

Effect of acid modification on the thermal, morphological and pasting properties of starch from mango kernel (*Mangifera indica* L.) of Palmer variety

Bet, C.D., Cordoba, L.P., Ribeiro, L.S. and *Schnitzler, E.

State University of Ponta Grossa, Av. Carlos Cavalcanti, 4748, 84030-900, Ponta Grossa, PR,
Brazil

Article history

Received: 21 July 2016
Received in revised form:
20 September 2016
Accepted: 23 September 2016

Abstract

Mango kernels are residues generated by the food industry and they have a significant amount of starch which can be exploited for applications. The aim of this study was to extract and modify the starch from mango kernels by acid hydrolysis with hydrochloric acid (HCl) at different temperatures (25°C and 50°C) and different acid concentrations (0.1 mol L⁻¹ and 0.3 mol L⁻¹). The starches were characterised using thermal, morphological, pasting and colorimetric analysis. The modified starch showed higher values in relation to thermal stability and gelatinisation enthalpy, as well as lower peak temperatures than the native starch. The viscosity decreased in proportion to the acid concentration and temperature. After the modification, three new bands appeared from the infrared analysis. The acid hydrolysis was not able to change the shape and the size of the granules and the colorimetric analysis showed a slight tendency to light red.

Keywords

Mango kernel starch
Acid hydrolysis
Thermal analysis
Byproduct valorisation

© All Rights Reserved

Introduction

Mangoes (*Mangifera indica* L.) are one of the most important tropical fruits in the food industry and have many technological applications. Brazil has a significant production of this fruit, which is used primarily in juices, nectars, concentrated juices, jellies and fruit bars (Buenrostro-Figueroa *et al.*, 2010; Sogi *et al.*, 2013). Processing generates about 35 to 60% of waste, such as the peel (12-15%) and kernel (15-20%), which could be exploited for other uses (Kaur *et al.*, 2004; Sandhu and Lim, 2008; Sogi *et al.*, 2013).

In Brazil 0.6 million tonnes of mango kernels are discarded each year because it is considered as an industrial waste, although mango kernels contain a high content of starch (55-58% in dry basis) (Chowdary *et al.*, 2000; Kaur *et al.*, 2004). Several studies have evaluated the application of mango kernels in the production of natural antioxidants, fat substitutes, starch, flour and biodiesel. Mango kernel starch can be easily produced from this industrial residue. Consequently, the re-use of this residue is important for financial reasons and also to protect the environment (Kaur *et al.*, 2004; Sultana *et al.*, 2012; Saddique *et al.*, 2014).

Alternative sources of starch have been studied to provide new properties and functionalities in the food, cosmetic, paper and pharmaceutical industries,

suppressing the limitations which are found in native starches, such as low thermal resistance (Kittipongpatana and Kittipongpatana, 2011; Chang *et al.*, 2014). Modified starches present the following benefits: better flowability, reduction in viscosity and hydrophobicity; and also a lower tendency for retrogradation (Singh *et al.*, 2007; Arocas *et al.*, 2010; Polesi *et al.*, 2016). The application of chemically modified starch with hydrochloric acid (HCl) is mainly used in the gum, confectionery and fat-replacement industries (Wuttisela *et al.*, 2008).

In the present study, the starch from mango kernels was extracted and modified by acid hydrolysis (standard HCl solutions) and then characterised using the following techniques: differential scanning calorimetry (DSC); thermogravimetry/derivative thermogravimetry (TG/DTG); rapid viscoamylographic analysis (RVA); field emission gun scanning electron microscopy (FEG-SEM); colorimetric analysis; and fourier transform infrared spectroscopy (FTIR).

Materials and Methods

Materials

The starch used in the development of this study was extracted from kernels contained in the core of mangoes (*Mangifera indica* L.) of the Palmer variety,

*Corresponding author.
Email: egons@uepg.br

which were obtained in the local market in the city of Ponta Grossa. The extraction and analyses were performed in the laboratories of the Ponta Grossa State University (UEPG).

Starch isolation

The extraction process was adapted from Bello-Pérez *et al.* (2006). After the extraction of the kernel contained in the mango core, it was sliced into small pieces and dried at 40°C for 24 h, crushed in a mill (Ika Werke M20, Wilmington, North Carolina, USA), suspended in water (4:1 w/w, water:starch) and passed consecutively through sieves of 150 and 270 mesh. The suspension was kept resting until all the contents were decanted; they were separated by gravity from the supernatant. After re-suspension in water, the decanted content was centrifuged (Rotina 420R - Hettich Zentrifugen/UK) at 9500 rpm for 5 minutes. The supernatant was discarded and the bottom layer was dried in an oven with air circulation at 40°C for 24 h. It was subsequently powdered and kept in a desiccator until the start of the analysis.

