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Spray-drying and extrusion processes: Effects on morphology and physicochemical characteristics of starches isolated from Peruvian carrot and cassava

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ABSTRACT

The Peruvian carrot and cassava starches were processed by spray-drying and extrusion processes. The amylose content, molecular weight of amylopectin, morphology, granule size, crystalline fraction, and thermal and pasting properties were investigated and compared with those native starches. The spray-dried starches showed reduction on molecular weight of amylopectin and reduction on crystallinity. This process caused change in surface granules as folds and wrinkles, and consequence reducing in granule size, when compared to native starch. There were partial gelatinization of spray-dried starches, with the development of viscosity at room temperature. The Peruvian carrot starch was most susceptible by spray-drying process. Extruded starch showed great reduction on molecular weight and complete degradation on crystalline fraction. The surface morphology of these starches showed a melting mass, due to the fully gelatinization. With these unique properties induced by both processes, the possibilities of industrial applications of these starches are significantly increased.

1. Introduction

Starch applications are dependent on their physical and chemical properties, environmental and agronomic factors, as well as the variations in properties across diverse cultivars [1]. Starch is biodegradable, derived from renewable sources, and is relatively cheap, because of the factors it could be used in food, chemical, textile, papermaking, medicine and other industries. Native starch granules are insoluble at room temperature and their application in industrial processes are limited due to their quick loss of viscosity, and therefore, their tendency to produce thin, elastic, and cohesive pastes. To overcome such drawback, physical, chemical, and enzymatic processes can be used to modify starch properties [2]. These methods could improve the functional properties of native starches and thereby, contribute to increasing their use in many industries sectors.

Pregelatinized starches can be divided in two groups: fully and partially gelatinized starches. Fully gelatinized starches can be used in pharmaceutical formulations and as main ingredients, bulking agents, or thickening agents for many food and non-food products. Partially gelatinized starches present a mixture of properties inherent to both native and fully gelatinized starches [3–6]. In many cases, the use of pregelatinized starch instead of native starch allows for simplified and shortened production processes. Pregelatinized starch can be produced by heating a starch suspension at a certain temperature for a specific time, before applying spray- or drum-drying, and it can also be obtained through extrusion process.

The spray-drying has being used as a common technique in starch products due to its low cost and available equipment [7]. Spray-drying is a rapid drying process, which converts a dispersion in amorphous particles or suspension in semi-amorphous particles, respectively. Pregelatinized starch has been produced by spray-drying for decades, without losing the granular integrity [8–10]. Moreover, spray-drying produces uniformly cooked or gelatinized starch granules with minimal shear and heat damage [11]. The spray-drying process can disrupt the ordered starch structure, producing an amorphous starch. The process is intense, as high-pressure can affect the granule integrity more severely [10].

Extrusion process, the starch is subject at high temperatures and mechanical shear at relatively low moisture [12]. This process can

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cause the breaking of covalent bonds between the components of the starch, causing the loss of the integrity of its granules and also a partial depolymerization of its components. This intense structural destruction facilitates the modification of the functional properties of the starch.

Peruvian carrot (*Arracacia xanthorrhiza*) is a crop grown on a large scale in South America. The high starch content of this root, which ranges between 20 and 25% (wet basis), and the relatively high agronomic yields achieved under low technology field conditions [13] make it suitable as a potential starch source for large scale uses [14, 15]. The characteristics of Peruvian carrot starch include low amylose content and gelatinization temperature, and low levels of setback and syneresis. It forms a clear paste with a high viscosity, and the ease of digestibility makes it useful in many food products. It has frangible granules, probably due to a weak crystalline structure [16]. The Peruvian carrot starch is crystallographically classified a B-type polymorphic starch, containing amylopectin chains with high degree of polymerization [17, 18]. Therefore, it is less thermodynamically stable it compared with A-type polymorphic starches.

Cassava (*Manihot esculenta*) is globally one of the main sources of starch and has low production costs. The world production of cassava was 268 million tons in 2014, with the highest production levels in Africa [19]. According to the International Starch Institute [20], the world production of starch has grown at an average rate of 4% per year. Cassava starch is increasing its market share and commands about 7.5% of the global starch market. Cassava starch is characterized by high hot viscosity, low setback, a clear and high transparent paste, and light flavor [21]. Due to global production and some characteristics cited, this starch was suitable for comparisons in this study.

Spray-drying and extrusion cooking processes may be applied as an alternative modification to improve the properties of native starches without the use of chemical reagents, and may also increase their value compared to that of native starches. The effect of extrusion [2, 5, 6, 11, 22–30] and spray-drying [7, 9–11, 30, 31] processes on starches of different sources has been investigated. However, the effect of spray-drying on tuberous starches has yet to be elucidated. From an industrial point of view, it is important to understand the changes in tuberous starch properties during the processes in order to improve the functional properties of cassava and Peruvian carrot starches, increase the production, and improve the processing of tuberous crops.

This study aimed to investigate the effect of the spray-drying process on the morphology and physicochemical characteristics of Peruvian carrot starch, and to compare its properties to those of cassava starch. We also aimed to compare the effects of the extrusion cooking process. The extrusion cooking process was considered, as it is already well known for the production of pregelatinized starch, and the hypothesis is that applying the spray-drying process to tuberous starches could improve the use of these starches in the food industry, because of its development of viscosity at low temperature. This study is of significance, since there is a growing interest in processed starches for industrial applications and in new sources of starch with potential for use in industry as partially or fully gelatinized starches.

2. Material and methods

2.1. Materials

Peruvian carrot (*Arracacia xanthorrhiza*) plants were cultivated in Experimental Farm of CERAT/UNESP, located in São Manuel city, São Paulo state, Brazil. The plants of Peruvian carrot, cultivar Amarela de Senador Amaral, grown in agreement with the technical recommendations for the culture and it were harvested after 9 months of the planting. This cultivar shows a dark green color in the foliage and green in the veins and in the insertion of the petiole, and an intense yellow color in the roots. The plants have 5 to 7 commercial roots per plant, and the roots have average length of 15 to 20 cm. The average productivity of this cultivar is 25 t ha^{-1} [32].

The plants of cassava (*Manihot esculenta*), cultivar IAC 90, were cultivated in according to the technical recommendations for the crop and harvested after 22 months of planting. The cassava IAC 90 is resistant to bacteriosis and it has roots with high dry matter content. This cultivar has productive stability in different environments being cultivated on a large scale in the Brazilian states of São Paulo, Paraná and Mato Grosso do Sul [33].

2.2. Starch isolation

Peruvian carrot starch was extracted following the methodology described by Santos, Leonel, Garcia, Carmo, and Franco [34], 24 h after harvesting. The extraction was performed in the CERAT laboratory. Roots were washed and peeled, then disintegrated in an industrial blender with water (5 °C). The material obtained was washed on the sieves (0.170 mm screen and 0.200 mm screen). The filtrate was left overnight for decantation, at 5 °C. The starch was washed three times, and cleaned starch was dried at 40 °C in an air circulation oven.

