

## THERMAL ANALYSIS, RHEOLOGY, X-RAY DIFFRACTOMETRY AND ATOMIC FORCE MICROSCOPY IN THE EVALUATION OF BINARY MIXTURES OF “STARCH-HYDROCOLLOIDS”

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### ABSTRACT

Starch is arguably the most investigated biopolymer in the world and the cassava starch that is extracted from *Manihot esculenta* Crantz, represents an important vegetal crop in tropical countries, where its roots and derivatives serve as food and a source of energy. The main composition of these roots is 70-80% water, 16-24% starch and small quantities (<4%) of protein, lipids vitamins and minerals. Hydrocolloids, or gums, are substances consisting of a hydrophilic long-chain with colloidal properties that, in water-based systems, produce gels. Starches and hydrocolloids are often used together in food systems to provide texture, water mobility, control moisture, improve product quality and stability, facilitate processing and reduce costs. In this study, the interactions between cassava and starch-hydrocolloids (1% of the following gums: CMC, jatahy, pectin and xanthan) were investigated. The TG/DTG method made it possible to determine the thermal decomposition of each sample, which under air atmosphere occurs in three steps. Little difference was observed in the degree of relative crystallinity (XRD) and in the average roughness or average diameter of the starch granules (NC-AFM). The viscosity and pasting properties (RVA) increased, and were higher for starch treated with jatahy gum. A large decrease was observed in peak temperature and gelatinisation enthalpy for the treated samples (DSC).

**Keywords:** Modified starches, hydrocolloids, thermal analysis, enthalpy, pasting properties

### INTRODUCTION

Root and tuber crops are grown widely in the tropical and subtropical regions of the world. They are plants that yield starchy roots and tubers which contain around 16-24% starch, 70-80% water, 2% fibres and minor quantities of lipids, proteins, vitamins and minerals. Cassava (*Manihot esculenta*, Crantz) is a species from the *Euphorbiaceae* family and is one of the most important root crops in these regions. On a food energy production basis cassava is one of the main industrial sources of starch in various countries (Colman *et al.* 2012; Andrade *et al.* 2013).

Starches are one of the most important and flexible food ingredients, with innumerable industrial applications. They are natural carbohydrates with several benefits, such as being non-toxic, biodegradable, abundantly available and they can be treated, with various possibilities of modifications (Tharanathan, 2005; Komulainen *et al.* 2013).

Starch granules are synthesised in a broad array of plant tissues and within many plant species. They have a very complex structure that, regardless of their botanical origins, is mainly composed of two types of  $\alpha$ -glucan: amylose and amylopectin, which represent approximately 98-99% of the dry weight. These glucose polymers (amylose and amylopectin), which are found inside vegetable cells, are extracted for industrial applications in the food, textile and paper industries, and many others. Amylose is predominantly a linear polymer of  $\alpha(1\rightarrow4)$  linked glucose, whereas amylopectin is a highly branched polysaccharide consisting of  $\alpha(1\rightarrow4)$  linked glucose with  $\alpha(1\rightarrow6)$  linkages at the branch points. Starches in their native form do not always have the physical or chemical properties appropriate for certain types of processing. Some of these constraints include insolubility in cold water, low stability to freeze-thawing, and syneresis, which in some cases makes them difficult to use (Leivas *et al.* 2012; Lacerda *et al.* 2008; Lacerda *et al.* 2009).

Starches also differ from each other; each starch is unique. The differences are in the fine structures of the amylose and amylopectin molecules and granule behaviour (Ji *et al.* 2004).

Unprocessed or native starches are structurally too weak and functionally too restricted for application in today's advanced technologies; processing is necessary to engender a range of functionality. The production of modified

starches is an alternative that is in continuous development to surpass one or more of the limitations of native starches, and thus to increase the utility of this polymer for industrial applications. The starch market has grown rapidly in the last few years, leading to the search for products with specific characteristics that support the requirements of the industry (Lacerda *et al.* 2008; Rudnick *et al.* 2006).

Hydrocolloids or so-called “gums”, are non-starchy polysaccharides that have a variety of different structures, such as differences in branching, flexibility, molecular weight ranges, ionic charge, all of which influence their behaviour and the rheologic properties of their solutions (BeMiller, 2011).

