

## Effect of dual modification on structural, functional and dielectric properties of cassava starch

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### ABSTRACT

The combined effect of hydrocolloid addition and microwave heating on the structural, physical and functional properties of cassava starch remains underexplored, despite individual studies on these modification methods. The dielectric properties, important for the microwave treatment of starch, have received little attention in recent studies. Cassava starch with and without addition of hydrocolloids (guar and xanthan gums) was modified by microwave heating for two different exposure times, and its structural, functional, and dielectric properties were studied. The dual modification enhanced the swelling power and oil holding capacity of the starch, reduced its gelatinization temperature, and did not alter its crystallinity. Notably, xanthan-modified starch microwaved for 6 min exhibited higher color variation ( $\Delta E^*$ ) and increased granules agglomeration, while the microwave treatment alone roughened the surface of the starch granules. The mean diameters  $D[4,3]$  of starch increased with xanthan gum addition, microwave treatment (6 min), and their combination. The relative permittivity ( $\epsilon'$ ), loss factor ( $\epsilon''$ ) and penetration depth ( $D_p$ ) were lower for samples modified by the combined method. Considering the type of

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hydrocolloid and the microwave exposure time, the combined modification significantly influenced the properties of starch, offering a promising approach to producing starch with enhanced functional properties.

## 1. Introduction

Cassava (*Manihot esculenta*: Crantz) is a key crop in agribusiness, largely due to its starch content. This starch, a renewable, inexpensive, and easily processed biopolymer, is composed of amylose (a linear molecule formed by D glucopyranosyl monomers linked in  $\alpha$ 1,4 bonds) and amylopectin, a highly branched molecule formed by D-glucopyranosyl monomers joined in  $\alpha$ 1,4 and  $\alpha$ 1,6 linkages). These components are organized into a complex semi-crystalline structure, in granular form [1–3]. The global market for cassava-based products exceeded US\$55 billion in 2020 and is projected to grow at an annual rate of approximately 5.7 % until 2026 [4]. Cassava starch's biodegradability, biocompatibility, and non-toxicity make it suitable for applications in the food and others industries. Additionally, its widespread availability and low cost render it an attractive material for modifications. Such modifications can alter its properties, including gelatinization, paste formation, swelling, solubility in water, retrogradation, and viscosity, thereby enhancing its functionality as thickening, colloidal stabilization, bulking agent, gelling, and water retention agent [5–10].

The application of starch in various products and manufacturing processes is determined by its functional properties, which are influenced by its composition and molecular structure. As a consequence of limitations on its structure and unfavorable properties of starch in native form, such as low solubility, high hydrophilicity and instability of the granules during processing, the properties are not always ideal for applications [6,10]. For instance, native cassava starch is unsuitable for producing foods that require specific textures, such as sauces and desserts that demanding a smooth, stable consistency. Its tendency toward retrogradation, which causes recrystallization and hardening after cooking and cooling, leads to undesirable changes in food texture [7].

To overcome these limitations, starch can be modified through chemical, physical, enzymatic, or genetic methods, as well as combinations thereof, to enhance its functional properties. Such modifications broaden its application potential, introducing new functionalities and adding value, thereby providing competitive advantages [1,5,11–13]. Notable examples include pre-gelatinization, which allows the starch to dissolve quickly in cold water for instant products like soups, sauces, and purees, and extrusion, which imparts diverse textures and expansion capacities, allowing use in snacks, breakfast cereals, and confectionery. Demand for modified starches has been increasing alongside with the rapid development of the food industry. Therefore, starch modification techniques and characterization of modified starches have attracted academic and industrial interest [7,8,12,14].

Physical modifications, including thermal and non-thermal treatments, and without intervention of chemicals, do not chemically alter starch beyond limited cleaving of glycosidic bonds. However, they can modify its morphology, three-dimensional structure, and, consequently, its functional properties, such as particle size, surface characteristic, solubility in water, swelling, gelation, and adhesion capacity [15,16]. These methods are simpler, more economical, safer, and environmentally sustainable compared to chemical or enzymatic modifications. Among these methods, microwave treatment, a form of non-ionizing electromagnetic radiation (EMR), is particularly effective. The high frequency of EMR induces rapid movement of water molecules and ions, resulting in rapid and uniform heating, without the need for overheated surfaces or temperature gradients [2,17,18]. Microwave heating of moist materials operates through two mechanisms: (i) dipolar rotation of water molecules, which are unable to keep up polarized with the rapid changes in the electric field, and (ii) ionic conduction, since the electric field induces the movement of dissolved ions [3]. This method is a simple and safe heat treatment for starch, as it does not generate effluents and the products obtained do not present traces of chemical compounds, aligning with concept of “green technology”. Consequently, microwave modification has been receiving research interest, with several studies evaluating its effects on the properties of starch [6,10,17–25].

In the process of energy transformation, where water molecules and ions present in the material interact with EMR waves, the dielectric properties of the material play a very important role in the heating rate and temperature distribution. Thus, knowledge of these properties is fundamental to understanding the phenomena. However, Tao et al. [4], in their review on the impact of dielectric properties in microwave- treated starch, cited that many studies focusing on structural changes induced by microwaves neglected the importance of dielectric properties. Starch, as a macromolecule, primary responds to microwaves through dipolar polarization; however, but its interaction is weak at low moisture content. The presence of moisture content or small polar molecules alters the dielectric properties of the starch system; hence investigating the polarization mechanism is essential in the study of the dielectric properties of modified starch systems [3].

The dielectric properties of modified starches systems have been studied over the years [7,26–28], for instance, but no studies on the dielectric properties of cassava starch modified by mixture with hydrocolloids and microwave treatment were found in the literature, which is the differential of this study. Effects of hydrocolloids on starch have been well-documented [5,9,29–34]. BeMiller [35] summarized over 250 results of pasting and gel properties of 21 native starches combined with 32 hydrocolloids with different molecular structures. Studies on starch-hydrocolloid systems have indicated a synergistic effect, resulting in higher viscosity of the mixtures compared to starch or hydrocolloid alone [36,37]. The addition of hydrocolloids to starch modified its rheological and pasting properties, preventing syneresis [5,31]. Probably, this modification was provoked by strong hydrogen interactions between the starch and hydrocolloid chains, allowing for changes in macromolecular mobility and reducing the tendency toward crystallization, for instance.

Xanthan gum, as a polyelectrolyte, interacts differently with starch compared to guar gum, which is neutral, and can influence the rheological and functional properties of the modified starch. Xanthan gum provides excellent stability under various processing

conditions, including high temperatures and shear forces, important for maintaining the quality and consistency of starch during cooking and processing [38]. Both gums are stable across a wide range of pH levels, making them suitable for use in acidic or alkaline environments without significant degradation of their properties [32]. Sun, Xu and Xiong [6] studied the effect of microwave-assisted dry heating with xanthan on normal and waxy corn starch, finding that this treatment altered the pasting properties, crystalline structure, syneresis, gelatinization and morphological properties of the starch.

Oyeyinka et al. [39] reviewed dual modification methods for various starch sources, mentioning only the microwave and lipid modification of cassava starch. The combination of microwave and hydrocolloids, central to this study, was not addressed. This study explored modifying cassava starch through simple and combined methods as a possibility to expand its applications by enhancing its technological and industrial properties, such as thickening, stabilizing, gelling, and film-forming capacity. Therefore, this study aimed the modification of cassava starch through the incorporation of hydrocolloids (guar or xanthan gums), the application of microwave treatment, or a combination of these approaches, in order to assess their impact on the starch's structural, functional, thermal, and dielectric properties. Microwave treatment or hydrocolloid addition have been independently, but the synergistic effects of these methods on starch properties remained underexplored. This research addresses this gap by evaluating the combined effects on starch properties, especially dielectric properties, which is important for understanding the interaction between microwave energy and starch molecules.

## 2. Materials and methods

### 2.1. Material

Commercial native cassava starch (11.7 % moisture content; 0.21 % total lipids, 0.03 % ash; 0.05 % protein) was supplied by Technoamido Indústria e Comércio de Amido e Derivados Ltda - Brazil. Guar and xanthan gums were purchased from Synth, Brazil. All reactants used were of analytical grade.

### 2.2. Starch modification with hydrocolloids and microwave

The starch modification was based on the studies by Chandanasree et al. [8] and Yang et al. [24]. Initially, guar or xanthan gum (0.4 g) was slowly mixed into distilled water (70 mL) under stirring, followed by the addition of starch (39.6 g) at room temperature. The resulting dispersion was stirred with a magnetic stirrer for 30 min at room temperature, placed in a Petri dish and dried at 45 °C in a convection oven until a constant weight was reached. The granulometry of the modified starch was standardized using a #100 mesh sieve (0.15 mm aperture).

