increasing the peak temperature. Dried masa samples stored for 7 days, showed a transition temperature (retrogradation) that was significantly higher for DM_H, than

Table 2
Effect of temperature on (A) water retention capacity (g H_2O/g sample) and (B) solubility of dispersions (%) of dried nixtamalized maize masa control and with hydrocolloid addition (average of three repetitions ± standard error)

Temperature (°C)	Control	CMC 0.2%	CMC 0.5%	Xanthan 0.2%	Xanthan 0.5%
(A) 30	5.5 ± 0.54	5.7 ± 0.37	5.9 ± 0.45	5.9 ± 0.51	6.9 ± 0.26
50	6.1 ± 0.32	6.3 ± 0.22	6.8 ± 0.11	7.1 ± 0.44	9 ± 0.25
70	6.4 ± 0.58	6.6 ± 0.31	8.2 ± 0.29	8.1 ± 0.51	11.3 ± 0.34
80	8.1 ± 0.19	10.1 ± 0.54	11.2 ± 3.19	10.5 ± 0.55	14.6 ± 0.54
95 (b)	11.2 ± 0.27	13.4 ± 0.33	14.8 ± 1.74	14.6 ± 0.50	18.4 ± 0.23
95 (f)	12.1 ± 0.35	13.6 ± 0.35	15.6 ± 2.16	15.2 ± 0.21	19.9 ± 0.35
40 (b)	12 ± 0.33	13.7 ± 0.20	15.7 ± 0.51	15.3 ± 0.56	19.8 ± 0.11
40 (f)	12.3 ± 0.44	13.5 ± 0.52	15.6 ± 0.57	15.2 ± 0.23	19.9 ± 0.55
(B) 30	1.7 ± 0.47	2.3 ± 0.25	2.5 ± 0.50	3.3 ± 0.20	6.2 ± 0.30
50	2 ± 0.36	2.7 ± 0.29	3.1 ± 0.25	4.6 ± 0.48	6.8 ± 0.30
70	2.3 ± 0.42	3.4 ± 0.40	4.1 ± 0.36	5.7 ± 0.13	8 ± 0.35
80	5.2 ± 0.14	5.4 ± 0.26	6.6 ± 0.14	7.9 ± 0.30	12.1 ± 0.32
95 (b)	6.1 ± 0.44	7.9 ± 0.45	8.3 ± 0.48	12.9 ± 0.22	19.2 ± 0.43
95 (f)	13.9 ± 0.13	23.1 ± 0.33	27.5 ± 0.54	33.8 ± 0.44	37.9 ± 0.41
40 (b)	10.8 ± 0.31	22.4 ± 0.42	27.9 ± 0.46	32.3 ± 0.30	37.4 ± 0.35
40 (f)	10.9 ± 0.48	22.3 ± 0.28	26.4 ± 0.17	32.3 ± 0.56	37.1 ± 0.34

(b) Beginning of the isothermal stage; (f) end of the isothermal stage.

that of the control, but without significant differences ($\alpha = 0.05$) between concentration and type of hydrocolloid (Table 2). At a longer storage time (14 days), a significant increase in the transition temperature was found respect to the value at 7 storage days in the control and DM_H with xanthan (w/w) 0.5%, indicating a higher degree of amylose alignment (re-ordering) in those samples. However, no statistical differences ($\alpha = 0.05$) among all transition temperatures of the gum treated samples respect to the control were detected, suggesting that even at longer storage time, the hydrocolloid did not affect the thermal stability of the crystals formed during starch retrogradation.

In the case of the enthalpy values of the retrogradation phenomenon with 7 days of storage, all gum treated samples had significantly lower enthalpies than the control, it was seen however, that for samples with CMC, the concentration did not affect the ΔH_r value, but for samples with xanthan gum, significant differences ($\alpha = 0.05$) were found between the two concentrations used. The lower ΔH_r values of treated $samples_s$ compared with that of the control is because more water molecules are retained by the hydrocolloid and thus a lower energy is needed for crystal disorganization. The interaction amylose-hydrocolloid is crucial as postulated by Ferrero, Martino, & Zaritzky (1994) and Mali, Ferrero, Redigonda, Belia, Grossmann, & Zaritzky (2003). They have suggested that the network formed by the hydrocolloid in some degree, prevents the amylose to be realigned through hydrogen bonds that play a critical role in the retrogradation phenomenon. The chemical structure of the two hydrocolloids tested could again explain the difference between those samples.

