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EFFECT OF BALL MILLING ON THERMAL, MORPHOLOGICAL AND STRUCTURAL PROPERTIES OF STARCHES FROM *Zingiber officinale* AND *Dioscorea sp*.

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ABSTRACT

Ginger and yam can be considered alternative sources of starch with specific properties, which can be modified through physical modifications, considered efficient and environmentally friendly. Thus, this study aimed to modify starches isolated from *Zingiber officinalle* and *Dioscorea* sp through ball milling at different times, verifying its effects on the thermal, morphological and structural properties. After milling treatment an increase in the thermal stability was observed for ginger and yam starches with the increase of milling time. A decrease in the gelatinisation parameters for two sources of the ball-milled starches was identified, which was related to the weakening of amylopectin chains and amylose depolymerisation. A decrease in the size of both starch granules was obtained, with the appearance of surface fissures. The degree of relative crystallinity decrease with the higher exposition to ball milling, reflecting in an amorphous state, although the diffraction pattern has not changed for both starches. Slight changes can be observed by Fourier transform infrared spectra due the damages caused by milling process.

1.Introduction

Starch is one of the most important and abundant carbohydrates available in nature, in addition, it presents low cost even after the extraction process. This natural biopolymer is composed of two polysaccharides: amylose considered a mostly linear macromolecule, and amylopectin, a highly ramified one. Starch represents an important input for industries in different sectors such as food, textile, pharmaceutical, among others. Due to the wide application, industries are looking not only for new process technologies, but also for new sources of starch with different properties that make its production feasible (Lawal et al., 2005; Vieira and Sarmento, 2008).

An alternative source of starch is from ginger, with a starch content around 13-18% according to Wang et al. (2008). Ginger is a plant belonging to the family of *Zingiberaceae*, originated in Asia and considered a popular spice used mainly in India for medicinal purposes. It can also be found in tropical and subtropical areas such as China, Indonesia and Nigeria (Madeneni et al. 2011; Sukhija, Singh and Ria, 2016; Li et al., 2016). Another source of starch of interest is from yam (*Dioscorea* sp.), which is a monocotyledonous herbaceous climbing plant. Around eight genera are known worldwide, with approximately 600 species, 95% belonging to the genus *Dioscorea* (Hornung et al, 2016). These tubers may have

different names depending on where they are grown. They are cultivated mainly in tropical and subtropical regions, and because of their easy handling they have become very consumed by millions of people in Africa, Asia and South America (Ramos et al., 2014; Zhu, 2015).

In addition to the search for new sources of starch, polysaccharides modifications are interesting, because in their native form, they can present some technological limitations. The main treatments applied on starch granules are: enzymatic, physical or chemical modifications, with the aim of obtaining starches with desirable and specific properties in order to meet a range of industrial applications (Park et al., 2009; Shima et al., 2015). Thus, several studies are carried out to investigate special starch characteristics obtained after these treatments. Although chemical modification has been widely applied in industry, physical modification regards to a market trend when used in natural products. It has potential to alter the functionality of starch at low cost in addition to being environmentally friendly (Zavareze and Dias, 2011).

Ball milling is a process that uses thermal and mechanical energy to modify the physicochemical properties of a material, presenting a high efficiency. Therefore, it has been largely used to grind minerals, foods, drugs, chemical products and construction material (Shi et al., 2015). In this type of treatment, the granular structure of the starch can be destroyed, with the formation of an amorphous material, with particles of smaller diameters (Sanguanpong et al., 2003). Consequently, the conformation of double helices is altered, promoting a decrease in relative crystallinity. Moreover, the fragmentation of the amylopectin chains improves the dilatation capacity, aiding the gelatinisation process (Alcázar-Alay and Meireles, 2015). Changes in the solubility, thermal and morphological properties, as well as in the digestion of starches can also occur (Moraes, Alves and Franco, 2013; He et al., 2014).

Therefore, this study aimed to modify starches isolated from ginger (*Zingiber officinalle*) and white yam (*Dioscorea* sp) through ball milling at different times (20, 30 and 40 min), verifying the results of this modification by thermal, morphological and structural analysis.

2. Materials and methods

2.1. Materials

Ball milling was used at Paulista State University Júlio de Mesquita Filho (Bauru, SP, BR). Extraction and instrumental analysis were made at Laboratories of Food Engineering Department and at Complex of Multi-Users Laboratory of State University of Ponta Grossa (UEPG).