The moisture content of the modified starches was adjusted to 25 wt% by the addition of water. Then, 28 g of native and modified starches was distributed in a Petri dish (diameter 15 cm), forming a thin layer (~1 mm), and taken to the microwave oven (CM020BFBNA, Consul, São Paulo, Brazil) at a frequency of 2450 MHz and 630 W for 4 or 6 min, according to previous research [6]. The treatment was carried out with a rotating dish and the Petri dish centered at 90 % microwave power, with an internal volume of 20 L. Therefore, the specific power in the treatment was 0.03 W/mL. The samples were removed from the microwave and cooled to room temperature.

Nine different starch samples with the appearance of white dispersed granules were analyzed. These included native starch (S) and modified starches subjected to microwave treatment for 4 and 6 min (S4 and S6), mixed with hydrocolloids, either individually (SG, guar and SX, xanthan) or in combination with microwave treatment (SG4, SX4, SG6, SX6). The numbers 4 and 6 correspond to the microwave treatment time.

### 2.3. Color measurements

The color of the native and modified starches was measured using a colorimeter (Mini Scan XE Plus, HunterLab, Virginia, USA) and Universal Software V4.10. The CIELab color parameters were determined in triplicate:  $L^*$  for luminosity (ranging from 0 for black to 100 for white),  $a^*$  for green (-) to red (+), and  $b^*$  for blue (-) to yellow (+). The instrument was calibrated with standard white and black tiles. Average color parameters were calculated based on three repetitions. The total color difference ( $\Delta E^*$ ) was calculated using Eq. (1).

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (1)$$

where  $\Delta L^*$ ,  $\Delta a^*$  and  $\Delta b^*$  are the difference between the sample and the native starch.

Additionally, the whiteness index (WI) of the samples was calculated using Eq. (2) [40].

$$WI = 100 - \sqrt{(100 - L^*)^2 + (a^*)^2 + (b^*)^2} \quad (2)$$

### 2.4. Moisture content and water activity

The moisture content of the samples (1.0 g) was determined using an Infrared Moisture Balance (Top Ray, Bel Engineering, Piracicaba, São Paulo, Brazil), at 105 °C, in triplicate. Water activity was measured using a water activity meter (Decagon Devices, Aqualab, 3 T series) in duplicate.

## 2.5. Oil holding capacity

The oil holding capacity (OHC) was determined according to a modified methodology described by Uzomah and Ibe [41]. A mass of 0.5 g (d.b.) of starch was weighed into a centrifuge tube (PAS) and mixed with 5 mL of refined soybean oil through vortex stirring. The suspension was allowed to stand for 30 min at 25 °C before centrifugation at 1200 × g for 20 min. The supernatant was removed, and the tubes containing the precipitate (PT) were weighed. The OHC was calculated using Eq. (3).

$$OHC = \frac{PT - PAS}{PAS} \times 100 \quad (3)$$

## 2.6. Particle size distribution

The particle size of native and modified starch granules was determined using a Laser Scattering Particle Size Distribution Analyzer (LA-950, Horiba, Japan) in triplicate. Starch (0.5 % w/v) was dispersed in a 95:5 ethanol:water solution and vortexed at 25 °C for 10 s. The volume-weighted mean diameter (De Brouckere Mean Diameter, D[4,3]), which is influenced by larger particles, was calculated using Eq. (4) [42].

$$D[4, 3] = \frac{\sum n_i D_i^4}{\sum n_i D_i^3} \quad (4)$$

## 2.7. Swelling power and solubility index in water

The swelling power (SP) and solubility index (SI) in water were determined according to Schoch's methodology [43] with some modifications and calculated using Eqs. (5) and (6), respectively. Starch (0.5 g, d.b.) (Si) was mixed with 20 g of distilled water in a tube and incubated in a thermostatic bath (MA-184, Marconi, Piracicaba, São Paulo, Brazil) at 90 °C for 30 min, with intermittent shaking every 5 min. After centrifugation at 3,200xg for 15 min (5430 R, Eppendorf, Hamburg, Germany), the supernatant was separated, spread in a pre-weighed Petri dish, and dried in an oven at 105 °C for 12 h to obtain the evaporation residue mass (Sd). The tubes containing the centrifugation precipitate (Sm) were also weighed.

$$SP = \frac{Sm}{Si - Sd} \quad (5)$$

$$SI = \frac{Sd}{Si} \times 100 \quad (6)$$

where Si represents the initial mass of the dry starch sample, Sm is the mass of the swollen starch sample (including absorbed water), and Sd is the mass of the solid residue obtained from the supernatant after evaporation. The supernatant is the liquid phase remaining above the starch sediment post-centrifugation, and Sd represents the mass of solutes or dissolved starch within this liquid.

## 2.8. Differential scanning calorimeter (DSC)

The thermal properties of native and modified starches were determined in triplicate using a differential scanning calorimeter (DSC) (TA 2010, TA Instrument, New Castle-DE, USA) controlled by a TA5000 system (TA 2010, TA Instrument, New Castle-DE, USA) and equipped with a cryogenic quench cooling accessory. Approximately 2 mg of sample (d.b.) and distilled water (1:3 w/v starch:water ratio) were hermetically sealed in an aluminum pan and equilibrated for 2 h. The samples were heated from 25 to 125 °C at a rate of 10 °C/min. An empty aluminum pan served as the reference. The peak temperature (Tp) and enthalpy of gelatinization (ΔH) were determined by analyzing the endothermic peak using the Universal Analysis 2000 software (version 4.2.E). The enthalpy was calculated as the total area under the peak.

## 2.9. Scanning electron microscopy (SEM)

The morphology of native and modified starches was analyzed using a HITACHI Tabletop microscope (SEM) (TM3000, Hitachi Ltd, Tokyo, Japan) at an accelerating voltage of 15 kV. Prior to analysis, starch samples were conditioned in a desiccator with silica gel under vacuum for 12 h. Subsequently, samples were placed onto conductive carbon tape fixed to aluminum stubs without further preparation.

## 2.10. X-ray diffraction (XRD)

The x-ray diffraction patterns of the starches were obtained using an X-ray diffractometer (MiniFlex 600, Rigaku, Akishima, Tokyo, Japan) to evaluate the crystallinity of the starch granules under the following conditions: 2θ angle ranging from 4 to 50°, scan rate of 2°·min<sup>-1</sup>, 40 kV and 15 mA. The samples were kept in a desiccator containing distilled water (25 °C) for 3 days to ensure constant water activity. The resulting diffraction curves were analyzed using Origin software (version 8, Microcal Inc., Northampton, USA). Relative crystallinity was estimated quantitatively using Eq. (7) [44].

$$X_c = \frac{I_c}{(I_c - I_a)} \times 100 \quad (7)$$

Where  $I_c$  represents the area of the crystalline peak, and  $I_a$  is the area of the amorphous peaks.

### 2.11. Dielectric properties

Dielectric properties were determined using the open-ended coaxial cable method, employing an 85070E dielectric probe kit and an 85093 C electronic calibration module connected to an E5061B network analyzer (Agilent Technologies, Penang, Malaysia), described by Franco et al. [45]. Calibration was conducted by measuring the properties of air (open circuit), the metallic calibration block provided in the equipment kit (short circuit) and distilled water at 25 °C, respectively. Then, measurements of a sodium chloride and sucrose solution with known dielectric properties [46] were performed to verify the instrumentation calibration. A 10 mL cylindrical sample holder (3.1 cm diameter and 3.3 cm height) containing approximately 7 g of powdered starch was elevated to touch the sensor with the aid of a laboratory support Jack for the measurement of dielectric properties at room temperature (~25 °C). The network analyzer software performed a linear frequency sweep from 500 MHz (lower limit of the probe) to 3000 MHz (upper limit of the network analyzer), providing 101 measurements of the complex reflection coefficient of the sample at the probe tip. This was converted to the complex permittivity and reported as relative permittivity, traditionally referred to as the “dielectric constant” ( $\epsilon'$ ) and dielectric loss factor ( $\epsilon''$ ). The measurements were performed in triplicate.