For each sample the ΔH_r at 14 storage days was similar to that at 7 storage days, but maintaining a significantly lower value than the control, concluding that even at longer storage time, the hydrocolloids maintained its effect on the retrogradation phenomenon.

3.4. Amylographic study

During the heating stage (30–95 °C), the viscosity (UB) increased gradually until obtaining a maximum value (maximum or peak viscosity) (Fig. 2). When starch is heated up in excess of water, its grains are swollen and at the same time, part of its components (amylose and low molecular-weight amylopectin molecules) is solubilized, giving rise to a swollen and dispersed particle suspension in a continuous phase (Thebaudin, Lefebvre, & Doublier, 1998).

The viscosity values of the DM_H are higher than those of the control, this is mainly due to the three-dimensional network formed by the hydrocolloid and to its ability to link water molecules within the system, giving as a result an increase on the viscosity (Andrew, 2004). For each gum type, the concentration had influence in the viscosity, because at 0.5% (w/w) solids, the DM presented higher viscosity. Again, samples with xanthan showed higher viscosity values than samples with CMC. This difference might be because the xanthan gum in its chemical structure has a higher number of free carboxyl groups than the CMC, which causes the xanthan gum to have a greater water absorption capacity (Alloncle and Doublier, 1991). When reaching the stage of cooking (molecular dissociation) of the paste (95 °C), a slight decrease of the viscosity values of the DM_H with CMC was observed, probably because its interaction with starch is weaker than that produced between xanthan and starch. During the reassociation and cooling steps, DM_H samples showed a higher increase in the viscosity than that presented by the control sample. This

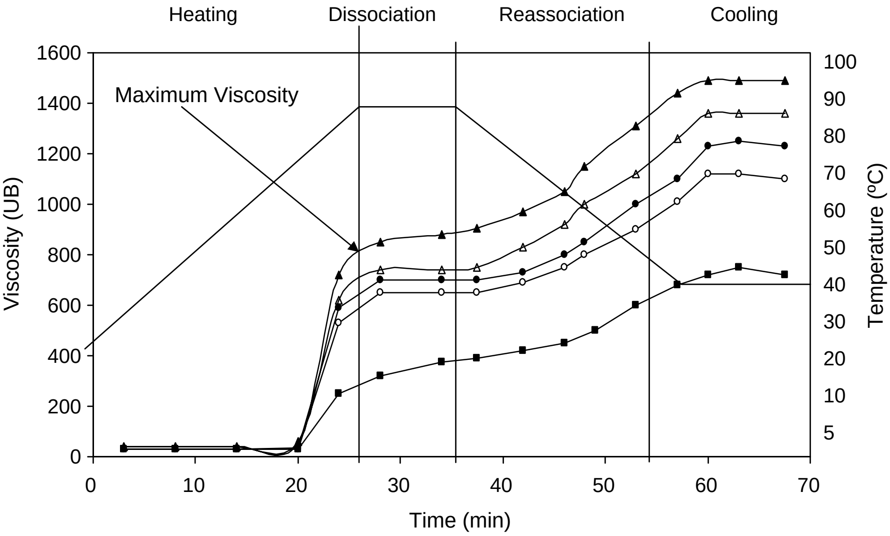

Fig. 2. Amylogram of dried nixtamalized maize masas with 10% (w/v) of total solids, control and with hydrocolloid addition. (■) Control; (○) CMC 0.2%; (●) CMC 0.5%; (△) xanthan 0.2%; (▲) xanthan 0.5%.

pattern is due to starch–hydrocolloid reorganization, originating a higher number of crosslinks during the process of conformation of the gel (Gimeno, Moraru, & Kokini, 2004; Mali, Ferrero, Redigonda, Belia, Grossmann, & Zaritzky, 2003), producing a network that retains a higher amount of water molecules.

