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In vitro digestibility, physicochemical, thermal and rheological properties of banana starches

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ABSTRACT

Banana starches (BS) were isolated from Enano, Morado, Valery and Macho cultivars. The BS possessed B-type crystallinity and an amylose content varying from 19.32 to 26.35%. Granules had an oval morphology with different major-to-minor axis ratios, exhibiting both mono- and bi-modal distributions and mean particle sizes varying from 32.5 to 45 μm. BS displayed zeta-potential values ranging between −32.25 and −17.32 mV, and formed gels of incipient to moderate stability. The enthalpy of gelatinization of BS affected the crystalline order stability within the granules. In-vitro digestibility tests showed fractions as high as 68% of resistant starch. Rheological oscillatory tests at 1 Hz showed that BS dispersions (7.0%, w/w) exhibited Type III behaviour, attributed to the formation of a continuous phase complex three-dimensional amylose gel reinforced by swollen starch granules acting as fillers. Amylose content and granules morphology were the main factors influencing the BS properties.

1. Introduction

Starch is the main reserve carbohydrate synthesized by superior plants, representing an important component of a large number of agricultural products, including cereals with polysaccharide content in the range 30–80%, legumes with 25–50% and tubers with 60–90% (Guilbot & Mercier, 1985). Traditionally, starch has constituted a major source of energy for many living organisms, especially to man (Buleon, Colonna, & Leloup, 1990; Luallen, 1998). In the recent decades, starch has found diverse applications in food and non-food industries as additive for modifying microstructure and functionality of commercial products (Bello-Pérez & Paredes-López, 2009; Maurer & Kearney, 1998; Meshram, Patil, Mhaske, & Thorat, 2009). Starch is composed mainly of two glucose polymers (amylose and amylopectin) spatially organized in granules with morphology, chemical composition and relative arrangement of macromolecules in the solid state depending of the botanical source. The relative proportion of amylose and amylopectin and the organization within solid granules determine the physicochemical and functional properties of starch, as well as the susceptibility for physical (e.g., gelatinization) and chemical modifications (e.g., hydrolysis).

Traditionally, cereals and tubers have been the main starch botanical sources. However, in the recent decades, the promotion of regional economies by different worldwide agencies and the search of sustainable agricultural activities have motivated the exploration of alternative starch botanical sources, such as tropical fruits (Zhang, Whistler, BeMiller, & Hamaker, 2005), tubers and roots (Hoover, 2001), among others. In particular, banana is widely harvested in tropical and semi-tropical regions with developing and emerging economic activities. World gross exports of banana were of 13,893.7 thousand metric tonnes in 2010 (FAO, 2011). Starch is the main component of green bananas and their systematic isolation and characterization can be traced back to the work by Kasiyu, Hood, and Vansoest (1981). In the recent two decades, a tight characterization of banana starch has been carried out, including digestibility in human intestine (Faisant et al., 1995), changes by physical and chemical modifications (Hernández-Jaimes, Bello-Pérez, Vernon-Carter, & Alvarez-Ramírez, 2013; Waliszewski, Aparicio, Bello, & Monroy, 2003), structure and digestibility (Zhang & Hamaker, 2012), among many other studies.

Some studies have shown that the physicochemical and functional properties of banana starch are not unique, and that they

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depend on variety, regional climatic conditions and harvesting periods (Bello-Pérez, Agama-Acevedo, Sánchez-Hernández, & Paredes-López, 1999). Although the so-called Criollo variety is the most commercialized banana cultivar worldwide, diverse varieties are still produced at regional level. For instance, the Enano and Macho varieties are widely cultivated in Southern Mexico, representing an important economic income for low-intensity farmers. Thus, studies on the digestion and functional properties of starches from regional banana cultivars have gained increasing importance, as they might help boost their application in processed foods and become a commercially viable commodity (Zhang et al., 2005). In particular, the examination of the morphological and rheological properties of banana starches is an important step in the characterization and understanding of their functional properties.

The aim of this work was to characterize the chemical composition, morphology, average particle size and distribution, zeta-potential, X-ray diffractograms, swelling, solubility, thermal properties, rotational and oscillatory rheological properties, and in vitro digestibility of starch (or starch dispersions) isolated from the Enano, Morado, Valery and Macho banana cultivars from Southern Mexico. By doing this, it is hoped that useful technical information is shed about the physico-chemical and functional properties of these starches, contributing to boost their application in the food industry in substitution of commercially available starches.

2. Materials and methods

2.1. Materials and reagents

Edible green (unripe) pre-climateric bananas (*Musa* sp.) from the Enano, Morado, Valery and Macho cultivars were purchased in the local market of Tuxtepec, State of Oaxaca, Mexico, immediately after harvest without any postharvest treatment. All the chemicals (sulphuric acid, citric acid, sodium hydroxide, potassium hydroxide, hydrochloric acid, iodine, sodium acetate) used were reagent grade (J.T. Baker, Mexico City, Mexico). The hydrolytic enzymes of pancreatic α-amylase (Sigma–Aldrich, Toluca, State of Mexico, Mexico; Nr. A3176; 23 IU mg^{-1}), pepsin (Merck, Naucalpan, State of Mexico, Mexico; Nr. 7190; 2000 FIP-U g^{-1}), amyloglucosidase (Boehringer, Mexico City, Mexico; Nr. 102857) and glucose oxidase-peroxidase kit (SERAPAK Plus, Bayer de Mexico, S.A. de C.V., State of Mexico, Mexico) were used in the in vitro starch digestibility test. Amylose (Nr. A-0512) and amylopectin (Nr. A-8515) were used as standards and were purchased from Sigma–Aldrich (Toluca, State of Mexico, Mexico). Deionised water was used in all the experiments.