Starches can be modified by chemical, physical, genetic or enzymatic means that promote specific functional properties (Beninca *et al.* 2013; Andrade *et al.* 2013).

Chemical modifications bring about structural alterations and the introduction of new functional groups, thus affecting the physicochemical properties of the starches and making them fit for various industrial uses (Shandu, Singh, Lim, 2007).

Hydrocolloids are widely used as food additives to improve the stability and texture of foods, for better water mobility and moisture control, to provide proper texture, reduce costs, facilitate processing, and to improve the overall product quality and/or stability. They are largely used in the food processing industry combined with different starches to modify their main rheological and pasting properties and several studies had been described in the literature (Xiaohong, BeMiller, 2002).

The main objective of the present study was to understand the interactions between cassava starch with some hydrocolloids and the functionalities that they can impart to foods. Some of these properties were analysed by the following techniques: thermogravimetry and derivative thermogravimetry (TG/DTG), differential scanning calorimetry (DSC), rheological properties by viscometer (RVA), structural properties by X-ray diffractometry (XRD) and atomic force microscopy (AFM).

**MATERIAL AND METHODS**

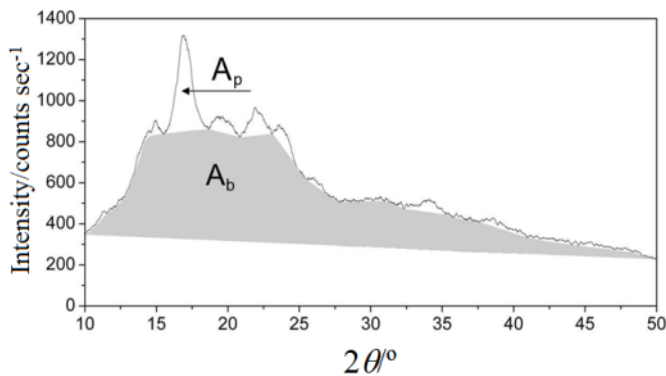
The starch and hydrocolloids used in this work were food grade. The hydrocolloid dispersion were prepared by suspension the hydrocolloids in distilled water at 1% (w/w) with constant stirring for 15 minutes; subsequently 15 g of starch was added slowly and maintained stirring for 15 minutes. The resultant slurry was filtered under reduced pressure and the solid was dried at 40 °C in an oven with forced air circulation for 24 hours.

The thermogravimetric curves (TG) were obtained using the thermal analysis system TGA-50 (Shimadzu, Japan), where the samples were heated from 35 °C to 650 °C using open alumina crucibles with approximately 5.0 mg of the sample under a synthetic air flow of 150 mL min<sup>-1</sup> at a heating rate of 10 °C min<sup>-1</sup>. The instrument was preliminarily calibrated with standard weight and with standard calcium oxalate monohydrate. All mass loss percentages were determined using TA-60 WS data analysis software, as well as first derivative (DTG) were calculated and was and was useful in determining the main steps and temperatures of mass loss.

The DSC curves were obtained using the thermal analysis system model DSC-Q200 (TA-Instruments, USA). The DSC curves were carried out with the objective of studying the gelatinisation process: the curves were recorded under an air flow of 50 mL min<sup>-1</sup>, heating rate of 5 °C min<sup>-1</sup> and samples weighing about 2.5 mg. A 4:1 (water:starch w/w) mixture was prepared and maintained for 60 minutes in order to equilibrate the moisture content. The aluminum crucibles were sealed and then the curves were performed. The instrument was previously calibrated with Indium 99.99% purity, melting point with T<sub>p</sub> = 156.6 °C, ΔH = 28.56 J g<sup>-1</sup>. The results were calculated using Universal Analysis 2000 software.

The pasting properties of the samples were obtained by using a RVA-4 (Newport Sci., Australia) viscometer. A suspension of 3 g (6% moisture) of starch in 25 g of accurately distilled water underwent a controlled heating and cooling cycle under constant shear, where it was held at 50 °C for two min, heated from 50 to 95 °C at 6 °C min<sup>-1</sup>, and held at 95 °C for 5 min, cooled to 50 °C at 6 °C min<sup>-1</sup> and held at 50 °C for 2 min. At the beginning of the heating the swelling of the starch granules occurred, which caused an increase in the viscosity slurry (time and temperature pasting) when the polymers with low molecular weight begin to be leached from the granules. The viscosity peak was observed when the granules were completely swollen and while maintaining the pasting temperature at 95 °C under constant stirring. The granules began to break down and solubilisation of the polymers provided a reduction in viscosity (break). Analysis followed, with a cooling cycle that caused reorganisation of some amylose and amylopectin polymers, increasing the opacity and viscosity of the paste in a process called setback (Colman et al. 2012; Andrade et al. 2013; BeMiller, 2011; Beninca et al. 2013) that occurs due to the strong tendency to form hydrogen bonds between adjacent molecules.

