

Thermoplastic Processing of Blue Maize and White Sorghum Flours to Produce Bioplastics

Grissel Trujillo-de Santiago · Cecilia Rojas-de Gante ·
Silverio García-Lara · Letizia Verdolotti ·
Ernesto Di Maio · Salvatore Iannace

Published online: 28 January 2015
© Springer Science+Business Media New York 2015

Abstract In this study, we evaluated the feasibility of producing bioplastics from blue maize (BM) and white sorghum (WS) flours by thermoplasticization using sorbitol and glycerol as plasticizers and by using extrusion and compression molding. The analyzed variables were screw speed rotation (50–70 rpm), extrusion temperature (100–140 °C), number of extrusion passes (1 or 2), and chemical modification of the flours with maleic anhydride. Mechanical characterization revealed a major effect of the extrusion temperature among the processing variables studied, and the microstructure and slab color varied significantly with temperature. Chemical modification also had a major effect on the properties of the produced materials. Slabs made with chemically modified flours showed increases in their mechanical properties compared to their native counterparts. Consistently, scanning

electronic microscopy revealed a more uniform microstructure in slabs made with chemically modified flours, and dynamic mechanical analysis indicated a better matrix-plasticizer interaction in these slabs when compared to slabs made with native flours. The BM and WS flours were determined to be suitable raw materials for producing thermoplastic materials.

Keywords Cereals · Chemically modified flour · Mini extruder · Thermoplasticization · Bioplastics

Abbreviations

BM	Blue maize flour
mBM	Modified blue maize flour
WS	White sorghum flour
mWS	Modified white sorghum flour
SSR	Screw speed rotation

Introduction

The interest in developing biodegradable plastics from renewable resources has emerged as an attempt to mitigate the problems caused by the generation of synthetic plastic waste and the depletion of oil reserves [1]. This can be seen in the marked growth of bioplastic production, which is estimated to reach 1.71 million tons of produced bioplastics by 2015 [2]. This class of materials is mostly used for nondurable goods, like food packaging [3]. For instance, some researchers have investigated the possibility of using biodegradable materials for food packaging from renewable biopolymers like proteins, starch, and other kinds of polysaccharides [4–7]. Usually, these biodegradable materials are made from fractions of the raw material that

G. Trujillo-de Santiago · S. García-Lara
Centro de Biotecnología- FEMSA, Tecnológico de Monterrey at
Monterrey, Ave. Eugenio Garza Sada 2501 Sur Col.
Tecnológico, CP 64849 Monterrey, Nuevo León, Mexico

C. Rojas-de Gante
Departamento de Ingeniería en Biotecnología, Tecnológico de
Monterrey at Ciudad de México, Calle del Puente 222 Col.
Ejidos de Huipulco, CP 14380 Tlalpan México, Distrito Federal,
Mexico

L. Verdolotti · S. Iannace
Institute for Polymers, Composites and Biomaterials of the
National Research Council of Italy (IPCB-CNR), P.le E. Fermi
1, 80055 Portici, NA, Italy

E. Di Maio (✉)
Dipartimento di Ingegneria Chimica, dei Materiali e della
Produzione Industriale, University of Naples Federico II, P.le
Tecchio 80, 80125 Naples, Italy
e-mail: edimaio@unina.it

must first undergo through an extractive process. However, using cereal flours as raw materials for obtaining thermoplastics do not require these extractive unitary operations, thereby making the process more sustainable. In this regard, some recent studies have reported the use of flours for producing flexible plasticized materials. For instance, the research groups of Menegalli and Rojas De Gante have produced films via casting from achira, amaranth and banana flours, and cereals flours, respectively [8–12].

In the same vein, but focused on the materials obtained using thermoplastic technologies, Ayadi et al. [13], Chanvrier et al. [14], and Chanvrier et al. [15] have reported the production of corn flour-based materials through thermoplastic extrusion and have studied the effect of their components, namely starch, zein, or lipids, on the structural, mechanical, and thermal behavior of the thermoprocessed materials. These studies report that both lipid and zein negatively affect the performance of these corn flour-based materials, particularly their mechanical properties, since phenomena such as phase separation and protein aggregation weaken the thermoplastic starch matrix. Chemical modification has been used elsewhere to improve the functionality of starch materials and to induce phase-compatibilization in starch-zein blends [16–18], but to our knowledge, flexible thermoplastic materials made from chemically modified flours have not yet been reported.

Adding value to regional agricultural resources is increasingly important for improving the sustainability of these products and supporting the local farmers. In Mexico, for instance, blue maize (*Zea mays Amylacea*; BM) and white sorghum (*Sorghum bicolor*; WS) are crops with the potential to produce novel high-value products. The sorghum is extensively produced mainly for animal feeding [19], while BM is produced at a very low scale in rural communities for auto-consumption and is commercially devaluated despite its high nutraceutical value [20]. Furthermore, these crops have significant advantages as they demand minimal care conditions and are adaptable to recalcitrant conditions like arid soil, which favors sustainability [19, 21].

BM and WS flours are potentially good materials for making bioplastics. These cereal flours contain starch and prolamins (zein in the maize and kafirin in the sorghum) with a demonstrated filmogenic capacity [5, 7, 11]. Although zein and kafirin are both prolamins and there is a high homology between them, there are important characteristics that differentiate them. For instance, kafirin has higher hydrophobicity and is richer in sulfur amino acids than zein. Sulfur amino acids are responsible for the disulfide cross-linking and aggregating capacity of kafirin during thermal processes [22]. Due to these dissimilarities, we expected WS to be a more challenging source for

producing flexible bioplastics than BM since phase separation between starch and prolamin and protein aggregation are more likely to occur at a higher extent in the former system.

This research was undertaken to evaluate the feasibility of producing flexible bioplastics using BM and WS flours and their chemically modified equivalents as raw materials. Flexible slabs were produced through extrusion-compression molding and studied by means of mechanical, dynamic mechanical analysis (DMA), color, scanning electronic microscopy (SEM), and Fourier transform infrared-attenuated total reflectance (FTIR-ATR) spectroscopy analysis.

Materials and Methods

Raw Materials

BM and WS were kindly provided by Eduardo Lovera (at Federación de Agricultores del Edomex) and Dr. L. W. Ronney (at Texas A&M University), respectively. Sorbitol (code: S1876) and glycerol (code: G9012), from Sigma-Aldrich, were used as plasticizers.