Cassava starch was extracted in the Flor de Lotus industry, located in Cândido Mota city, São Paulo state, Brazil.

2.3. Starch processes

Cassava and Peruvian carrot starches were processed by spray-drying and extrusion and the processes were repeated four times for each starch.

The spray-drying process followed the methodology of Fu et al. [10] with some modifications. Dispersions of 8% starch (w/w) were prepared. The suspensions were stirred in a thermostatic water bath at 57 °C for 10 min, and beakers containing the starch dispersions were covered with plastic films to minimize water evaporation. The hot dispersions of starch were then spray-dried (Spray-dryer, MSD 0.5 model, LABMAQ, São Paulo, Brazil) with a double-atomizer nozzle, with 0.7 mm diameter of the nozzle hole. The outlet temperature was 105 °C and the feed rate was 0.5 L h^{-1}. The flow of compressed air and hot air were 0.40 L min^{-1} and 3.8 m^3 min^{-1}, respectively, by compressed air pressure of 6 bar.

The extrusion process was carried out in a single-screw extruder using a complete line of INBRA RX 50, (Inbramaq, Brazil), which has a motor coupled with a speed reducer (extrusion by mechanical friction), with 130 mm barrel diameter and 440 mm extruder length, a hydraulic cooling system for temperature control, variable speed, and 50 kg h^{-1} capacity. The extrusion process parameters were: extrusion temperature in the 1st (20 to 25 °C), 2nd (40 to 45 °C), and 3rd (70 to 75 °C) zones; screw compression ratio (3:1); screw diameter (32.6 mm); die diameter (4 mm); feed rate (150 g min^{-1}), and cutting speed (90 rpm). The initial moisture of the starches was 20%.

2.4. Amylose and amylopectin

The determination of the amylose content was performed following the protocol of Kasemsuwan, Jane, Schnable, Stinard, and Robertson [35]. Prior to performing this, the starch samples were defatted with methanol (85%, v/v). The iodine affinity was determined using a potentiometric autotitrator (702 SM Titrino, Brinkmann Instrument, Westburn, NY, USA). The amylose count was calculated by dividing the value for iodine affinity by 20% [36].

The molecular weight (M_w) and gyration z-average radius (R_z) of amylopectin were assessed by high performance size exclusion chromatography with multi-angle laser light scattering and refractive index detectors (HPSEC-MALLS-RI), as reported by Yoo and Jane [37]. The HPSEC system included a HP 1050 isocratic pump (Hewlett Packard, Valley Forge, Pennsylvania, PA) with a Rheodyne injection valve (Model 7125, 100 μL sample loop), a multi-angle laser light scattering detector (Dawn DSP-F, Wyatt Technology Corp., Santa Barbara, California, USA) with a He-Ne laser source (632.8 nm), a K-5 flow cell, and a HP 1047A

RI detector (Hewlett Packard, Valley Forge, PA, USA). Amylopectin was separated from amylose by employing a Shodex OH pak KB-G guard column and KB-806 and KB-804 analytical columns (Showa Denko K.K., Tokyo, Japan). The filtered (0.22 μm) distilled-deionized water was used as effluent, it was degassed with helium gas for 30 min, and the flow rate was 0.6 mL min^{-1}. The temperature of injector and columns was kept at 50 °C using a CH-460 column heater and a TC-50 controller (Eppendorf, Madison, WI). The RI detector operated at 30 °C. The hot sample was filtered through a 5.0 μm nylon membrane and inject into a HPSEC system (100 μL) at a rate of 0.4 mg mL^{-1}. The results were interpreted using ASTRA software (version 4.7.07, Wyatt Technology Corporation, Santa Barbara, California, USA) according to Yoo and Jane [37].

2.5. Starch crystallinity

To analyze X-ray diffraction patterns and relative crystallinities, starches samples were incubated in a desiccator for 10 days with a saturated solution of $BaCl_2$ (Barium chloride, 25 °C, $a_w = 0.9$) in order to reach humidity equilibrium (90%). X-ray patterns were examined using a goniometer unit (RINT2000, Rigaku MiniFlex 300, Rotaflex, Tokyo, Japan), with copper K_α radiation ($\lambda = 0.1542$ nm). The scanning speed was 1° min^{-1} at 50 kV and 100 mA [34]. The relative crystallinity was calculated based on the relationship between the peak and total areas, using Origin software (v.7.5, Microcal Inc., Northampton, Massachusetts, USA) [38].

2.6. Morphology of starches

The granule morphology of native, spray-dried, and extruded starches was evaluated using Scanning electron microscopy (SEM) (Tecnai Spirit, Fey Company, Hillsboro, Oregon, USA). Starches samples were previously dehydrated in ethanol, and then were applied to an aluminum stub with double-sided tape, and the starches were coated with layer of gold (20 nm).

The average granule sizes of starches samples were determined using the laser light diffraction technique with a He-Ne laser (Mastersizer 2000, Malvern Instruments Ltd., Worcestershire, UK). Anhydrous ethanol was used as the solvent. The refractive indexes of the starch samples and the solvent were 1.500 and 1.360, respectively. Average granule sizes of the particles were obtained using the software provided by the manufacturer, and expressed as volume mean diameters (D [3, 4], μm) [39].

2.7. Thermal properties

Spray-dried starches samples (2.5 mg, dry basis) were evaluated using a differential scanning calorimeter (DSC, Pyris 1, Perkin Elmer, Norwalk, CT, USA), used distilled water (7.5 μL). The sealed pans were kept at room temperature for 2–3 h to equilibrate. The scanning temperature range was 25 to 100 °C and the heating rate was 10 °C min^{-1}, respectively [34].

2.8. Pasting properties

Samples were analyzed using a Rapid Visco Analyzer (RVA Super 4, Newport Scientific, Warriewood, New South Wales, AU). Starch samples (2.5 g, 14% w/w) were weighted, and 25 g of distilled water was added. Samples were analyzed using the *Extrusion 1* program. The samples were equilibrated at 25 °C for 1 min, heated to 95 °C at a rate of 6 °C min^{-1}, held at 95 °C for 5 min and then cooled down to 25 °C at a rate of 6 °C min^{-1}, while stirring at 160 rpm was applied throughout the whole experiment.

2.9. Statistical analysis

Data were analyzed using SAS statistical software. The analysis of variance was performed followed by the Tukey multiple comparison test ($p < 0.05$). All measurements were performed in triplicate and data are presented as mean ± standard deviation. Statistical analysis was carried out considering, separately, process and starch source, due to the fact that the selected starches and kind of process have contrasting properties.

3. Results and discussion

3.1. Starch components and crystallinity

The amylose content in native starches was 21.8% and 18.1% for cassava and Peruvian carrot, respectively (Table 1). The amylose content observed in cassava starch is in agreement with the variation observed in 4050 varieties of cassava genotypes from a worldwide collection (15.2 to 26.5%) [40]. Rocha et al. [16] and Moraes et al. [41] reported values ranging from 15.6 to 21.7% for starches from two varieties of Peruvian carrot.