Modification by acid hydrolysis

The acid modification was carried according to Beninca *et al.* (2013) with some modifications. Individual samples of 10 grams of native mango kernel starch were suspended in 200 mL of 0.1 mol L⁻¹ and 0.3 mol L⁻¹ standard hydrochloric acid (HCl) in 250 mL beakers and kept under constant stirring (330 rpm) at temperatures of 25°C and 50°C for one hour. After this time, the suspension was filtered and washed with distilled water. The silver nitrate (AgNO₃) test was performed to confirm the absence of HCl residue in the filtered solution. The samples were named as follows: (a) untreated mango kernel starch; mango kernel starch modified with: (b) HCl 0.1 mol L⁻¹ 25°C; (c) HCl 0.1 mol L⁻¹ 50°C; (d) HCl 0.3 mol L⁻¹ 25°C and (e) HCl 0.3 mol L⁻¹ 50°C.

Differential scanning calorimetry

The DSC analysis was performed using DSC-Q200 equipment (TA-Instruments, EUA). The equipment was initially calibrated using 99.99% purity indium, mp = 156.6°C, H = 28.56 J g⁻¹. The curves were obtained to study the gelatinisation process of the starches. The conditions of the analysis were as follows: air flow of 50 mL min⁻¹, heating rate of 10°C min⁻¹, aluminium crucibles with hermetic lid, and samples weighing about 2.5 mg. After weighing the samples, 10 µL of water was added using a micropipette in order to obtain a 4:1 ratio (water:starch, w/w); the aluminium crucibles were sealed and maintained like that for 30 minutes

(Ribeiro *et al.*, 2014).

Thermogravimetry/derivative thermogravimetry (TG/DTG)

The thermogravimetric and derivative thermogravimetric curves (TG/DTG) were obtained using a thermal analysis system TGA-50 (Shimadzu, Japan). In this analysis, the samples were heated from 15°C to 650°C. Then about 9 mg of the sample was weighed in an opened alumina crucible. The analysis was performed in the following conditions: air flow of 150 mL min⁻¹ and a heating rate of 10°C min⁻¹. The instrument was previously calibrated with monohydrated calcium oxalate standard. All the mass loss percentages were determined using TA-60WS software, as well as the derivative thermogravimetric curves (DTG), which were calculated to determine the peaks of the main mass losses (Costa *et al.*, 2013).

Rapid visco amylograph analysis (RVA)

The starch suspensions were prepared by the addition of 8% (approx. 2.24 g) of starch in distilled water into an aluminium sample holder, resulting in a total mass of 28 g. These were subsequently analysed using Rapid Visco Analyser (Newport Scientific, Australia) equipment. The samples were kept at 50°C for 1 min, heated to 95°C at 6°C min⁻¹, maintained at 95°C for 2.5 min, cooled to 50°C at 6°C min⁻¹, and then maintained at 50°C for 2 minutes (Dutta *et al.*, 2011).

Field emission gun scanning electron microscopy (FEG-SEM)

The size, shape, average length and width of the starch granules were analysed using field emission gun scanning electron microscopy (FEG-SEM) model MIRA 3 Tescan (Czech Republic). The tension of 15 kV on the field emission gun was generated by a lamp with a tungsten filament. The samples were sprayed over the carbon tape and, considering that starch is a non-conductive sample, it was necessary to metalise the samples with gold and palladium to promote the passage of the electrons (Pumacahua-Ramos *et al.*, 2015).

Colorimetric analysis

A spectrophotometer, model MiniScan EZ 4500L, (Hunter Associates Laboratory Inc., United States) was used to measure the colour parameters, which were based on the CIE (International Commission on Illumination). The parameters obtained were L*, a* and b*.

Lightness is represented by the parameter L* (representing black to white, from 0 to 100). The

Table 1. DSC gelatinisation and colour parameters results of: (a) untreated mango kernel starch and acid-modified mango kernel starch with: (b) HCl 0.1 mol L⁻¹ at 25°C; (c) HCl 0.1 mol L⁻¹ at 50°C; (d) HCl 0.3 mol L⁻¹ at 25°C and (e) HCl 0.3 mol L⁻¹ at 50°C

Sample	DSC gelatinisation				Colour parameters		
	T _o /°C	T _p /°C	T _c /°C	ΔH _{gel} /J g ⁻¹	L*	a*	b*
(a)	74.31±0.02 ^b	80.45±0.01 ^a	85.22±0.01 ^a	11.32±0.16 ^c	83.87±0.41 ^a	0.93±0.02 ^e	13.21±0.07 ^a
(b)	73.38±0.04 ^e	79.02±0.02 ^c	84.02±0.04 ^{cd}	13.82±0.26 ^b	83.29±0.39 ^a	2.83±0.04 ^b	10.50±0.03 ^e
(c)	73.61±0.01 ^d	79.15±0.01 ^b	84.34±0.01 ^b	15.48±0.03 ^a	83.19±0.18 ^a	2.73±0.03 ^c	10.90±0.04 ^d
(d)	75.14±0.01 ^a	78.58±0.01 ^e	83.98±0.07 ^d	13.47±0.15 ^b	83.62±0.23 ^a	3.00±0.03 ^a	11.76±0.07 ^c
(e)	74.02±0.03 ^c	78.92±0.01 ^d	84.18±0.10 ^{bc}	11.35±0.30 ^c	83.80±0.05 ^a	2.58±0.04 ^d	12.03±0.05 ^b

(*) T_o “onset” initial temperature, T_p peak temperature, T_c “endset” or conclusion temperature, ΔH_{gel} gelatinisation enthalpy. Values presented as mean values ± standard deviation after analysing in triplicate. Values followed by the same letter in the same column do not differ statistically by Tukey’s test (p<0.05)

colour approximation is evaluated by the a* and b* parameters. The a* parameter indicates the tendency to red (+) and green (-), and b* indicates the tendency to yellow (+) or blue (-).