2.2. Starch extraction

Starches were obtained from roots of ginger and yam according to the methodology describe by Costa et al. (2013).

2.3. Ball Milling modification

Starches from ginger (*Zingiber officinale*) and white yam (*Dioscorea* sp), were submitted to abrasive milling in a vibrating mill MM 400 (Retsch, Germany). The milling process was performed with the following parameters: sample mass about 0,6 g; milling time of 20, 30 and 40 minutes; and a milling frequency of 30 Hz. The stainless steel sample holder has a capacity of 10 mL, containing two balls of same material and diameter (5 mm), which remain in contact with the sample throughout the treatment.

The native and modified samples of ginger and white yam starches were coded as follows: (a) native ginger starch, and modified with ball milling during: 20 min (a1); 30 min (a2) and 40 min (a3); (b) native yam starch and modified with ball milling

during: 20 min (b1); 30 min (b2) and 40 min (b3).

2.4. Thermal analysis

2.4.1 Differential scanning calorimetry (DSC)

Each sample submitted to the DSC analysis was mixed with water (in the proportion of starch:water, 1:4) and kept at rest for 1 h for the granules swelling. The analysis was performed following the procedure described by Colman, Demiate and Schnitzler (2014).

The instrument used was the DSC Q200 (TA Instruments, USA). The equipment was previously calibrated with Indium standard, 99% purity, (m.p. = 156.6 ºC; ΔH = 28,56 J g^{-1}) The aim of this analysis was to obtain the gelatinisation parameters of the samples, then the following conditions were employed: sample mass of 2.5 ± 0,5 mg, heating rate of 10 °C min^{-1}, synthetic air atmosphere with a flow rate of 50 mL min^{-1}, with a temperature range from 30 to 100 °C. The results were analysed with the aid of the software Universal Analysis 2000.

2.4.2. Simultaneous Thermogravimetry and Differential thermal analysis (TG-DTA)

The TG-DTA curves were obtained according to the methodology described by Malucelli et al. (2015), using α-alumina crucibles for each sample (mass around 7 mg) in the equipment DTG-60 (Shimadzu, Japan), previously calibrated with calcium oxalate, using synthetic air atmosphere with flow rate of 100 mL min^{-1}. The heating rate was 10 °C min^{-1} in the range of 30 to 600 °C. The software used to obtain the results was TA-60 WS.

2.5. Morphological analysis

2.5.1. Field emission gun - Scanning electron microscopy (FEG-SEM)

The diameter and shape of the starch granules were verified using a field emission electronic microscope MIRA 3 (Tescan, Czech Republic), using the following parameters: the electrons beam tension was 15 kV in the field emission gun, generated by a lamp with tungsten filament. The samples were pulverised over a carbon tape, following by the metallisation process (120 s, 40 mA) with gold and palladium, to promote the passage of electrons, according to Bet et al. (2016).

2.5.2. Fourier Transform Infrared Spectroscopy (FTIR)

According to Ji et al. (2015), the conditions used for this analysis were: an average of 64 scans at 4 cm^{-1} of resolution, in the transmittance mode. The samples were prepared in a press, as pellets, consisting of 2 mg of sample in 100 mg of KBr. The wave number interval was 400 to 4000 cm^{-1}. It was used for this analysis the FT-IR 8400 (Shimadzu, Japan).

2.6. Structural analysis

2.6.1. X-ray powder diffractometry (XRD)

The samples were put in a glass support and analysed in the X-ray diffractometer Ultima 4 (Rigaku, Japan), exposed to CuKα radiation (λ = 1.542 Å), submitted to 40 kV and 30 mA, with scattered radiation detected from the angles of $5º \leq 2\theta \leq 50º$, with a scanning speed of 2° min^{-1} and a step of 0.02°. The diffractograms were treated in the software Origin 6.1 (OriginLab, USA), and the degree of relative crystallinity of the starches was calculated using the Equation 1 bellow (Colman, Demiate and Schnitzler, 2014):

$$Xc = \frac{Ap}{Ap+Ab} \times 100 \qquad (1)$$

Where: X_c = relative crystallinity; A_p = peak area; A_b = basis area which refers to amorphous area of diffractograms.