X-ray diffraction powder patterns (XRD) were obtained by using an X-ray diffractometer mod. Ultima 4 (Rigaku, Japan), employing Cu Kα radiation (λ = 1.541 Å) and settings of 40 kV and 20 mA. The scattered radiation was detected in the angular range of 5-50° (2θ), with scanning speed of 8° min<sup>-1</sup> and a step of 0.06°.



**Figure 1** XRD diffractogram of starch sample with the parameters to calculate the relative cristallinity.

The area above the smooth curve was taken as the crystalline portion, and the lower area between the smooth curve and the linear baseline which covered the 2θ range from 10° to 50° was taken as the amorphous section. The upper diffraction peak area and the total diffraction area over the diffraction angle 10-50° was integrated. The ratio of upper area to total diffraction was used as the “degree of relative crystallinity” (Rudnick et al. 2006). This method is largely used in starch studies and the equation for calculating the degree of relative crystallinity was as follows:

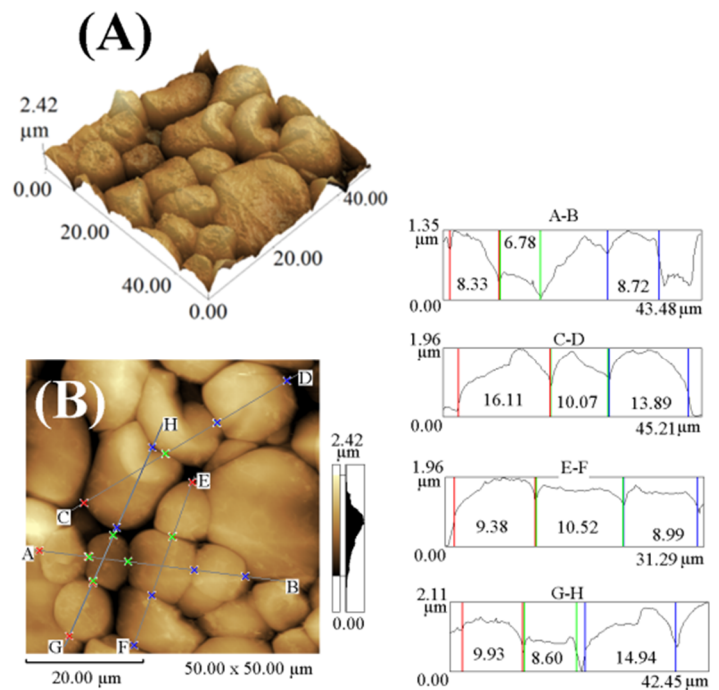
$$X_c = \frac{A_p}{(A_p + A_b)} \cdot 100 \tag{1}$$

where X<sub>c</sub> refers to the relative crystallinity degree, A<sub>p</sub> refers to the crystallized area on the X-ray diffractogram and A<sub>b</sub> refers to the amorphous area on the X-ray diffractogram. A smooth curve, with connect peak baseline, was computed and plotted on the diffractograms (Colman et al. 2012; Andrade et al. 2013; Rudnick et al. 2006; Oliveira et al. 2013).

The micro-images of each sample were observed with high resolution, using an atomic force microscope SPM-9600 (Shimadzu, Japan), by the non-contact method (NC-AFM). All the measurements were performed in triplicate in different points and resolutions (20 x 20, 50 x 50 and 100 x 100 μm); this technique allowed us to observe the surface of the studied starches and it was possible to calculate the average diameter and the average roughness of the samples (Juszczak, Fortuna, 2008; Colman et al. 2012; Andrade et al. 2013; Leivas et al. 2013; Beninca et al. 2013; Oliveira et al. 2013).