Before the colorimetric measurement, the instrument was calibrated with white and black plate standards. The samples were put in Petri dishes with a lid to determine the colour parameters. Each sample was measured in triplicate (Hornung, Oliveira, Lazzarotto *et al.*, 2015).

Fourier transform infrared spectroscopy (FTIR)

The FTIR analysis was performed using a Shimadzu FT-IR 8400 spectrophotometer (Shimadzu, Japan) and collected at a resolution of 4 cm⁻¹; 64 scans were performed. The spectra were obtained using KBr pellets containing a homogeneous mixture of 100 mg of dry KBr and 2 mg of the sample (dry basis). The wavenumber range of the spectra was between 400 and 4000 cm⁻¹ (Chi *et al.*, 2008).

Statistical analysis

Analysis of variance (ANOVA) and Tukey’s test were used to compare the averages of the samples with a 95% confidence interval (p<0.05), using SASM-Agri 8.2 software. All the analyses were performed in triplicate.

Results and Discussion

Yield of mango starch

The yield of mango starch from the kernels was 58.20%. This was similar to the values reported by Chowdary *et al.* (2000) and Silva *et al.* (2013), who found 55% and 59.82%, respectively.

Differential scanning calorimetry

Analysing the DSC curves, the values of the endothermic process were obtained and they are shown in Table 1. As can be seen, the beginning of the gelatinisation phenomenon occurred for all the samples at 73.38-75.14°C; the peak temperatures were about 78.58-80.45°C and the conclusion temperature (T_c) stayed from 83.98 to 85.22°C. Other studies (Bello-Pérez *et al.*, 2005), which involved the characterisation of starch from mango pulp found values for gelatinisation temperatures of about 69-70°C. Those values were lower than the values for mango kernel starch found in the present study, demonstrating different properties for the starch from the same fruit.

The native mango kernel starch presented higher peak temperatures than those found in studies of native cassava (64.56°C) and waxy corn starches (68.31°C) (Cordoba *et al.*, 2013; Oliveira *et al.*, 2014). The values obtained for the gelatinisation phenomenon were very similar to those found by Kaur *et al.* (2004), who studied mango kernels from five Indian cultivars.

With the exception of sample (d), after one hour of treatment the T_o values decreased in a similar behaviour to that found in another study of cassava starch, which was modified with HCl at different temperatures (Cordoba *et al.*, 2013). There was a decrease in the T_p value of the modified samples and it was observed that there were higher differences for the samples (d) and (e), which were modified with more concentrated acid solutions. Others authors (Oliveira *et al.*, 2014) reported decreases of about 3°C in the T_p of waxy corn starch with HCl. Kong *et al.* (2012) also observed lower T_o, T_p and T_c values for amaranth starch, with different contents of amylose, which was modified with 0.5 mol L⁻¹ hydrochloric acid for one hour.

Table 2. Results of the TG/DTG analysis of: (a) untreated mango kernel starch and acid-modified mango kernel starch with: (b) HCl 0.1 mol L⁻¹ at 25°C; (c) HCl 0.1 mol L⁻¹ at 50°C; (d) HCl 0.3 mol L⁻¹ at 25°C and (e) HCl 0.3 mol L⁻¹ at 50°C

Sample	TG and DTG Results			
	Step	$\Delta m/\%$	$\Delta T/^\circ\text{C}$	$T_p/^\circ\text{C}$
(a)	1 st	9.91	30-133	62.41
	stability	-	133-174	-
	2 nd	69.99	174-370	285.49
	3 rd	19.28	370-530	462.92
(b)	1 st	10.15	15-136	71.68
	stability	-	136-179	-
	2 nd	65.24	179-364	263.26
	3 rd	24.31	364-567	459.84
(c)	1 st	8.78	29-135	74.64
	stability	-	135-190	-
	2 nd	65.48	190-358	261.63
	3 rd	25.40	358-560	459.58
(d)	1 st	9.85	20-141	73.26
	stability	-	141-185	-
	2 nd	65.61	185-353	267.62
	3 rd	24.19	353-555	455.46
(e)	1 st	11.39	20-133	65.47
	stability	-	133-181	-
	2 nd	67.22	181-354	268.79
	3 rd	21.12	354-549	450.47

Δm , mass loss (%); ΔT , temperature range ($^\circ\text{C}$); T_p , peak temperature ($^\circ\text{C}$)

The gelatinisation enthalpy increased for the modified samples, contrary to the results of a study in which cassava starch was modified with HCl (Oliveira *et al.*, 2014), where the ΔH_{gel} values decreased. A study by Beninca *et al.* (2013) observed an increase of 5.86J g⁻¹ in the ΔH_{gel} of cassava starch modified with HCl at 30°C, and an increase of 4.50J g⁻¹ when the modification occurred at 50°C, compared to native starch.