Flours

Flours (150 mesh) from the two decorticated cereals (BM and WS) were obtained according the process described by Rojas De Gante et al. [11]. BM and WS were also chemically modified using maleic anhydride. The chemical modification was conducted using the method reported by Murúa-Pagola et al. [23] with some modifications. The process was carried out in a 3 L fully instrumented control reactor (Applikon Biotechnology model EZ, Schiedam, the Netherlands) using eccentric agitation as described by Bulnes-Abundis and Alvarez [24] and Sánchez Cervantes et al. [25]. A dispersion of 585 g of flour (d.b.)/1.3 L of distilled water was prepared at 500 rpm. The pH was maintained at 8.5–9.0 using a 1 M NaOH solution. About 2 g of maleic anhydride/50 g of flour (d.b.) were slowly added over 2 h. Agitation was increased as needed, reaching 1,000 rpm when the slurry was very viscous. The reaction was kept for 6 h and was stopped by lowering the pH to 4.8–5.2 using 1 M HCl solution. The modified flour was centrifuged for 20 min at 4,500 rpm. The precipitated was washed-centrifuged three times and dried for 24 h in a convection oven at 45°C. The dried modified flour was milled and sieved to obtain a 150 mesh powder.

Moisture, protein, ether extract, and ashes content were analyzed at least in duplicate according to the procedures established in Mexican standards (NOM-116-SSA1-1994, NMX-F-608-NORMEX-2011, NMX-F-615-NORMEX-2004,

NMX-F-607-NORMEX-2002 respectively) [26–29] based in AOAC standard methods. Crude fiber was analyzed by the AOAC 962.09 [30] standard method.

Mixing and Composition

The flours, either BM, WS, maleated blue maize (mBM), maleated white sorghum (mWS), and the plasticizers were premixed with a spatula to provide a crude blend. The mixture consisted of 70 % flour and 30 % plasticizer, and the plasticizer was a mix of sorbitol and glycerol (1.4:1). Moisture content was adjusted to 10 % (b.s.) by the addition of distilled water.

The blends were thermoplasticized in a twin conical screw mini extruder (Haake MiniLab, Thermo Scientific, USA) in continuous mode. About 30 g of material was fed into the extruder and collected as a thread. The process lasted for about 24–28 min, from the very first amount fed to the last extruded material collected. Slabs were obtained by compression molding. The extruded materials were pressed at 20 MPa for 4 min with a P300P (Collin, Germany) at the same temperature used for extrusion and were then cooled to 35 °C under pressure. Spacers of 0.5 mm were used between the press plates.

Setting of the Extrusion Conditions

Extrusion conditions were established using BM blends and considering results from the tensile tests of the produced slabs. An analysis of variance and *t* test were carried out to evaluate significant differences ($p < 0.05$) among the treatments. Three variables were explored independently: speed of screws rotation (SSR) (50, 60, and 70 rpm), temperature (100, 110, 120, 130, and 140 °C), and extrusion passes (1 or 2). The values of the variables analyzed were selected based on preliminary assays. In the first experimental round, effect of SSR was evaluated by setting the temperature and extrusion passes at 130 °C and one pass, respectively. In a second stage, effect of temperature was explored using the selected SSR from the first stage and one extrusion pass. Finally, in the third experimental stage, both one and two extrusion passes were tested at the temperature and SSR previously established.

Tensile Testing

The tensile strength and elongation properties of the slabs were evaluated using standard microtensile test specimens according to the ASTM D1708. Mechanical test were performed on slabs conditioned at room temperature (about 25 °C) and 50 % RH prior to testing by using a universal testing machine (Tensile T2020, Alpha Technologies, USA).

Color

Since changes in color could be related to physic-chemical changes during processing, color measurements were conducted on selected slabs to assess the effect of extrusion temperature this parameter. The parameters L^* , a^* , and b^* (L^* : lightness from 0 = black to 100 = white; a^* : +a = redness, -a = greenness; b^* : +b = yellowness, -b = blueness) [31] were determined in the CIELAB system using a spectrophotometer X-Rite Color i5 (Neu-Isenburg, Germany) with standard illuminant D_{65} and a 10° observer angle.

SEM

To evaluate the effects of the extrusion conditions and the type of flours on the materials morphology, cross-sectional surfaces of selected samples were observed by means of SEM. The SEM analysis was performed by means of an FEI Quanta 200 FEG (Eindhoven, The Netherlands). All samples were liquid nitrogen fractured and vacuum metallized with gold–palladium using the Baltec MED 020 Coating System.

FTIR-ATR

The effects of thermoplasticization on the molecular interactions were evaluated by means of FTIR-ATR analysis. Infrared spectra of the materials produced were acquired using an FTIR spectrophotometer (Nicolet 6700, Thermo Scientific, USA) with a diamond horizontal ATR sampling device (Thermo Scientific, USA). Spectra (16 scans at a 4 cm^{-1} resolution) were collected within the frequency range of $4,000$ – 650 cm^{-1} . The empty diamond was used as background. Automatic baseline correction was applied to all spectra, and an automatic corrected height of the selected bands was measured using OMNIC software.

DMA

The glass transition temperature (T_g) was measured using DMA according to Oliviero et al. [32] with a DMA Tritec 2000 (Triton Technology, UK) in the tensile-deformation mode. Temperature scan tests were performed by applying a tensile displacement of 10 μm at 1 Hz frequency and a heating rate of 4 °C/min from –80 to 140 °C. The T_g was determined as the tan δ maximum. The sample dimensions were 8.8 mm wide and 0.5–0.56 mm thick (depending on the sample), and the gauge length was 10 mm.

Results and Discussion

Flours Proximate Composition

Table 1 shows the proximate composition of BM, WS, mBM, and mWS 150 mesh flours. The chemical modification process had an effect on the composition of flours by lowering protein and lipid content (ether extract) and increasing the crude fiber and ashes content. Since the process of chemical modification was conducted in aqueous conditions, protein loss can be attributed to the washing away of the water-soluble proteins. In addition, some low-density fractions such as lipids might be eliminated during centrifugation and washing operations.

Effect of Extrusion Conditions on Tensile Properties of BM Slabs

Figure 1 shows the effect of three processing variables (SSR, temperature, and extrusion passes) on the tensile properties of BM slabs. Tensile properties strongly depended on the extrusion conditions. Our results suggest that two competing phenomena occur during processing: (a) thermoplasticization, which requires sufficient shear stress and temperature to allow the macromolecules to undergo the conformational modification that leads to the occurrence of a melt state by an increase in mobility assisted by plasticizers, and (b) degradation phenomena, which are the fragmentation and oxidation of functional groups in the matrix that become important at high temperatures or high shear stress.

The results presented in Fig. 1a suggest that thermoplasticization was better achieved at higher SSR values. Materials produced at 50 and 60 rpm showed higher tensile strengths ($p < 0.05$) than those produced at 70 rpm. Strain at break reached higher values at 60 and 70 rpm than at 50 rpm ($p < 0.05$). This suggests that the lowest SSR value tested (50 rpm) does not provide a sufficient shear stress to

achieve a complete melt state of the BM blend. Based on these results, SSR was set at 60 rpm in subsequent tests using chemically modified flours. In regards to extrusion passes, Fig. 1c shows that a single extrusion pass gave slabs that had a significantly ($p < 0.05$) higher tensile strength than those produced after two extrusion passes. In addition, a brownish material (see Table 2) was obtained after two extrusion passages, indicating that degradation phenomena prevailed over thermoplasticization.