2.7. Statistical analysis

All the analysis were made in triplicate, except otherwise stated, such as the TG-DTA, which was made in duplicate. The results were denoted in average ± standard deviation. Due the small numbers of repetition (n=3), the normality of the samples were assumed. The Brown-Forsythe's test was realized to verify the homoscedasticity of the variances (α = 95%). When observed homoscedastic variances, the results were compared using One-Way ANOVA, with α = 95%, in order to verify significant differences. Then, Tukey's HSD post-hoc test (α = 95%) was realized in order to elucidate where the differences occurred. The inferential statistics was realized using the software Statistica 13.2 (Dell, USA).

3.Results and discussions

3.1. Thermoanalytical techniques

3.1.1.Differential scanning calorimetry

It was noted (Figure 1) that the endothermic event readily identified for native ginger and white starch samples (samples ‘a’ and ‘b’) became always lower for starches after ball milling.

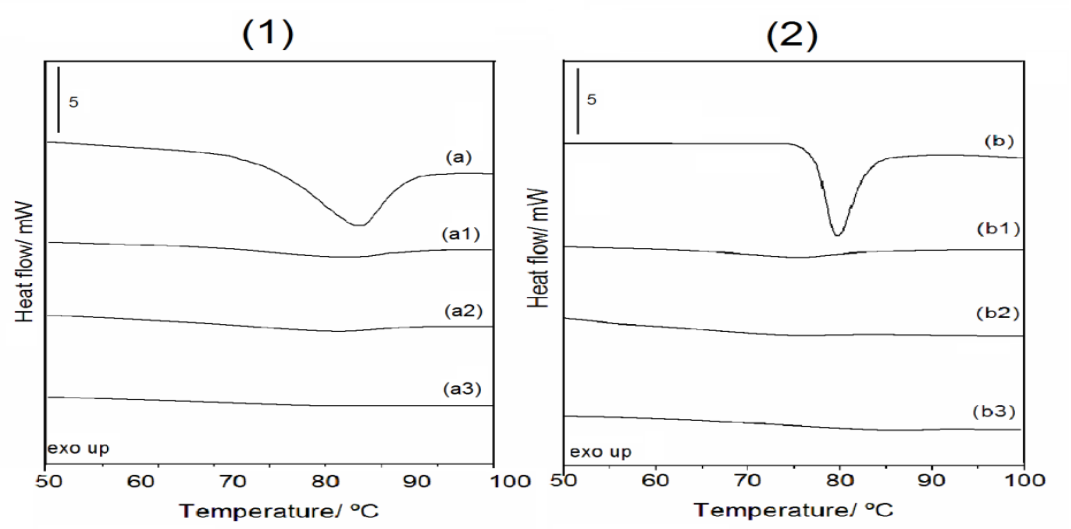

Figure 1. Differential scanning calorimetry curves of the native and modified starches from ginger (1) and white yam (2).

Ball milling compromises the crystalline structure of the starch, in an effect known as mechanical activation, associated with the friction, collision or shear, for example. During this modification, the temperature may also increase due to the frictional forces between the starch granules or between the small steel balls and the granules (Shi et al., 2015).

Thus, ball milling may cause damage to the granules, especially in the amylopectin chains, as well as observed by XRD, making gelatinisation difficult or shifting the thermal event, as identified for yam and ginger starch in the three times of treatment.

Moraes, Alves and Franco (2013) also reported broader endothermic peaks after the ball milling process, which were attributed to greater heterogeneity of the crystals. Therefore, the gelatinisation temperature range may vary according to the heterogeneity of the crystals. The transitions temperatures and gelatinisation enthalpy for all the samples can be identified in Table 1:

Table 1. Results of the differential scanning calorimetry (DSC)

Sample		DSC gelatinisation results			
	T_o (ºC)	T_p (ºC)	T_c (ºC)	$T_c - T_o$ (ºC)	ΔH_{gel} (J g^{-1})
(a)	80.01 ± 0.05^a	87.73 ± 0.21^c	92.01 ± 0.16^a	12.00	15.15 ± 0.39^a
(a1)	80.37 ± 0.14^a	87.08 ± 0.26^b	89.80 ± 0.73^b	9.44	1.56 ± 0.20^b
(a2)	77.38 ± 1.02^b	85.97 ± 0.26^a	90.99 ± 0.44^{ab}	13.61	1.43 ± 0.38^b
(a3)	80.68 ± 0.75^a	84.43 ± 0.24^a	88.03 ± 0.34^c	7.34	0.15 ± 0.02^c
(b)	72.39 ± 0.22^b	75.71 ± 0.12^a	79.55 ± 0.12^c	7.16	15.13 ± 0.15^a
(b1)	66.78 ± 0.14^c	75.43 ± 0.25^a	81.10 ± 1.02^b	14.32	2.27 ± 0.15^b
(b2)	64.66 ± 0.92^d	73.77 ± 0.73^b	76.06 ± 0.28^d	11.40	0.98 ± 0.10^c
(b3)	76.58 ± 0.43^a	74.90 ± 0.51^c	87.50 ± 0.50^a	10.92	0.51 ± 0.12^c