A lower gelatinisation enthalpy was required for the samples (a) and (e) and a higher one for sample (c). There was no significant difference in the enthalpy values of the samples (b) and (d); both were treated at 25°C, despite the difference in the concentrations of acid, which in this case did not influence this parameter.

Thermogravimetry/derivative thermogravimetry (TG/DTG)

Similar profiles were found in the analysis of the curves for the native and acid modified starch samples; they presented three characteristic mass losses, which is common in starchy samples, as has been observed in other studies (Cordoba *et al.*, 2013; Oliveira *et al.*, 2014; Pumacahua-Ramos *et al.*, 2015). The first mass loss refers to the dehydration of the samples, and the second and the third refer to the

degradation and oxidation of the organic matter.

Table 2 shows the results of the TG/DTG curves for the native starch samples and those treated with HCl. After dehydration, there was a period of stability for the native sample until 174°C, and between 179-190°C for the treated samples. An increase in the thermal stability was observed before the decomposition process of the starch.

The native starch sample had a value of 530°C for the final temperature of the last mass loss, when the decomposition process had finished. It can be observed that there was an increase in this value, after the acid treatment. Accordingly, it is possible to observe a shift in the last mass loss, with an increase in the thermal stability of the samples that were treated with acid. Similar behaviour has been described in the literature for cassava starch modified with HCl (Beninca *et al.*, 2013; Cordoba *et al.*, 2013) and HNO₃, with a larger temperature interval in the last mass loss and, consequently, higher stability.

Rapid visco amylograph analysis (RVA)

Table 3 shows the values obtained for the pasting properties of the studied starches. Mendes *et al.* (2012) found a pasting temperature (76.72°C) for native kernel mango starch (Tommy Atkins variety) that was very similar to the present study. These authors observed an increase in the pasting temperature after the oxidative treatment, unlike the results found in the present study, which showed a decrease in this parameter after the treatment with HCl. Another study (Kaur *et al.*, 2010) also reported an increase in the pasting temperature of banana, sweet potato and wheat starch treated with HCl.

Comparing the results of the present study with a study by Mendes *et al.* (2012), the values for peak viscosity, final viscosity and setback were considerably higher than those obtained for mango kernel starch from the Tommy Atkins variety. The peak viscosity and the final viscosity of the modified samples decreased proportionally in relation to the treatment that was made, considering the concentrations of acid and temperature; the lowest value was found for the sample treated with HCl 0.3 mol L⁻¹ at 50°C (sample (e)). Hydrolysis results in a decrease in the molar mass of the starch due to the cleavage of the chains, so the viscosity is lower (Ulbrich *et al.*, 2014). Furthermore, this decrease in the pasting temperature indicates that modified starches are more susceptible to the dissociation of the intermolecular hydrogen chains (Leonel *et al.*, 2005).

Furthermore, the treated samples also had their setback (tendency to retrogradation) decreased

Table 3. Results of the pasting properties of: (a) untreated mango kernel starch and acid-modified mango kernel starch with: (b) HCl 0.1 mol L⁻¹ at 25°C; (c) HCl 0.1 mol L⁻¹ at 50°C; (d) HCl 0.3 mol L⁻¹ at 25°C and (e) HCl 0.3 mol L⁻¹ at 50°C

Sample	Pasting temperature/ °C	Viscosity peak/ mPa.s	Setback/ mPa.s	Breakdown/ mPa.s	Final viscosity/ mPa.s	Peak time/ s
(a)	77.23±0.04 ^a	2474.35±1.91 ^a	930.50±0.71 ^a	1362.00±1.41 ^a	2039.50±2.12 ^a	444.25±0.35 ^a
(b)	75.26±0.01 ^d	2092.00±2.83 ^b	794.10±1.56 ^b	1161.00±1.41 ^b	1725.10±0.14 ^b	408.50±0.71 ^d
(c)	76.47±0.02 ^c	1351.00±1.41 ^c	426.75±1.06 ^d	741.50±0.71 ^c	1036.65±0.92 ^c	412.10±0.14 ^c
(d)	76.77±0.02 ^b	1318.50±1.20 ^d	443.85±1.20 ^c	741.55±0.78 ^c	1021.05±1.48 ^d	420.80±1.13 ^b
(e)	76.82±0.02 ^b	790.50±0.71 ^e	221.50±0.71 ^e	553.65±0.92 ^d	456.00±1.41 ^e	408.35±0.49 ^d

(*) mPa.s “millipascal second”, s “seconds”. Values presented as mean values ± standard deviation after analysing in triplicate. Values followed by the same letter in the same column do not differ statistically by Tukey’s test (p<0.05)

compared to the native starch (a), given that the amorphous region, which is responsible for the higher degree of retrogradation, was affected by the hydrolysis. This phenomenon fact also occurred in other studies found in the literature in relation to acid-treated starch samples (Sandhu *et al.*, 2007).

