STRUCTURAL, MORPHOLOGICAL AND THERMAL CHARACTERIZATION OF GINGER STARCH *(Zingiber officinale)* ISOLATED FROM RHIZOME

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Abstract:
Ginger starch (GS) was isolated directly from ginger rhizome. The structure, morphology, crystallinity and thermal stability of granular starch were characterized by Fourier transform infrared analysis (FTIR), Field emission gun scanning electron microscopy (FEG-SEM), X-ray diffraction (XRD) and Thermogravimetric analysis (TG). The structural result suggested the presence of the fatty acid in the resulting starch. Morphologic analyzes revealed that the granular ginger had a smooth surface with elliptical, oval and spherical forms. The average granular size, width, and thickness were 19.55 ± 2.7µm, 4.50 ± 1.19 µm, 3.0 ± 0.49 µm respectively. The crystal structure was an A-type pattern typical of cereal grains with a crystallinity index of around 43%. The initial temperature and the maximum temperature of thermal degradation for GS granules in a nitrogen atmosphere were 287.6°C and 310.0°C respectively. The results were an initial study of the characterization of ginger starch, aiming to increase as applications of these in other fields besides the food industry, such as the biomass-based plastics sector.

Keywords:
Ginger. *Zingiber officinale.* Starch ginger characterization.

CARACTERIZAÇÃO ESTRUTURAL, MORFOLÓGICA E TÉRMICA DO AMIDO DE GENGIBRE *(Zingiber officinale)* ISOLADO A PARTIR DO RIZOMA

Resumo:
O amido de gengibre (GS) foi isolado diretamente do rizoma de gengibre. A estrutura, morfologia, cristalinidade e estabilidade térmica do amido granular foram caracterizadas por

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análises de espectroscopia do infravermelho com transformada de fourier (FTIR), microscopia eletrônica de varredura com de emissão de campo (FEG-SEM), difração de raios X (DRX) e análise termogravimétrica (TG). A análise estrutural revelou a presença de ácido graxo no amido resultante. As análises morfológicas revelaram que o gengibre granular apresentou uma superfície lisa com formas diversas como elípticas, ovais e esféricas. O tamanho médio do grânulo, largura e espessura foram de 19,55 ± 2,7 µm, 4,50 ± 1,19 µm, 3,0 ± 0,49 µm, respectivamente. A estrutura cristalina foi a Tipo-A, característica de grãos de cereais com um índice de cristalinidade em torno de 43%. A temperatura inicial e a temperatura máxima de degradação térmica do GS, em atmosfera de nitrogênio, foram 287,6°C e 310,0°C, respectivamente. Os resultados constituíram-se em um estudo inicial de caracterização do amido de gengibre, a fim de aumentar as aplicações deste em outros campos como o do setor de plásticos à base de biomassa, além da indústria de alimentos.

Palavras-chave:
Gengibre. *Zingiber officinale*. Caracterização do amido de gengibre.

CARACTERIZACIÓN ESTRUCTURAL, MORFOLÓGICA Y TÉRMICA DEL ALMIDÓN DE JENGIBRE *(Zingiber officinale)* AISLADO DESDE EL RIZOMA

Resumen:
El almidón de jengibre se ha aislado directamente del rizoma de jengibre. La estructura, morfología, cristalinidad, estabilidad térmica del almidón granular se han examinado. El análisis de la espectrocopia del infrarrojo en la transformada de Fourier (FTIR); microscopia electrónica de barrido con emisión de campo (FEG SEM), difración de rayos X (DRX) y análisis de termogravimetría (TG). El análisis estructural han demonstrado la presencia del ácido graso em el almidón resultante de dicha transformácion. El análisis morfológicas han demonstrado que el jengibre granular presentó una superfície lisa con diferentes formas: elíptica, ovaladas y esféricas. El tamaño médio del granulo, anchura, espesor fueran de 19,55 ± 2,7 µm; 4,5 ± 1,19 µm; 3,0 ± 0,49 µm, respectivamente. La estructura cristalina examinada fue el tipo A. Las características de los granos de cereales con índice de cristalinidade alrededor de 43%. La temperatura inicial y la temperatura máxima de la degradación térmica de almidón de jengibre (JS), en atmosfera de nitrógeno se ha visto 287,6ºC y 310,0ºC, respectivamente. Los resultados del análisis representáron el estúdio inicial de la caracterización del almidón de jengibre, com el fin de aumentar las aplicaciones de esos análisis para otras áreas del conocimiento, como por ejemplo: el sector de plásticos a base de la biomasa, además, la aplicácion en la industria alimentaria.

Palabras clave:
Jengibre. *Zingiber officinale*. Caracterización del almidón de jengibre.