(*) To inicial temperature, Tp peak temperature, Tc conclusion temperature, ΔHgel gelatinization enthalpy. Values that have the same letter, from the same sample type, don't present significative difference by Tukey's Test ($p<0.05$).

The gelatinisation enthalpies of the modified samples of ginger and yam were intensely decreased, as the milling time increased, as related by Loubes and Tolaba (2014). This suggests that the starches may have undergone pregelatinisation. Cavallini and Franco (2010) explain that ball milling can induce a partial gelatinisation, with similar results to that caused by heating. Pregelatinised starches are formed of damaged granules, soluble in room-temperature water, and with a crystalline disorder, because during this process can occur the depolymerisation or fragmentation of starch molecules (BeMiller and Huber, 2015). In addition, this modification can break down the double helices of amylopectin, due to the rupture of the hidrogen bonds, which stabilise the molecules in the starch granule contributing to the decrease of the enhtalpy (Tester, Karkalas and Qi, 2004).

Shi et al. (2015) also verified a decrease in the gelatinisation enthalpy of maize starch, and the onset temperature was shifted to higher temperature. This was related to the destruction of the crystallinity portion of the granules, implying a weaker expansion capacity of the granules during gelatinisation.

Besides of the enthalpy, the gelatinisation temperatures of the two starch sources also showed a tendency to decrease after the milling treatment as well as identified for cassava starches (Huang et al., 2006), which indicates that the amylose chains were affected too. The amylose depolymerisation and amylopectin degradation by breakage of intermolecular bonds can occur in starches exposed to ball-milling, favouring the appearance of disordered amorphous regions which are easily accessible to water, allowing the gelatinisation at lower temperatures (Liu et al., 2017; Martínez-Bustos et al., 2007; Kim and Kim, 2014).

Loubes and Tolaba (2014) observed an increase in the water absorption capacity, dilatation and solubility of the ball-milled rice flour, and reported that the rate and the time of milling had a negative effect on the temperatures and enthalpy of gelatinisation.

Due to the decrease of crystallinity and the new chain arrangements acquired by the starches exposed to the mechanical forces, as well as the partial gelatinisation of these polysaccharides, Liu et al. (2011) have suggested the use of these as stabilizers, adsorbents, food additives and moisture retention agents.

3.1.2. Simultaneous Thermogravimetry and Differential Thermal Analysis (TG-DTA)

The TG-DTA curves are exposed in Figure 2, for ginger and yam starches. According to Ionashiro, Caires and Gomes (2015), Thermogravimetry (TG) shows the mass loss of sample and differential thermal analysis (DTA) can monitor the heat effects associated with physicochemical changes in the sample. Phase transitions, dehydrations, and reductions produce endothermic effects, whereas crystallisations, oxidations and some decomposition reactions produce exothermic effects.