### 2.12. Calculation of the energy penetration depth

The penetration depth of an electromagnetic wave into a material is defined as the depth at which the power density of the incident wave on a semi-infinite solid is reduced to  $1/e$  (~37%) of its value on the surface of the material. This parameter is important for selecting the appropriate thickness of the material to ensure uniform heating. It depends on the frequency of the electric field, the relative permittivity ( $\epsilon'$ ) and the loss factor ( $\epsilon''$ ), being calculated using Eq. (8).

$$D_p = \frac{\lambda_0}{2\pi\sqrt{2\epsilon'}} \left[ \sqrt{1 + \left(\frac{\epsilon''}{\epsilon'}\right)^2} - 1 \right]^{-\frac{1}{2}} \quad (8)$$

where  $D_p$  is the penetration depth (m),  $\lambda_0 = c_0/f$  is the electromagnetic wavelength in free space (m),  $c_0$  is the speed of light in free space ( $c_0 = 2.9979 \times 10^8$  m/s), and  $f$  is the frequency (Hz) [47,48].

### 2.13. Statistical analysis

The mean and standard deviation of the experimental data were calculated from independent replicates. The data were analyzed by analysis of variance (ANOVA) with the Statistical Analysis System software (SAS, Cary, North Carolina, USA). The effects of hydrocolloid type and microwave time were evaluated separately using the Tukey test ( $p < 0.05$ ).

## 3. Results and discussion

### 3.1. Color measurements

Cassava starch is typically characterized by a less intense color compared to other starch varieties. Few studies have reported the color of this starch and its relationship with other properties. As a critical organoleptic, color influences consumer acceptance of starch-based products. Therefore, achieving a homogenous color is essential for product appeal and marketability [49]. Table 1 presents the color parameters, total color difference, and whiteness values of the native and modified starches. The parameter  $L^*$ , indicative of lightness, ranged between 85.1 (SG6) and 87.7 (S), aligning with previous findings by Eke et al. [50] who reported average  $L^*$  values ranging from 87.66 to 93.73. Ladeira et al. [51] also reported similar  $L^*$  values (83.65–87.22) along with  $a^*$  and  $b^*$  values ranging from  $-0.24$ – $0.33$  and  $3.57$ – $5.02$ , respectively, for cream-fleshed Brazilian cassava starches. Single modification with hydrocolloid did not affect the  $L^*$  values, whereas dual modification with both hydrocolloid and microwave for 6 min resulted in a significant reduction in  $L^*$  ( $p < 0.05$ ) compared to native starch (Table 1).

Higher values of  $b^*$  ( $5.0 \pm 0.0$ ) and  $\Delta E^*$  ( $3.1 \pm 0.1$ ) were observed for SX6.  $\Delta E^*$  represents the overall color change of the samples, and according to Francis & Clydesdale [52], only values higher than 3 may be considered visually noticeable to the human eye. Samples subjected to dual modification (hydrocolloids and 6 min of microwave treatment) exhibited higher  $\Delta E^*$  values, suggesting a more pronounced color change induced by heating, although still near the threshold of human. Hydrocolloid addition and microwave treatment significantly decreased ( $p < 0.05$ ) the whiteness of cassava starch, with the lowest values observed for samples SG6 and SX6.

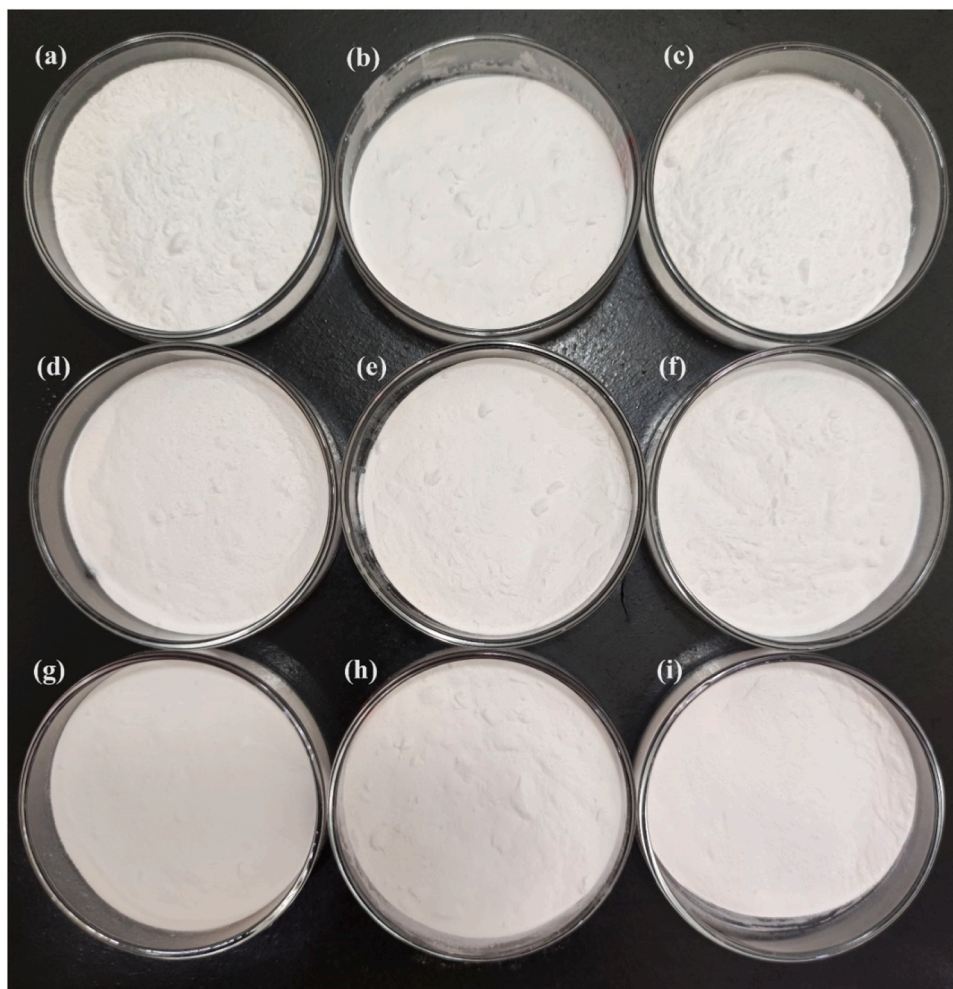
In general, the color measurements indicated that the modified starches exhibited a light color high whiteness index (WI), suggesting that the treatments caused minimal darkening of the samples, mostly below the threshold detectable for the human eye. This characteristic allows for the application of these starches in products requiring uniform coloration (Fig. 1). In this figure, it is evident that the samples were homogeneous in terms of color and did not show notable darkening with the treatments applied.

**Table 1**

Color parameters ( $L^*$ ,  $a^*$ ,  $b^*$ , total color difference [ $\Delta E^*$ ] and whiteness index [WI]) of native starch (S) and starch modified by microwave treatment for 4 (S4) and 6 min (S6), hydrocolloids addition (guar (SG), xanthan (SX)), or both treatments (SG4, SX4, SG6, SX6).

Cassava		Microwave treatment (min.)		
Starch		0	4	6
$L^*$	Native (S)	87.7 ± 0.0 aA	87.2 ± 0.0 aA	86.3 ± 0.0 aB
	with guar (SG)	86.6 ± 0.0 bA	85.4 ± 0.0 cB	85.1 ± 0.0 bB
	with xanthan (SX)	86.5 ± 0.0 bA	86.3 ± 0.0 bA	85.4 ± 0.0 bB
$a^*$	Native (S)	0.5 ± 0.0 bB	0.5 ± 0.0 aB	0.6 ± 0.0 bA
	with guar (SG)	0.5 ± 0.0 aA	0.4 ± 0.0 bB	0.5 ± 0.0 cA
	with xanthan (SX)	0.5 ± 0.0 aB	0.5 ± 0.0 aB	0.7 ± 0.0 aA
$b^*$	Native (S)	2.8 ± 0.0 cC	3.2 ± 0.0 aB	3.9 ± 0.0 bA
	with guar (SG)	3.6 ± 0.0 aB	3.4 ± 0.0 aB	3.9 ± 0.0 bA
	with xanthan (SX)	3.3 ± 0.0 bB	3.4 ± 0.0 aB	5.0 ± 0.0 aA
$\Delta E^*$	Native (S)	NA	0.6 ± 0.0 cB	1.8 ± 0.1 bA
	with guar (SG)	1.3 ± 0.0 aC	2.3 ± 0.3 aB	2.8 ± 0.4 aA
	with xanthan (SX)	1.3 ± 0.2 aB	1.5 ± 0.0 bB	3.1 ± 0.1 aA
WI	Native (S)	87.3 ± 0.0 aA	86.8 ± 0.1 aB	85.7 ± 0.1 aC
	with guar (SG)	86.2 ± 0.1 bA	85.0 ± 0.2 bB	84.6 ± 0.5 bC
	with xanthan (SX)	86.1 ± 0.1 bA	85.9 ± 0.1 cA	84.6 ± 0.1 bB

Values are expressed as the mean ± standard deviation. Different lowercase letters in the same column indicate a significant difference between treatments at each time ( $p < 0.05$ ). Different capital letters in the same row indicate a significant difference between treatments for each hydrocolloid ( $p < 0.05$ ).