Process temperature was the most important factor affecting the tensile properties of the samples produced. Figure 1b shows that processing at 120 °C resulted in materials with the highest tensile strength, while slabs obtained at the temperatures below and above 120 °C exhibited lower values of tensile strength. At temperatures below 120 °C, the thermoplasticization of the biopolymer was incomplete, while at temperatures above 120 °C, the material was brownish and developed a popcorn-like odor, which suggests a higher degree of fragmentation and breaking of more hydrogen bonds. This finding is discussed elsewhere for thermoplastic starch [33]. The lower mechanical performance of slabs produced at temperatures above 120 °C could also be explained by the occurrence of less efficient thermoplasticization—since the blend melts more rapidly, the viscosity decreases accordingly and a mechanical shear sufficient to modify the conformation of the starch and the proteins does not build up. This phenomenon has been previously documented for thermoplasticized zein elaboration by Di Maio et al. [5].

Effect of Extrusion Conditions on Physical Properties

The data for the color of the BM flour slabs produced at different temperatures are presented in Table 2. The slabs produced at 100 and 110 °C had a lighter color (higher values in L^*) consistent with their opaque and whitish-purple hue. The value of a^* increased with the process temperature, which is congruent with the bright purple color (since purple is a mixture of blue and red) of the slab made at 120 °C, and the brownish red color of the slab made at 140 °C. The slab with the bluest color (lowest b^*) was obtained at 120 °C, which is again consistent with the purple color showed by this slab. Anthocyanins, mainly cyanidin and malvidin, have been reported as the compounds responsible for the purple tonalities in BM kernels; these colors were observed mainly in the slabs obtained at or below 120 °C [34]. Moreover, brown tonalities are related to the oxidation of anthocyanins in red wines [35]; thus, high processing temperatures (130 and 140 °C) may have given rise to oxidized anthocyanins, which could explain the brownish color of slabs made at these

Table 1 Proximate compositions of BM, WS, mBM and mWS flours

Parameter	BM	WS	mBM	mWS
Moisture (%)	12.3(0.06)	10.5(0.21)	11.2(0.06)	12.7(0.08)
Protein (%)	6.5(0.69)	9.1(0.37)	3.5(0.29)	4.0(0.02)
Ether extract (%)	1.5(0.26)	1.7(0.14)	0.8(0.01)	0.6(0.03)
Crude fiber (%)	0.5(0.03)	0.3(0.02)	0.7(0.01)	0.4(0.01)
Ash (%)	1.0(0.06)	0.9(0.02)	1.3(0.004)	1.0(0.02)

Percentages are in dry base. Values are means (standard deviations of at least two replicates)

BM Blue maize, WS White sorghum, mBM Modified blue maize, mWS Modified white sorghum

Stage 1				
Screw speed rotation (rpm)	Temperature (°C)	Extrusion cycles	Tensile strength (MPa)	Strain at break (mm/mm)
50			1.38(0.08) ^a	0.11(0.009) ^b
60	130	1	1.27(0.04) ^{ac}	0.14(0.004) ^a
70			1.23(0.07) ^{bc}	0.14(0.012) ^a

Selected speed: 60 rpm

Stage 2				
Screw speed rotation(rpm)	Temperature (°C)	Extrusion cycles	Tensile strength (MPa)	Strain at break (mm/mm)
60	100	1	0.70 (0.04) ^d	0.08(0.005) ^c
	110		0.071(0.08) ^d	0.12(0.012) ^b
	120		1.93(0.17) ^a	0.12(0.009) ^b
	130		1.27(0.04) ^b	0.14(0.004) ^a
	140		0.94(0.2) ^c	0.13(0.017) ^{ab}

Selected temperature: 120°C

Stage 3				
Screw speed rotation (rpm)	Temperature (°C)	Extrusion cycles	Tensile strength (MPa)	Strain at break (mm/mm)
60	120	1	1.93(0.17) ^a	0.12(0.009) ^a
		2	1.21(0.11) ^b	0.13(0.015) ^a

Fig. 1 Effect of extrusion conditions on tensile properties of blue maize slabs. Lettered panels are strain versus strain curves of slabs made at different (a) screw speed rotation, (b) temperatures and

(c) extrusion passes. Values in parentheses are standard deviations. Letters indicate statistical differences calculated with a *t* test ($p < 0.05$)

Table 2 Color of BM flour slabs made at different extrusion/compression temperatures

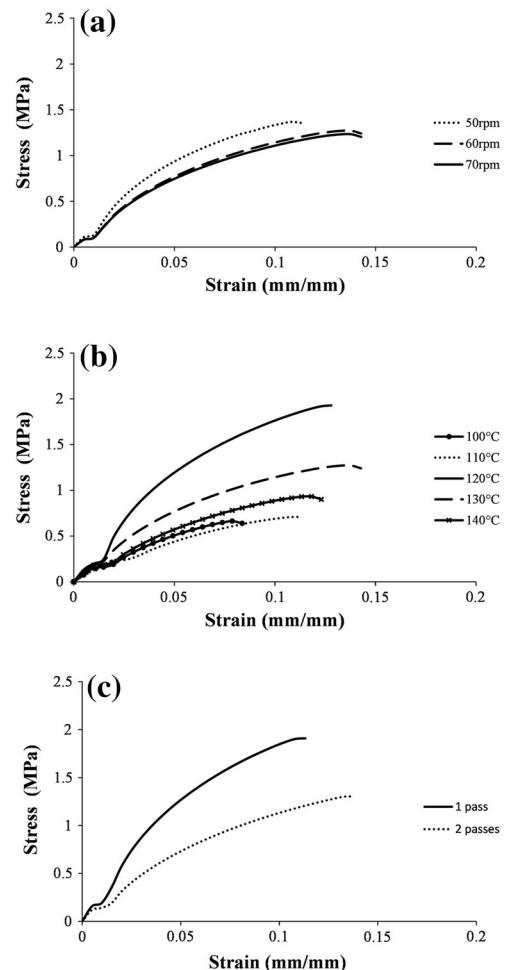
Procces temperature	Color parameters		
	L*	a*	b*
100	57.28	6.98	8.03
110	54.77	8.22	11.53
120	38.26	11.42	3.68
130	39.81	11.89	9.62
140	39.08	13.10	15.18

All slabs were produced at speed of screws rotation equals to 60 rpm and 1 extrusion pass

Values originated from one single measurement

L*: lightness from 0 = black to 100 = white; a*: +a = redness, -a = greenness; b*: +b = yellowness, -b = blueness. BM: Blue maize

temperatures. The color of the materials therefore acted as an indicator of the performance of the thermoplasticization process: the whitish color of the slabs made at 100 and



110 °C was evidence of incomplete thermoplasticization and the brownish color obtained at 130 and 140 °C indicated the occurrence of degradation.