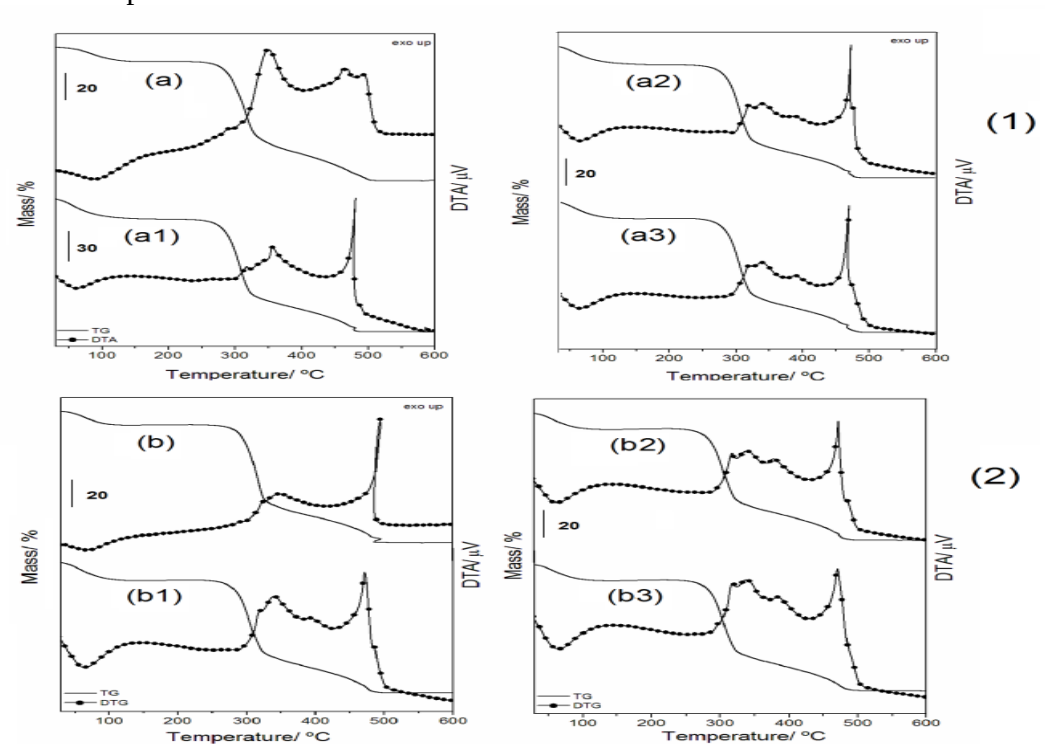

Figure 2. TG-DTA curves of the native and modified starches from ginger (1) and white yam (2).

It was noted that the thermal decomposition of the samples occurred in three consecutive mass losses, where the first one was related to sample dehydration, comprising temperatures between 30 – 157 ºC for ginger starches, and 30-140 ºC for white yam starch samples. A stability plateau can be observed after water loss, which increased after milling process. The white yam starch that remained in the ball mill for 40 min presented a higher stability in relation to the native sample, with increased of 11 ºC, and for ginger starch, after 20 min of milling, the stability increased 8 ºC.

The second step referred to the decomposition of the organic matter of the samples, occurring between 247-375 ºC for the samples of ginger starch and between 245-372 ºC for the white yam starch samples.

At temperatures above 300 ºC the starch depolymerisation occurs, and in oxygen atmosphere this decomposition is exothermic (Cordoba, Bet and Schnitzler, 2015). According to Aggarwall et al. (1997) in some cases, the breakdown of amylopectin binds contributes to the decomposition of starch granules at high temperatures.

The third mass loss was attributed to the oxidation of organic matter occurring

between 338-512 ºC and 341-519 ºC for ginger and white yam starch samples, respectively.

The ash content of each sample was: (a) 0.4; (a1) 0.7; (a2) 0.5; (a3) 0.5; (b) 0.8; (b1) 0.7; (b2) 0.2; (b3) 0.2 %, respactively.

Table 2. Results of the thermogravimetry-differential thermal analysis for the untreated (a) and modified starches from ginger (a1, a2 and a3); and untreated white yam (b) and modified white yam (b1, b2 and b3).

	Steps	**TG Results**		**DTA results**
		Δ_m(%)	ΔT (ºC)	T_p (ºC)
a	1st	10.9	30-149	87.58
	Stb.	-	149-247	-
	2nd	67.5	247-375	350.2
	3rd	21.2	375-512	460.4
a1	1st	13.3	30-157	61.9
	Stb.	-	157-249	-
	2nd	62.2	249-357	239.7
	3rd	23.8	357-506	480.9
a2	1st	14.1	30-145	62.3
	Stb.	-	145-255	-
	2nd	60.9	255-339	290.7
	3rd	24.5	339-508	470.2
a3	1st	12.8	30-131	62.7
	Stb.	-	131-247	-
	2nd	60.8	247-338	240.1
	3rd	25.9	338-512	468.4
b	1st	11.6	30-135	67.5
	Stb.	-	135-245	-
	2nd	65.5	245-372	347.3
	3rd	22.1	372-519	493.9
b1	1st	13.9	30-136	64.2
	Stb.	-	136-252	-
	2nd	59.6	252-341	276.2
	3rd	25.8	341-517	471.4
b2	1st	12.5	30-140	62.3
	Stb.	-	140-254	-
	2nd	62.7	254-341	275.6
	3rd	24.6	341-524	472.4
b3	1st	12.1	30-137	64.82
	Stb.	-	137-256	-
	2nd	61.6	256-341	252.9
	3rd	26.1	341-511	470.8

Δm, mass loss (%); ΔT, temperature range (°C); Tp, peak temperature (°C), Stb., stability.