2.2. Starch isolation

Starch from the different banana cultivars was isolated following the procedure proposed originally by Flores-Gorosquera et al. (2004) and implemented to pilot plant scale by Utrilla-Coello, Bello-Pérez, Vernon-Carter, Rodríguez, and Alvarez-Ramírez (2013). The fruit was peeled (ca.100 kg), cut into cubes (~125 cm^3), immediately submerged in aqueous citric acid solution (0.5 g L^{-1}), and then macerated at low speed in a Waring blender (10 kg of fruit to 10 L of solution) for 2 min. The homogenate was subsequently sieved through screens (40, 100, 200, and 325 US mesh) until the wash distilled water was clear. The starch dispersion (300–400 g kg^{-1}) was fed to a spray-dryer (Niro Atomizer model P-6.3, Copenhagen, Denmark) using an inlet air temperature of 130–150 °C and an air outlet temperature of 70–80 °C as reported by Casarrubias-Castillo, Hamaker, Rodríguez-Ambriz and Bello-Pérez (2012). These authors found that under these drying conditions the damage to starch structure was negligible (0.37%). During spray drying the surface area produced by atomization of the liquid feed enables a short gas residence time (3–40 s), which permits the drying of sensitive materials without thermal degradation.

The resulting powder was ground to pass through a 100-mesh sieve and finally stored at room temperature (25 °C) in a sealed glass container until required.

2.3. Chemical composition

Moisture content was determined by gravimetric heating (130 ± 2 °C for 2 h) using 2–3 g sample. Ash, protein and fat were analyzed according to AACC (1983) methods 08–01, 46–13 and 30–25, respectively. Amylose content of the banana starches was determined by following the method of Williams, Kuzina, and Hlynka (1970). Starch samples (20 mg) were added with 10 mL of 0.5 N KOH and the resulting suspension was thoroughly mixed. Afterwards, the dispersed sample was transferred into a 100 mL volumetric flask and diluted to the mark with distilled water. An aliquot (10 mL) was pipetted into a 50 mL volumetric flask and 5 mL of 0.1 N HCl was added followed by 0.5 mL of iodine reagent. The volume was diluted to 50 mL and the absorbance was measured at 625 nm. The measurement of the amylose was determined from a standard curve developed using amylose and amylopectin blends.

2.4. Swelling and solubility

Starch solution (1.0%, w/w) was prepared in a flask and then heated at different temperatures in the range from 30 to 90 °C for 30 min, with shaking each 5 min. The slurry was centrifuged for 10 min at 5000 × *g*. The supernatant was decanted, and the volume was measured; aliquots were used to estimate total carbohydrates (Dubois, Gilles, Hamilton, Rebers, & Smith, 1956). The precipitate was used to determine the moisture content (2 h at 130 °C).

2.5. Scanning electron microscopy (SEM)

The BS particles were mounted on carbon sample holders using double-side sticky tape and were observed using a JEOL JMS 7600F scanning electron microscope (Akishima, Japan) with the GB-H mode at 1 kV accelerating voltage. Micrographs at 2000× and 2200× magnification are presented. Samples were not metalized since the microscopy equipment operates under ultra-vacuum conditions (Hernández-Jaimes et al., 2013).

2.6. X-ray diffraction (XRD)

BS particles were stored in a sealed container at a relative humidity of 85% for achieving constant moisture content. XRD patterns were measured at room temperature following the procedure of Hernández-Nava, Bello-Perez, San Martin-Martinez, Hernandez-Sanchez, and Mora-Escobedo (2011) with slight modifications. A Siemens D-5000 diffractometer (Karlsruhe, Germany) using Cu Kα radiation ($\lambda = 1.543$) and a secondary beam graphite monochromator was operated at 40 kV and 30 mA. Intensities were measured in the 5–70° 2θ range with a 0.03° step size and measuring time of 1.0 s per point.

2.7. Granules average particle size and distribution

The particle size distribution of the BS was determined with laser diffraction using a Mastersizer 2000 (Malvern Instruments Ltd., Malvern, Worcestershire, UK), with the help of a Scirocco dry disperser unit used for dispersing the powders at a feed pressure of 2 bars and a feed rate of 40%. The obscuration was in the interval of 0.5–5%. The Fraunhofer approximation was used for calculation

of the starch granules size distribution and the corresponding volume fraction-length mean diameter ($d_{4,3}$) (Palma-Rodríguez et al., 2012).

2.8. Starch digestibility

The total starch (TS), rapidly digestible starch (RDS), slowly digestible starch (SDS) and resistant starch of the different banana varieties were determined using the Englyst, Kingman and Cummings (1992) assay and slightly modified by Casarrubias-Castillo et al. (2012). Samples of native and gelatinized BS (400 mg), 25 mg of guar gum powder, and 8 mL of water were cooked in a boiling water bath for 20 min. Then, 5 mL of pepsin/hydrochloric acid solution was added and equilibrated at 37 °C for 30 min. Then, 5 mL of 0.25 M sodium acetate solution were added, agitated gently to disperse the contents; 2.5 mL of enzyme mixture were added to tubes in intervals of 1 min, and tubes were placed in a water bath adjusted to a speed of 160 strokes min^{-1}. After 20 min (G_{20}), 0.5 mL aliquot was removed and placed into a tube containing 20 mL of 66% ethanol; after another 120 min (G_{120}), a second 0.5 mL aliquot was removed and treated in the same way. Glucose content of the hydrolyzates was determined using glucose oxidase/peroxidase assay kit. Values for RDS, SDS, RS, and TS were calculated from the measured G_{20}, G_{120}, and TG values. Values for the starch fractions were expressed as mg of glucose × 0.9 (Vatanasuchart, Niyomwit, & Wongkrajang, 2012).