3.5. Water retention capacity and solubility

Table 2a, shows the effect of the temperature on the water retention capacity (WRC) of the DM and DM_H suspensions. All samples presented an increase in the WRC in an interval of temperature between 30 and 95 °C (heating stage), showing the highest values at 95 °C. However, during the isothermal and cooling stages, the WRC did not change. This pattern is because the starch granules and hemicellulose components present in the masa link water molecules. Overall, DM_H had higher WRC than the control sample ($\alpha = 0.05$), this could be because of the high affinity to water of the hydrocolloids, due to their branched structure. During hydration, the water molecules orient towards the hydroxyl (or carboxyl) groups found in the individual units of components (sugars) of the hydrocolloid molecule, this association usually induces an increase in the WRC (Dickinson, 2003). Significant differences ($\alpha = 0.05$) in WRC were shown in the samples at different gum concentration, and also the effect was more pronounced for samples with xanthan gum, results that agree with those found in the viscoamylographic and thermal studies, where the chemical structure of the hydrocolloid play an important role.

In the case of the solubility (Table 2b), it was observed the same tendency as for WRC; i.e. solubility values increased with the temperature. Amylose and some amylopectin chains, which lixiviated during the heating stage contributed to these values. The DM_H samples showed higher solubility values than the control, this is probably because some hydrocolloids molecules were cleaved during the heating, contributing to the total carbohydrate content determined as the material solubilized during the experiment.

3.6. Dynamic viscoelastic method

Fig. 3. shows the strain amplitude sweep of the control and hydrocolloids added masa samples, throughout the kinetic (heating, cooking and cooling) involved. The rheological profiles of both moduli G' (elastic modulus) and G'' (viscous modulus) throughout the three stages were similar shaped plots, with higher values of G' than G'', indicating that the elastic character predominated in those gels. All plots are essentially flat without inflexion points that could indicate disruption of the structure of the system under test. It was observed in all cases, an increase in the moduli values when going from the 1st to the 2nd and 3rd stages of the kinetic, this indicates that the increase in the temperature is causing some strengthening of the DM and DM_H structure when the systems pass from a suspension (1st stage) to conform a paste (2nd stage), and finally to yield a gel (3rd stage).

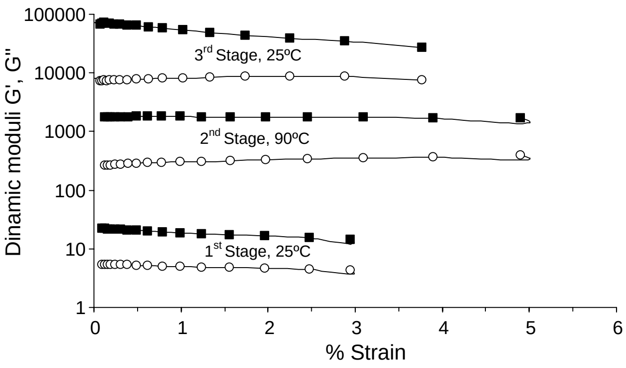

Fig. 3. Strain amplitude sweep ($w = 1$ Hz) of dried nixtamalized maize masa with 10% (w/v) of total solids, control and with hydrocolloid addition, following a heating/cooling kinetics of three stages. (■ G', ○ G'').

In the three stages, it was observed that $G' > G''$, usual in viscoelastic gels, being consistent with the values of tan δ, which were in the range from 0.1 to 0.3, typical of 'weak' viscoelastic gels (Ferry, 1980). From the RVL shown in Fig. 3, the values of deformations used to run the frequency sweeps were chosen (0.3% for the 1st stage and 0.5% for 2nd and 3rd stages, respectively).