**Fig. 1.** Image of the samples of native starch (S (a)) and starch modified by microwave treatment for 4 (S4 (b)) and 6 min (S6 (c)), hydrocolloids addition (guar, SG (d), xanthan, SX (g)), or both treatments (SG4 (e), SX4 (h), SG6 (f), SX6 (i)).

Generally, darkening is correlated with thermal degradation of the starch or Maillard reaction, which was not observed in the samples, as the intensity of the heat treatment (time and temperature) was insufficient to cause degradation. Additionally, the protein content in the starch is too low for the Maillard reaction to occur, which typically involves interactions between reducing sugars and protein amino acids.

### 3.2. Moisture content and water activity

Microwave treatment of starch, either with or without a hydrocolloid, significantly impacted its moisture content; however, it did not affect the water activity, which remained stable at approximately  $0.59 \pm 0.02$ . This low water activity enhances its versatility for various industrial applications that demand stability, solubility, and food safety. The low water activity also ensures the microbiological stability of this starch during storage.

Native starch and hydrocolloid-starch samples (SG, SX) showed significantly higher moisture content, ranging from 12.6 % to 13.0 % ( $p < 0.05$ ), compared to microwave-treated samples, which had moisture contents in the range from 2.0 % to 5.2 % (Table 2). The type of gum influenced moisture content only after 4 min of heating, with guar-starch sample showing higher moisture content retention than xanthan-starch ( $X_{SG4} > X_{SX4}$ ). The addition of xanthan gum may have increased microwave absorption due to its polyelectrolyte nature, which enhances the system's polarity, thereby causing internal moisture removal from the starch granules [8]. Samples modified with 6 min of microwave heating displayed the lowest moisture contents. This is important to guarantee the observed low water activity and then microbiological stability during storage or in powdered products containing this starch. Moreover, in the pharmaceutical industry, low-moisture starches serve as excipients in tablets and capsules, enhancing drug efficacy over time.

### 3.3. Oil holding capacity

Microwave modification increased the oil holding capacity (OHC) of the starch (Table 2). There was no significant variation ( $p < 0.05$ ) in the OHC among starches modified either by microwave treatment or solely with hydrocolloids. Pramodrao and Riar [5] and Chandanasree et al. [8] reported higher OHC for modified starches through dry heating and the addition of gums. The OHC observed in this study exceeded the values obtained by Pramodrao and Riar [5] (OHC ~80 %) but was lower than those related by Chandanasree et al. [8] (OHC ~180 %). Larger OHC values are desired in the food industry to enhance the texture of the final product and in the development of food emulsions [53,54].

**Table 2**

Moisture content (X), oil holding capacity (OHC), de Brouckere Mean Diameter (D[4,3]), solubility index in water, swelling power, and thermal properties of native starch (S) and starch modified by microwave treatment for 4 (S4) and 6 min (S6), hydrocolloids addition (guar (SG), xanthan (SX), or both treatments (SG4, SX4, SG6, SX6).

	Cassava Starch	Microwave treatment (min.)		
		0	4	6
X (%)	Native (S)	12.6 ± 0.1 aA	3.4 ± 0.2bB	2.0 ± 0.3bC
	with guar (SG)	12.6 ± 0.8 aA	5.2 ± 0.3aB	3.9 ± 0.4aC
	with xanthan (SX)	13.0 ± 0.6 aA	4.2 ± 0.2abB	3.5 ± 0.2aB
OHC (%)	Native (S)	111.0 ± 0.1aB	142.1 ± 12.0 aA	139.7 ± 7.6 aA
	with guar (SG)	119.6 ± 1.8aB	139.8 ± 8.4 aA	139.4 ± 2.1 aA
	with xanthan (SX)	114.7 ± 4.2aB	137.8 ± 0.5 aA	138.3 ± 5.4 aA
D[4,3] (µm)	Native (S)	29.5 ± 1.2bB	32.7 ± 0.6cB	55.5 ± 2.7bA
	with guar (SG)	22.2 ± 0.6cC	65.5 ± 1.8 aA	47.0 ± 1.1cB
	with xanthan (SX)	49.7 ± 2.5aC	56.5 ± 0.5bB	62.8 ± 1.7 aA
	Guar (G)	80.9 ± 0.5	-	-
	Xanthan (X)	55.4 ± 1.9	-	-
Solubility index 90 °C	Native (S)	79.9 ± 3.0aB	83.2 ± 0.6aAB	87.5 ± 0.7 aA
	with guar (SG)	55.5 ± 2.6bB	68.8 ± 3.0bA	65.0 ± 3.8bA
	with xanthan (SX)	76.8 ± 1.9 aA	81.4 ± 2.1 aA	52.9 ± 2.2cB
Swelling power 90 °C	Native (S)	16.3 ± 1.7 aA	11.0 ± 0.7cB	12.4 ± 0.8cB
	with guar (SG)	14.5 ± 3.6aB	19.8 ± 1.0aAB	22.4 ± 1.4 aA
	with xanthan (SX)	15.4 ± 1.3 aA	14.9 ± 1.9bA	17.9 ± 0.2bA
Tp (°C)	Native (S)	66.9 ± 0.4 aA	65.6 ± 0.2bB	63.3 ± 0.1cC
	with guar (SG)	67.1 ± 0.1 aA	66.5 ± 0.4 aA	65.1 ± 0.4aB
	with xanthan (SX)	67.4 ± 0.4 aA	66.3 ± 0.2abB	64.3 ± 0.1bC
ΔH (J/g)	Native (S)	14.2 ± 0.4 aA	13.1 ± 0.4aB	12.5 ± 0.5aAB
	with guar (SG)	12.8 ± 0.2 aA	12.5 ± 0.7aB	11.8 ± 0.5aAB
	with xanthan (SX)	12.6 ± 0.6 aA	11.7 ± 0.7aB	11.1 ± 0.1aB

Values are expressed as the mean ± standard deviation; Different lowercase letters in the same column indicate a significant difference between treatments at each time ( $p < 0.05$ ). Different capital letters in the same line indicate a significant difference between for each hydrocolloid ( $p < 0.05$ ).

### 3.4. Particle size distribution

The particle size distribution was monomodal for S, S4, S6, SG, and guar gum, and bimodal for xanthan gum (Fig. 2). However, starches modified by both treatments, as well as those with only xanthan gum added, exhibited an altered profile characterized by a shoulder at the end of the distribution.

The De Brouckere Mean Diameter,  $D[4,3]$ , of starches ranged from 22.2 (SG) to 65.5  $\mu\text{m}$  (SG4) (Table 2).  $D[4,3]$  did not show significant variation ( $p < 0.05$ ) for S4 compared to native starch. Microwave treatment increased  $D[4,3]$  ( $p < 0.05$ ) compared to