Field emission gun scanning electron microscopy (FEG-SEM)

Kaur *et al.* (2004) analysed the starch granules from the kernels of some species of mango and they reported that the granules had an oval shape with some pores on the surface, similar to maize starch. However, these pores were not observed in the starches in the present study (Figure 1), only some rugosity in the granules, which can be explained by the aqueous extraction method, which does not use any chemical treatment for the total purification of the granules. There are literature reports from studies that observed starch granules with a smooth surface because NaOH was used during the extraction (Novelo-Cen and Betancur-Ancona, 2005; Ruiz-Ruiz *et al.*, 2012). The results obtained in this study were similar to those of Silva *et al.* (2013), who obtained granules with irregular shape (mainly spherical and ellipsoidal) with a smooth surface and less grooves, which was due to extraction with sodium bisulphite.

Because the granules in the present study had an ellipsoidal shape, their width and length were measured. The average length of the granules for each sample was as follows: (a) 17.89±3.83a µm, (b) 18.30±3.44a µm, (c) 17.64±3.21a µm, (d) 18.16±2.79a µm and (e) 15.98±2.71a µm. Consequently, it was observed that the degree of hydrolysis did not affect the structure of the granules. Furthermore, it was noticed that the granules treated with higher temperatures were shorter in length. Bello-Pérez *et al.* (2005) reported that native starches extracted from mango pulp using sodium sulphite

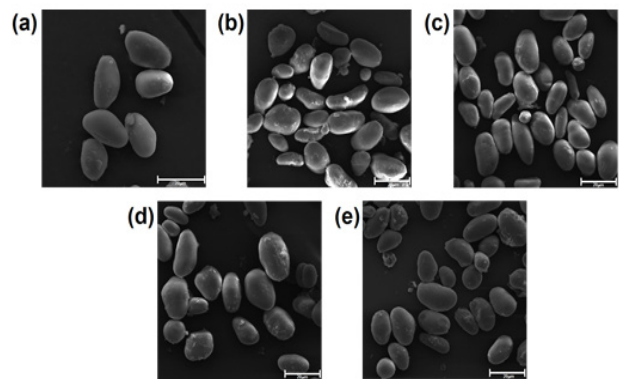


Figure 1. FEG-SEM micro-images of: (a) untreated mango kernel starch and acid-modified mango kernel starch with: (b) HCl 0.1 mol L⁻¹ at 25°C; (c) HCl 0.1 mol L⁻¹ at 50°C; (d) HCl 0.3 mol L⁻¹ at 25°C and (e) HCl 0.3 mol L⁻¹ at 50°C

were shorter in length; the values for the “Manilla” variety were around 5-10 µm and they were rounded and oval in shape. Ulbrich *et al.* (2014) studied the conservation of the structure of starch granules after hydrolysis at 40°C with HCl (0.36 and 0.72 N, 4h and 24 h, respectively) and found superior partial fragmentation for pea starch compared to potato and wheat starch, which was associated with the acid concentration, independent of the treatment time.

The widths of the granules of the samples in the present study were as follows: (a) 12.82±2.36a µm, (b) 11.81±2.29a µm, (c) 11.17±1.51a µm, (d) 12.54±1.84a µm and (e) 12.46±1.78a µm. The values for length and width were close to the ones found by Kaur *et al.* (2004) which were from 10.9 to 27.2 µm and from 6.5 to 16.3 µm, respectively.

Colorimetric analysis

The colour parameters for the native and treated samples are shown in Table 1. Three colour parameters were evaluated: L*, a* and b*. The acid treatment with HCl did not affect the L* parameter, with no significant difference at 5% significance by

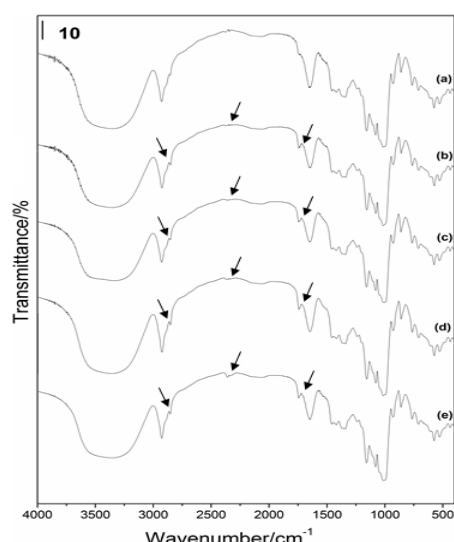


Figure 2. FTIR spectrum of: (a) untreated mango kernel starch and acid-modified mango kernel starch with: (b) HCl 0.1 mol L⁻¹ at 25°C; (c) HCl 0.1 mol L⁻¹ at 50°C; (d) HCl 0.3 mol L⁻¹ at 25°C and (e) HCl 0.3 mol L⁻¹ at 50°C

Tukey's test for all the the samples. When the cassava starch was treated with UV-light and modifying agent (NaClO and H₂O₂), the L* parameter also did not present great variations (Hornung, Granza, de Oliveira *et al.*, 2015; Hornung, Oliveira, Lazzarotto *et al.*, 2015).

