

Physicochemical and Thermal Characterization of Starch from Three Different Plantain Cultivars in Puerto Rico

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Abstract—Plantain contains starch as the main component and represents a relevant source of this carbohydrate. Starches from different cultivars of plantain and bananas have been studied for industrialization purposes due to their morphological and thermal characteristics and their influence in food products. This study aimed to characterize the physical, chemical, and thermal properties of starch from three different plantain cultivated in Puerto Rico: Maricongo, Maiden and FHIA 20. Amylose and amylopectin content, color, granular size, morphology, and thermal properties were determined. According to the amylose content in starches, FHIA 20 presented lowest content of the three cultivars studied. In terms of color, Maiden and FHIA 20 starches exhibited significantly higher whiteness indexes compared to Maricongo starch. Starches of the three cultivars had an elongated-ovoid morphology, with a smooth surface and a non-porous appearance. Regardless of similarities in their morphology, FHIA 20 exhibited a lower aspect ratio since its granules tended to be more elongated. Comparison of the thermal properties of starches showed that initial starch gelatinization temperature was similar among cultivars. However, FHIA 20 starch presented a noticeably higher final gelatinization temperature (87.95°C) and transition enthalpy than Maricongo (79.69°C) and Maiden (77.40°C). Despite similarities, starches from plantain cultivars showed differences in their composition and thermal behavior. This represents an opportunity to diversify plantain starch use in food-related applications.

Keywords—Aspect ratio, morphology, *Musa* spp., starch, thermal properties, amylose content.

I. INTRODUCTION

PLANTAIN (*Musa paradisiaca*) is considered one of the most important sources of energy for millions of people in Africa, the Caribbean, Latin America, Asia, and the Pacific [1]. For 2019, statistics from the Food and Agriculture Organization of the United Nations (FAO) showed a slight increase in the value of global gross production (0.86% annually between 2018 and 2019) [2]. Latin America and the Caribbean alone produce more than 9 million of tons of plantain and banana annually [2] and most of it is exported, reaching an annual value higher than US \$ 7600 million. Ecuador is the first ranked exporter in Latin America [3].

In Puerto Rico, plantain is a staple crop. There is a diversity of plantain cultivars in the Puerto Rican market; Maricongo being the predominant variety. However, this clone does not

keep uniformity in the number of hands and fruits per bunch [4]-[6]. This characteristic affects fruit yield and quality.

New plantain cultivars have been incorporated to the Puerto Rican market to increase the offer and availability of this fruit. Goenaga and Irizarry evaluated two varieties of plantain (*Musa*, AAB) Congo type, Maiden and Red Dominican, to determine the effect of bunch pruning on fruit size and yield [7]. In this study, it was stated that Maiden fruits with pruned bunches overpassed the average weight of 270 g (important criteria in the marketability of fresh product).

From a nutritional viewpoint, plantains contain more than 70% of carbohydrates [8] and starch represents the largest constituent of this macronutrient. This component is responsible for functional and structural properties of flours such as plantain flour [9]. Plantain could be considered by some to be an unconventional starch source despite the high amount of starch it contains [10]. As such, the starch influence on the rheological characteristics of the processed product should be considered. To identify potential uses of this starch, its thermal properties, morphology, and amylose content need to be studied.

Although plantain is consumed through a variety of local dishes in Puerto Rico, there is not enough research about the physicochemical and nutritional properties of plantains and the application or use of their starch in the formulation of other processed foods. For this reason, the objective of this study was to characterize the physical, chemical, and thermal properties of starch from three different plantain cultivated in Puerto Rico: Maricongo, Maiden and FHIA 20.

II. MATERIALS AND METHODS

A. Materials

Plantains Maricongo, Maiden, and FHIA 20 at stage 1 of ripeness (Fig. 1) were provided by Juana Diaz Agricultural Experimental Station and processed in the pilot plant of Food Science and Technology program of University of Puerto Rico, Mayaguez Campus. Flour and starch were obtained.

For flour preparation, plantains were peeled, sliced, and immersed in citric acid 0.3%, with a 1:1.5 (w/v) fruit/solution relation for 5 min. Fruit slices were dried in a forced air

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dehydrator at 40°C for 24 h, then ground and sieved through a 600-µm mesh.