Introduction

Ginger (*Zingiber officinale*) is a rhizome widely used in the food industry as spices and as a phyto-therapeutic aiding in the treatment of health problems such as inflammation, flu, diseases caused by bacteria and viruses and analgesic agent (CHANTARODSAKUN *et al.*, 2014; KOGA, BELTRAME & PEREIRA, 2016). In general, the chemical composition of ginger rhizome are oleoresins and essential oils, such as trans-6-shoagol and α-zingiberene, respectively, starch, minerals, proteins, fibers and fatty acids (REYES *et al.*, 1982; BARTLEY & JACOBS, 2000; SINGH *et al.*, 2005; KOGA, BELTRAME & PEREIRA, 2016).

The ginger starch (GS) corresponds to around 15% of fresh rhizomes and 40% of ginger of a dry basis (SUKHIJA, SINGH & RIAR, 2016). Seasonal, crop changes and methodology used for determination of GS content can affect the content value of the starch on the rhizome. (MADENENI *et al.*, 2011). Fatty acids are also present in GS. Reyes and collaborators (REYES *et al.*, 1982) determined that 50% of these acids are saturated such as palmitic acid (C16:0, 30.5%), lauric acid (C12:0, 7.8%) and myristic acid (C14:0, 5.0%). Among unsaturated fatty oleic acid (C18:1, 16.1%) and linoleic acid (C18:2, 21.1%) were mainly found. (MADENENI *et al.*, 2011; REYES *et al.*, 1982; TALELE *et al.*, 2015; SUKHIJA, SINGH & RIAR, 2016). The GS gelatinization temperature (76° to 88°C) is higher than compared with other starch source.

Starch-based materials for non-food applications are considered an attractive material for short-life products, especially in the plastics industry, due to its low cost and biodegradability. The GS has low retrogradation tendency (good structural stability), higher gelatinization temperature (76°C to 88°C) than other botanical starches sources and low granular solubility in water and dimethylsulfoxide (REYES *et al.*, 1982). These peculiar characteristics of GS make an attractive material to be explored in the area of new environmentally friendly plastic materials.

The use of ginger starch in non-food applications, particularly in the plastic packaging sector, is still little explored. This work was investigated the structural, chemical, and thermal properties of ginger starch, which are essential for its application as bio-based plastic.

Methodology

Extraction of ginger starch

Ginger rhizomes were supplied by a local market in Barra do Garças, Brazil. Ginger rhizomes were peeled, cut into small pieces and then grounded in a household blender with a proportion of 500 mL water for each 50 g rhizome. The resultant material was composed of starch and soluble components of rhizome in suspension and solid fibrous waste. It was sieved and the suspension being separated from solid residues. After that, the suspension was allowed to settle for starch decantation. The supernatant was discarded, and the starch was washed with water successively until it was clear-looking. The resulting slurry was immersed in 70% commercial ethanol solution (J. FRES) and washed with distilled water for further clarification of ginger starch. The starch was dried at room temperature. The white powder obtained was sieved (170 mesh sieve) and stored in a suitable container protected from moisture. Figure 1 summarizes this process.

Figure 1 - Representative scheme of the process of obtaining ginger starch from the rhizome.
Source: The authors.

Characterization of ginger starch

Fourier transformed infrared analysis (FTIR)

FTIR spectra of SG and its films were obtained by transmittance in a Nicolet iS10FT-IR spectrometer, using 32 scans, with 4 cm^{-1} resolution over a wavelength range of 400 to 4000 cm^{-1}.

Scanning electron microscopy (SEM)

The morphology of granular starch was investigated using a JEOL microscope, model JSM 6510 at 10kV. The grains were dispersed in water, and a drop of this dispersion was deposited on aluminum specimen stubs, and let dry at room temperature. The dried solution was sputter-coated with a thin (ca. 15 nm) layer of gold.

X-ray diffraction (XRD)

The diffractogram of GS was recorded on a Shimadzu XRD 600 diffractometer operating at 30 kV, 30 mA and CuKα radiation (k = 1,540 Å). The sample was scanned in 2Θ ranges varying from 5° to 40° (2° min^{-1}). The crystallinity index for GS was estimated based on the method proposed by Hulleman et al. (HULLEMAN *et al.*, 1999).

Thermogravimetry (TG)

Thermogravimetric analysis was obtained in a TA Instrument model Q500, in temperature ranging from 25 to 600°C, at a heating rate of 10°C min^{-1} in nitrogen atmosphere (60 mL min^{-1}). Approximately 10 mg of GS was used for analysis.

Results and discussions

The structure of starch sample was evaluated by FTIR (Figure 2a).