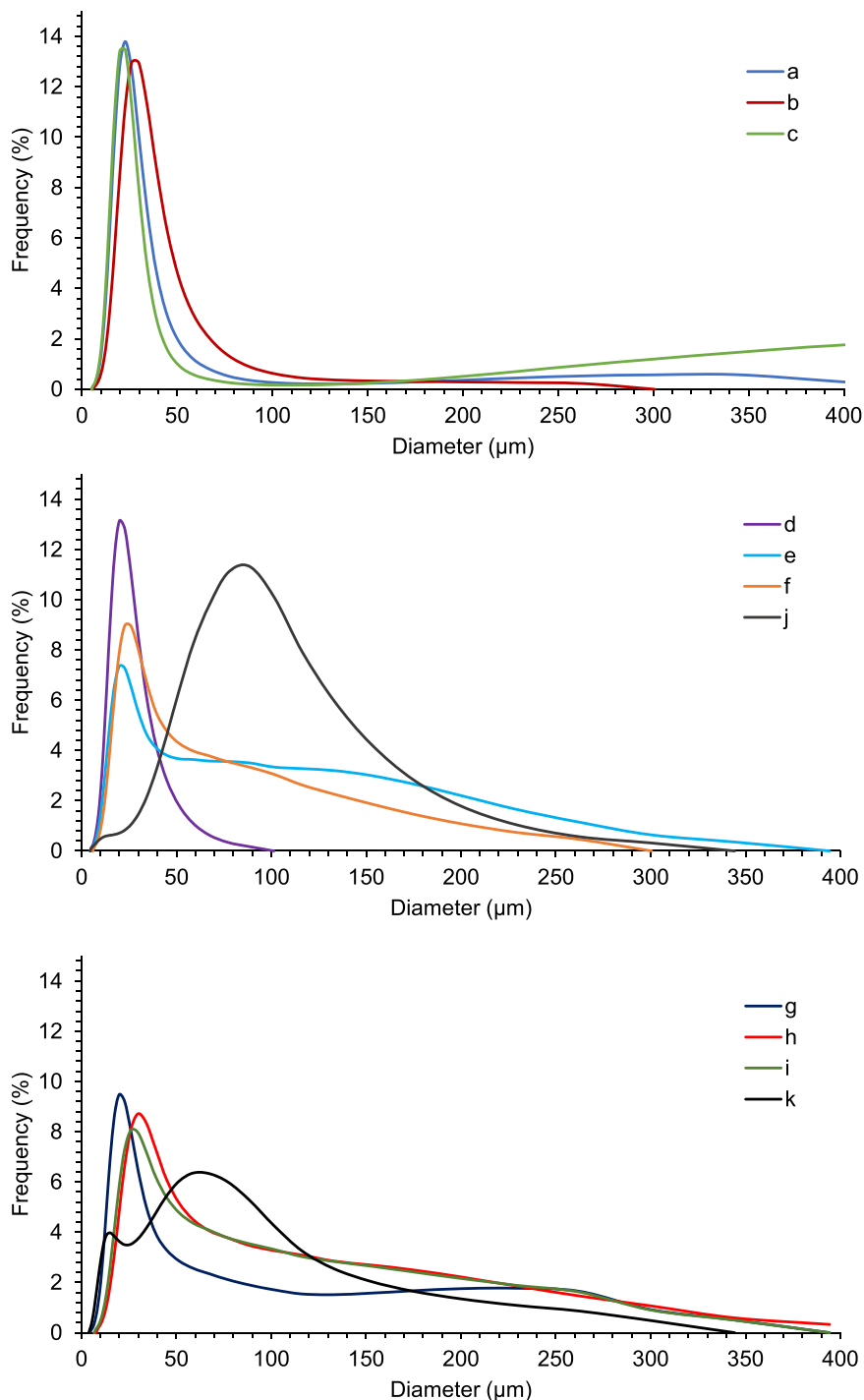


Fig. 2. Particle size distribution of native starch (S (a)) and starch modified by microwave treatment for 4 (S4 (b)) and 6 min (S6 (c)), hydrocolloids addition (guar SG (d), xanthan SX (g)), or both treatments (SG4 (e), SX4 (h), SG6 (f), SX6 (i)), along with the hydrocolloids alone (guar (j) and xanthan (k)).



native starch and starch-hydrocolloid mixture, suggesting granule agglomeration as observed by SEM (Section 3.7; Fig. 4). This behavior aligns with findings by Sun et al. [6] for native and waxy corn starch granules modified with xanthan gum and microwave heating (600 W for 4–6 min.). Xanthan gum induced greater agglomeration than guar gum in starch modification with hydrocolloid, indicating differences in the interactions between the gums and starch. Guar gum is neutral, whereas xanthan gum, being anionic, binds to starch more readily, resulting in an increase in D[4,3] [55].

### 3.5. Swelling power and solubility index in water

Starch modified with xanthan showed a significant difference from native starch only after microwave heating for 6 min ( $52.9 \pm 2.2\%$ ). Guar gum addition decreased the solubility index in water (SI) of cassava starch, irrespective of microwave treatment (Table 2). The reduction may be attributed to structural changes in the starch granule during gelatinization and the degree of molecular association within the starch granule [33]. Conversely, microwave treatment enhanced SI, with S6 exhibiting the highest value ( $87.5 \pm 0.7\%$ ).

Lower SI values are advantageous for applications such as the encapsulation of controlled-release flavors or bioactive compounds and biodegradable film production with good barrier properties for packaging. Chandanasree et al. [8] also observed the reduction of SI for carboxymethylcellulose-modified cassava starch.

The addition of hydrocolloids at the concentration employed in this study did not significantly influence the swelling power (SP) of cassava starch at 90 °C (Table 2). Microwave treatment markedly reduced the SP of native starch, with no significant difference ( $p > 0.05$ ) among the exposure time. Similarly, the swelling power of Bambara groundnut starch decreased following microwave treatment, but with a more pronounced decline at longer heating time [56]. There was a significant increase in the SP after the dual modification, with the highest value recorded for SG6 ( $22.4 \pm 1.4\%$ ).

### 3.6. Thermal properties

Microwave treatment promoted changes in the gelatinization properties of cassava starch as determined by DSC (Table 2, Fig. 3). A single endothermic peak was observed for all samples. Compared to native cassava starch, the peak temperature decreased with increasing microwave treatment time.

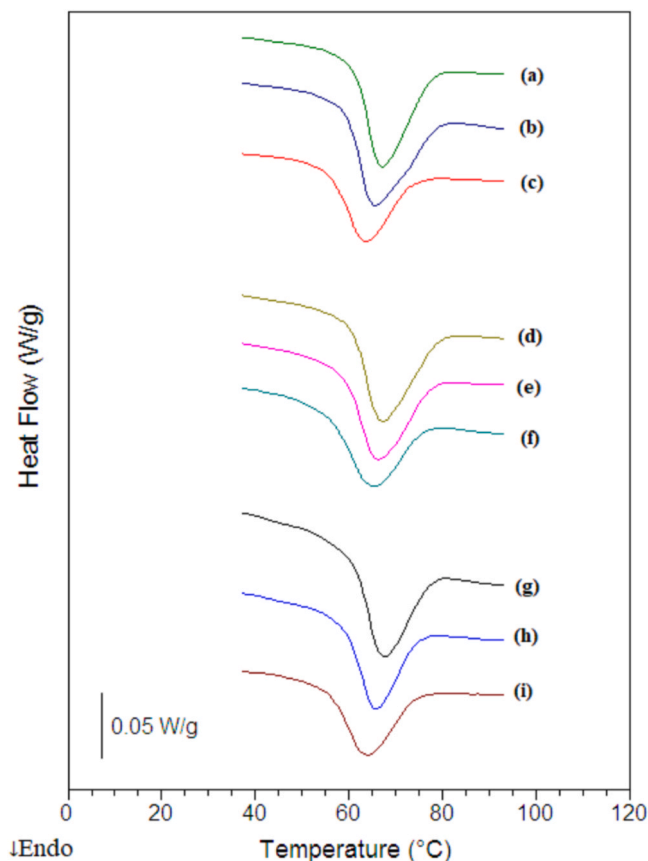


Fig. 3. Heat flow curves of native starch (S (a)) and starch modified by microwave treatment for 4 (S4 (b)) and 6 min (S6 (c)), hydrocolloids addition (guar SG (d), xanthan SX (g)), or both treatments (SG4 (e), SX4 (h), SG6 (f), SX6 (i)).

Overall, the gelatinization temperature ( $T_p$ ) decreased with increasing of the microwave treatment duration (Table 2). The heat treatment likely caused some structural disruption in the starch granules, leading to a slight loss of thermal stability. This effect was also confirmed by the decrease in gelatinization enthalpy ( $\Delta H$ ), with the lowest value of 11.1 J/g observed for SX6. Similar reductions in  $\Delta H$  have been reported for chestnut starch [30], normal and waxy corn starch [6], hydrocolloid-modified cassava starch subject to oven heating for 2 and 4 h [8], and microwave-modified Bambara groundnut starch [56].

Hydrocolloids (guar or xanthan gums) at the studied concentration did not significantly influence ( $p > 0.05$ )  $T_p$  or  $\Delta H$  for non-microwaved samples. Nevertheless, a small but significant ( $p < 0.05$ ) effect was observed for microwaved samples. Notably, hydrocolloids appeared to enhance the thermal stability of microwaved starch, as evidenced by an increased  $T_p$  for samples containing guar gum. However, this interaction did not sufficient to affect  $\Delta H$  (Table 2). Sun et al. [57] observed a significant decrease in  $T_p$  of potato starch with ionic gums (1 % sodium alginate, CMC and xanthan), after heating in an electric oven (130 °C, for 2 and 4 h). According to Sun, Xu and Xiong [6], the modification with xanthan and microwave for 4 and 6 min also reduced the  $T_p$  of normal and waxy corn starch.