2.9. Thermal analysis

The thermal properties of the BS were measured using a differential scanning calorimeter (TA Instrument, Q1000, New Castle, NJ, USA) previously calibrated with indium. The gelatinization temperature was evaluated as indicated by Palma-Rodríguez et al. (2012), with slight modifications. A 3.0 mg sample (dry basis) was weighed in an aluminium pan and 6 mL of deionized water were added. The pan was sealed tightly and allowed to stand for 1 h before carrying out the analysis. The sample was subjected to a heating ramp of 10–140 °C and a heating rate of 5 °C. An empty aluminium pan was used as reference. The onset (T_o), peak (T_p), end temperatures (T_e), and the gelatinization enthalpy (ΔH_{gel}). The data were obtained directly from the instrument's software.

2.10. Zeta-potential

The zeta-potential (ξ-potential) of 7.0% (w/w) BS dispersions at pH 5.0 was determined using the Zetasizer Nano ZS90 equipment (Malvern Instruments, Worcestershire, UK).

2.11. Rheological properties

BS dispersions (7.0%, w/w) were heated up to 90 °C with mild agitation until gelatinization was achieved (~30 min). Gelatinized banana starches (GBS) were left to cool to achieve room temperature (25 °C) and the water lost during heating was added back to the gels with gentle mixing and let to rest for 1 h to allow structure recovery. Rheological measurements were made at 25 ± 0.1 °C with a Physica MCR 300 (Physica Meßtechnik GmbH, Stuttgart, Germany) modular compact rheometer, with a cone-plate geometry, in which the rotating cone was 50 mm in diameter, and the cone angle was 2.0°. The apparent viscosity (η_{app})-shear rate ($\dot{\gamma}$) behaviour of the GBS was determined by increasing the shear rate from 0.0001 to 1000 s^{-1}. The viscoelastic properties were determined under oscillatory shear conditions. To this end, amplitude sweep experiments were performed with constant frequency of 1 Hz and strain varying from 0.1 to 1000%. The storage modulus (G'), loss modulus (G'') and loss ratio = tan δ (G''/G') responses were obtained from the equipment software in all cases.

2.12. Statistical analysis

Results are presented as means ± SE from the analysis of replicates ($n = 3$). Data analysis was done using the Statgraphics Plus software (Statistical Graphics Corp., Manugistics, Inc, Cambridge, MA, USA).

3. Results and discussion

3.1. Chemical composition

The chemical composition of the different banana starches is presented in Table 1. The moisture content varied between 7.03% for the Enano cultivar to 8.96% for the Valery cultivar. The moisture contents of our BS were significantly lower than those reported for Macho (12.9%) and Criollo (11.1%) starches by Bello-Pérez et al. (1999), probably because in this work starch dispersions were spray-dried, which is a more efficient drying technique than convection drying used by the aforementioned authors. Our BS had protein (0.83–0.98%) and fat (0.73–0.82%) contents that were significantly lower than those reported for the Macho and Criollo varieties (Bello-Pérez et al., 1999), despite that their samples had considerable higher moisture content. These results indicate that our starch preparation technique produced samples with higher purity, and that residual protein and fat were removed almost completely during the alkali stepping. Bello-Pérez et al. (1999) reported higher values of ash content for "Macho" banana starch, although other authors (Kasiyu et al., 1981; Lii, Chang, & Young, 1982) reported lower ash contents (about 0.02–0.04%). The results in Table 1 are within the range reported recently for these components by Carmona-Garcia, Sánchez-Rivera, Mendez-Montealvo, Garza-Montoya, and Bello-Pérez (2009). Surely, the chemical composition of isolated starches from different botanical sources depends on various factors, such as regional climate, agronomic methods, harvesting conditions, isolation methods, among others (Lawal, 2004; Lawal et al., 2011).

The amylose content plays a central role in affecting diverse physico-chemical parameters of starches, since the amorphous fraction of starch granules is built up mainly of amylose. The amylose contents of our BS was in the range from 19.32 to 26.35% with the lowest and highest values belonging to Valery and Macho varieties, respectively. Reported amylose contents for banana starches have been: 17–19.5% for Cavendish cultivar (Garcia & Lajolo, 1988; Ling, Osman, Fernandes, & Reilly, 1982); 40.7% for Valery cultivar (Waliszewski et al., 2003); 38.6–43.8% for six Kluai cultivars (Vatanasuchart et al., 2012). Interestingly, the amylose contents reported in Table 1 are within the values (20–25%) for cereal starches. Similar results have been reported for rice starches from different sources (Lawal et al., 2011; Wani et al., 2013).

3.2. Solubility and swelling

The dependence of solubility and swelling with temperature in the range of 30–90 °C is shown in Fig. 1. The starch solubility % and swelling capacity of all BS was not higher than ~5.0% for temperatures lower than 50 °C. For higher temperatures, both the solubility % and swelling capacity increased in a nearly linear fashion, with the Enano and Morado varieties presenting relative higher values. Similar trends were found for starch Macho variety solubility-swelling behaviour by Núñez-Santiago, Bello-Pérez, and Tecante (2004) for starch pastes with concentrations between 3 and 6% (w/w). The swelling capacity is the ability of starch granules to hydrate under excess water conditions. It has been argued

Table 1
Chemical composition of native banana starches.