Analysing the a* parameter, which assumes values from green (-) to red (+), a small tendency to red was observed in the native starch sample (a). When the samples were treated, the a* parameter was increased, which could be observed visually by the slight tendency to light red. Regarding the b* parameter, from blue (-) to yellow (+), it was identified that this coordinate decreased its value for the modified samples compared to the native one.

Fourier transform infrared spectroscopy (FTIR)

The molecular structure of starch as well, as its conformation, crystallinity and water content, can be investigated by infrared analysis (Capron *et al.*, 2007). The FTIR spectra for the native and modified samples are shown in Figure 2. These showed similar behaviour to that found by Li *et al.* (2014) for the phosphodiester bonds in sweet potato starch, with similar bands and characteristics for the starch.

Three bands after the acid modification were identified, which corresponded to the spectral bands between 1722 and 2867 cm⁻¹. According to Kizil *et al.* (2002), the spectral band in the interval of 1550-1750 cm⁻¹ shows the amorphous region of starch granules, which is most susceptible to acid hydrolysis, and, as reported by Hoover (2000), confirms the modification of mango kernel starch in the interval (1722-1752 cm⁻¹), with the appearance of a peak in the band between

1743-1745 cm⁻¹. This peak can be associated with the presence of carbonyls of the ester group (2000-1500 cm⁻¹) (Colussi *et al.*, 2015), and more specifically with the aliphatic ester (RCOOR'). This agrees with a study by Bai *et al.* (2009), which reported that the reaction of solid starch granules with an inorganic acid anhydride in an aqueous slurry produced ester links with OH groups in glucose units.

The bands of 2360-2368 cm⁻¹ in the modified starch samples corresponded to C≡N, which could be formed because of the proteins in the samples; bearing in mind that denaturation possibly makes them reassociate with glucose chains (Kumar *et al.*, 2014). The 2852-2854 cm⁻¹ bands corresponded to the CH₂ deformations, with lesser contributions from C-H stretch, aldehyde, COOH and OH, according to Kizil *et al.* (2002).

Conclusion

The mango kernel starch presented higher peak temperatures of gelatinisation than the starch extracted from mango pulp. After the acid modification there was a decrease in the peak temperature and an increase in the gelatinisation enthalpy as well as in the thermal stability of the samples. There was a decrease in the viscosity and also a lesser tendency to the retrogradation, which were proportional to the acid concentration and the modification temperature. The mango kernel starch granules showed an ellipsoidal shape and they remained unchanged after the acid modification. There was a tendency to light red for the modified starches, but there was no difference in the luminosity parameter. With the FTIR, three bands appeared after the acid modification. After the acid modification, the mango kernel starch, a byproduct obtained from mango processing, showed interesting characteristics to be used in the gum and confectionery industries.

Acknowledgements

The authors would like to thank the Brazilian organization CAPES and CNPq for the financial support and also to thank C- LABMU (UEPG) for help in the analysis.

References

- Arocas, A., Sanz, T., Salvador, A., Varela, P. and Fiszman, S. M. 2010. Sensory properties determined by starch type in white sauces: Effects of freeze/thaw and hydrocolloid addition. *Journal of Food Science* 75(2):