The AFM visualisation of starch granules and measurements were performed at ambient conditions; the starch samples were spread directly onto a sticking tape fixed on an AFM sample holder, which was enough to immobilize the granules and prevented contamination of starch surface.

In Figure 2 are depicted: (A) the 3D and (B) the 2D acquisition micro-images of starch granules. The segments A-B, C-D, E-F and G-H were obtained with the software from the instrument and which represents the height profile of the surfacial morphology.



**Figure 2** (A) 3D micro-image of starch granules (scan-size 50 x 50 μm); (B) 2D micro-image of starch granules (scan-size 50 x 50 μm), with the measurements

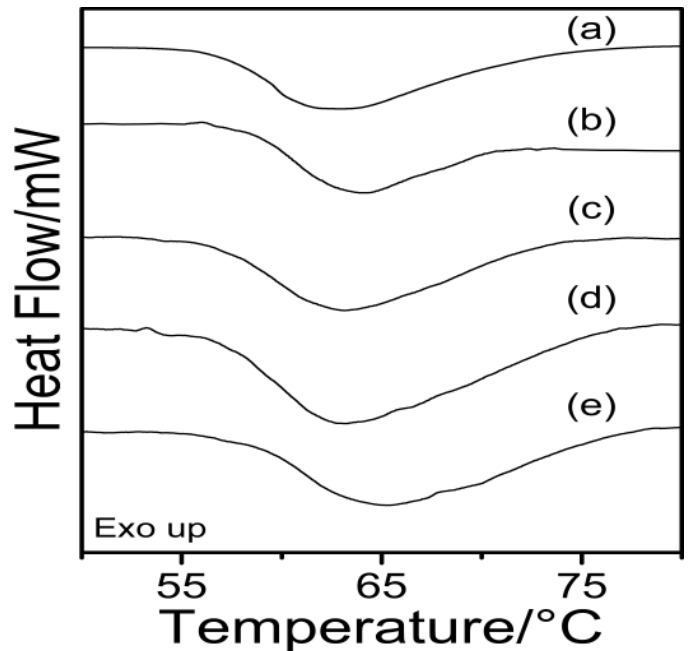
In Table 1 are gathered the obtained results from TG/DTG curves. All the samples showed similar thermal behaviour, with displacement of temperatures of each thermal event; the cassava starch treated with 1% jatahy gum (c) displaced the least mass loss to higher temperature, and the cassava starch when treated with 1% xanthan gum (e) showed the lowest dehydration and decomposition temperatures.

The DSC curves are depicted in Figure 4 and the main results are shown in Table 2. Each sample was prepared in a proportion 4:1 (water:starch, w/w) mixture and maintained for 60 minutes in order to equilibrate the moisture content, with the aim of verify the gelatinisation parameters. The gelatinisation enthalpy (ΔH<sub>gel</sub>) of the studied samples was calculated, as well as the “onset”, the “peak” and the “endset” or “conclusion” temperatures. As can be observed, the untreated cassava starch had the highest ΔH<sub>gel</sub> and it occurred with higher peak temperature (T<sub>p</sub> = 68.79 °C). The treatment with these hydrocolloids caused a small decrease in the gelatinisation and peak temperatures, as well as the difference between the onset and conclusion temperatures.

**Table 1** TG and DTG results of: (a) untreated cassava starch, (b) starch treated with carboxymethylcellulose, (c) starch treated with jatahy gum, (d) starch treated with pectin gum, (e) starch treated with xanthan gum.

Samples	TG Results			DTG Results		
	Step	$\Delta m/\%$	$\theta/^\circ\text{C}$	$T_p/^\circ\text{C}$	$T^*/^\circ\text{C}$	
(a)	1 <sup>st</sup>	10.63	30-193	-	71	
	stability	-	193-277	-	-	
	2 <sup>nd</sup>	75.52	277-429	344	-	
(b)	3 <sup>rd</sup>	13.53	429-561	-	516	
	1 <sup>st</sup>	9.40	30-185	-	71	
	stability	-	185-288	-	-	
(c)	2 <sup>nd</sup>	71.67	288-444	356	-	
	3 <sup>rd</sup>	18.35	444-580	516	-	
	1 <sup>st</sup>	9.37	30-193	-	66	
(d)	stability	-	193-306	-	-	
	2 <sup>nd</sup>	76.58	306-457	362	-	
	3 <sup>rd</sup>	13.35	457-624	-	556	
(e)	1 <sup>st</sup>	8.17	30-172	-	79	
	stability	-	172-297	-	-	
	2 <sup>nd</sup>	73.95	297-458	355	-	
(e)	3 <sup>rd</sup>	17.03	458-627	-	551	
	1 <sup>st</sup>	8.46	30-180	-	66	
	stability	-	180-264	-	-	
(e)	2 <sup>nd</sup>	68.68	264-425	348	-	
	3 <sup>rd</sup>	22.29	425-558	494	-	