Besides color variations, processing at different temperatures caused other obvious physical differences in the extrudates. The collected extrudates processed below 120 °C had a dry, opaque, and rough surface, described as “shark skin.” This extrusion instability (shark skin) is related to local stresses that occur at the die exit, although the exact mechanism that causes this phenomenon is under debate [36]. Some mechanisms reported in the literature are wall-slip, fracture at the die exit, failure of adhesion at the polymer/die interface, and cavitation due to negative pressures close to the die exit. Some other factors, such as changes in flow boundary conditions, the shape of the dies, shear stress, rheology of the material, temperature of the die, melt/wall interfacial interactions, and lubricating effects, have also been considered [36–39]. For the BM compositions, and as it is found in most thermoplastics, temperature appears to have

a strong impact on the occurrence of this phenomenon, since the extruded materials were obtained as smooth and continuous threads at temperatures of 120 °C and above.

Effect of Chemical Modification on the Tensile Properties of the Slabs

Based on the results previously discussed using native BM flours, the extrusion conditions for a second round of experiments, now using WS and chemically modified flours (mBM and mWS), were set at 60 rpm of SSR, 120 °C, and one extrusion pass. Overall, these extrusion conditions rendered bioplastics with the best mechanical performance.

The tensile properties of the slabs made with native and chemically modified flours, (BM, WS, mWS, and mBM) are shown in Fig. 2. In the literature, the low mechanical performance of materials containing native starch and zein has been attributed to (a) the starch-zein incompatibility and (b) material weakening by a matrix-particle effect due to zein aggregation [15, 16, 40]. However, the chemical modification of starches has been suggested and used in the past to produce thermoplasticized materials from starch-zein blends and has resulted in materials with improved

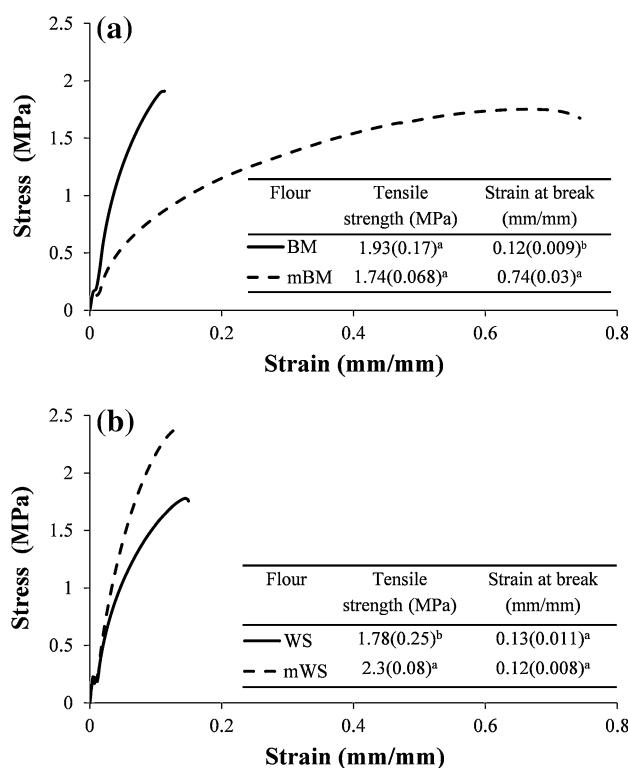


Fig. 2 Tensile properties of slabs made from different flours. (a) BM (solid line) and mBM (dashed line); (b) WS (solid line) and mWS (dashed line). Values in parentheses are standard deviations. Letters indicate statistical differences calculated with a *t* test ($p < 0.05$)

mechanical properties that are attributed to the reaction between functional groups of starch and zein [16–18]. In this vein, materials made from chemically modified flours were expected to exhibit improved mechanical properties. Our results are consistent with this idea.

Stress-strain curves show that the slabs made with the modified flours were tougher than those made with their native counterparts. Tensile strength was increased 1.3-fold in slabs made with mWS compared with those made with native WS. The effect of maleation was even more evident in the BM slabs—the strain at break of the mBM slabs was 6.3 times larger than the strain at break of the slabs made with native BM. Both native and modified WS flours slabs were weaker than their respective counterparts made with BM flours. This weaker behavior in the WS slabs could be due to starch-prolamин incompatibility, which may have been exacerbated by the increased hydrophobic behavior and cross-linking capability of kafirin (sorghum prolamин) by disulfide bond formation [41].

The proximate analysis of native and chemically modified flours, as reported in Table 1, indicates that a significant amount of protein was lost during the modification process. Conceptually, the lower protein content in the modified flours may have contributed to some extent to the improvement of the mechanical properties by decreasing the heterogeneity of the matrix, *per se*—a higher starch-to-prolamин ratio would imply a lower occurrence of prolamin aggregates. However, we believe that the effect of the protein loss was minor. Prolamins are insoluble in water, and exclusively aqueous conditions were used during the process of chemical modification. Most of the observed protein loss can be attributed to washing away of water-soluble proteins. Mechanical performance is certainly hampered by prolamin bodies but water soluble proteins should not have a significant effect.

SEM

SEM micrographs of the BM flour and BM slabs obtained at different process temperatures are compared in Fig. 3. Starch granules in the range of 7–17 μm and protein bodies of about 1–3 μm were seen in the native flour micrograph (see Fig. 3a); these dimensions were consistent with previously reported data for maize flours [42]. The slab obtained at 100 °C (see Fig. 3b) had a rough surface with intact starch granules and protein bodies dispersed throughout the (un) thermoplasticized matrix. Figure 3c shows the fracture surface of the slab obtained at 120 °C, where a smoother surface can be seen compared to the other SEM images. Although residual starch granules and protein bodies are still present, they are less evident than in the slabs obtained at 100–130 °C. Besides, Fig. 3d shows