Analysis of the amylose contents of the spray-dried and extruded starches showed that these starches had lower amylose contents than native starches (Table 1). The characteristics of the spray-drying process could result in a greater molecular entanglement between amylose and other molecules, reducing iodine alignment in the helical structure of the amylose [31]. Furthermore, extrusion may promote molecular degradation, resulting in shorter amylose molecules with reduced iodine binding capacity, thereby interfering in the quantification of the amylose content in the starch [42].

Results of the molecular weight (M_w) analysis of the starches showed that cassava amylopectin displayed a higher molecular weight than its Peruvian carrot counterpart (Table 1). Results for M_w and gyration radius (R_z) analysis of amylopectin in cassava starch were very close to those reported for this starch by Demiate et al. [43], who observed M_w of 4.7×10^8 and R_z of 295 nm. A minor reduction in the M_w of amylopectin was observed after spray-drying. Significant reduction, however, was observed with extruded starch, as expected. The changes caused by shear forces and temperature in the extrusion process decreased the M_w and R_z of amylopectin.

Table 1
Amylose content, molecular weight (M_w) and gyration radius (R_z) of amylopectin, and relative crystallinity of starches.

Starchess	Amylose (%)	$M_w \times 10^8$ (g mol^{-1})	R_z (nm)	Relative crystallinity (%)
Cassava				
Native	22.6 ± 1.3aA	4.54 ± 0.11aA	315.70 ± 1.56aA	35.57 ± 1.70a
Spray-dried	18.7 ± 0.3b	4.15 ± 0.32a	307.66 ± 16.4a	26.50 ± 1.51b
Extruded	20.8 ± 0.4A	0.51 ± 0.27B	135.33 ± 11.1B	0.0
Peruvian carrot				
Native	18.1 ± 0.3aA	1.51 ± 0.05aA	254.36 ± 1.34aA	18.09 ± 0.17a
Spray-dried	16.3 ± 0.5b	1.33 ± 0.11b	250.70 ± 1.10b	11.60 ± 0.57b
Extruded	17.1 ± 0.2B	0.35 ± 0.09B	143.66 ± 0.89B	0.0

Values followed by the same lower case or upper case letter within same column for each process do not differ statistically from each other, Tukey's HSD test ($p < 0.05$).

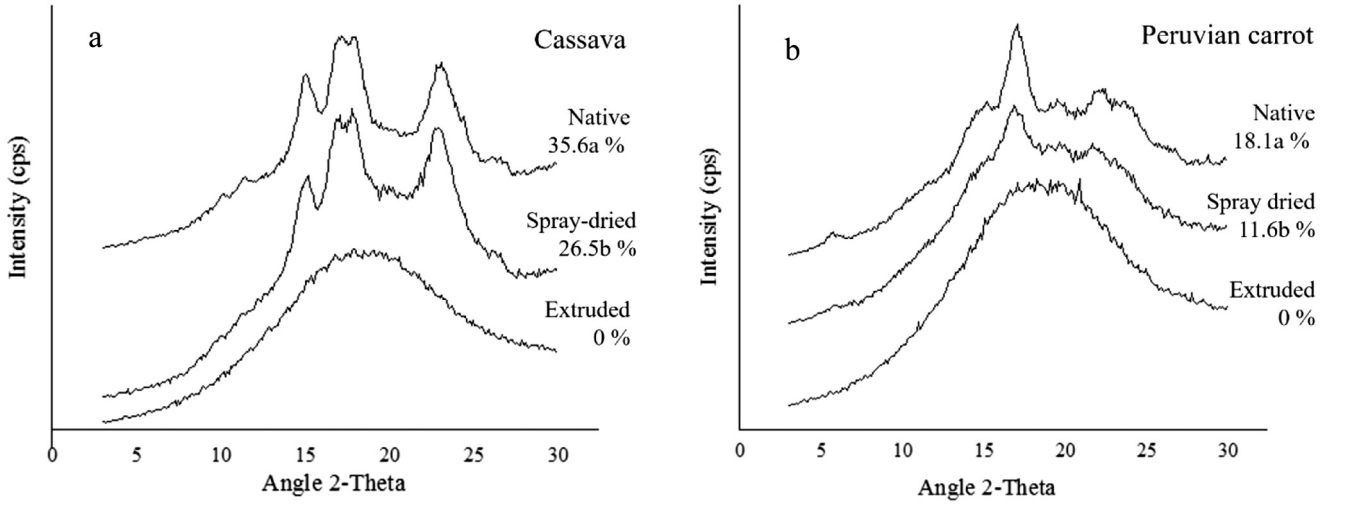

Fig. 1. Diffractograms and relative crystallinities of native and processed starches. The numbers stand for relative crystallinity. Values followed by the same lower case letter, for spray-drying process, do not differ statistically from each other, Tukey's HSD test ($p < 0.05$). Cassava starch (a); Peruvian carrot starch (b).

Native cassava starch displayed an A-type diffraction pattern, in which the most intense peaks were at 15, 17, 18 and 23° 2θ (Fig. 1a). Zhu [30] reported that all the cassava starch exhibited A- or C_a-type patterns.

Native Peruvian carrot starch showed a diffractogram with main peaks at 5.6; 15; 17; 24° 2θ, which is a B-type pattern, and had already been reported in the literature (Fig. 1b) [17, 18, 41].

Spray-dried cassava starch showed a reduction in the intensity of the peaks but no change in the diffraction pattern (A-type). Spray-dried Peruvian carrot starch changed its diffraction pattern, showing a very small peak at 5.6° 2θ (Fig. 1b), which may be related to the B-type pattern. Starches with a B-type pattern are less thermodynamically stable compared with starches having an A-type pattern, due to the lower packing density [44–46].