Banana variety	Moisture (%)	Ash (%)	Protein (%)	Fat (%)	Amylose (g/100 g)
Enano	7.03 ± 0.03	1.43 ± 0.02	0.92 ± 0.06	0.73 ± 0.05	25.38 ± 0.94
Morado	8.75 ± 0.03	1.17 ± 0.02	0.83 ± 0.04	0.73 ± 0.04	21.99 ± 0.46
Valery	8.96 ± 0.03	1.27 ± 0.03	0.93 ± 0.05	0.78 ± 0.05	19.32 ± 0.95
Macho	7.72 ± 0.03	1.11 ± 0.03	0.98 ± 0.05	0.82 ± 0.05	26.35 ± 1.16

Values expressed are mean ± standard error ($n = 3$).

that starch solubility and swelling capacity are directly related to the amylose-amylopectin relative content (Ratnayake, Hoover, & Warkentin, 2002). Also, swelling capacity is an indication of the strength of water binding forces in starch granules. In fact, the mobility of starch molecules is increased with temperature, thereby weakening binding forces. Hence, the leaching of soluble components is augmented, yielding improved starch solubility and increased granule porosity. An effect of this process is the increase of the effective diffusivity of water into the granule structure and, together with the flexibility of high molecular number of starch molecules, improves water retention. Since amylose is related to the amorphous fraction of starch granules, water penetration is more important in these granule regions. In this way, in line with the results in Fig. 1, higher solubility and swelling can be attributed to high amylose contents (Lawal et al., 2011).

3.3. Starch granule morphology

Starch granules from Enano and Macho varieties exhibited nearly mono-modal size distributions (Fig. 2). In contrast, the Morado and Valery varieties presented bimodal size distributions. A small shoulder was observed for particle sizes smaller than 10.0 μm. For all starches, the granule size ranged from 1.0 to about 200.0 μm, while the mean particle size ranged from 30 to about 45 μm. Enano and Valery varieties presented the lowest and higher mean particle size. For Núñez-Santiago et al. (2004) reported a mean particle size of the order of 10–20 μm for non-pasted Macho starch, and values similar to those found in this work for starch pastes. In this way, it is apparent that the bi-modal size distributions can be attributed to partial or incomplete swelling of some of starch granules. In turn, this would mean that hydration of some starch granules was not complete enough.

SEM was used for determining the morphological differences of the four starch varieties. In agreement with previous findings, Fig. 3 shows that the starch granules exhibited regular shapes with oval appearance (Eggleston, Swennen, & Akoni, 1992; Jane, Kasemsuwan, Leas, Zobel, & Robyt, 1994; Kasiyu et al., 1981; Lii et al., 1982). Major axes ranged from 10 to 80 μm, mostly between 30 and 50 μm. The Enano variety granules were more elongated while the Macho granules were nearly spheroidal. An estimation of the major-to-minor axis ratio is presented in Fig. 4, showing that the larger value was found for the Enano variety. The conditions under which starch biosynthesis occurs yield a natural variability in amylose content, which may be responsible for granule diversity. The diversity of size distribution and shape is expected to affect the functional and rheological properties of materials added with starch granules (Peterson & Fulcher, 2001; Soh, Sissons, & Turner, 2006).

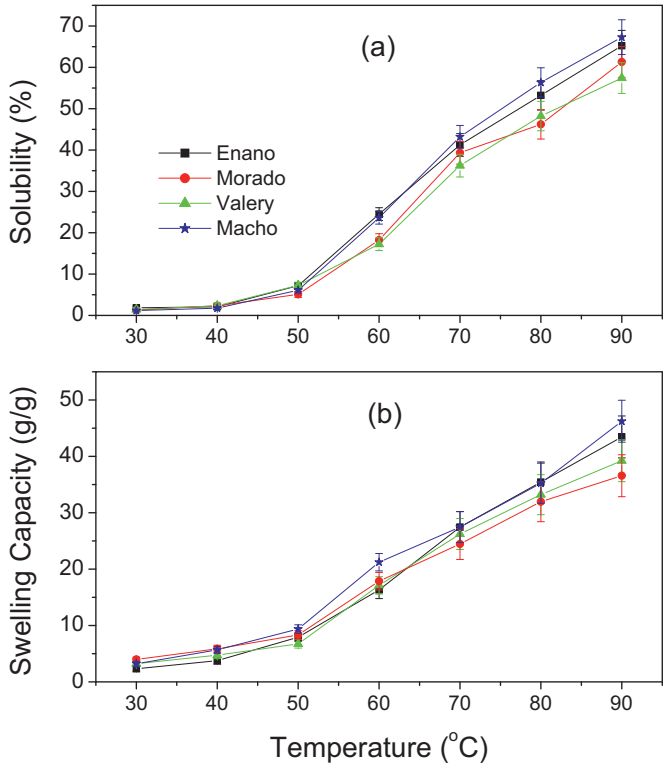

Fig. 1. Dependence of banana starch solubility and swelling with temperature (30–90 °C). Marginal solubility and swelling is observed for relatively small temperatures.

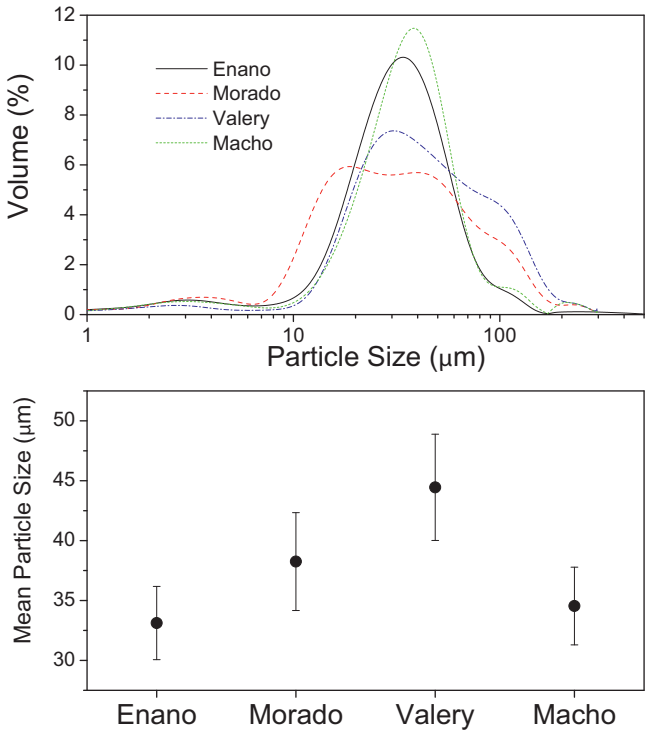

Fig. 2. (a) Particle size distribution for the four banana starches. The Enano and Macho varieties exhibited nearly mono-modal size distributions (Fig. 2). In contrast, the Morado and Valery varieties presented bimodal size distributions. (b) Mean particle size for the four banana varieties.