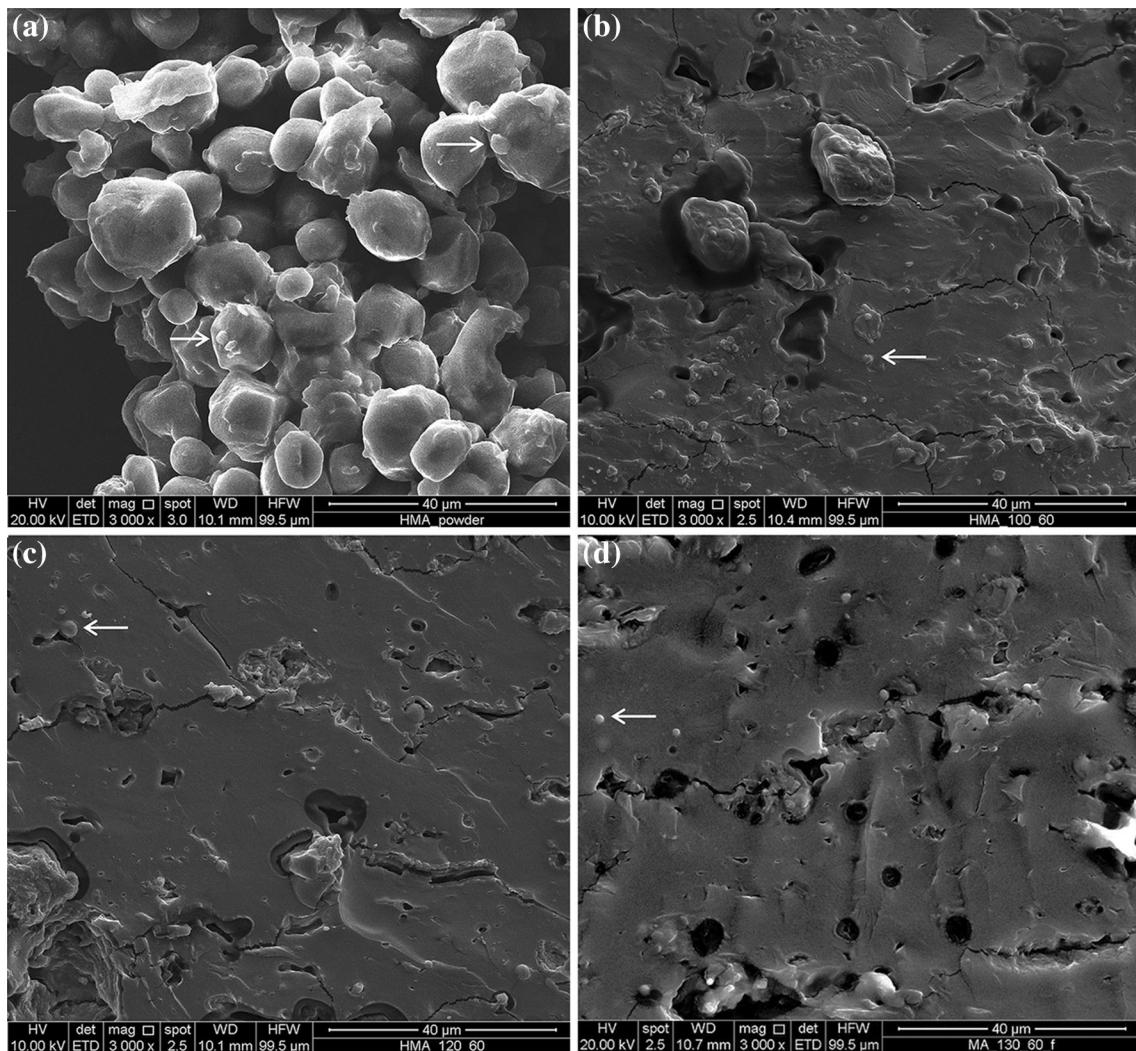


Fig. 3 SEM micrographs at $\times 3,000$ magnification of (a) Native BM flour; BM slab extruded at (b) 100; (c) 120; (d) 130 °C

that the process at 130 °C led to a material with rougher and more irregular morphology than that processed at 120 °C. Protein bodies were also present, and small holes were observed, which are assumed to be the space that was occupied by partially fragmented starch granules. The morphology observed in the slab processed at 130 °C is consistent with the hypothesis of an incomplete destructure given by the lack of enough shear stress during the process, due to the low viscosity, which has been previously reported for other biopolymers [5].

Figure 4 shows the microstructure of materials made with the different flours processed under the same conditions. The modified flours, mBM and mWS, showed smoother and more homogeneous surfaces than their native counterparts, being the number of protein bodies and starch granules significantly reduced in both systems. The mBM slab microstructure, unlike the BM slab, showed almost no zein bodies and very few starch granules (only partially destructured). Moreover,

although mWS micrograph revealed the presence of some kafirin bodies and starch granules, they were present to a significantly less extent than in the WS. It is worth noting that the WS slab showed the most uneven microstructure of all of the samples; starch granules and several protein bodies were observed in the micrograph (Fig. 4c). In this regard, kafirin bodies are difficult to disrupt because of their high capacity for aggregation caused by disulfide cross-linking polymerization; they also act as an obstacle to reaching starch granules to be destructured [41]. Chanvrier et al. [15] stated that, in thermoprocessed maize-based materials, protein aggregates and starch granules act as particles with no or poor adhesion within the amorphous starch and weaken the material. Our results are consistent with this statement; for instance, mBM presented the most continuous and particle-free microstructure and showed the highest toughness, while the WS micrographs presented the greatest number of particles and had the lowest mechanical performance among the tested flours.