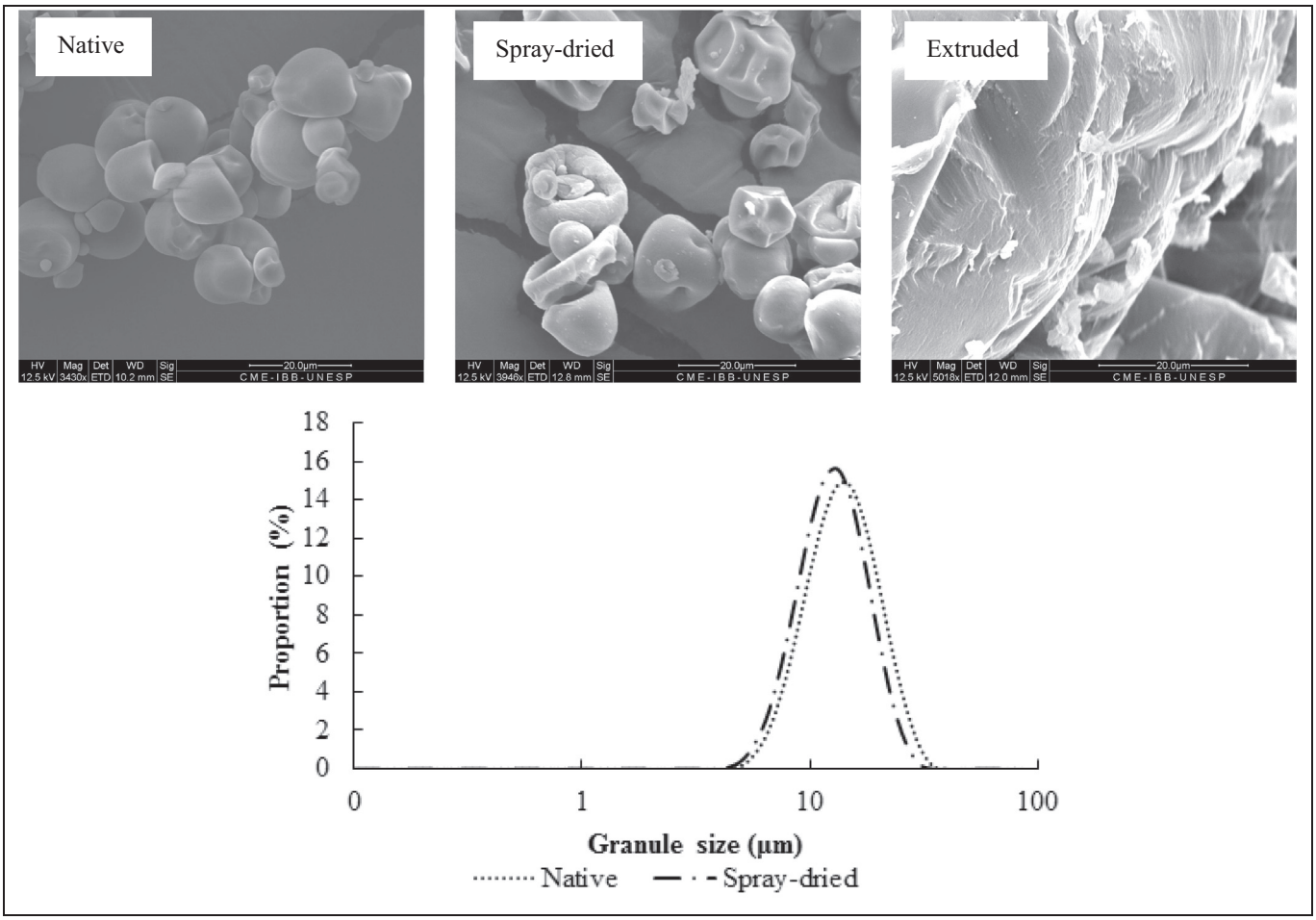

Fig. 2. Microphotographs of scanning electron microscope of cassava starches and granule size distribution of native and spray-dried cassava starches.

After the extrusion process the diffraction peaks disappeared completely, indicating that both starches had been converted to amorphous structures (Fig. 1), an effect also described by Colonna and Mercier [22]. In this process, owing to shear forces and temperature, the material undergoes a process of melting and forms a continuous amorphous mass, with the loss of diffraction peaks [27].

3.2. Morphology

Native cassava starch predominantly displayed round and concavo-convex granules, with few depressions (Fig. 2). The cassava starch granules had an average size of 15.7 μm, which is within the range 2–32 μm reported by Zhu [30] and also by Rolland-Sabate et al. [47] (7–20 μm), with a unimodal distribution.

The surface structure and the shape of the cassava starch granules were not drastically changed by processing. However, there was a reduction in the distribution of the average granule size (from 15.7 to 14.3 μm). Starch was partially gelatinized and swollen during the spray-drying, but upon cooling, the swollen granules shrank and displayed wrinkles and reduced sizes.

Microscopic analysis of the native Peruvian carrot starch showed granules with irregular shapes, mainly round, and smooth surfaces with some depressions (Fig. 3). The size of the granules varied greatly with an average of 19.4 μm. Other authors have also reported this variability in granule size. Santacruz, Kock, Svensson, Ruales, and Eliasson [48] reported granules with sizes ranging from 7 to 23 μm for Peruvian carrot and indicated the presence of pores on the surface. Rocha, Carneiro, and Franco [49] observed round shapes and 7.8% of granules with sizes larger than 20 μm, 12.7% with sizes of 1–5 μm, and 67.8% with sizes ranging from 5.1 to 15 μm.

When we observed the spray-dried Peruvian carrot starch with SEM, we saw a marked change in the shape of granules, with the formation of surface folds and wrinkles (Fig. 3). The most marked change in the shape of granules of Peruvian carrot starch may be due to high levels of absorption of water into the granules during processing, which promoted swelling and altered the granule shape during drying.

These changes in pregelatinized starches processed by spray-drying have also been reported in other studies. Fu et al. [10], who studied the effects of spray-drying on the structure of corn starch, observed that the surface morphology of partially gelatinized starch granules appeared more shriveled with the increase in temperature, and the granule size of this starch was smaller than that of native starch.

The spray-drying process led to an increased in proportions of granules size between 5 and 15 μm and a decreased in those one between 16 and 60 μm (Fig. 2). These results suggest that during the pregelatinization stage, the application of temperature and agitation may have caused the granules to break, resulting in an increase in the proportion of small granules, which may correspond to pieces of granules, or because the granules have become wrinkled and shrunken.

After the extrusion process, it was observed that the two starches were a molten mass. Starch granules are subjected to high shear and temperature during the extrusion. The transformation involves the absorption of water into the granules at elevated temperatures, followed by granule swelling and eventual disintegration to form a homogeneous gel. Thus, extrusion of starches is a complex process leading to physicochemical changes in the starches. This process results in the destruction