Fig. 4 shows typical frequency profiles for DM (control) with 10% (w/v) of total solids, it can be observed that the rheological behavior was essentially linear throughout the three stages, observing that in the three stages $G' > G''$, with some frequency-dependency of both moduli seen solely on the third stage. The tan δ values ranged from 0.097 to 0.106 in the 1st stage (25 °C), increasing to 0.113–0.16 in the 2nd stage (90 °C) and then it went up to the range 0.186–0.31 in the last stage (25 °C). The materials can be classified, according to the value of tan δ, i.e. the values obtained during the 1st and 2nd stage (about 0.1), correspond to that of a glassy and crystalline polymer whereas in the 3rd stage, the values of tan δ (about 0.2–0.3), correspond to that of an amorphous polymer (Ferry, 1980). This is consistent with the known fact that by heating, normal starch experiment changes from a mainly crystalline structure to an amorphous one. Since the relation $G' > G''$ was maintained constant during the three stages of the kinetics involved, suggesting that the behavior of G'' was probably the same or similar as G', it was decided to only apply two way ANOVA to the values of G'.

Fig. 5a shows the rheological behavior (G', frequency sweep) of all masa samples, during the 1st stage (25 °C). The value of G' for the DM_H was lower than the one of the DM, being observed that when increasing the hydrocolloid concentration (0.2–0.5%), the value of G' decreased. When comparing the DM_H with 0.2 and 0.5% (w/w) solids, significant differences ($\alpha = 0.05$) were detected for effect of the hydrocolloid concentration (data not shown). This

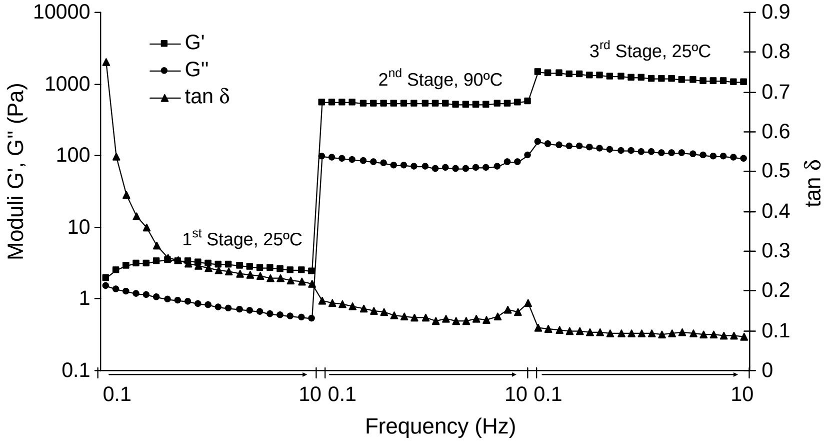

Fig. 4. Typical frequency sweep of dried nixtamalized maize masa with 10% (w/v) of total solids, following a heating/cooling kinetics of three stages. The strain was 0.3% on the 1st stage and 0.5% on the 2nd and 3rd stages.

suggests that an increase in the hydrocolloid concentration had induced a ‘weakening’ of the existing structures, that could be because the hydrocolloid in aqueous solution tends to dissociate partially in the system, ‘interfering’ with any network structure present. This is consistent with the trend observed for the gelatinization enthalpies (ΔH values decreased as the hydrocolloid concentration increased). During this stage, the carboxyl (or hydroxyl) groups of the hydrocolloid form anions, which interact directly with water, favoring the physical unions of its molecules, effect that is enhanced when increasing the concentration. No significant differences ($\alpha = 0.05$) were found between the two DM_H samples with 0.5% (w/w) of gum solids, probably because during this stage, the components of the DM_H with Xanthan and DM_H with CMC are in suspension, without interacting significantly so as to detect real differences. The tan δ values ranged from 0.07 to 0.09, which is slightly lower than the control one shown previously (Fig. 4), but still corresponding to a crystalline structure, suggesting that although the hydrocolloids addition induced some changes in the storage modulus, the rheological system remained essentially the same.