3.2. Morphological results

The micro-images of the native and grinded granules of ginger and yam starches are shown in Figure 3. Native ginger starch presented oval shape with some spherical granules, without evidence of cracks, as also obtained by Zhang et al. (2012). Native yam starch granules exhibited an oval shape with some triangular granules and a smooth surface, as reported by Hornung et al. (2017).

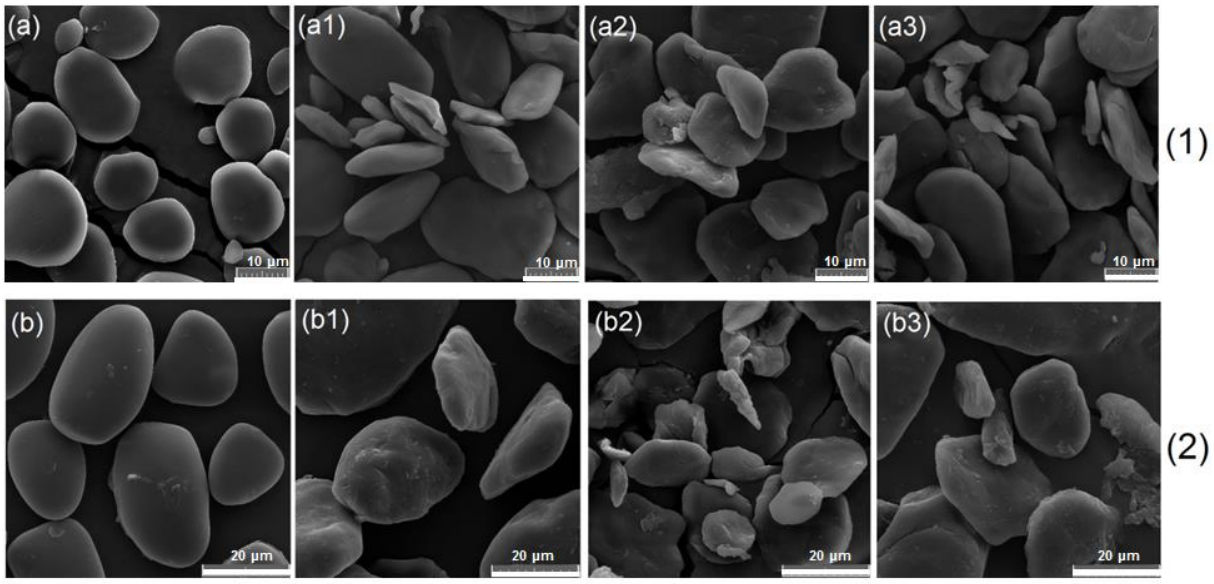

Figure 3. Micro-images of: (1) native and modified ginger starch granules, and (2) native and modified white yam starch granules.

According to Diop et al. (2012), during the milling process the starch granules are peeled layer by layer, transforming into anomalous and small granules. There was a physical degradation in the grinded starches, which were losing their shape as the milling time increased. These deformations can be caused by the friction between the starch granules, water molecules, milling balls and the wall of the cylinder, resulting in the production of heat, which, in addition to mechanical energy, contributed to change the shape and the properties of the starch (Martínez-Bustos et al., 2007).

Ball-milling process can cause cracks on the surface of the granules, which favour the passage of water, leading to the formation of fragments that can swell in cold water. Any starch subjected to the milling may contain damaged and fragmented granules (BeMiller and Huber, 2015).

The cracks that appear after the modification facilitate the diffusion and increase the susceptibility to hydrolysis, since the fragments present a larger surface area, as discussed by He et al. (2014).