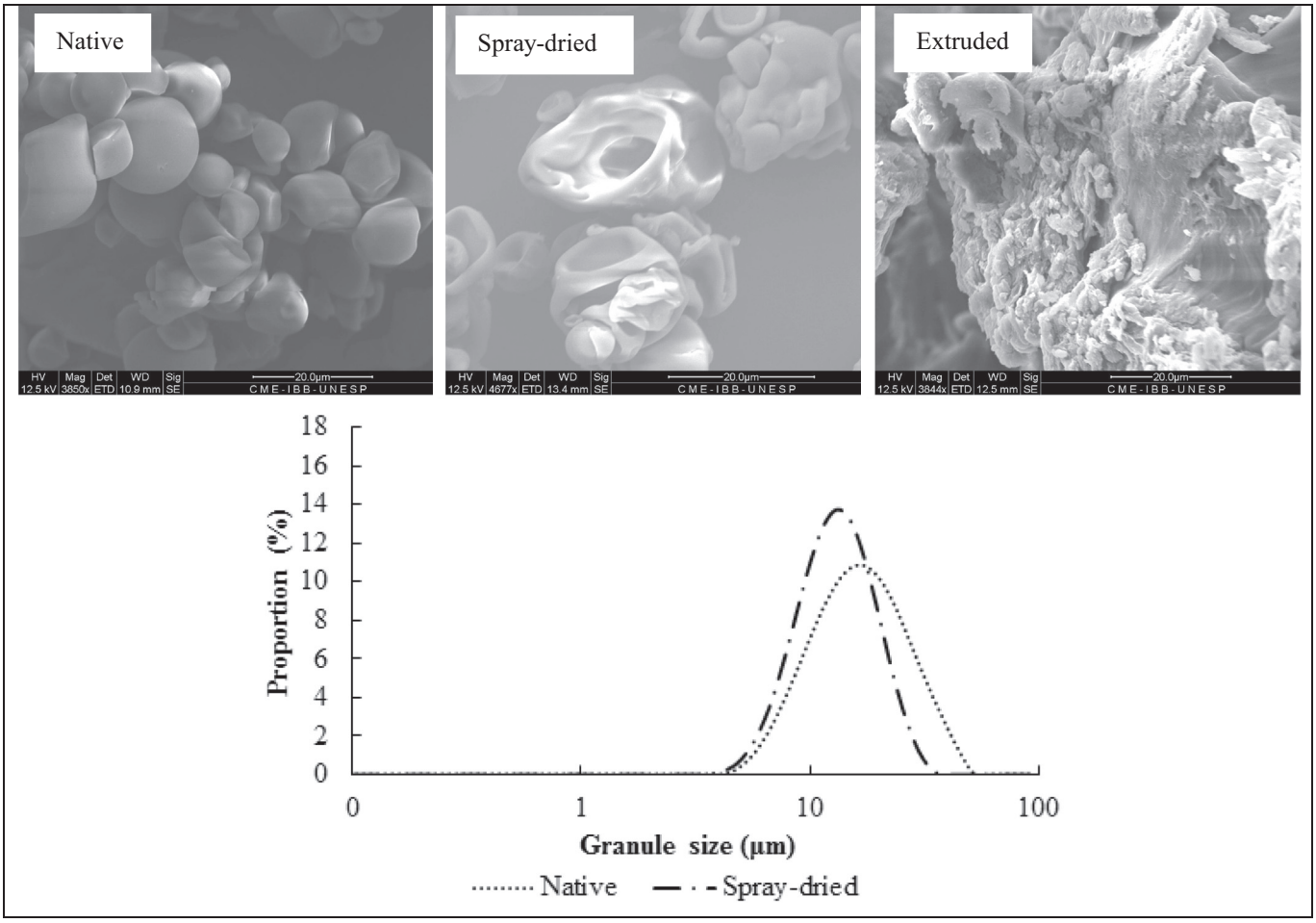

Fig. 3. Microphotographs of scanning electron microscope of Peruvian carrot starches and granule size distribution of native and spray-dried Peruvian carrot starches.

Table 2
Thermal parameters of native and spray-dried starches.

	Thermal properties				
	T_{onset} (°C)	T_{peak} (°C)	$T_{conclusion}$ (°C)	ΔT (°C)	ΔH (J g^{-1})
Cassava					
Native	59.4 ± 0.3b	65.6 ± 0.3a	73.7 ± 0.8a	14.4 ± 0.6a	14.2 ± 0.3a
Spray-dried	62.0 ± 0.2a	65.9 ± 0.2a	72.5 ± 0.4a	10.5 ± 0.6b	7.0 ± 0.1b
Peruvian carrot					
Native	57.9 ± 0.2a	61.6 ± 0.2a	64.8 ± 0.3a	6.9 ± 0.2a	15.3 ± 0.4a
Spray-dried	57.9 ± 0.2a	60.6 ± 0.3b	63.5 ± 0.4b	5.6 ± 0.3b	8.3 ± 0.2b

T, temperature; ΔT, ($T_{conclusion}$-T_{onset}); ΔH, enthalpy change. Values followed by the same lower case letter within same column, for the same starch source, do not differ statistically from each other, Tukey's HSD test ($p < 0.05$).

of granules, elimination of the crystalline structure, and also the formation of an amorphous molten mass [26, 50].

3.3. Thermal properties

The energy required for the dissociation of the helical structures present in the starch varies according to the starch source. The gelatinization temperatures (T_{onset}, T_{peak}, and $T_{conclusion}$) of native cassava and Peruvian carrot starches showed that these starches have different structures (Table 2, Fig. 4). Peruvian carrot starch displayed lower gelatinization temperatures than cassava starch, which was related to the larger proportion of short branch-chain amylopectin in Peruvian carrot [44]. The difference between starches in relation to morphological changes after processing may be associated with the T_{onset} of the starches.

Results of thermal properties evidenced a small variation between the native starches and spray-dried starches (Fig. 4). This means that conditions of the spray-dried process provoke a partial gelatinization of the crystalline structure of these starches.

The enthalpy change of the starch is attributed to amylopectin crystallite disorder. As observed in X-ray diffraction (Fig. 1), it can be observed that the extent of crystallinity decreased with modification of the starches, and as a result, the ΔH values of spray-dried starches were lower than those of native starches. Fu et al. [10] also reported similar results. Extruded starches did not shown gelatinization peaks (Fig. 4). The absence of residual enthalpy of gelatinization suggests that all starch was completely gelatinized. From the results obtained from X-ray diffraction, it can be concluded that the extent of crystallinity decreases with increasing intensity of processing.

3.4. Pasting properties

Our results for the pasting properties of cassava and Peruvian carrot native starches are shown in Table 3. Native starches of cassava and Peruvian carrot showed very low viscosity at room temperature, indicating integrity of granules, considerable peak viscosity, low resistance to heat and agitation, and tendency to setback. The setback viscosity was more pronounced in cassava starch because of its larger amylose contents. These results agreed with those reported in the literature for these starches [16, 30].

Ungelatinized starch can absorb limited water at room temperature. The results showed significant effects of both processes on the pasting properties of the starches with more changes caused by extrusion process. We observed a significant increase in cold viscosity for spray-dried Peruvian carrot starch, but it was not observed for spray-dried cassava starch, which can be related to the higher loss of crystalline structure of Peruvian carrot starch. In starch granules, amylopectin molecules form rigid crystallites, which are more susceptible to shear degradation than the flexible, amorphous amylose molecules [28].

Peak viscosity indicates hot water swelling of the starch granules, which reflects the ability of the ordered starch to hydrate and swell. Results showed that starches lost their ordered structure during spray-drying and extrusion processes and their swelling ability was reduced.

The final viscosity in RVA curves is a measure of the dispersion of the macromolecules and can relate to their hydrodynamic volume and hence their molecular weight [29]. Decrease in final viscosity of the starches after processing indicates degradation of macromolecules and this effect was more severe in extruded starches.