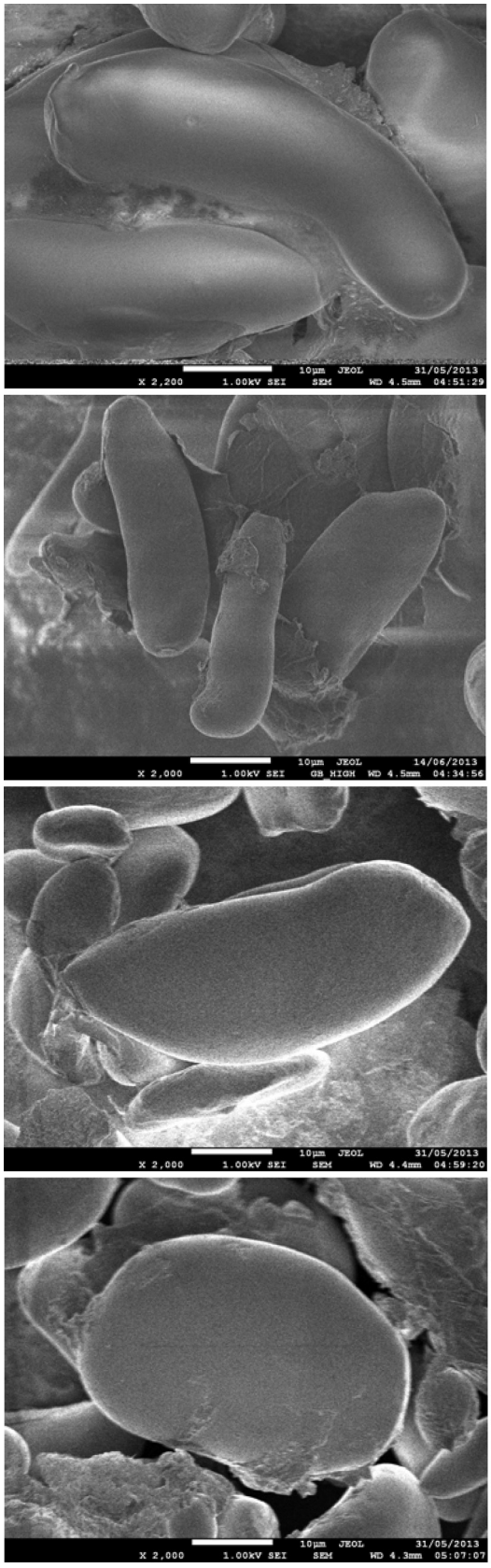

Fig. 3. Morphology of the banana starch granules as determined by scanning electron microscopy (SEM). The shape is regular with an oval appearance.

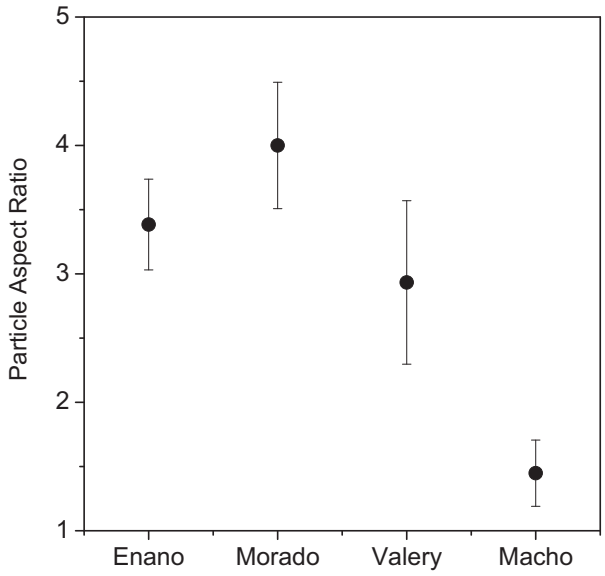

Fig. 4. Major-to-minor axis ratio estimations for the four banana starches. The larger value is found for the Enano variety.

3.4. X-ray diffraction (XRD)

The X-ray diffraction patterns of the four banana starches are presented in Fig. 5. All the BS displayed similar diffraction patterns, with crystallinity indexes of the order of 28–30%. The diffractograms showed a region of prominent peaks in the range from 12 to 25 diffraction angles. The highest peak was located at about 17 degrees, while other two minor peaks were located at about 15 and 23 diffraction angles. In line with previous reports (Faisant et al., 1995; Lii et al., 1982; Teixeira, Ciacco, Tavares, & Bonezzi, 1998), this diffraction pattern is consistent with B-type crystallinity. Zhang et al. (2005) commented that the crystallinity type of banana starches is not clear as other researchers have reported A-type (Bello-Pérez, Romero-Manilla, & Paredes-López, 2000) and C-type (Jane et al., 1994; Waliszewski et al., 2003) crystallinity patterns. Surely, the detected crystallinity pattern depends on plant growing conditions. In particular, the starch isolation technique (e.g.,