### 3.7. Scanning electron microscopy (SEM)

Scanning electronic micrographs of native and modified starch granules are presented in Fig. 4. Cassava starch granules exhibited spherical, oval, and bell shapes of varying sizes, typical of this kind of starch [58]. No notable change in the granule surface morphology were observed upon modification. While starch granules mixed with hydrocolloids displayed a slightly rougher surface, potentially due to gum adhesion, as also observed by Sun, Xu and Xiong [6] on the surfaces of corn starch granules after the addition of xanthan gum. Microwave treatment did not induce pronounced changes in granule shape or the formation of cracks, which was consistent with results of other studies of starch systems with low moisture content ( $< 30\%$ ) subjected to microwave heating [59–61]. The controlled low moisture content (25 %) limited energy conversion and absorption, preventing granule destruction [3].

Interestingly, the type of gum influenced granule clustering, with higher agglomeration observed after the addition of xanthan

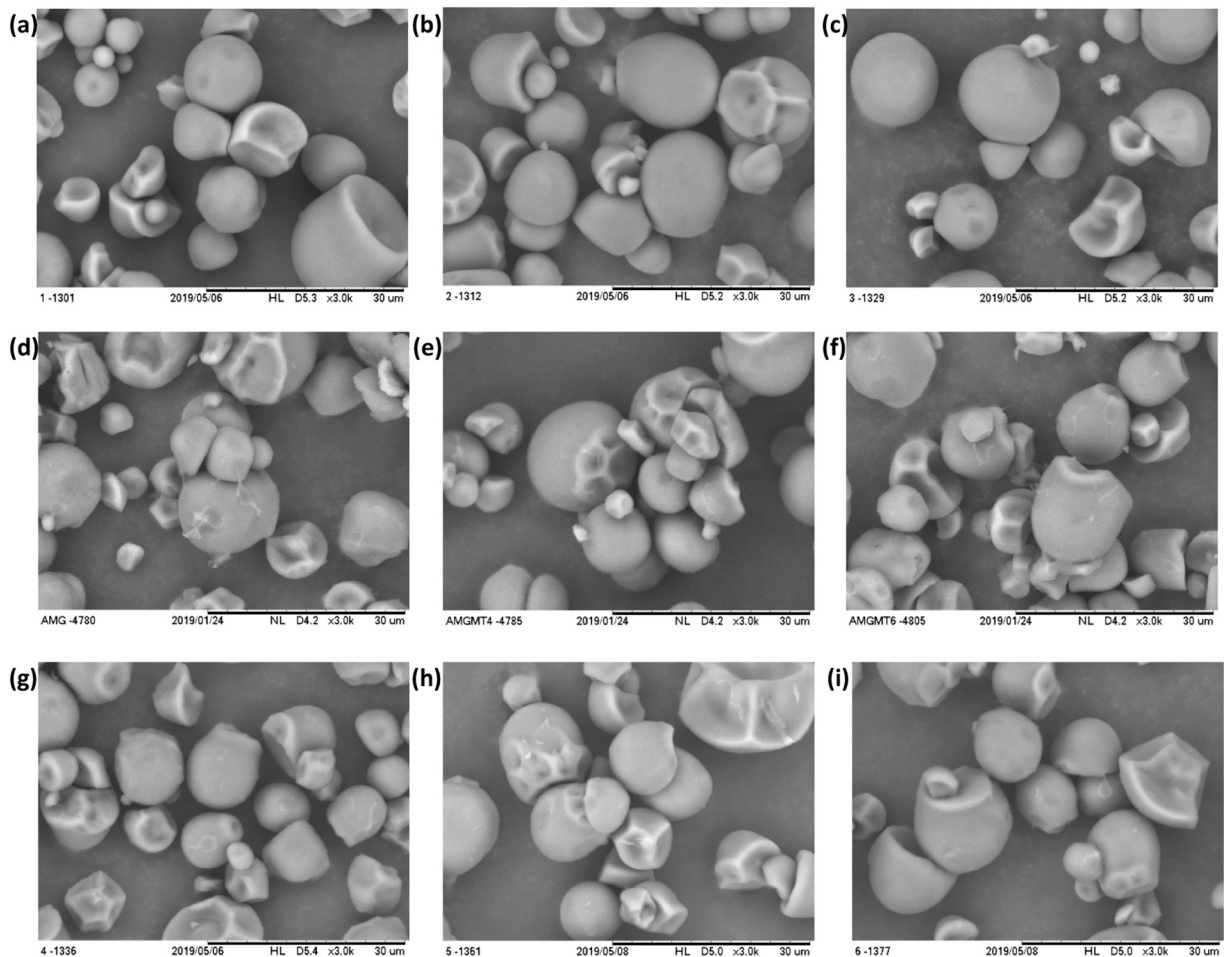


Fig. 4. Scanning electron microscopy (SEM) of native starch (S (a)) and starch modified by microwave treatment for 4 (S4 (b)) and 6 min (S6 (c)), hydrocolloids addition (guar, SG (d), xanthan, SX (g)), or both treatments (SG4 (e), SX4 (h), SG6 (f), SX6 (i)). Scale bars: 30  $\mu\text{m}$ , magnification:  $\times 3\text{k}$ .

gum. Larger clusters were formed after dual modification with addition xanthan gum and microwave heating, a result that corroborates the D[3,4] (Table 2 or Fig. 2). This observation is consistent with previous reports of agglomerate formation in hydrocolloid-modified starch after oven heating [8].

### 3.8. X-ray diffraction (XRD)

Internally, the starch granule is structured in concentric rings, known as radial growth rings, which develop from a nucleation center, termed the hilum [49]. In the growth rings the crystalline and amorphous regions alternate, characterizing the starch as a semi-crystalline or partially crystalline biopolymer. In the amorphous region, branching points of the amylopectin side chains and probably amylose molecules are present, which do not have a particular orientation, being positioned in a disorderly manner. Meanwhile, the crystalline region is formed by the double helices of the amylopectin chains, which are packaged in an orderly manner [62–64].

X-ray diffraction patterns and relative crystallinity of the granules are presented in Fig. 5. As a root starch, the cassava starch exhibited a characteristic type C diffraction pattern with prominent peaks at  $2\theta$  angles of  $15^\circ$ ,  $17^\circ$ ,  $18^\circ$  and  $23^\circ$ . The observed diffraction peaks did not change with the modification proposed in this work. These diffractograms are in accordance with that presented by Sun, Xu and Xiong [6] in a study of normal and waxy corn starch modification with xanthan gum (1 %) and microwave heating for 4 and 6 min. Similar peaks were identified by Bet et al. [57] for starch from common pea seeds, which showed no change after mixing starch with hydrocolloids (5 % carrageenan, CMC, guar, locust bean, xanthan and pectin).

The lowest intensities for each peak were found for cassava starch with addition of guar gum, regardless of microwave treatment (SG, SG4, SG6), followed by cassava starch with addition of xanthan gum and microwave treatment (SX4 and SX6). Native starch exhibited the highest peak intensities.

Relative crystallinity values remained around  $14 \pm 2\%$  for the analyzed samples. The addition of 1 % hydrocolloids (guar or xanthan) did not significantly alter the relative crystallinity degree of cassava starch, except for SG, which showed a significant reduction. Alberton et al. [58] also observed no significant change in the relative crystallinity of cassava starch with the addition of 1 % hydrocolloids (pectin, CMC, locust bean and xanthan). However, contrasting results have been observed, with increases in relative crystallinity for various hydrocolloid-modified starch [65], except for guar gum, which did not differ significantly from native starch. Interestingly, the crystallinity degree of SG6 was higher than that of SG, contrary to several studies that report a decrease in starch crystallinity after microwave treatment.

### 3.9. Dielectric properties

The dielectric properties reflect a system's response to microwaves and its ability to transform incoming electrical energy into heat. In the microwave frequency range, dielectric loss consists primarily of dipolar loss and ionic loss [66]. The effect of field frequency (500–3000 MHz) on the relative permittivity ( $\epsilon'$ ) and loss factor ( $\epsilon''$ ) at  $25^\circ\text{C}$  for native and modified cassava starches in powder form is illustrated in Fig. 6(a) and 6(b), respectively.