- S132-S140.
- Bai, Y., Shi, Y. C. and Wetzel, D. L. 2009. Fourier transform infrared (FT-IR) microspectroscopic census of single starch granules for octenyl succinate ester modification. *Journal of Agricultural and Food Chemistry* 57(14): 6443-6448.
- Bello-Pérez, L. A., Aparicio-Saguilán, A., Méndez-Montealvo, G., Solorza-Feria, J. and Flores-Huicochea, E. 2005. Isolation and partial characterization of mango (*Mangifera indica* L.) starch: Morphological, physicochemical and functional studies. *Plant Foods for Human Nutrition* 60(1): 7-12.
- Bello-Pérez, L.A., García-Suárez, F.J., Méndez-Montealvo, G., Nascimento, J.R.O., Lajolo, F.M. and Cordenunsi, B.R. 2006. Isolation and characterization of starch from seeds of *Araucaria brasiliensis*: a novel starch for application in food industry. *Starch-Stärke* 58(6): 283-291.
- Beninca, C., Colman, T. A. D., Lacerda, L. G., Carvalho Filho, M. A. S., Bannach, G. and Schnitzler, E. 2013. The thermal, rheological and structural properties of cassava starch granules modified with hydrochloric acid at different temperatures. *Thermochimica Acta* 552: 65-69.
- Buenrostro-Figueroa, J., Garza-Toledo, H., Ibarra-Junquera, V. and Aguilar, C. N. 2010. Juice extraction from mango pulp using an enzymatic complex of *Trichoderma* sp. produced by solid-state fermentation. *Food Science and Biotechnology* 19(5): 1387-1390.
- Capron, I., Robert, P., Colonna, P., Brogly, M. and Planhot, V. 2007. Starch in rubbery and glassy states by FTIR spectroscopy. *Carbohydrate Polymers* 68(2): 249-259.
- Chang, F., He, X., Fu, X., Huang, Q. and Qiu, Y. 2014. Preparation and characterization of modified starch granules with high hydrophobicity and flowability. *Food Chemistry* 152: 177-183.
- Chi, H., Xu, K., Wu, X., Chen, Q., Xue, D., Song, C., Zhang, W. and Wang, P. 2008. Effect of acetylation on the properties of corn starch. *Food Chemistry* 106(3): 923-928.
- Chowdary, G. V., Krishna, S. H. and Rao, G. H. 2000. Optimization of enzymatic hydrolysis of mango kernel starch by response surface methodology. *Bioprocess Engineering* 23(6): 681-685.
- Colussi, R., El Halal, S. L. M., Pinto, V. Z., Bartz, J., Gutkoski, L. C., Zavareze, E.R. and Dias, A.R.G. 2015. Acetylation of rice starch in an aqueous medium for use in food. *LWT-Food Science and Technology* 62(2): 1076-1082.
- Cordoba, L. P., Ribeiro, L. S., Colman, T. A. D., Oliveira, C. S., Andrade, M. M. P., Costa, F. J. O. G. and Schnitzler, E. 2013. Effect of hydrochloric acid in different concentrations and temperatures up to some properties of organic cassava starch. *Brazilian Journal of Thermal Analysis* 2(1): 6-11.
- Costa, F.J.O.G., Leivas, C.L., Waszczynskyj, N., Godoi, R.C.B., Helm, C.V., Colman, T.A.D. and Schnitzler, E. 2013. Characterisation of native starches of seeds of *Araucaria angustifolia* from four germplasm collections. *Thermochimica Acta* 565(10): 172-177.
- Dutta, H., Paul, S.K., Kalita, D. and Mahanta, C.L. 2011. Effect of acid concentration and treatment time on acid-alcohol modified jackfruit seed starch properties. *Food Chemistry* 129(2): 284-291.
- Goñi, O., Escribano, M. I. and Merodio, C. 2008. Gelatinization and retrogradation of native starch from cherimoya fruit during ripening, using differential scanning calorimetry. *LWT-Food Science and Technology* 41(2): 303-310.
- Hoover, R. 2000. Acid-treated starches. *Food Reviews International* 16(3): 369-392.
- Hornung, P. S., Granza, A. G., de Oliveira, C. S., Lazzarotto, M. and Schnitzler, E. 2015. Study of the Effects of Ultraviolet Light and Sodium Hypochlorite Solutions on Properties of Cassava Starch Granules. *Food Biophysics* 10(3): 368-374.
- Hornung, P.S., Oliveira, C.S., Lazzarotto, M., Lazzarotto, S.R.S. and Schnitzler, E. 2015. Investigation of the photo-oxidation of cassava starch granules. Thermal, rheological and structural behaviour. *Journal of Thermal Analysis and Calorimetry* 120(3): 1-10.
- Kaur, M., Oberoi, D.P.S., Sogi, D.S. and Gill, B.S. 2010. Physicochemical, morphological and pasting properties of acid treated starches from different botanical sources. *Journal of Food Science and Technology* 48(4): 60-465.
- Kaur, M., Singh, N., Sandhu, K. S. and Guraya, H. S. 2004. Physicochemical, morphological, thermal and rheological properties of starches separated from kernels of some Indian mango cultivars (*Mangifera indica* L.). *Food Chemistry* 85(1): 131-140.
- Kittipongpatana, O. S. and Kittipongpatana N. 2011. Preparation and physicochemical properties of modified jackfruit starches. *LWT - Food Science and Technology* 44: 1766-1773.
- Kizil, R., Irudayaraj, J. and Seetharaman, K. 2002. Characterization of irradiated starches by using FT-Raman and FTIR spectroscopy. *Journal of Agricultural and Food Chemistry* 50(14): 3912-3918.
- Kong, X., Kasapis, S., Bao, J. and Corke, H. 2012. Influence of acid hydrolysis on thermal and rheological properties of amaranth starches varying in amylose content. *Journal of the Science of Food and Agriculture* 92(8): 1800-1807.
- Kumar, S., Chaudhary, S. and Jain, D. C. 2014. Vibrational Studies of Different Human Body Disorders Using FTIR Spectroscopy. *Open Journal of Applied Sciences* 4(03): 103-129.
- Leonel, M., Ferrari, T. B., Sarmiento, S. B. S. and Oliveira, M. A. D. 2005. Planting time, developmental stages and characteristics of roots and starch of *Pachyrhizus ahipa*. *Scientia Agricola* 62(6): 528-533.
- Li, G., Liu, B., Zhang, G., Zeng, J., Sun, J. and Ma, H. 2014. Characterization of Digestion Resistance Sweet Potato Starch Phosphodiester. *Tropical Journal of Pharmaceutical Research* 13(9): 1393-1400.
- Mendes, M.L.M., Bora, P.S. and Ribeiro, A.P.L. 2012. Morphological and functional characteristics and other properties of the native and oxidized starch paste produced from mango kernels of Tommy Atkins