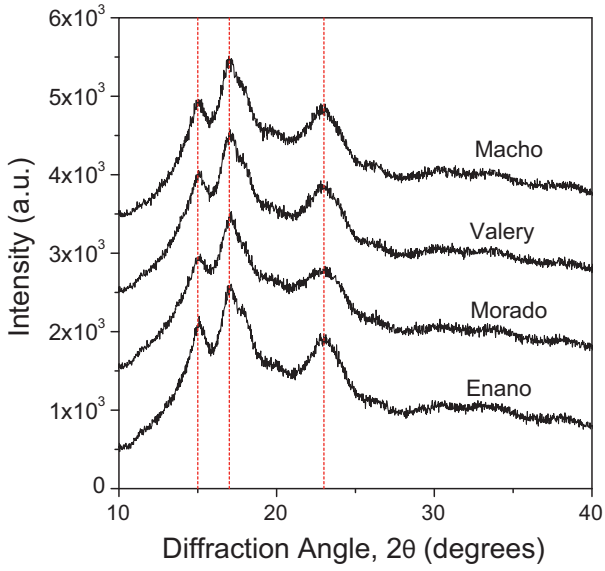

Fig. 5. X-ray diffraction patterns of the four banana starches had similar diffraction patterns, with crystallinity index of the order of 28–30%.

Table 2
Gelanisation properties of banana starches measured by differential scanning calorimetry.

Banana variety	T_o (°C)	T_p (°C)	T_e (°C)	ΔH_{gel} (J g^{-1})
Enano	71.3 ± 0.1	78.4 ± 0.4	91.5 ± 0.7	14.9 ± 0.7
Morado	60.9 ± 0.1	70.2 ± 0.2	83.2 ± 0.6	10.4 ± 0.2
Valery	71.9 ± 0.1	76.2 ± 0.1	88.71 ± 0.6	14.8 ± 0.5
Macho	74.6 ± 0.1	78.7 ± 0.5	92.4 ± 1.0	15.1 ± 0.1

T_o, onset temperature; T_p, peak temperature; T_e, end temperature; ΔH_{gel}, enthalpy of gelatinization. Values expressed are mean ± standard error (n = 3).

alkaline or non-alkaline) can affect largely the internal organization of banana starch granules.

3.5. Thermal properties

The thermal properties of the BS are presented in Table 2. The Morado variety presented the lowest values for T_o (60.9 °C) and T_p (70.2 °C), while the Macho variety exhibited the highest T_o (74.6 °C) and T_p (78.7 °C) values. A similar pattern was found for ΔH_{gel}, the Morado variety showing the lowest value (10.4 J g^{-1}) and the Macho variety the highest value (15.1 J g^{-1}). Similar values of thermal properties have been reported for Macho variety (Bello-Pérez et al., 2000; Núñez-Santiago et al., 2004). However, Table 2 indicates important differences in the internal organization of starch granules depending on the banana variety. It was observed that the Morado and Valery varieties had lower values for the end temperatures (83.2 and 88.7 °C) than the Enano and Macho starches (91.5 and 92.4 °C), respectively. This suggests that the former starches had more regular internal order than the latter starches. Amylose has been related to the irregular patterns in starch granules, which are displayed over a broad range of entropic conditions. In turn, higher temperature values are required for gelatinizing the internal arrangements for starches with high amylose content. On the other hand, gelatinization enthalpy is a measure of the internal order of starch granules (Chiotelli & Le Meste, 2002; Hoover & Vasanthan, 1994). Lower values of ΔH_{gel} indicate poor starch molecules organization. The Morado variety, with relatively low amylose content, exhibited the lowest ΔH_{gel} and the lowest onset and end temperatures. In contrast, Macho starch, which had the highest amylose content, also presented highest T_o, T_e and ΔH_{gel} values.

3.6. ξ-Potential

Starch in diverse forms (e.g., native, gelatinized, chemically modified) has been proposed as an additive for stabilizing emulsions in the food industry (Tan et al., 2012; Tesch, Gerhards, & Schubert, 2002). The surface charge plays a central role when starch is combined with other biopolymers for coating droplets in different emulsion configurations (Mao & McClements, 2013). The ξ-potential is an index commonly used for quantifying charges in biopolymers and the results for the four BS dispersions are presented in Table 3. All the BS were negatively charged, with the Macho variety presenting the lowest (−32.26 ± 0.86 mV) and the Enano variety the highest (−17.32 ± 2.34 mV) zeta-potential values. A positive correlation between amylose content and ξ-potential is apparent (R = 0.85), suggesting that amylose molecules affect largely the electrochemical activity of colloidal systems. Following the notions by Hanaor, Michelazzi, Leonelli, and Sorrell (2012), colloidal systems formed by banana starches should display incipient-moderate stability, so their use for emulsion applications should be considered in combination with other biopolymers (e.g., gums, proteins).

Table 3
Zeta potential of native banana starches.

Banana variety	Zeta potential (mV)
Enano	−18.52 ± 0.62
Morado	−32.26 ± 0.86
Valery	−28.41 ± 1.26
Macho	−17.32 ± 2.34

Values expressed are mean ± standard error (n = 3).

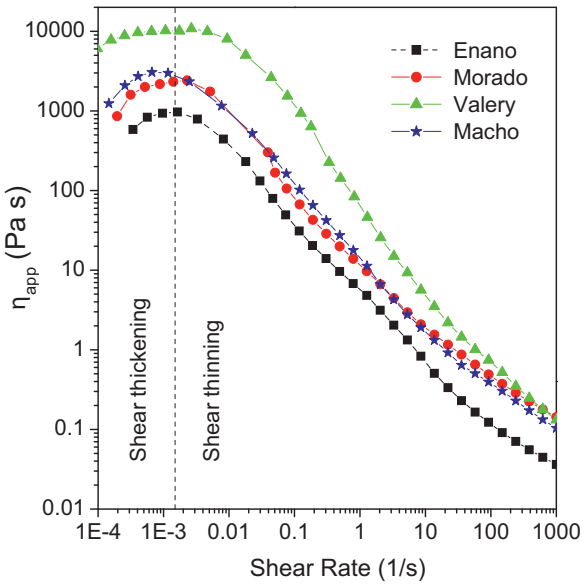

Fig. 6. Flow curves for the banana starch dispersions. Shear thickening and shear-thinning behaviours were observed for low and high shear rates, respectively.