The frequency data obtained during the 2nd stage (90 °C), are shown in Fig. 5b. The behavior was similar to that of the 1st stage, i.e. in all cases, the addition of the hydrocolloid decreased the G' values, being notorious the

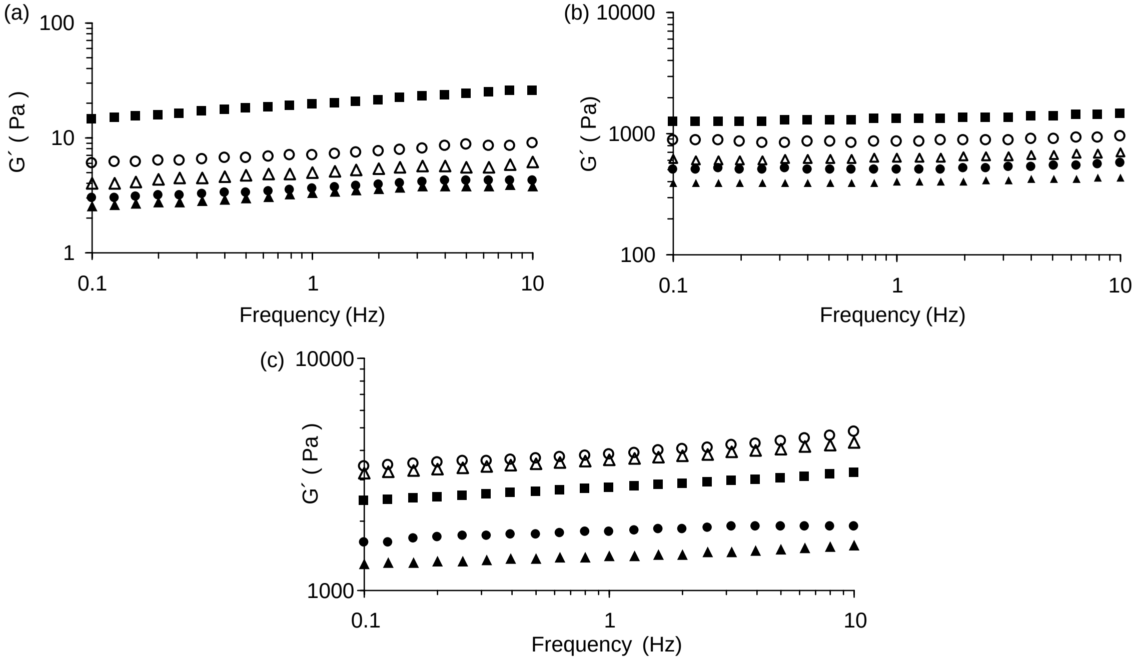

Fig. 5. Frequency sweep (0.3% strain), during the three stages of the heating/cooling kinetics of nixtamalized maize masa with 10% (w/v) of total solids and hydrocolloids addition. (a) 1st stage (25 °C); (b) 2nd stage (90 °C); (c) 3rd stage (25 °C). (■) Control; (○) CMC 0.2%; (●) CMC 0.5%; (△) xanthan 0.2%; (▲) xanthan 0.5%.

reduction in the modulus, as the hydrocolloid concentration increased. This is also similar to the above mentioned behavior observed for the gelatinization enthalpies, where a decrease in ΔH values was correlated with an increase in gum concentration, which as mentioned above, retained more water molecules causing a higher mobility, leading to a decrease in the G' values. However, unlike the 1st stage, the G' values changed of magnitude going from the range 1–30 (Pa) to about 450–1500 (Pa) in the 2nd stage. At this temperature, the maize starch amylose is being solubilized in the aqueous media, during this heating process, the interaction between amylose and the hydrocolloid takes place, the incorporation of water in the system (amylose-hydrocolloid) increases and thus the modulus (G') values increase, overcoming the weakening effect of the hydrocolloid mentioned above (Rojas, Rosell & Barber, 1999; Shi and Bemiller, 2002).