When the starch is heated to higher temperatures, the structure of the granules becomes frangible and large granules can disintegrate

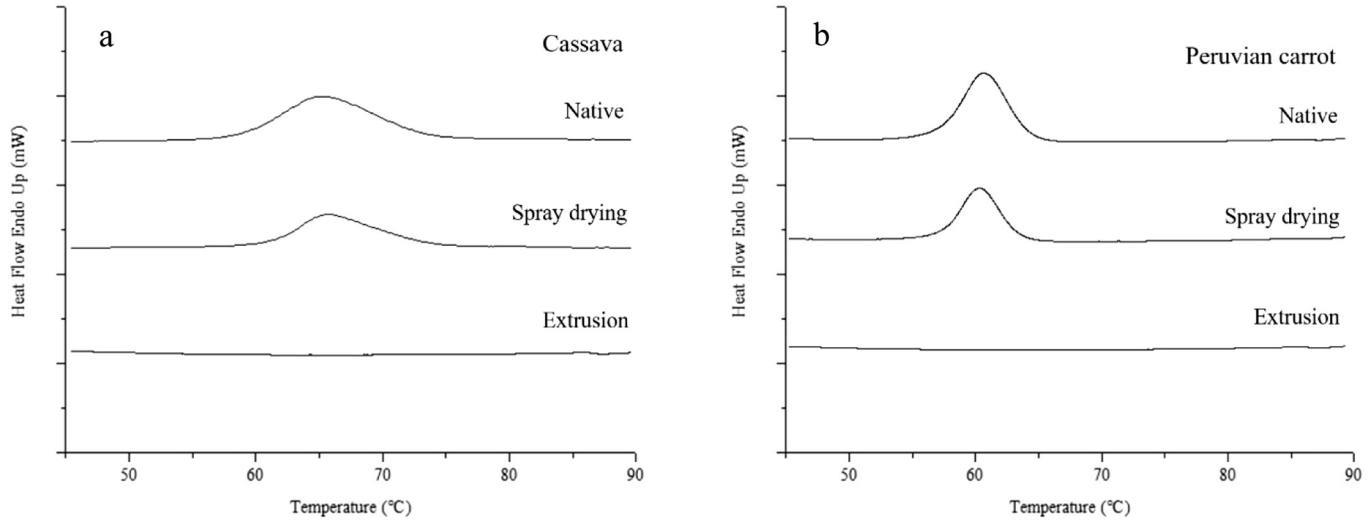

Fig. 4. DSC curves of native and processed starches from cassava and Peruvian carrot. Cassava starch (A); Peruvian carrot starch (B).

Table 3
Rapid Visco Analyzer results of native and processed starches.

Starches	Pasting properties (RVU)				
	Cold peak	Peak	Breakdown	Final viscosity	Setback
Cassava					
Native	1.2 ± 0.0bB	323.1 ± 9.6aA	186.8 ± 9,5aA	332.8 ± 7.4aA	196.4 ± 4.2aA
Spray-dried	2.4 ± a	287.5 ± 3.6b	163.1 ± 2.2b	268.3 ± 0.3b	144.0 ± 6.0b
Extruded	11.0 ± A	9.8 ± 1.6B	5.0 ± 1.6B	9.8 ± 0.4B	5.0 ± 0.3B
Peruvian carrot					
Native	1.3 ± 0.0bB	338.6 ± 12.1aA	194.7 ± 7.5aA	217.4 ± 0.8aA	73.5 ± 3.7aA
Spray-dried	9.3 ± 0.4a	215.7 ± 5.7b	117.4 ± 1.6b	197.9 ± 6.4b	99.6 ± 2.4b
Extruded	8.7 ± A	8.1 ± 0.8B	4.2 ± 0.8B	7.5 ± 0.2B	3.6 ± 0.2B

Values followed by the same lower case letter or upper case column for each process do not differ statistically from each other, Tukey's HSD test ($p < 0.05$). RVU, Rapid Visco Unit.

[10]. According to the cited literature, the treatments carried out at higher temperatures exhibit starch granules at breaking point, and also some already broken granules, resulting in increased granule size and cold viscosity, and a decrease in crystallinity.

In spray-drying process, the starch is partially converted to an amorphous mass [10, 51], showing reduced crystallinity, increased granule size and gelatinization, and viscosity development at room temperature. These factors make the spray-dried starch able to be used in products that require high viscosity during production, and also in the final product. The extrusion process converts granular starch to an amorphous mass [52, 53], with molecular and structural degradation, loss of crystalline fraction, total gelatinization, and increased viscosity at room temperature. These changes are very important because they will provide the extruded starchy materials with new and relevant properties either for food or non-food applications [52].

In addition, in food and pharmaceutical applications, extrusion and spray-drying processing are also often applied to encapsulate flavors, nutrients and drugs respectively. Extrusion is applicable to production of matrix formulations for controlled drug delivery and drugs with not-very-high melting points [54–56]. Spray drying is useful for drugs soluble in at least one volatile solvent [57], microcapsules, controlled release particles, composite microparticles, nanoparticles, and liposomes [51, 58]. Spray-drying process has seen increasing application as a tool for the incorporation of bioactive ingredients into foods, as flavorings and functional ingredients, especially since it protects them from moisture, heat, oxygen, and other adverse conditions [59–61].

Peruvian carrot and cassava starches differed in both pasting and thermal properties. Peruvian carrot starch has shown lower final viscosity, consistency indices, and gelatinization temperature. The Peruvian carrot starch also has shown lower crystallinity pattern and molecular weight. Some differences in rheological features were observed between Peruvian carrot and cassava starches, which may be due to inherent structural and molecular dissimilarities. Lower gelatinization temperature shown by the Peruvian carrot starch may be a factor contributing to higher degradation during extrusion and spray-drying processes. However, the difference of sensitivity between cassava and Peruvian carrot starches is likely rather due to the larger content of amylopectin of the latter. Indeed, amylopectin is known to be more easily degraded than amylose by shear, because of its larger size and compact, less flexible, structure [52]. Peruvian carrot starch displays special characteristics, which make it appropriate for industrial application in many processed foods like soups, infant foods, purees, breads and cakes as well as for other non-food uses [16, 18]. Due to the thermal and structural characteristics of Peruvian carrot starch, processes such as spray-drying and extrusion of this starch can be carried out at lower temperatures, which can favor its use as a vehicle for the process of encapsulation and pelletizing in the food and pharmaceutical industry.

4. Conclusion

This study showed that the spray-drying process allowed us to obtain partially pregelatinized starches, observed by changes in surface granules with the formation of surface folds and wrinkles, reduction of crystallinity and development of viscosity at room temperature. The extrusion process led to obtaining fully pregelatinized starches. This resulted was demonstrated by loss of crystallinity, formation of a melting mass, and viscosity at the room temperature. With these unique properties induced by both processes, the possibilities of industrial applications of these starches are significantly increased. Both starches studied changed significantly after spray-drying and extrusion processes, indicating the possibility of using Peruvian carrot as a source of starch at industrial levels.

Conflict of interest

The authors declare that they have no conflict of interest.