(\*)  $\Delta m$  mass loss (%),  $\theta$  temperature range,  $T_p$  peak temperature,  $T^*$  minimum temperature of the endothermic event.



**Figure 4** DSC gelatinisation curves of (a) untreated cassava starch, (b) starch treated with carboxymethylcellulose, (c) starch treated with jatahy gum, (d) starch treated with pectin gum, (e) starch treated with xanthan gum.

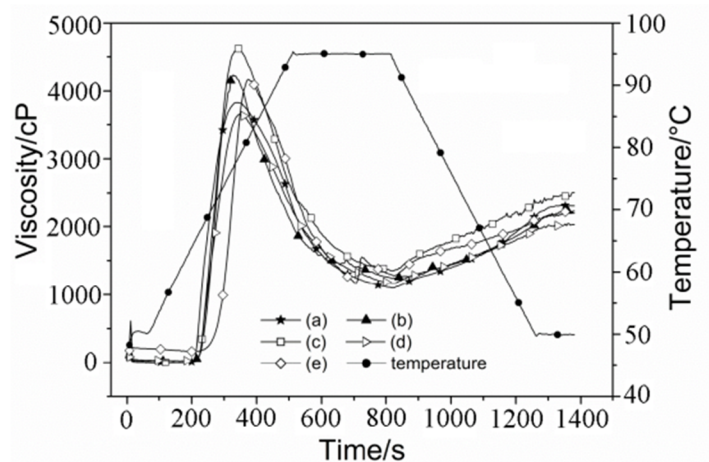
**Table 2** DSC gelatinization, NC-AFM and XRD of: (a) untreated cassava starch, (b) starch treated with carboxymethylcellulose, (c) starch treated with jatahy gum, (d) starch treated with pectin gum, (e) starch treated with xanthan gum

Samples	DSC gelatinisation				AFM		XRD
	$T_o/^\circ\text{C}$	$T_p/^\circ\text{C}$	$T_c/^\circ\text{C}$	$\Delta H_{gel}/\text{J}\cdot\text{g}^{-1}$	$d_a/\mu\text{m}$	$r_a/\mu\text{m}$	Degree of relative crystallinity
(a)	62.53±0.02 <sup>a</sup>	68.79±0.04 <sup>a</sup>	79.08±0.06 <sup>a</sup>	21.10±0.28 <sup>a</sup>	12.19±3.25 <sup>a</sup>	357.39	24.09±0.62 <sup>a</sup>
(b)	55.98±1.01 <sup>b</sup>	58.46±0.65 <sup>c</sup>	70.93±0.98 <sup>b</sup>	5.51±0.16 <sup>c</sup>	10.56±2.88 <sup>a</sup>	236.28	23.69±0.38 <sup>a</sup>
(c)	55.98±0.96 <sup>b</sup>	57.62±0.61 <sup>c</sup>	71.66±0.8 <sup>b</sup>	9.88±1.04 <sup>b</sup>	9.87±2.39 <sup>a</sup>	258.08	21.24±0.28 <sup>b</sup>
(d)	55.97±1.00 <sup>b</sup>	57.40±0.59 <sup>c</sup>	69.88±2.06 <sup>b</sup>	9.63±1.30 <sup>b</sup>	10.84±3.15 <sup>a</sup>	274.68	23.49±0.72 <sup>a</sup>
(e)	55.97±0.96 <sup>b</sup>	59.16±0.49 <sup>b</sup>	67.56±2.77 <sup>b</sup>	8.28±1.23 <sup>b</sup>	11.5±2.92 <sup>a</sup>	254.15	21.34±0.67 <sup>b</sup>

(\*)DSC:  $T_o$  "onset" or initial temperature,  $T_p$  peak temperature,  $T_c$  "endset" or final temperature,  $\Delta H_{gel}$  gelatinisation enthalpy; NC-AFM: ( $d_a$ ) Average diameter, ( $r_a$ ) Average roughness; XRD: the degree of relative crystallinity was calculated as percentage; peaks are determined in 2 $\theta$ .