Liu et al (2011) identified that after 1 h of milling, the surface of the corn starch granules became rough, losing smoothness and flatness. They observed grooves, cracks and a few small fragments of granules with 2 h of treatment, maintaining the integrity in the granule periphery. And finally, after 3 h of milling, the granules were divided into smaller pieces and agglomerates. In the present study it were not identified agglomerates, maybe due the lower milling time employed.

Su et al. (2016) observed after 6 h of milling, the appearance of rough and exfoliated surfaces, due to the removal of small pieces of the external layer of corn starch granules, by the action of the pressure and friction of the balls

The average lengths (Table 3) of the ball-milled granules decreased compared to the

native starches, as observed by Ren et al. (2010) for cassava starch. In this treatment, starch granules are subjected to various forces such as compression, impact and shear, which contributes to damage and decrease the size of the granules (Huang et al., 2007).

For the ginger starch, the average size of the granules decreased proportional to the time spent on the ball mill. The same happened with the white yam starch, except after 40 min.

3.3. Structural parameters

3.3.1. Powder diffraction and relative crystallinity

The X-ray diffractograms of the native and modified ginger and white yam starches are shown in Figure 4. It was identified an A-type diffraction pattern for native ginger starch as reported by Zhang et al (2009) for yellow ginger starch. And the native white yam starch was classified as B-type diffraction pattern, as also obtained by Hornung et al (2016).

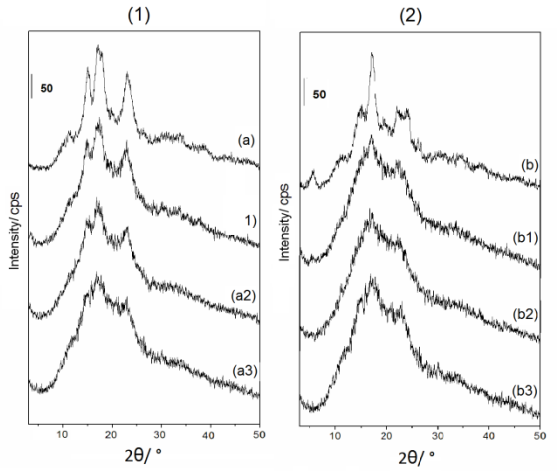

Figure 4: X-ray diffractograms of: (1) native and modified ginger starch granules, and (2) native and modified white yam starch granules.

Greater exposure of the granules to the grinding caused a decrease in the intensity of each peak and in the relative crystallinity of the samples (Table 3), as discussed by Anzai et al. (2011). Shi et al. (2015), found that ball-milled corn starch maintained A-type pattern, but had a drastically decrease in its crystallinity.

Ground samples lose their crystalline structure due to the high energies and mechanical force employed during ball milling. As the amorphous regions tend to increase, the degree of relative crystallinity decreases, since a change occurs in the amylopectin and amylose arrangements (Roa et al., 2014).

Table 3. Results of relative crystallinity by XRD and average length of the starch granules, by SEM.

Samples	Relative crystallinity (%)	Average length (µm)
a	30.09 ± 0.87^{a}	20.47 ± 1.13^{a}
a1	23.18 ± 0.44^{b}	14.12 ± 0.97^{b}
a2	20.08 ± 0.68^{c}	13.68 ± 1.15^{bc}
a3	19.50 ± 0.58^{c}	11.99 ± 0.75^{c}
b	27.91 ± 0.90^{a}	30.01 ± 2.49^{a}
b1	17.54 ± 0.22^{b}	15.29 ± 1.04^{c}
b2	13.31 ± 0.28^{c}	10.55 ± 1.20^{d}
b3	13.69 ± 0.40^{c}	18.32 ± 0.69^{b}

(*) Values that have the same letter, from the same sample type, don't present significant difference by Tukey's Test ($p<0,05$).

Starch is considered a semi-crystalline polymer due to lateral branching of amylopectin, which forms a double helix structure. However the hydrogen bonds which maintain stable this structure can be broken during grinding, exposing the hydroxyls and giving a more amorphous character (Anzai et al., 2011). It is probable

that this occurred in this study, observing the fall in the relative crystallinity, associated with the decrease in the gelatinisation enthalpy, evidenced by DSC.

Roa et al. (2014) studied an enriched fraction of amaranth starch (*Amaranthus cruentus*) modified with ball mill and observed the destruction of the ordered structure of the starch, proportional to the degree of energy used. There was a decrease in crystallinity with increasing amorphous regions. As a consequence, a higher capacity of water absorption and cold solubility of the flour was obtained.