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References

[1] K.O. Adebowale, T.A. Afolabi, B.I. Olu-Owolabi, Hydrothermal treatments of finger millet (*Eleusine coracana*) starch, Food Hydrocoll. 19 (2005) 974–983.
[2] C.W. Chiu, D. Solarek, Modification of Starches, in: J. Bemiller, R. Whistler (Eds.), Starch Chemistry and Technology, 3 ed.Academic Press, Burlington 2009, pp. 629–655.
[3] H. Lai, Effects of hydrothermal treatment on the physicochemical properties of pregelatinized rice flour, Food Chem. 72 (2001) 455–463.
[4] M.O. Adedokun, O.A. Itiola, Material properties and compaction characteristics of natural and pregelatinized forms of four starches, Carbohydr. Polym. 79 (2010) 818–824.
[5] W.C. Liu, P.J. Halley, R.G. Gilbert, Mechanism of degradation of starch, a highly branched polymer, during extrusion, Macromolecules 43 (2010) 2855–2864.
[6] Y. Zhang, Z. Huang, C. Yang, A. Huang, H. Hu, Z. Gong, G. Sun, K. Huang, Material properties of partially pregelatinized cassava starch prepared by mechanical activation, Starch/Stärke 65 (2013) 461–468.
[7] A. Gharsallaoui, G. Roudaut, O. Chambin, A. Voilley, R. Saurel, Applications of spray-drying in microencapsulation of food ingredients: an overview, Food Res. Int. 40 (2007) 1107–1121.
[8] E. Pitchon, J.D. O'Rourke, T.H. Joseph, Process for cooking or gelatinizing materials. (1981) US Patent, 4280851.
[9] R.W. Rubens, Method and apparatus for cooking and spray-drying starch. (1992) US Patent, 5149799.
[10] Z. Fu, L. Wang, D. Li, B. Adhikari, Effects of partial gelatinization on structure and thermal properties of corn starch after spray drying, Carbohydr. Polym. 88 (2012) 1319–1325.
[11] G. Haghayegh, R. Schoenlechner, Physically modified starches: a review, J. Food Agric. Environ. 9 (2011) 27–29.
[12] M.E. Camire, A. Camire, K. Krumhar, Chemical and nutritional changes in foods during extrusion, Crit. Rev. Food Sci. Nutr. 29 (1990) 35–57.
[13] E.E. Pérez, R. Borneo, C.G. Melito, J. Tovar, Chemical, physical and morphometric properties of peruvian carrot (*Arracacia xanthorrhiza* b.) starch, food technology, Acta Cient. Venez. 50 (1999) 240–244.
[14] S. Pérez, E. Bertoft, The molecular structures of starch components and their contribution to the architecture of starch granules: a comprehensive review, Starch/Stärke. 62 (2010) 389–420.