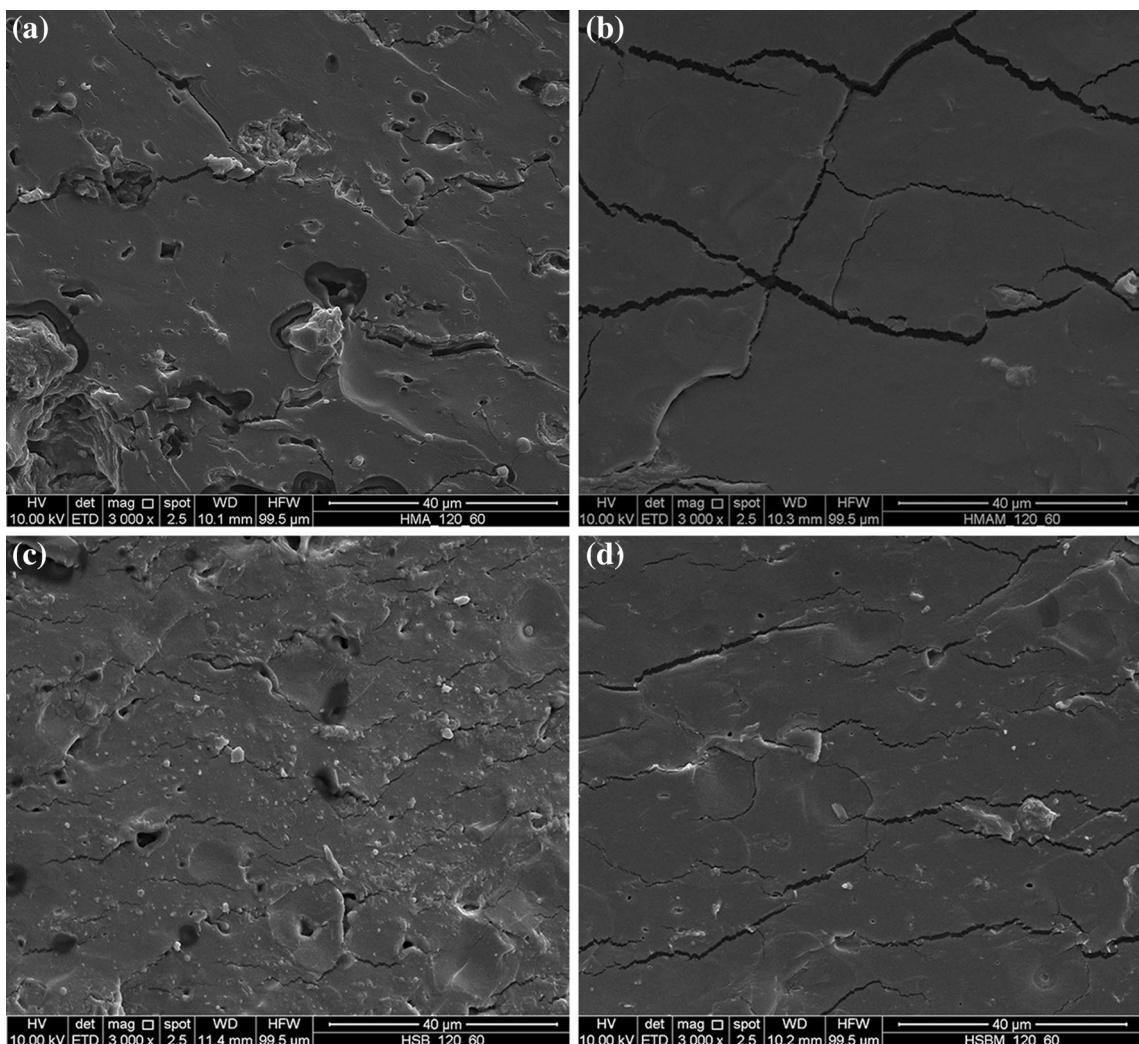


Fig. 4 SEM micrographs at $\times 3,000$ magnification of slabs made with different flours. **(a)** BM; **(b)** mBS; **(c)** WS; **(d)** mWS

FTIR-ATR

Figure 5a, b show the FTIR spectra of the slabs produced at different temperatures. The phenomena of degradation and thermoplasticization induced chemical changes that can be observed in these spectra. For instance, changes in the range of $1,900\text{--}1,500\text{ cm}^{-1}$ (see Fig. 5a) suggest that degradation occurred. A band at $1,745\text{--}1,746\text{ cm}^{-1}$ was detected in materials made at 100 and 110 °C; this vibration is characteristic of saturated C=O stretching, which was apparently oxidized to carboxylic acid at higher temperatures—this band disappeared in the spectra of materials made at 120, 130, and 140 °C but another appears at $1,709\text{ cm}^{-1}$. Indeed, a shoulder at $1,712\text{ cm}^{-1}$ was detected in slabs made at 100 and 110 °C, indicating that oxidation started to occur at these temperatures. Furthermore, a shoulder at $1,684\text{ cm}^{-1}$, which corresponds to amide C=O stretching, was also observed in the spectra of slabs

made at 130 and 140 °C. Feasible explanations of these observations include the formation of secondary oxidation products from lipids and phytocompounds and/or the occurrence of Maillard reactions as has been previously reported for extruded maize [43]. In fact, the bands observed in our spectra are consistent with the chemical vibrations of expected Maillard-derived compounds. For instance, the carbonyl signals may correspond to intermediate compounds that condense with terminal amino groups of proteins, giving place to the amide bonds that are observed in the spectra of materials obtained at the higher temperatures [44]. Moreover, differences in the $1,018/999\text{ cm}^{-1}$ absorbance ratio points to the thermoplasticization phenomena, taking into account that increases in the $1,022/995\text{ cm}^{-1}$ absorbance ratio in starches have been associated with decreases of molecular order [45, 46]. Figure 5b shows the differences in the $1,018/999\text{ cm}^{-1}$ absorbance ratio that occurred in materials processed at