- variety. *Revista Instituto Adolfo Lutz* 71(1): 76-84.
- Novelo-Cen, L. and Betancur-Ancona, D. 2005. Chemical and functional properties of *Phaseolus lunatus* and *Manihot esculenta* starch blends. *Starch-Stärke* 57(9): 431-441.
- Oliveira, C. S., Andrade, M. M. P., Colman, T. A. D., da Costa, F. J. O. G. and Schnitzler, E. 2014. Thermal, structural and rheological behaviour of native and modified waxy corn starch with hydrochloric acid at different temperatures. *Journal of Thermal Analysis and Calorimetry* 115(1): 13-18.
- Polesi, L. F., Sarmiento, S. B. S., Moraes, J., Franco, C. M. L. and Canniatti-Brazaca, S. G. 2016. Physicochemical and structural characteristics of rice starch modified by irradiation. *Food Chemistry* 191: 59-66.
- Pumacahua-Ramos, A., Demiate, I.M., Schnitzler, E., Bedin, A.C., Telis-Romero, J. and Lopes-Filho, J.F. 2015. Morphological, thermal and physicochemical characteristics of small granules starch from *Mirabilis jalapa* L. *Thermochimica Acta* 602: 1-7.
- Ribeiro, L. S., Cordoba, L. P., Andrade, M. M. P., Oliveira, C. S., Silva, E. C., Colman, T. A. D. and Schnitzler, E. 2014. Thermoanalytical study on the action of nitric acid up cassava starch granules. *Brazilian Journal of Thermal Analysis* 3: 20-25.
- Ruiz-Ruiz, J. C., Dávila-Ortíz, G., Chel-Guerrero, L. A. and Betancur-Ancona, D. A. 2012. Wet Fractionation of Hard-to-Cook Bean (*Phaseolus vulgaris* L.) Seeds and Characterization of Protein, Starch and Fibre Fractions. *Food and Bioprocess Technology* 5(5): 1531-1540.
- Saddique, M. S., Sultan, M. T., Akhtar, S., Riaz, M., Sibte-Abass, M., Ismail, A. and Hafeez, F. 2014. Utilization of Mango Kernel Lipid Fraction to Replace Normal Shortenings in Cereal Baked Products. *Food Science and Technology Research* 20(1): 3-21.
- Sandhu, K. S. and Lim, S. T. 2008. Structural characteristics and in vitro digestibility of mango kernel starches (*Mangifera indica* L.). *Food Chemistry* 107(1): 92-97.
- Sandhu, K. S., Singh, N. and Lim, S. T. 2007. A comparison of native and acid thinned normal and waxy corn starches: Physicochemical, thermal, morphological and pasting properties. *LWT-Food Science and Technology* 40(9): 1527-1536.
- Silva, G. A., Cavalcanti, M. T., Almeida, M. C. D. M., Araújo, A. D. S., Chinelate, G. C. and Florentino, E. R. 2013. Use of starch of almond of Tommy Atkins mango as thickener for dairy beverages. *Revista Brasileira de Engenharia Agrícola e Ambiental* 17(12): 1326-1332.
- Singh, J., Kaur, L. and McCarthy, O. J. 2007. Factors influencing the physico-chemical, morphological, thermal and rheological properties of some chemically modified starches for food applications—A review. *Food Hydrocolloids* 21(1): 1-22.
- Sogi, D. S., Siddiq, M., Greiby, I. and Dolan, K. D. 2013. Total phenolics, antioxidant activity, and functional properties of 'Tommy Atkins' mango peel and kernel as affected by drying methods. *Food Chemistry* 141(3): 2649-2655.
- Sultana, B., Hussain, Z., Asif, M. and Munir, A. 2012. Investigation on the antioxidant activity of leaves, peels, stems bark, and kernel of mango (*Mangifera indica* L.). *Journal of Food Science* 77 (8): C849-C852.
- Ulbrich, M., Natan, C. and Flöter, E. 2014. Acid modification of wheat, potato, and pea starch applying gentle conditions—impacts on starch properties. *Starch-Stärke* 66(9-10): 903-913.
- Wuttisela, K., Shobsngob, S., Triampo, W. and Triampo, D. 2008. Amylose/amylopectin simple determination in acid hydrolyzed tapioca starch. *Journal of the Chilean Chemical Society* 53(3):1565-1567.
- Yadav, B. S., Guleria, P. and Yadav, R. B. 2013. Hydrothermal modification of Indian water chestnut starch: Influence of heat-moisture treatment and annealing on the physicochemical, gelatinization and pasting characteristics. *LWT-Food Science and Technology* 53(1): 211-217.