As shown in Fig. 6(a), samples without microwave treatment (S, SX and SG) exhibited higher values of  $\epsilon'$ . However, samples modified with hydrocolloids and microwave treatment showed lower values of  $\epsilon'$ . This result agrees with the moisture content of samples (Table 2), since water is the main contributor to permittivity. Generally, the  $\epsilon'$  and  $\epsilon''$  values obtained for all samples were small due to the low moisture content of the cassava starch powder and low water activity ( $\sim 0.6$ ). This suggests that the measurement of  $\epsilon'$  was highly influenced by the electronic and atomic polarization mechanism of the macromolecules [47,67]. Li et al. [61] observed the similar behavior in a study of the dielectric properties of almond grains with a moisture content of 4.2%. Normally, relative permittivity and loss factor are higher in systems with high moisture content [3,68]. The  $\epsilon'$  values found in this study were consistent with those reported in the literature, such as  $\epsilon' = 2.25$  for granular cassava starch at  $30^\circ\text{C}$  and a frequency of 2450 MHz [69].

The  $\epsilon'$  of SG or SG6 was superior to SX or SX6 ( $\epsilon'_{\text{SG}} > \epsilon'_{\text{SX}}$  and  $\epsilon'_{\text{SG6}} > \epsilon'_{\text{SX6}}$ ). The higher relative permittivity of SG is attributed to the more flexible molecular structure and less intense intermolecular interactions of guar gum, which allow greater mobility and the formation of electric fields within the material. The less intense intermolecular interactions in guar gum result in a more open matrix, facilitating the formation and movement of electric fields. Additionally, the structure of guar gum allows greater mobility of water molecules and other dipoles within it [38,70]. Higher D[4,3] values were observed for SX compared to SG, and for SX6 compared to SG6, which may explain the higher dielectric constant of starch modified with guar gum compared to xanthan gum. Larger or more rigid molecules have less freedom to reorient, which can reduce polarization and, consequently, the relative permittivity.

The loss factors of the analyzed samples remained practically constant with increasing frequency, with a peak observed at approximately 2450 MHz. The lowest  $\epsilon''$  values were found in SX4, while the highest values were observed in S, SX and SG. The  $\epsilon''$  values obtained were consistent with those reported in the literature for granular cassava starch at  $30^\circ\text{C}$  and a frequency of 2450 MHz ( $\epsilon'' = 0.08$ ). Overall, the relative permittivity ( $\epsilon'$ ) decreased, and the loss factor ( $\epsilon''$ ) showed a peak with increasing frequency, likely due to a delay in the dipole moment [68].

### 3.10. Penetration depth

The electromagnetic energy penetration depth ( $D_p$ ) is influenced by microwave frequency and dielectric properties of the sample, and is generally used to describe the extent to which the sample can be penetrated by microwaves at a given frequency. It typically attenuates exponentially as a function of the distance within the sample [3,45]. Based on the measured dielectric properties, the

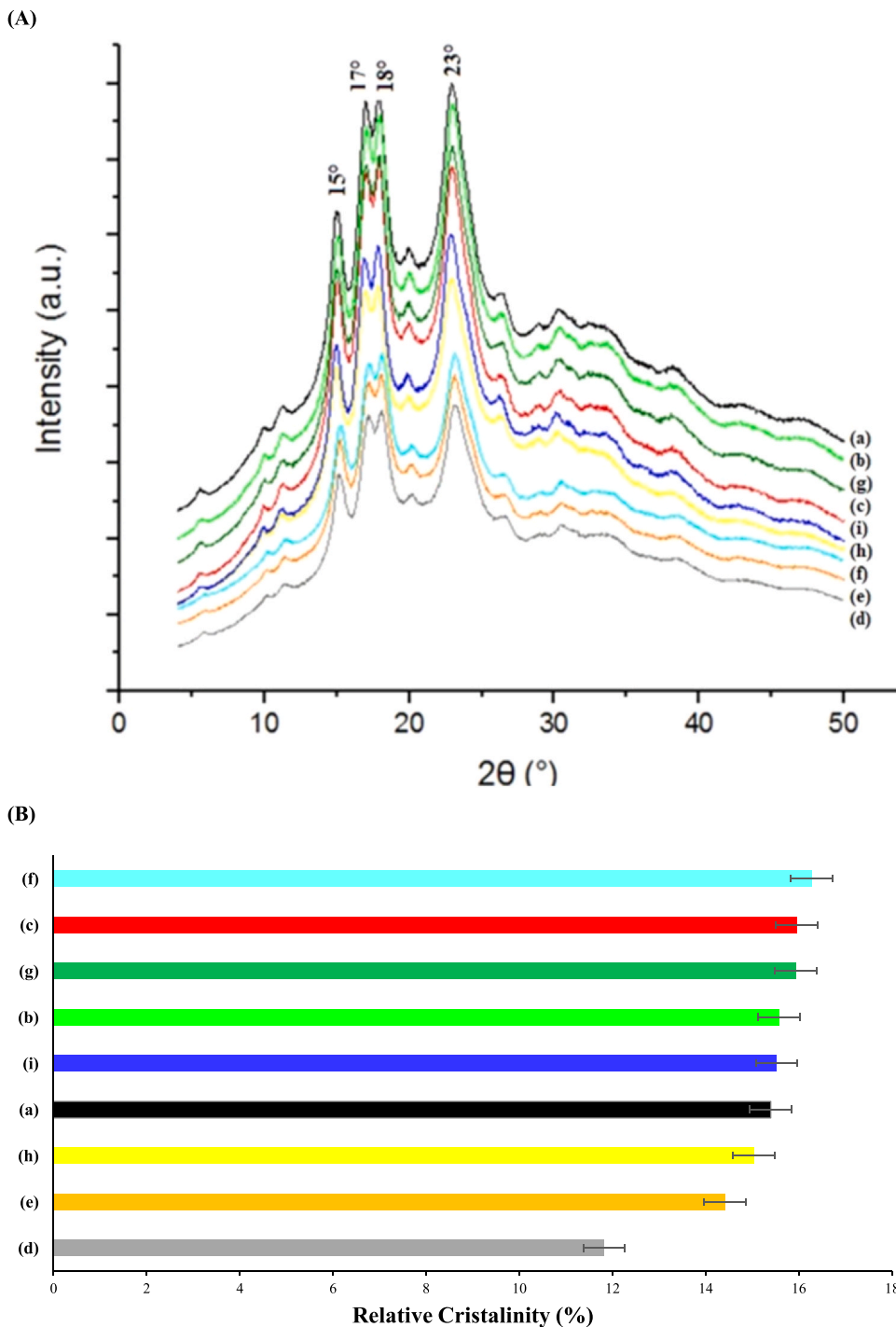
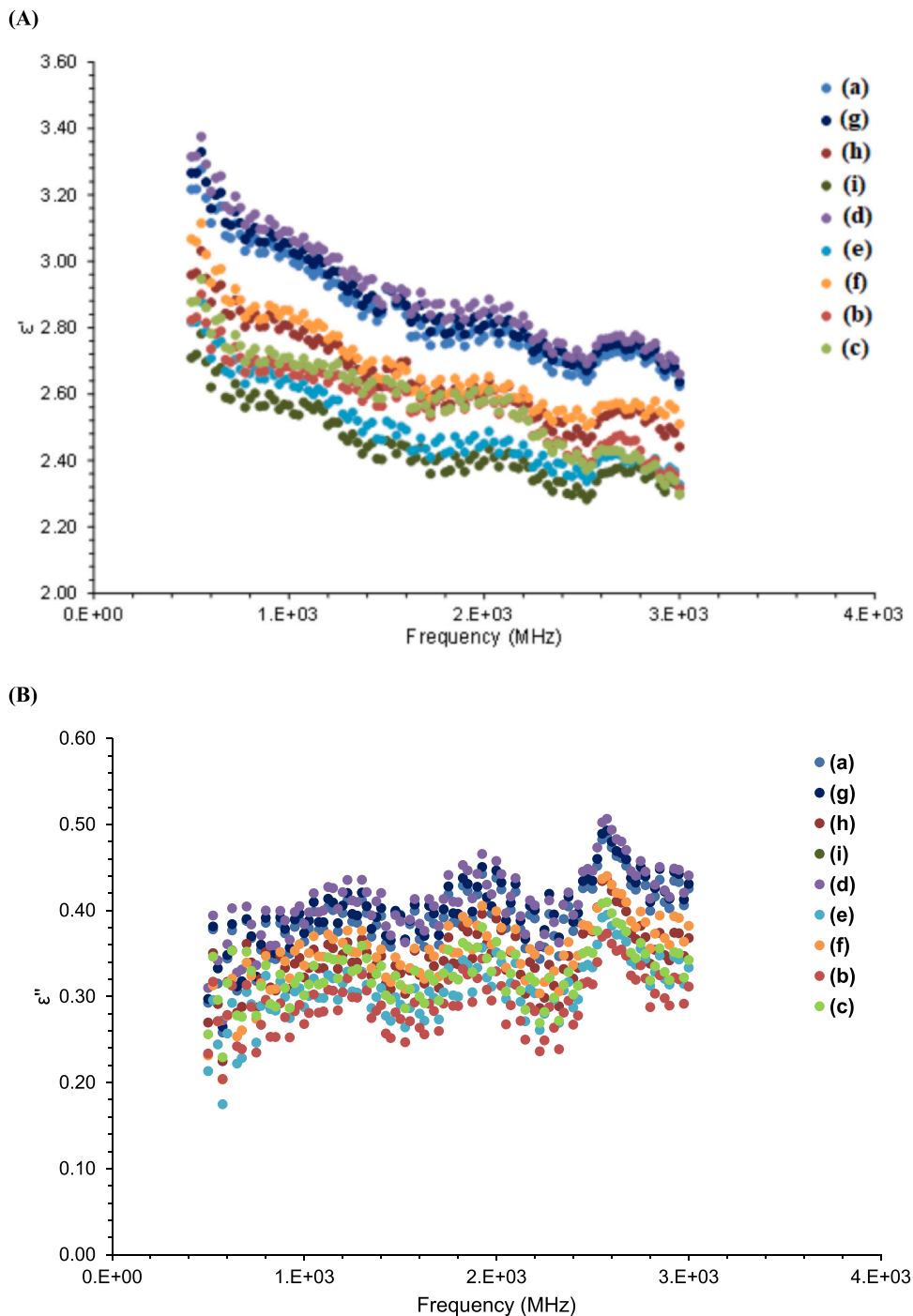