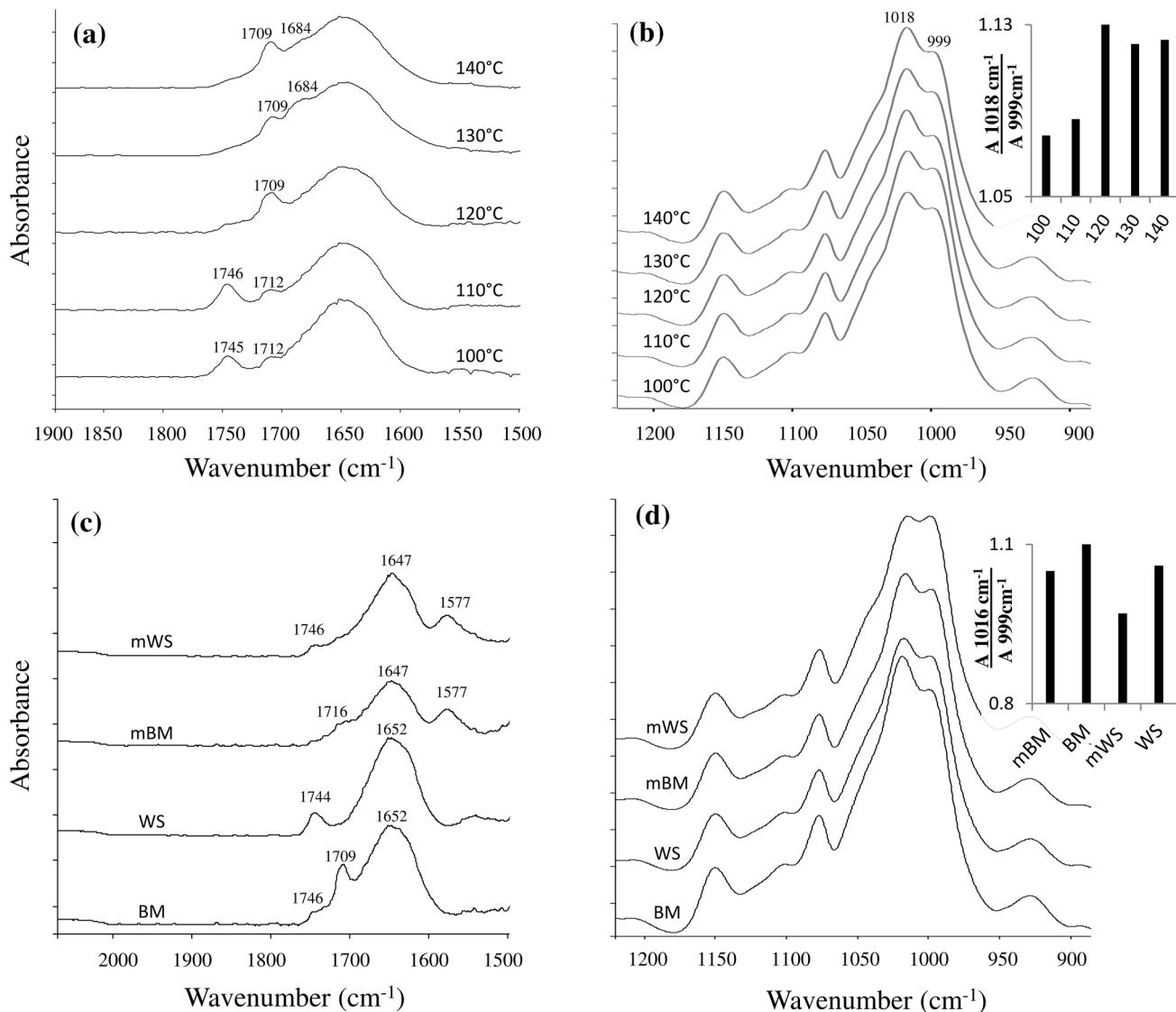


Fig. 5 FTIR spectra of slabs produced by extrusion/molding press. **(a, b)** BM slabs produced at different temperatures; **(c, d)** slabs made with different flours

different temperatures. The slabs obtained at 120 °C showed the highest value, which suggests that the highest molecular mobility was obtained at this processing temperature. This is consistent with the higher deformability exhibited by these slabs. Slabs obtained at temperatures below and above 120 °C showed lower values of the 1,018/999 cm⁻¹ absorbance ratio. On the one hand, the higher molecular order of the slabs obtained at 100 and 110 °C could be due to the scarce thermoplasticization achieved at these temperatures. On the other hand, at temperatures of 130 and 140 °C, the lower ratio value could be due to the presence of undestructured starch granules that remained in the materials as shown in the SEM micrographs.

Figure 5c shows the FTIR spectra of slabs produced from different flours. Differences can be observed between the

spectra corresponding to modified and native flours. For instance, the area and height of the peaks corresponding to the N–H stretching signals of amides I (1,647 cm⁻¹ [47]) were lower for the modified flours. In addition, a band in the region of amides II and double bonds C=C and C=N (1,577 cm⁻¹) was only present in samples corresponding to modified materials. This suggests that chemical modification in flours promoted the formation of secondary amines at the expenses of primary amines, which may be due to the interaction between proteins and carbohydrates in the matrix. Besides, high temperatures could have generated furanic compounds from starch via 1–2 enolisation and pyridines, which contributed to the C=C and C=N stretching signals observed in spectra [43, 48]. These new bonds may have been responsible for the improved mechanical properties performed by these slabs.

Figure 5d shows that changes in the 1,016/999 cm^{-1} ratio also occurred in materials made with different flours. Compared with the materials made with native flours, materials made with chemically modified flour presented lower ratio absorbances between these peaks (1.05 vs. 1.12 for mBM and BM materials, and 0.97 vs. 1.06 for mWS and WS materials) indicating that these presented a higher molecular order than the former, which is consistent with the presence of the double bonds elucidated by the band at 1,577 cm^{-1} .

DMA

Figure 6 shows the $\tan \delta$ versus temperature plots obtained by DMA. Two maxima in $\tan \delta$ were detected in all samples, which could be associated with the T_g of the plasticizers-rich and flour-rich fractions as reported for other plasticized biopolymer systems [33, 49, 50]. The slabs made with modified flours presented a decrease of the T_g , for instance BM slab shows a peak at 25 °C which shifts to 11 °C in mBM slab, similarly occurs in WS and mWS slabs (shifting from 20 to 9 °C). This suggest that the slabs made with modified flours presented increased mobility of polymer chains and a better compatibility with the plasticizers, as also confirmed by FTIR [50]. Consistently with the tensile properties and SEM analysis, these results indicate that a more effective thermoplasticization was achieved with slabs made with modified flours than those made with native flours.

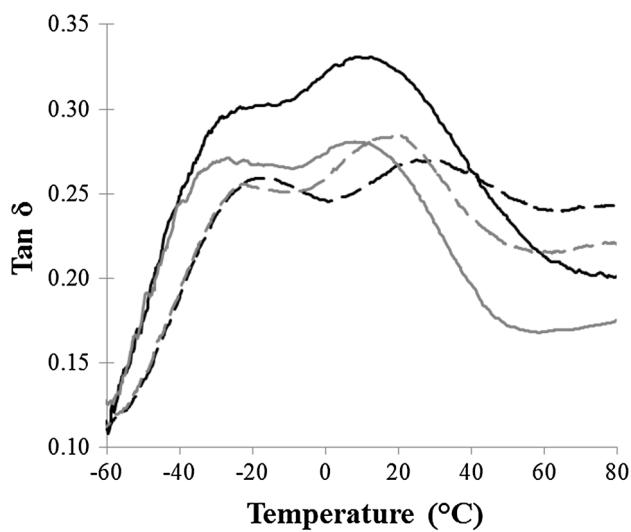


Fig. 6 $\tan \delta$ of films made from different flours. Blue maize: *dashed black line*; Modified blue maize: *solid black line*; White sorghum: *dashed gray line*; Modified white sorghum: *solid gray line*

Conclusions

In this work, thermoplasticization of BM and WS flours were performed to achieve thermoplastic materials from natural occurring polymers. The produced slabs presented tensile strength values in the range of 0.7–2.3 MPa and strain at break in the range of 0.08–0.74 mm/mm, which are close to but below the values previously reported for similar biopolymer systems [13, 33, 51] and in the range of the values reported for amaranth flour [12]. Results on extrusion proved that the investigated processing conditions were appropriate for producing flexible slabs, although at 120 °C, 60 rpm, and one extrusion pass, we obtained the BM slabs with the best mechanical properties. Extrusion temperature had a significant effect on the tensile properties, color, and microstructure of the materials. Out of all of the temperatures tested, 120 °C produced materials that were the most plasticized and resistant and had a more continuous microstructure and a more desirable color (purple). The slabs produced at higher and lower temperatures showed incomplete thermoplasticization or degradation. The WS slabs were weaker than those produced from BM, which was probably caused by the kafrin bodies, which are more recalcitrant to be destructured during the process and hinder the proper thermoplasticization of the flour. Slabs made from chemically modified flours were more deformable and resistant than those made from native flours. This enhanced resistance could be explained by the formation of secondary amines detected by the FTIR analysis and by the better thermoplasticization and compatibility with plasticizers, as also confirmed by DMA. Micrographs showed that the modified flour slabs have a more uniform surface with less protein bodies than native flours slabs. BM and WS flours and their chemically modified counterparts were determined to be suitable raw materials for producing bioplastics by thermoplastic processing, although more effective strategies for developing starch/prolamin-based materials with mechanical performances more comparable to oil-based plastics are needed.