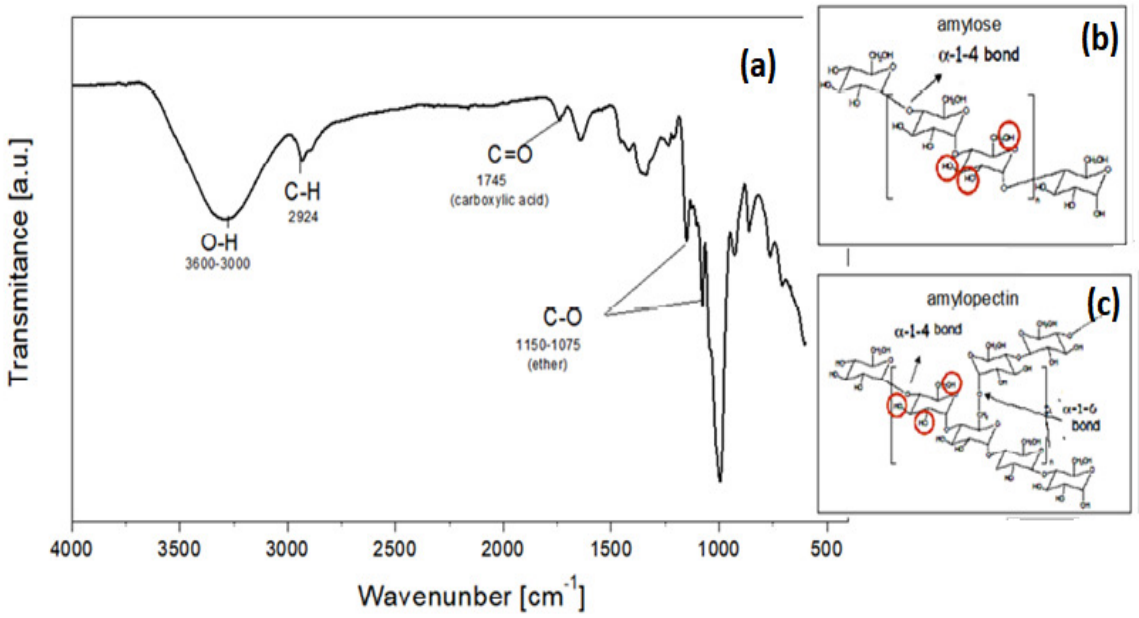

Figure 2 - (a) IR spectrum of ginger starch (GS); (b) and (c) representative structures for the major starch components amylose and amylopectin respectively.
Source: The authors.

According with the structures of amylose and amylopectin, (Figure 2 (b) e (c), the signals around 2900-2800 cm^{-1} bands were ascribing to -CH signal for $-CH_2$ and $-CH_3$ vibrations (asymmetric and symmetric stretching, respectively). A discreet band next to 1740 cm^{-1} was regarding stretching of glycerol esther group of fatty acid. The broad band around 3690-3015 cm^{-1} present in GS was attributed to the vibration of -OH groups. Around 1012 cm^{-1}, C-O-C vibration was related to the vibration of glucose units of starch chains. For starch and starch-based films, a band at 1640 cm^{-1} was attributed to absorbed water.

The X-ray diffractogram and FEG-SEM micrograph of GS are shown in Figure 3. The native ginger starch had a semi-crystalline structure with characteristic crystallinity peaks of A-type pattern as indicated in Figure 2A. A similar crystalline pattern can be observed for corn and rice starches that are typical to the starches A-type, whereas potato has a B-type pattern and cassava show a C-type (COLLONA, BULEON & MERCIER, 1987). The granular GS crystallinity was 43%, while the crystallinity indexes for corn, rice, potato, and cassava starch are 44%, 53%, 55%, and 50% respectively (GUINESI *et al.*, 2006). The granular crystallinity depends mainly on the crystalline amylopectin chains (VAN SOEST & VLIEGENTHART, 1997). The GS amylose content can vary between 12.5 and 25.5% (MADENENI, *et al.*, 2011; REYES *et al.*, 1982; TALELE *et al.*, 2015; SUKHIJA, SINGH & RIAR, 2016). The proximity between the crystallinity index for ginger starch and corn starch

suggests that the amylose content of GS is next to 28%. Further additional investigations in this direction must be realized.

The granular ginger had a smooth surface with elliptical, oval and spherical forms. The average granular size, width, and thickness were 19.55 ± 2.7 µm, 4.50 ± 1.19 µm, 3.0 ± 0.49 µm respectively. The GS granular size was next to granular potato and cassava starch (20 –33 µm and 11 – 18 µm intervals, respectively) (GUINESI *et al.*, 2006).