3.3.2. Fourier Transform Infrared Spectroscopy (FT-IR)

Figures 5 and 6 show the Fourier transformed infrared spectra of ginger and yam starches, respectively.

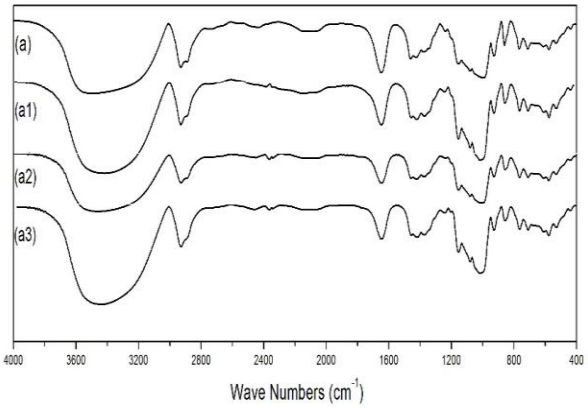

Figure 5. Fourier transformed infrared spectra for native and modified ginger starch granules.

Bands commonly observed in starch spectra correspond to the wavenumbers of 850, 996, 1014, 1039, 1145 and 1075 cm^{-1}. They are related to bending and stretching of C-O-C groups and C-O, C-O-H of the glycosidic bonds, according to Roa et al., (2014). In this study, these bands can be visualised in the spectra of ginger and yam starches, which underwent slightly changes caused by ball milling treatment, as observed for ball-milled maize starch (Liu et al., 2011).

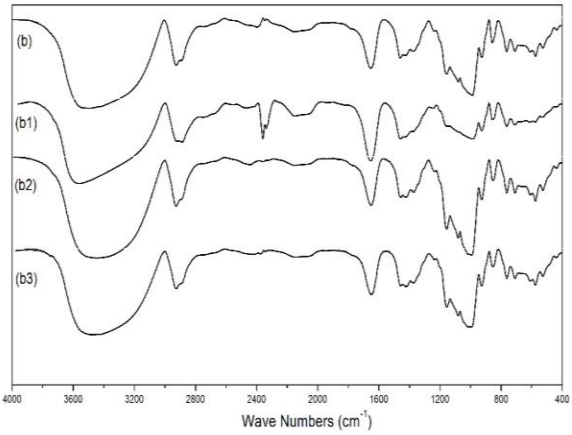

Figure 6. Fourier transformed infrared spectra for native and modified white yam starch granules.

Changes in the starch bonds are expected after treatment with ball mill, as it may cause the depolymerisation of the starch chains, reorganizing its structure (He et al., 2014).

The band at 3500 cm^{-1} was attributed to the stretching vibration of OH- molecules (complex stretching vibration associated with free intra- and inter-molecular bound hydroxyl groups), and the band closest to 3000 cm^{-1} was related to C-H bond stretching (Chang et al., 2014).

The band at 2400 cm^{-1}, observed in the spectra of b1 sample was attributed to the stretching of CO_2 molecule, associated in the preparation of the sample pellet.

Bands at 1480 cm^{-1} were related to stretching vibration of C-N bond (Wang and Xie, 2010). This band may point to a presence of proteins in the ginger and yam starches.

4. Conclusions

From the study of ball milling applied to ginger and white yam starches, it was possible to observe changes on the thermal, morphological and structural properties of the granules.

The gelatinisation enthalpy and transition temperatures of the modified samples, both ginger and white yam, suffered a decrease compared with the native starches, mainly at higher milling times.

By differential thermal analysis it was observed three mass losses. For the ginger starch, it was identified that the ball-milled samples for 20 and 40 minutes had an increase in their stability period. As for the white yam starch, it was observed that the stability period of the modified samples increased in proportion to the exposition time in the ball milling process.

It was observed a substantial change in the samples morphology. The granules lost their surface smoothness, had a decrease in the size and showed fissures and roughness after the modification.

The relative crystallinity of the ground starches decreased with the increase of the milling time.

Slight changes occurred in the infrared spectra, especially in bands smaller than 1000 cm^{-1}, corresponding to the glycosidic bonds.

It was concluded, therefore, that the time utilised on this paper was enough to modify the studied starches. Also, 20 minutes modification caused as much alteration on the starches properties as the 40 minutes one, possibility a save in time and energy.

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