Acknowledgments We gratefully acknowledge the financial support of Tecnológico de Monterrey through the seed fund CAT-121 and CDB-181 (Centro de Biotecnología FEMSA, Tecnológico de Monterrey, Monterrey, Nuevo Leon, Mexico). CONACyT (Mexico) provided the doctoral scholarship 45964 to GTdeS. The authors deeply appreciate the donation of the BM and WS by Eduardo Lovera (at Federación de Agricultores del Edomex) and Dr. L. W. Ronney (at Texas A&M University). We are grateful to Massimo Lombardo (Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale, University of Naples Federico II, P.le Tecchio 80, 80125 Naples, Italy.), Cristina del Barone (Institute of Polymers, Composites and Biomaterials, Consiglio Nazionale delle Ricerche,

P.le E. Fermi 1, 80055 Portici (Na), Italy), Fabio Docimo and Maria Rosaria Marcedula (Istituto per i Materiali Compositi e Biomedici, CNR, Naples, Italy), and Vincenzo Scognamiglio (Icimen S.p.A., Marcianise (Ce), Italy) for the technical support provided for producing and studying the materials addressed in this paper.

References

1. Luckachan GE, Pillai CKS (2011) *J Polym Environ* 19:637
2. Smith C (2012) Compounding World 45. <http://www.chem.umn.edu/csp/pdfs/CWJune2012%20article.pdf>
3. Kuruppalil Z (2011) *Int. J. Eng. Res. Innov.* 3:59
4. Chen CH, Kuo WS, Lai LS (2010) *Food Hydrocoll* 24:200
5. Di Maio E, Mali R, Iannace S (2010) *J Polym Environ* 18:626
6. Fadel SM, Hassan ML, Oksman K (2013) *J Compos Mater* 47:1977
7. Zullo R, Iannace S (2009) *Carbohydr Polym* 77:376
8. Andrade-Mahecha MM, Tapia-Blácido DR, Menegalli FC (2012) *Carbohydr Polym* 88:449
9. Pelissari FM, Andrade-Mahecha MM, Sobral PJA, Menegalli FC (2013) *Food Hydrocoll* 30:681
10. Pelissari FM, Andrade-Mahecha MM, Sobral PJA, Menegalli FC (2013) *LWT Food Sci Technol* 52:1
11. Rojas De Gante C, Rios Licea JM, Tinoco Pérez B (2010) Patent application number: PCT/MX2009/000092
12. Tapia-Blácido D, Mauri AN, Menegalli FC, Sobral PJA, Añón MC (2007) *J Food Sci* 72:E293
13. Ayadi F, Bliard C, Dole P (2011) *Starch-Stärke*. 63:604
14. Chanvrier H, Colonna P, Della Valle G, Lourdin D (2005) *Carbohydr Polym* 59:109
15. Chanvrier H, Della Valle G, Lourdin D (2006) *Carbohydr Polym* 65:346
16. Habeych E, van der Goot AJ, Boom R (2009) *Chem Eng Sci* 64:3516
17. Spence KE, Jane J, Pometto AL (1995) *J Environ Polym Degrad* 3:69
18. Lim S, Jane J (1994) *J Environ Polym Degrad* 2:111
19. Pérez-Carrillo E, Serna-Saldívar SO, Alvarez MM, Cortes-Callejas ML (2008) *Cereal Chem* 85:792
20. De la Rosa-Millán J, Agama-Acevedo E, Jimenez-Aparicio AR, Bello-Pérez LA (2010) *Starch-Stärke* 62:549
21. Moreno-Calles AI, Casas A, García-Frapolli E, Torres-García I (2012) *Agrofor Syst* 84:207
22. Belton PS, Delgadillo I, Halford NG, Shewry PR (2006) *J Cereal Sci* 44:272
23. Murúa-Pagola B, Beristain-Guevara CI, Martínez-Bustos F (2009) *J Food Eng* 91:380
24. Bulnes-Abundis D, Alvarez MM (2013) *AIChE J* 59:3092
25. Sánchez Cervantes MI, Lacombe J, Muzzio FJ, Álvarez MM (2006) *Chem Eng Sci* 61:8075
26. Norma Oficial Mexicana NOM-116-SSA1-1994
27. Norma Mexicana NMX-F-608-NORMEX-2011
28. Norma Mexicana NMX-F-615-NORMEX-2004
29. Norma Mexicana NMX-F-607-NORMEX-2002
30. AOAC Official Method 962.09
31. Trujillo-de Santiago G, Rojas-de Gante C, García-Lara S, Ballesca-Estrada A, Alvarez MM (2014) *J Chem Educ* 91:1729
32. Oliviero M, Verdonotti L, Di Maio E, Aurilia M, Iannace S (2011) *J Agric Food Chem* 59:10062
33. Pushpadass HA, Marx DB, Hanna MA (2008) *Starch-Stärke* 60:527
34. Salinas Moreno Y, Salas Sánchez G, Rubio Hernández D, Ramos Lobato N (2005) *J Chromatogr Sci* 43:483
35. Boulton R (2001) *Am J Enol Vitic* 52:67
36. Miller E, Rothstein JP (2004) *Rheol Acta* 44:160
37. Arda DR, Mackley MR (2005) *J Nonnewton Fluid* 126:47
38. Denn MM (2001) *Annu Rev Fluid Mech* 33:265
39. Wang X, Wang Z, Wu Q (2005) *J Appl Polym Sci* 96:802
40. Corradini E, de Carvalho AJF, Curvelo AAS, Agnelli JAM, Mattoso LHC (2007) *Mater Res* 10:227
41. Wang Y, Tilley M, Bean S, Sun XS, Wang D (2009) *J Agric Food Chem* 57:8366
42. Dombrink-Kurtzman MA (1994) *J Cereal Sci* 19:57
43. Bredie WLP, Mottram DS, Guy RCE (1998) *J Agric Food Chem* 46:1479
44. Martins SIF, Jongen WM, van Boekel MAJ (2000) *Trends Food Sci Technol* 11:364
45. Sevenou O, Hill S, Farhat I, Mitchell J (2002) *Int J Biol Macromol* 31:79
46. van Soest JJG, Tournois H, de Wit D, Vliegenthart JFG (1995) *Carbohydr Res* 279:201
47. Sivam AS, Sun-Waterhouse D, Perera CO, Waterhouse GIN (2012) *Food Chem* 131:802
48. Rufián-Henares JA, Delgado-Andrade C, Morales FJ (2008) *Eur Food Res Technol* 227:1447
49. Mylläriinen P, Partanen R, Seppälä J, Forssell P (2002) *Carbohydr Polym* 50:355
50. Oliviero M, Di Maio E, Iannace S (2010) *J Appl Polym Sci* 115:277
51. Lourdin D, Bizot H, Colonna P (1997) *J Appl Polym Sci* 63:1047