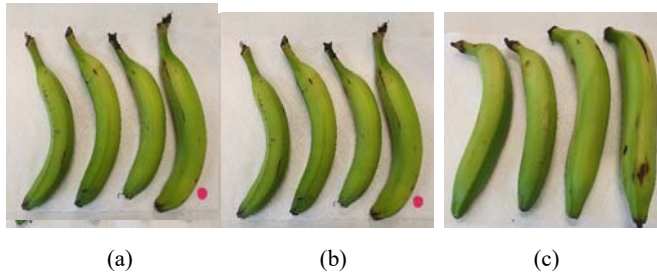


Fig. 1 Plantain at stage 1 of ripeness (a) Maricongo (b) Maiden (c) FHIA 20

Plantain starch was obtained by the method of Flores-Gorosquera et al., with some modifications [11]. Plantains were peeled, sliced, and immersed in citric acid 0.3%, with a 1:1.5 fruit/solution relation for 5–10 min. Fruit slices were blended in an industrial blender at maximum speed for 2 min. Blended fruit was passed through a cheesecloth and the suspension stored at 5°C for 24 h to facilitate starch precipitation. Suspension was centrifuged at 4700 rpm for 15 min and rewashed six times to guarantee absence of residues in the starch samples. Final paste was dried in a forced air dehydrator at 40°C for 24 h.

B. Total Starch Content

Starch hydrolysis was carried out according to the method described by Vatanasuchart, Niyomwit, & Wongkrajang [12]. Flour samples of 50 mg were weighted in centrifuge tubes and dispersed in 6 mL KOH 2M. After 30 min of repose at ambient temperature, samples were incubated with amyloglucosidase at 60°C for 45 min with constant shaking. Hydrolyzed glucose from starch was quantified by phenol-sulphuric acid method by Sadasivam & Manickam [13].

C. Apparent Amylose and Amylopectin Content

Apparent amylose content of starch of flour samples was determined according to AACC (2010) method 61–03(10), which is based on the maximum absorption at 620 nm of amylose-iodine complex [14]. Amylopectin content was determined by difference.

D. Color

Starch color was determined using Hunter lab (HunterLab MiniScan XE, VA, USA) configured with D65 illuminant and observation angle of 10°. L* a* and b* color values were measured. Whiteness Index (WI), Chroma (C*) and Hue (h*) were calculated [15], according to the following formulas:

$$WI = 100 - \sqrt{(100 - L^*)^2 + a^{*2} + b^{*2}} \quad (1)$$

$$C^* = \sqrt{a^{*2} + b^{*2}} \quad (2)$$

$$h^* = \arctan\left(\frac{b^{*2}}{a^{*2}}\right) \quad (3)$$

E. Granular Size and Morphology

Granular size and morphology were obtained by scanning electron microscopy. Samples were attached to circular specimen tubs, covered with electroconductive charcoal tape and a layer of gold, and viewed under a scanning electron microscope using acceleration voltage of 5 kV. Starch granule images were obtained with a 500X magnification.

Diameter and length were measured using Eleif photo measure program. Aspect ratio (A_R) then was calculated using the following formula:

$$A_R = \frac{D_{min}}{D_{max}} \quad (4)$$

where D_{min} and D_{max} are the diameter and the length of the starch granule, respectively.

F. Thermal Properties

Starch samples (approximately 6 ± 0.1 mg) were weighed into aluminum pans and deionized water added to obtain a starch/water ratio of 1:4 (w/v) (24 ± 1 µL). Pans were sealed and equilibrated at room temperature for 12 h before DSC analysis. Samples were heated from 20°C to 120°C at a heating rate of 5°C/min, using an empty aluminum pan as the reference. Thermal transition parameters (i.e., onset temperature (T_o), peak temperature (T_p), end temperature (T_e) and enthalpy change (ΔH)) were determined.

III. RESULTS AND DISCUSSION

A. Total Starch and Apparent Amylose Content

Total starch content data appears in Table I and ranged from 89.70% to 93.40%. These values agree with previous works, where starch content of plantains ranged from 72.7% to 99.6% [8], [10], [12], [16]. Differences in starch content depends on the cultivar and region cultivated. In this study, Maiden had the highest starch content (93.40%), followed by FHIA (91.40%) and Maricongo (89.10%).

Amylose content of starches ranged from 21.82% to 28.75%. These values were within ranges reported in literature for plantain starch [12], [17], [18]. Maricongo (27.78%) and Maiden (28.75%) starch showed similar amylose content while FHIA 20 (21.82%) exhibited lowest content. High amylose values have been associated with greater values of resistant starch [19]-[21].