3.7. Starch digestibility

In vitro starch digestibility measured in terms of rapidly digestible starch (RDS), slowly digestible starch (SDS) and resistant starch (RS) is presented in Table 4. It has been shown that banana starch appears to be resistant to enzyme-catalyzed hydrolysis (Zhang et al., 2005; Vatanasuchart et al., 2012). Table 4 shows that native banana starches presented an important amount of SDS and RS. Native Macho and Morado starches presented the lowest (9.4 g per 100 g) and highest values (19.7 g per 100 g) of RDS. These results indicate that banana cultivars, grown in Southern Mexico, have a low digestibility index. It has been pointed out that the digestion performance of cooked banana starch would be of importance to the food industry, since the consumption of cooked starch in human food is much more common than that of native starch. Table 4 shows that the RS contained in banana starch is relatively fragile under cooking conditions as about 90% of RS is converted in RDS and SDS after gelatinization. The RS in Macho variety presented the highest cooking robustness as about 25% of RS remained after gelatinization. These results suggest that for avoiding high glycemic indices and for exploiting the prebiotic advantages of SDS and RS, banana starch should be used in its native state in food products.

3.8. Rheological properties

The flow curves of the BS dispersions are presented in Fig. 6, and are all qualitatively similar. In the shear rate range of (~10–1000 s^{-1}) the apparent viscosity profiles can be described by a power-law equation of the form $\eta_{app} = K\dot{\gamma}^{n-1}$. The parameter values of the power-law fitting are shown in Table 5. The smaller (0.013) and higher (0.26) n values correspond to the Valery and Macho varieties, respectively. Interestingly, the Valery starch has the lowest amylose content, suggesting that amylose plays an

Table 4
Total starch (TS), rapidly digestible starch (RDS), slowly digestible starch (SDS) and resistant starch (RS) content from native and gelatinized banana starches.

Banana variety	TS	Native			Gelatinized		
		RDS	SDS	RS	RDS	SDS	RS
Enano	92.7 ± 1.9	13.3 ± 0.8	36.9 ± 2.5	42.4 ± 1.9	72.9 ± 0.7	18.4 ± 1.7	3.6 ± 0.7
Morado	87.1 ± 1.8	19.7 ± 1.7	39.9 ± 1.7	27.4 ± 1.6	67.4 ± 1.4	17.0 ± 1.7	0.76 ± 0.2
Valery	95.0 ± 1.8	11.0 ± 0.9	38.9 ± 2.0	45.0 ± 1.0	78.0 ± 1.8	11.0 ± 1.9	3.6 ± 0.9
Macho	99.6 ± 0.7	9.4 ± 1.0	22.5 ± 1.4	67.6 ± 0.9	72.0 ± 1.2	14.1 ± 1.1	13.4 ± 1.9

Values expressed are mean ± standard error ($n = 3$).

important role in the apparent viscosity drop with respect to the applied shear rate. Indeed, in agreement with reports for other starches (Xie et al., 2009), a positive linear relationship ($R = 0.88$) between amylose content and power-law exponent is apparent. The decaying apparent viscosity indicates that, for high shear rates, BS dispersions exhibited a shear thinning or pseudo-plastic behaviour, which was more pronounced for the Valery starch. These results suggest that the alignment of the starch granules along the flow direction is responsible for the shear-thinning behaviour, particularly at relatively high shear rates, and that when amylose is lixiviated from the partially swollen granules, the viscosity of the continuous phase is increased reducing the drag among starch particles. However, for relatively small shear rates (below $10^{-3}\ s^{-1}$), the BS dispersions exhibited a shear thickening behaviour (the apparent viscosity increased) with increased shear rate. Here, the shear rate is high enough for breaking the granules flocs and causing their alignment in the direction of flow, and rather a spatial rearrangement of the dispersed starch granules accompanied by entrapment of continuous phase within the flocs, causing an increase in the apparent viscosity.

The combined viscous and elastic behaviour of the BS dispersions can be determined by examining the movement of the material as a function of an oscillatory force. If the n caused by shear stress during oscillatory movement is reversible and returns to zero after stopping the applied force, the material will behave as an elastic solid. In contrast, if the strain is completely irreversible, the material will exhibit a viscous (i.e., liquid) behaviour. Complex fluids, like starch dispersions, behave as a combination of both viscous and elastic models. For an oscillation frequency of 1 Hz, Fig. 7a and b exhibit the elastic (G') and the viscous (G'') moduli as function of strain %. For the small strain range (up to 10%), the elastic modulus was nearly constant, indicating a linear elastic behaviour. At strains higher than about 10% all BS incurred in a power law decrease of G'. In line with the results of apparent viscosity as function of the applied shear rate, it can be suggested that the power-law behaviour observed in Fig. 7a is associated to the onset of the microstructure breakdown that is hastened as strain % increases until a constant structural deconstruction is achieved at relative high strain %. As a consequence, the dispersion BS structures increasingly tend to behave more as a viscous liquid. Fig. 8 presents the behaviour of the loss ratio ($G''/G' = \tan(\delta)$), which reflects the dominance of liquid-like over solid-like behaviour for values larger than one. The crossover between elastic and viscous dominance is located at about 40% for the four BS. A more

Table 5
Parameters of the power-law used for describing the shear thinning behaviour at intermediate shear rates.

Banana variety	K (Pa s^n)	n (−)
Enano	4.98 ± 0.23	0.24 ± 0.03
Morado	11.86 ± 0.97	0.22 ± 0.02
Valery	67.31 ± 1.56	0.08 ± 0.02
Macho	14.91 ± 1.05	0.26 ± 0.04

Values expressed are mean ± standard error ($n = 3$).