Fig. 5. (A) Diffractogram and (B) relative crystallinity of native starch (S (a)) and starch modified by microwave treatment for 4 (S4 (b)) and 6 min (S6 (c)), hydrocolloids addition (guar SG (d), xanthan SX (g)), or both treatments (SG4 (e), SX4 (h), SG6 (f), SX6 (i)).

penetration depths of the electromagnetic wave in the samples were calculated (Fig. 7). The penetration depths exhibited very similar trends, decreasing with increasing frequency, with the decrease being greater at low frequencies. This behavior was also observed by Guo and Zhu [71] in their study of red pepper powder with moisture contents ranging from 10.4% to 30.8% (w.b.).

$D_p$  values for cassava starches ranged from approximately 0.7 cm (SX6) to 2.0 cm (SG), at 500 MHz, from 0.8 cm (S4 and SX6) to 1.2 cm (SX, SG and S) at 915 MHz, and from 0.3 cm (SX6 and SG6) to 0.5 cm (SX, SG and S) at 2450 MHz. This information is important, for example, for drying processes, in which the material thickness must not exceed two to three times the penetration



**Fig. 6.** (A) Dependence of relative permittivity ( $\epsilon'$ ) and (B) dielectric loss factor ( $\epsilon''$ ) with frequency of native starch (S (a)) and starch modified by microwave treatment for 4 (S4 (b)) and 6 min (S6 (c)), hydrocolloids addition (guar SG (d), xanthan SX (g)), or both treatments (SG4 (e), SX4 (h), SG6 (f), SX6 (i)) at room temperature ( $\sim 25$  °C).

depth to ensure uniform drying [71]. Additionally, lower frequencies (915 MHz) generally provide more uniform dielectric heating due to their greater  $D_p$  compared to 2450 MHz [65]. The unmodified microwave samples (S, SX and SG) showed relatively larger penetration depths than those that underwent heat treatment. Lower penetration depth at microwave frequencies results in greater heating of the material surface, with the lowest penetration depth found for SX6, which may explain the modifications of the other starch properties being more pronounced for samples modified in microwave for 6 min.

The penetration depth of microwaves in starch is affected by several factors, which can be categorized into those related to the starch (moisture content, chemical composition, particle size), the microwaves (frequency and power), and the environmental

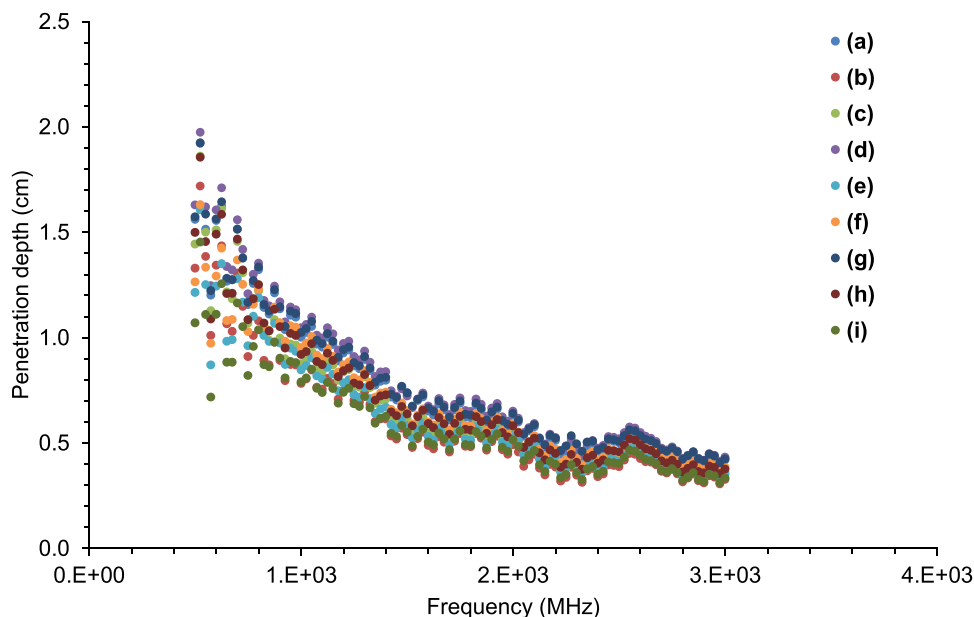


Fig. 7. Calculated penetration depths (in cm) of the incident electromagnetic field in the native starch (S (a)) and starch modified by microwave treatment for 4 (S4 (b)) and 6 min (S6 (c)), hydrocolloids addition (guar SG (d), xanthan SX (g)), or both treatments (SG4 (e), SX4 (h), SG6 (f), SX6 (i)) in the 500–3000 MHz frequency range.

conditions (initial temperature of the starch and surroundings, pressure, and the presence of other materials with different dielectric properties). The native starch and non-microwave-modified starch (S, SX, and SG) exhibited smaller particle sizes compared to the microwave-modified samples, and therefore tend to absorb microwaves more uniformly.

#### 4. Conclusion

The combined effects of microwave and hydrocolloid modification offer an alternative approach to chemical modification methods and can alter the properties of cassava starch. Dual modification of cassava starch resulted in notable variations in its properties, with the starch samples undergoing double modifications (SG6 and SX6) showing the most improvements.

In general, starch modified only with hydrocolloids did not show significant differences in its dielectric properties, with microwave treatment being the most relevant factor in changing these properties. Dual modification had a greater influence on the dielectric behavior of cassava starch, altering the morphology of the granules without being destructive, increasing the swelling power (SG6), and reducing the gelatinization temperature of the starch (SX6). These effects are probably due to the more flexible molecular structure and less intense intermolecular interactions of guar gum, which allow greater mobility and the formation of electric fields within the material, resulting in a more open matrix that facilitates the movement of these electric fields.

Depending on the need and functionality required for the starch, one can choose the most advantageous method. Further studies should be documented to confirm the advantages of microwave modification combined with other methods and their effects on the functional properties of starches.

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#### CRedit authorship contribution statement

**Paula Cremasco:** Writing – original draft, Methodology, Investigation. **Karine Mayuri Pistoni Siqueira:** Methodology. **Paulo José do Amaral Sobral:** Writing – review & editing, Validation. **Walter Ferreira Velloso Junior:** Writing – review & editing, Supervision. **César Gonçalves de Lima:** Methodology, Formal analysis. **Jorge Andrey Wilhelms Gut:** Writing – review & editing, Methodology, Investigation. **Izabel Cristina Freitas Moraes:** Writing – review & editing, Supervision, Project administration, Methodology, Investigation, Funding acquisition.

## Declaration of Competing Interest

The authors confirm that they have no conflicts of interest with respect to the work described in this manuscript.

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