Ferrero, Martino, & Zaritzky (1994) and Phillips and Williams (2000), reported that a starch-xanthan suspension, offered less resistance to the deformation compared with other hydrocolloids at the same concentration used in this study (0.5% (w/w) of solids), during a process of heating from 30 to 80 °C. This behavior is similar to the one obtained in this work, the G' value for DM_H with 0.5% (w/w) of xanthan solids was the lowest, showing lower resistance to the deformation. The tan δ values for this stage ranged from 0.16 to 0.19, similar to the control one.

The behavior of the DM and DM_H during the frequency sweep on the 3rd stage (cooling to 25 °C), is shown in Fig. 5c, the values of G', increased about one logarithmic cycle going from the interval 450–1500 (Pa) in the 2nd stage to about 1300–5000 (Pa) in this 3rd stage, this could be because the cooling temperature induced to a more elastic system, decreasing the molecular mobility during the conformation of the gel (Christianson, Hodge, Osborne, & Detroit, 1981). The values of G' for the DM_H with 0.2% (w/w) of gum solids, were higher than those of the control, possibly because at this concentration, the molecular mobility is restricted, increasing the rigidity of the system and as a consequence, causing an increase in the G' values.

This suggests that the high G' values observed in the DM_H with 0.2% (w/w) gum solids, during the stage of gel formation, are because the formulation used, forms a more compact structure compared with the control. i.e. probably at this stage the network formed by the hydrocolloid and the amylose presents a more ‘agglomerated’ structure as indicated by Gimeno, Moraru, & Kokini (2004).

However, when increasing the gum concentration (0.5% (w/w) of solids), the DM_H, showed lower G' values, because the water molecules and the linked components of the DM_H (amylose-hydrocolloid) in the system, form a gel with ‘smoother’ structure, which affects the G' values. At this concentration, the system maintained the same tendency as in the 1st and 2nd stage, the G' values of the samples, were also lower than those of the control and the DM_H with 0.2% (w/w) of gum solids, this formulation also consistently presented smaller resistance to the deformation respect to the other samples. When comparing samples with xanthan and CMC with 0.5% (w/w) of gum solids, the G' values for the DM_H with xanthan were smaller than those of DM_H with CMC. This could be because during the gel formation, the structural chains of the xanthan gum, are found interacting with the components of the DM by hydrogen bonds, ionic interactions and molecular crosslinks, which contributes to a higher gel flexibility. For the DM-CMC system however, these types of interactions, which maintains the structure of the gel, are in less amount, which presumably allow less mobility to the system than xanthan gum (Glicksman, 1969). The tan δ values for this last stage ranged from 0.18 to 0.33, similar to the one shown for the control, this again is consistent with the behavior of an amorphous polymer (Ferry, 1980).

4. Conclusions

The addition of either hydrocolloid (CMC, xanthan) increased the gelatinization temperature but decreased the enthalpy values of the dried maize masa, with effect of the gum concentration. The stored masa samples with hydrocolloid addition presented lower enthalpy values than the control sample and differences were found with the type of gum. Some changes in the transition temperature were observed at the 14 storage days, with no effect in the enthalpy values respect to 7 storage days.

The DM_H had higher viscosity (Bravender Unities) than DM, whose values were affected by the concentration and type of hydrocolloid. The chemical structure of the hydrocolloid played an important role in those patterns. The WRC and solubility increased with the temperature having the DM_H higher values than the DM.

All samples behaved as ‘weak’ viscoelastic gel-like systems, with G' (storage modulus) $>$ G'' (loss modulus), during the three stages of the heating–cooking–cooling kinetics applied. The moduli values increased as the kinetics advanced being highest at the last (cooling) stage, suggesting that some structure may be forming in the masa systems as going from stage to another of the kinetics. The hydrocolloid addition seemed to be interfering with the structure of the masa components in an aqueous environment, being the smoothest gel the one of DM_H-xanthan with 0.5% (w/w) of solids. In relation to the tan δ values, the gels formed with DM and DM_H, showed the change from a crystalline system in the 1st and 2nd stage to an amorphous one in the 3rd stage of the mentioned kinetics.

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Bello-Pèrez and Solorza-Feria are PhD; Aguirre-Cruz and Mèndez-Montealvo are MSc.