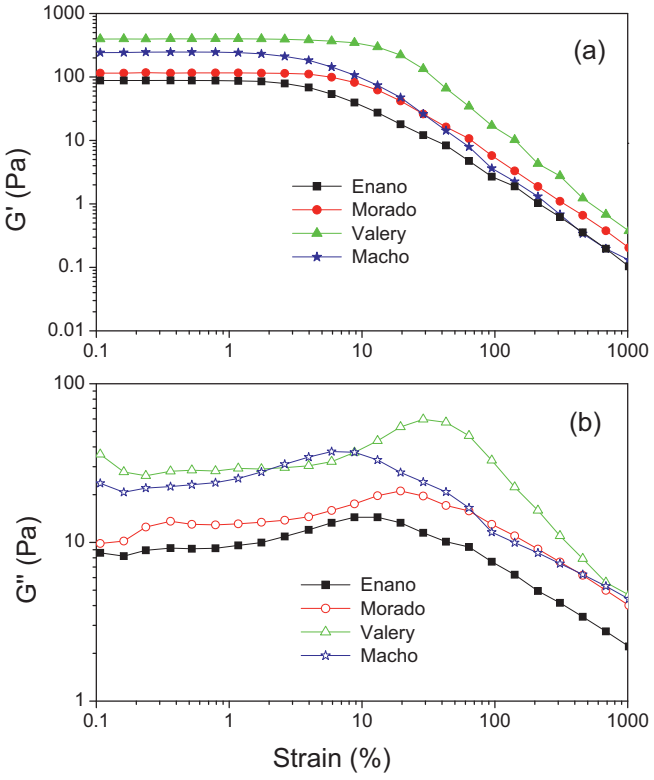

Fig. 7. (a) Elastic G' and (b) loss G' moduli dependence on strain % as obtained from oscillatory tests at 1 Hz. An overshoot for moderate strain % is observed for the loss modulus.

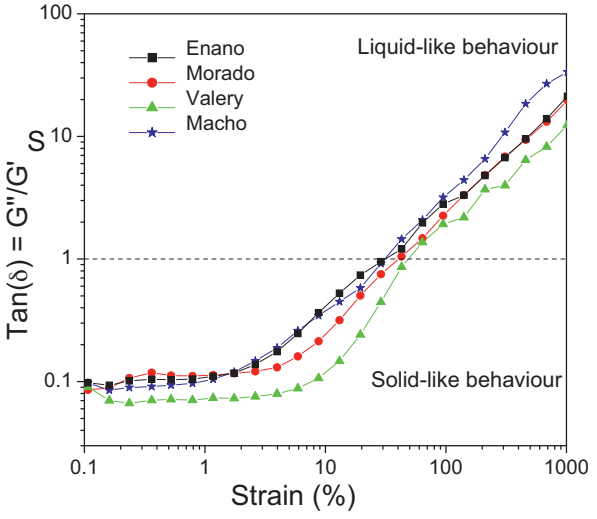

Fig. 8. Loss ratio G''/G' for the banana starch dispersions, showing the dominance of viscous effects over elastic effects for strain % values.

interesting behaviour is exhibited by the viscous modulus as exhibited in Fig. 7b. In contrast to the elastic modulus, the viscous modulus does not exhibit a well-defined linear behaviour at relatively low strain %, neither is it monotonously decreasing at relatively high strain %. Instead, the viscous modulus presents an overshoot for strains in the medium range, from about 1.0 to 100.0%. Similar oscillatory behaviour has been reported for starch isolated from several rice varieties (Lawal et al., 2011). In terms of the terminology by Hyun, Kim, Ahn, and Lee (2002) and Sim, Ahn, and Lee (2003), the behaviour described in Fig. 7b is classified as Type III and is often displayed by polymeric weak gels and disperse systems. In such systems, particle concentration, inter-particle interactions or inter-chain associations impose severe constraints to incipient flow of the internal structural units (e.g., particles, flocs or gel micro-domains). Núñez-Santiago et al. (2004) argued that a continuous network formed mainly by amylose occurred during gelatinization of banana starches. The swollen starch granules, mainly made by amylopectin matrices where the chains of this macromolecule entangled, allowed the granules to retain their rigidity. The result was the formation of a continuous phase three-dimensional complex fluid amylose gel that was reinforced by swollen starch granules acting as fillers of the gel (Eliason, 1986). This behaviour depends of the amylose content of the banana starch. In fact, Fig. 7b shows that the highest overshoot for G'' was exhibited by the Valery starch, which had the lowest amylose content. This result provides further evidence that the formation of a strong amylose gel reduces the effects of swollen particles within the complex structure.

4. Conclusions

This work provided a detailed report on the rheology, digestibility and functional properties of starches isolated from four banana cultivars from Southern Mexico. The results indicated that these banana starches presented differences in physico-chemical properties that can be caused by starch granule size and morphology, as well as amylose/amylopectin ratio. The thermal properties also exhibited some differences in gelation temperatures and enthalpy, which could be correlated to the amylose content of the banana starches. The rheological analysis showed that the starch dispersions behaved non-linearly and also were affected by granule size and amylose/amylopectin ratio. In particular, it was found that the rheological behaviour was consistent with a Type III classification, suggesting that the formation of a continuous phase three-dimensional complex fluid amylose gel reinforced by swollen starch granules acting as fillers of the gel for which a three-dimensional complex fluid formed by a continuous amylose gel reinforced by swollen starch granules that act as fillers of the gel took place. Although the native banana starches presented high values of resistant starch, it was substantially destroyed by cooking. Thus, in order to take advantage of the prebiotic properties of the resistant fraction, the banana starch should be used in its native state as additive for food products.

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