All the treated samples with the gums demonstrated a widening in the gelatinization peaks and a reduction in the enthalpy values. The obtained results ( $T_o$ ,  $T_p$ ,  $T_c$  and  $\Delta H_{gel}$ ) are collected in Table 2.

The pasting temperature (RVA) for each studied sample was always around 64-65 °C. The highest viscosity peak was for the starch treated with jatahy gum (c), followed by starch treated with CMC (b), starch treated with xanthan gum (e), untreated starch (a) and finally, the starch treated with pectin gum (d). The highest final viscosity was observed in cassava starch treated with jatahy gum and the lowest was for the cassava starch treated with pectin.



**Figure 5** RVA curves: (a) cassava starch native, (b) starch with carboxymethylcellulose, (c) starch with jataí gum, (d) starch with pectin gum, (e) starch with xanthan gum.

Other authors (Xiaohong, BeMiller, 2002; Chaisawang, Suphantharika, 2006) have also observed that jatahy, CMC and xanthan gums cause an alterations in the viscosity peak, although using lower concentrations (0.4%) of the gums.



In this study was observed that the pectin gum at 1% with cassava starch caused a slight decrease in the viscosity when compared to the untreated cassava starch. In the literature (Rojas, Rossel, de Barber, 1999), the authors of a study of wheat flour with pectin at 0.5 and 1.0% also observed this characteristic. These authors observed that each hydrocolloid (guar, xanthan and pectin) affected pasting properties in a different way.

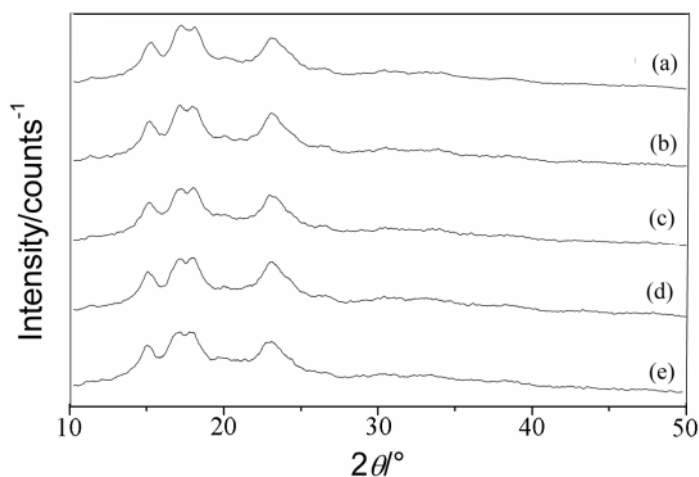
Babic et al. 2006, have stated that a hydrocolloid-starch mixture exerts a great effect on the rheological properties and that the extent of this variation is dependent on the concentration and type of the added hydrocolloid.

**Table 3** RVA results of: (a) untreated cassava starch, (b) starch treated with carboxymethylcellulose, (c) starch treated with jatahy gum, (d) starch treated with pectin gum, (e) starch treated with xanthan gum

Samples	Pasting temperature/°C	Viscosity peak/cP	Peak time/sec	Setback/cP	Break/cP	Final viscosity/cP
(a)	64.50±0.40 <sup>b</sup>	3830.00 ±1.40 <sup>d</sup>	338.00±2.80 <sup>cd</sup>	1208.50±7.80 <sup>a</sup>	2730.00±1.40 <sup>d</sup>	2303.50±0.70 <sub>b</sub>
(b)	65.30±0.30 <sup>ab</sup>	4231.00±4.20 <sup>b</sup>	330±2.80 <sup>d</sup>	960.50±3.50 <sup>c</sup>	2990.50±6.40 <sup>b</sup>	2203.00±8.50 <sub>c</sub>
(c)	65.80±0.20 <sup>ab</sup>	4621.50±4.90 <sup>a</sup>	342±2.80 <sup>bc</sup>	1152.00±5.70 <sup>b</sup>	3271.50±4.90 <sup>a</sup>	2504.50±2.10 <sub>a</sub>
(d)	65.60±0.10 <sup>ab</sup>	3653.50±0.70 <sup>c</sup>	350±2.80 <sup>b</sup>	861.50±3.50 <sup>d</sup>	2489.50±0.70 <sup>c</sup>	2029.00±1.40 <sub>d</sub>
(e)	67.10±1.00 <sup>a</sup>	4165.50±0.70 <sup>c</sup>	375±3.50 <sup>a</sup>	944.50±0.70 <sup>c</sup>	2882.50±0.70 <sup>c</sup>	2221.50±7.80 <sub>c</sub>