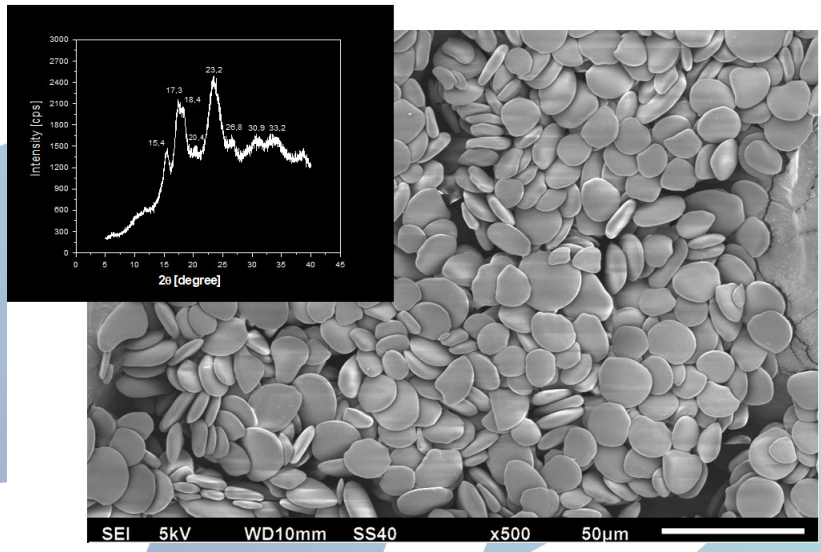

Figure 3 - X-ray diffraction (on upper left side) and FEG-SEM micrograph for GS sample. (Scale bar: 50 µm).
Source: The authors.

The TG and DTG curves obtained by thermogravimetric analysis are shown in Figure 4.

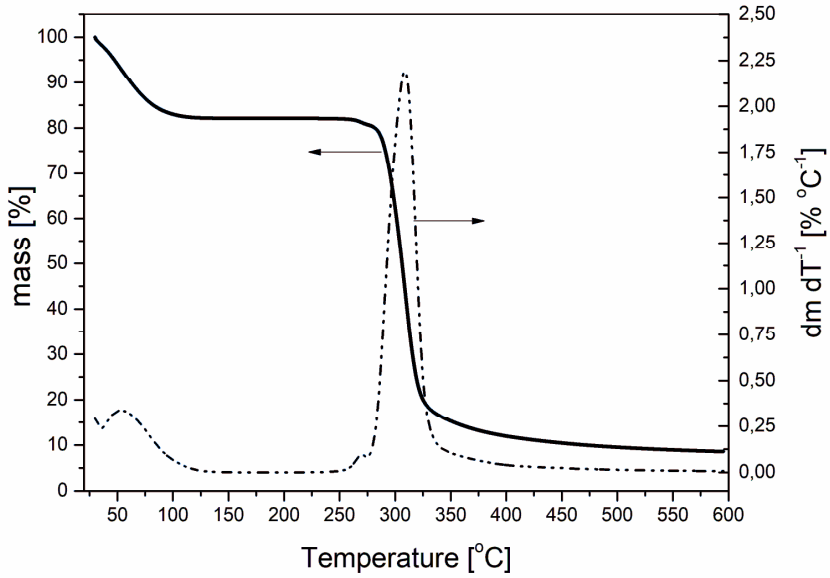

Figure 4 - TG and DTG curves of GS. Analyses in nitrogen atmosphere, heating rate of 10°C min^{-1}.
Source: The authors.

It can be observed in Figure 4 that up to 180°C there is a mass loss event (about 10% of mass), referring to water evaporation. The initial temperature (TG curve) and the maximum temperature of thermal degradation (DTG curve) for GS in nitrogen atmosphere were 287.6°C and 310.0°C respectively. The main event corresponds to 60% of loss mass is attributed to starch degradation. The residue after the thermal GS degradation (at a temperature higher than 350°C) corresponds to organic e inorganic constituents naturally present of GS.

Conclusions

Ginger starch was extracted from rhizomes and physically characterized. In the conditions of extractions used in this study, the granular structure, evaluated by FTIR, show be compatible with those of its major constituents (amylose and amylopectin) in addition to the presence of fatty acids. Morphologic analyzes revealed that the granular ginger had a smooth surface with elliptical, oval and spherical forms. The average granular size, width, and thickness were 19.55 ± 2.7 µm, 4.50 ± 1.19 µm, 3.0 ± 0.49 µm respectively. The crystal structure was an A-type pattern typical of cereal grains with a crystallinity index of around 43%. The initial temperature and the maximum temperature of thermal degradation for GS granules in a nitrogen atmosphere were 287.6°C and 310.0°C respectively. These characterizations are relevant in terms of determining processing parameters for the future use of ginger starch to obtain biodegradable plastics from biomass.

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