[15] M. Leonel, E.L. do Carmo, C.M.L. Franco, A.M. Fernandes, E.L. Garcia, T.P.R. dos Santos, Peruvian carrot (*Arracacia xanthorrhiza* Bancroft) as raw material for producing special native starches, Aust. J. Crop. Sci. 10 (2016) 1151–1157.
[16] T.S. Rocha, I.M. Demiate, C.M.L. Franco, Structural and physicochemical characteristics of Peruvian carrot (*Arracacia xanthorrhiza*) starch, Food Sci. Technol. 28 (2008) 620–628.
[17] FAO - Food and Agriculture Organization of the United Nations, FAOSTAT: Production-Crops, 2014http://faostat3.fao.org/home/E>.
[18] D.E. Mweta, M.T. Labuschagne, S. Bonnet, J.S. Warts, J.D.K. Saka, Isolation and physicochemical characterisation of starch from cocoyam (*Colocasia esculenta*) grown in Malawi, J. Sci. Food Agr. 90 (2010) 1886–1896.
[19] T.S. Rocha, V.A.G. Cunha, J. Jane, C.M.L. Franco, Structural characterization of Peruvian carrot (*Arracacia xanthorrhiza*) starch and the effect of annealing on its semicrystalline structure, J. Agric. Food Chem. 59 (2011) 4208–4216.
[20] International Starch Institute A/S, , Available in: http://www.starch.dk/isi/market/index.asp 2016.
[21] A. Rolland-Sabate, T. Sanchez, A. Buléon, P. Colonna, B. Jaillais, H. Ceballos, D. Dufour, Structural characterization of novel cassava starches with low and high-amylose contents in comparison with other commercial sources, Food Hydrocoll. 27 (2012) 161–174.
[22] P. Colonna, C. Mercier, Macromolecular modifications of manioc starch components by extrusion-cooking with and without lipids, Cabohydr. Polym. 3 (1983) 87–108.
[23] K.M. Lee, S.R. Bean, S. Alavi, T.J. Herrman, R.D. Waniska, Physical and biochemical properties of maize hardness and extrudates of selected hybrids, J. Agric. Food Chem. 54 (2006) 4260–4269.
[24] R.A. González-Soto, R. Mora-Escobedo, H. Hérnandez-Sánchez, M. Sánchez-Riviera, L.A. Bello-Pérez, Extrusion of banana starch: characterization of the extrudates, J. Food Agric. 87 (2007) 348–356.
[25] M. Leonel, T.S. Freitas, M.M. Mischan, Physical characteristics of extruded cassava starch, Sci. Agric. 66 (2009) 486–493.
[26] B. Su, F. Xie, M. Li, P.A. Corrigan, L. Yu, X. Li, L. Chen, Extrusion processing of starch film, Int. J. Food Eng. 5 (2009) 1–12.
[27] L. Mościcki, M. Mitrus, A. Wójtowicz, T. Oniszczuk, A. Rejack, L. Janssen, Application of extrusion-cooking for processing of thermoplastic starch (TPS), Food Res. Int. 47 (2012) 291–299.
[28] M. Li, J. Hasjim, F. Xie, P.J. Halley, R.G. Gilbert, Shear degradation of molecular, crystalline, and granular structures of starch during extrusion, Starch/Stärke 66 (2014) 595–605.
[29] T. Moisio, P. Forssell, R. Partanen, A. Damerau, S.E. Hill, Reorganization of starch, proteins and lipids in extrusion of oats, Innovative Food Sci. Emerg. Technol. 31 (2015) 45–53.
[30] F. Zhu, Composition, structure, physicochemical properties and modifications of cassava starch, Carbohydr. Polym. 122 (2015) 456–480.
[31] D.R. Izidoro, M.R. Sierakowski, C.W.I. Haminiuk, C.F. de Souza, A.P. Scheer, Physical and chemical properties of ultrasonically, spray-dried green banana (Musa cavendish) starch, J. Food Eng. 104 (2011) 639–648.
[32] F.F. Santos, Peruvian Carrot “Amarela de Senador Amaral”, Centro Nacional de Pesquisa de Hortaliças, Brasília, 1998 , Available in: http://www.cnph.embrapa.br/cultivares/Mandioquinha.html.
[33] M. Leonel, J.C. Feltran, E.B. Aguiar, A.M. Fernandes, V.A. Peressin, S.J. Bicudo, Mandioca (*Manihot esculenta* Crantz), in: M. Leonel, A.M. Fernandes, C.M.L. Franco (Eds.), Culturas amiláceas: batata-doce, inhame, mandioca e mandioquinha-salsa, 1. ed. Universidade Estadual Paulista, Centro de Raízes e Amidos Tropicais, Botucatu 2015, pp. 183–326.
[34] T.P.R. dos Santos, M. Leonel, E.L. Garcia, E.L. do Carmo, C.M.L. Franco, Crystallinity, thermal and pasting properties of starches from different potato cultivars grown in Brazil, Int. J. Biol. Macromol. 82 (2016) 144–149.
[35] T. Kasemsuwan, J. Jane, P. Schnable, P. Stinard, D. Robertson, Characterization of the dominant mutant amylose-extender (Ae1-5180) maize starch, Cereal Chem. 75 (1995) 457–464.
[36] Y. Takeda, S. Hizukuri, C. Takeda, A. Suzuki, Structures of branched molecules of amyloses of various origins, and molar fractions of branched and unbranched molecules, Carbohydr. Res. 165 (1987) 139–145.
[37] S. Yoo, J. Jane, Molecular weights and gyration radii of amylopectins determined by high-performance size-exclusion chromatography equipped with multi-angle laser-light scattering and refractive index detectors, Carbohydr. Polym. 49 (2002) 307–314.
[38] S. Nara, T. Komiya, Studies on the relationship between water-saturated state and crystallinity by the diffraction method for moistened potato starch, Starch/Stärke. 35 (1983) 407–410.
[39] C.B. Mesquita, M. Leonel, C.M.L. Franco, S. Leonel, E.L. Garcia, T.P.R. Santos, Characterization of banana starches obtained from cultivars grown in Brazil, Int. J. Biol. Macromol. 89 (2016) 632–639.
[40] T. Sánchez, E. Salcedo, H. Ceballos, D. Dufour, G. Mafla, N. Morante, F. Calle, J.C. Pérez, D. Debouck, G. Jaramillo, I.X. Moreno, Screening of starch quality traits in cassava (*Manihot esculenta* Crantz), Starch/Stärke 61 (2009) 12–19.
[41] J. Moraes, R.S. Branzani, C.M.L. Franco, Behavior of Peruvian carrot (*Arracacia xanthorrhiza*) and cassava (*Manihot esculenta*) starches subjected to heat-moisture treatment, Starch/Stärke. 66 (2014) 645–654.
[42] A. Htoon, A.K. Shrestha, B.M. Flanagan, A. Lopez-Rubio, A.R. Bird, E.P. Gilbert, M.J. Gidley, Effects of processing high amylose maize starches under controlled conditions on structural organization and amylose digestibility, Carbohydr. Polym. 75 (2009) 236–245.
[43] I.M. Demiate, A.M. Figueroa, M.E.B.Z. Guidolin, T.P.R. dos Santos, H. Yangcheng, F. Chang, J. Jane, Physicochemical characterization of starches from dry beans cultivated in Brazil, Food Hydrocoll. 61 (2016) 812–820.
[44] A.M. Donald, Understanding starch structure and functionality, in: A.C. Eliasson (Ed.), Starch in Food: Structure, Function and Applications, CRC Press, Boca Raton 2004, pp. 156–184.
[45] Q. Liu, Understanding starches and their role in foods, in: S.W. Cui (Ed.), Food Carbohydrates: Chemistry, Physical Properties and Applications, CRC Press, Boca Raton 2005, pp. 309–355p.
[46] D. Kuakpetoon, Y. Wang, Structural characteristics and physicochemical properties of oxidized corn starches varying in amylose content, Carbohydr. Res. (2006) 1896–1915.
[47] A. Rolland-Sabate, T. Sanchez, A. Buléon, P. Colonna, B. Jaillais, H. Ceballos, D. Dufour, Structural characterization of novel cassava starches with low and high-amylose contents in comparison with other commercial sources, Food Hydrocoll. 27 (2012) 161–174.
[48] S. Santacruz, K. Kock, E. Svensson, J. Ruales, A.-C. Eliasson, Three underutilised sources of starch from the Andean region in Ecuador Part I. Physico-chemical characterization, Carbohydr. Polym. 49 (2002) 63–70.
[49] T.S. Rocha, A.P.A. Carneiro, C.M.L. Franco, Effect of enzymatic hydrolysis on some physicochemical properties of root and tuber granular starches, Cienc. Tecnol. Aliment. 30 (2010) 544–551.
[50] H. Yan, G.U. Zhengbiao, Morphology of modified starches prepared by different methods, Food Res. Int. 43 (2010) 767–772.
[51] A. Sing, G. Van den Mooter, Spray drying formulation of amorphous solid dispersions, Adv. Drug Deliv. Rev. 100 (2016) 27–50.
[52] N. Logié, G.D. Della Valle, A. Rolland-Sabaté, N. Descamps, J. Soulestin, How does temperature govern mechanisms of starch changes during extrusion? Carbohydr. Polym. 184 (2018) 57–65.
[53] B. Zhang, S. Dhitala, B.M. Flanagan, P. Luckman, P.J. Halley, M.J. Gidley, Extrusion induced low-order starch matrices: Enzymic hydrolysis and structure, Carbohydr. Polym. 134 (2015) 485–496.
[54] D. Henrista, R.A. Lefebvre, J.P. Remon, Bioavailability of starch based hot stage extrusion formulations, Int. J. Pharm. 187 (1999) 185–191.
[55] M.M. Crowley, F. Zhang, M.A. Repka, S. Thumma, S.B. Upadhye, S.K. Battu, J.W. McGinity, C. Martin, Pharmaceutical applications of hot-melt extrusion: part I, Drug Dev. Ind. Pharm. 33 (2007) 909–926.
[56] S. Shah, S. Maddineni, J. Lu, M.A. Repka, Melt extrusion with poorly soluble drugs, Int. J. Pharm. 453 (2013) 233–252.
[57] A. Paudel, Z.A. Worku, J. Meeus, S. Guns, G. Van den Mooter, Manufacturing of solid dispersions of poorly water soluble drugs by spray drying: formulation and process considerations, Int. J. Pharm. 453 (2013) 253–284.
[58] D.M. Parikh, Handbook of Pharmaceutical Granulation Technology, third ed CRC Press, New York, 2009.
[59] K. Gosh, Functional coatings and microencapsulation: a general perspective, Functional Coating by Polymer Microencapsulation, Wiley-VCH, Weinheim, 2006.
[60] I. Tontul, A. Topuz, Mixture design approach in wall material selection and evaluation of ultrasonic emulsification in flaxseed oil microencapsulation, Dry. Technol. 31 (2013) 1362–1373.
[61] A.K. Anal, H. Singh, Recent advances in microencapsulation of probiotics for industrial applications and targeted delivery, Trends Food Sci. Technol. 18 (2007) 240–251.