(<sup>c</sup>) cP “centipoises”, sec “seconds”.

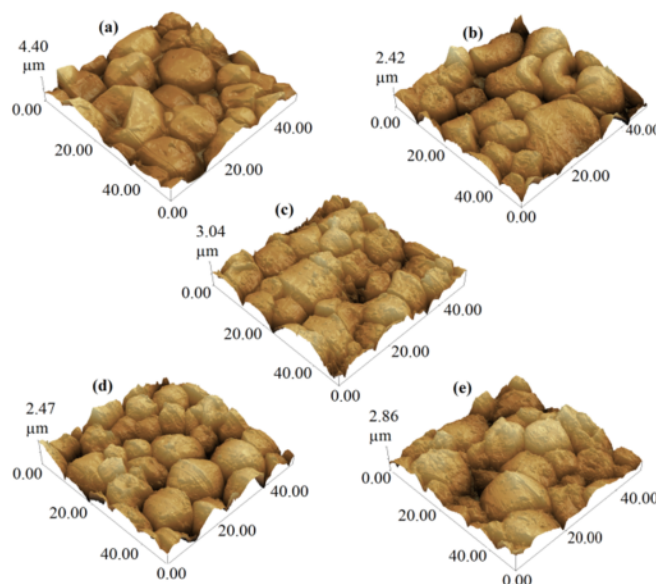
The relative crystallinity of the studied starches were calculated according to Equation 1 and demonstrated in Figure 1. As can be observed in Figure 6, no displacement occurred between the main peaks ( $2\theta = 15.00, 17.00, 17.75$  and  $22.90^\circ$ ) and the degree of relative crystallinity was around 21-24%. The results of relative crystallinity are gathered in Table 2



**Figure 6:** XRD diffractograms of (a) untreated cassava starch, (b) starch treated with carboxymethylcellulose, (c) starch treated with jatahy gum, (d) starch treated with pectin gum, (e) starch treated with xanthan gum.

When compared with the untreated starch, the degree of relative crystallinity was not severely affected by the treatment with the hydrocolloids; the highest decrease was for the starches treated with jatahy and xanthan gums.

The main results related to the viscosity behaviour of the cassava starch and the starches treated with gums are shown in Table 3.



**Figure 7** NC-AFM, 3D micro-images of: (a) untreated cassava starch, (b) starch treated with carboxymethylcellulose, (c) starch treated with jatahy gum, (d) starch treated with pectin gum, (e) starch treated with xanthan gum.

The atomic force microscopy by non-contact method (NC-AFM) technique was useful for viewing the shape and morphology of the granules, that present oval shape. On the surface of untreated and treated starches we can observed that it is relatively smooth with shallows depressions and furrows. It was possible to determine the average size and average roughness according literature (Juczak, Fortuna, Krok, 2008; Colman et al. 2012; Andrade et al. 2013; Oliveira et al. 2013), and the obtained results are summarised in Table 2.

**CONCLUSION**

The instrumental and analytical methods used in this work were important to establish some parameters that can serve to characterise starches for treatment according to industry requirements. The addition of hydrocolloids to cassava starch exerts a great effect on the gelatinisation of cassava starch, causing a broadening of the endothermic peaks ( $T_o$  and  $T_c$ ) with a decrease in the gelatinisation enthalpy ( $\Delta H_{gel}$ ). The pasting properties of the treated starches were characteristic and were influenced by the preparation methods; the differences were due to the characteristics of the gums. X-ray diffractometry and atomic force microscopy aided in the interpretation of the size and structure of the starch granules, which were not very pronounced.

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