TABLE I
TOTAL STARCH OF PLANTAINS AND APPARENT AMYLOSE CONTENT OF STARCH

Component	Maricongo	Maiden	FHIA 20
Total starch	89.70 ± 1.65^a	93.40 ± 2.77^{ab}	91.40 ± 1.47^b
Amylose	27.78 ± 2.87^a	28.75 ± 0.62^a	21.82 ± 0.98^b
Amylopectin	72.22 ± 2.87^a	71.25 ± 0.62^a	78.18 ± 0.98^b



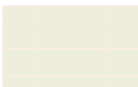
Values are means \pm standard deviation. Means with different letters in the same row differ significantly ($p < 0.05$).

B. Color

Color parameters starches can be observed in Table II. L* values for each cultivar were close to the range reported by different authors for plantain starch (i.e., 75.4 to 90.9) [16],

[22]-[24]. Maricongo starch had an L* value within the previously mentioned range. However, Maiden and FHIA 20 starches had slightly higher values. Higher L* values indicate high purity level [25]. Maricongo starch had the highest Chroma value (8.20), followed by Maiden (6.53) and, FHIA 20 (5.84).

TABLE II
 COLOR PARAMETERS OF PLANTAIN STARCHES

Parameter	Maricongo	Maiden	FHIA20
L*	88.49 ± 0.59 ^a	92.94 ± 0.51 ^b	91.76 ± 0.35 ^c
a*	2.33 ± 0.14 ^a	1.96 ± 0.09 ^b	1.61 ± 0.06 ^c
b*	7.86 ± 0.45 ^a	6.23 ± 0.18 ^b	5.61 ± 0.14 ^c
Chroma (C*)	8.20 ± 0.47 ^a	6.53 ± 0.19 ^b	5.84 ± 0.15 ^c
Hue (h*)	85.01 ± 0.10 ^a	84.35 ± 0.26 ^b	85.28 ± 0.15 ^c
Whiteness Index (WI)	85.87 ± 0.75 ^a	90.38 ± 0.49 ^b	89.90 ± 0.36 ^b
Color			

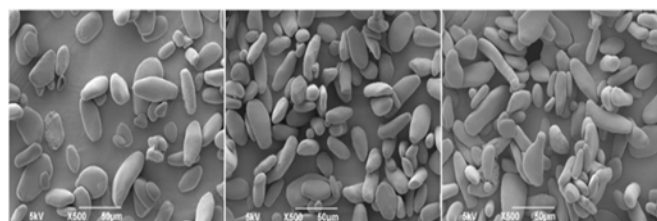
Values are means ± standard deviation. Means with different letters in the same row differ significantly (p < 0.05).

Whiteness Index (WI) correlate to consumer preference for white color. Starches had WI values between 85.87 and 90.30. Maiden starch had the highest value. These values were close to the ones reported for other botanical sources such as cocoyam (91.82 - 97.13), arrowroot (95.00), and cassava (95.92 - 96.07) [26]-[29].

Chroma (C*) is a qualitative parameter of color intensity. The higher values of chroma, the higher color intensity perceived by the human eye [30]. Regarding of Chroma values, Maricongo values had the highest value (8.20), followed by Maiden (6.53) and FHIA20 (5.84). Hue values for studied starches were within the range from 84.35 to 85.28, indicating that starches had a yellow-greenish tone.

C. Granular Size and Morphology

Fig. 2 shows micrographs of starch granules. In general terms, starches from studied cultivars had an elongated ovoid morphology, with smooth surface and non-porous appearance. This agrees with findings by Perez-Sira [16], Ramiro-Cortés et al. [31], and Chávez-Salazar et al. [10], for starches from different plantain cultivars. According with these reports, starch granules from this farinaceous have irregular morphology and a tendency towards elongated shapes. Smooth surface and non-porous appearance presented by granules also agree with results obtained by Kayisu and Hood [32].



(a) (b) (c)

Fig. 2 Scanning electron micrographs of plantain starch: (a) Maricongo, (b) Maiden, and (c) FHIA 20

Plantain starch granules have an ample range of length (7.8 - 61.3 μm) and diameter (16.4 - 35.1 μm) [33]. Diameter and length from Maricongo, Maiden, and FHIA20 starches was in the range reported in previous works [10], [34].

Maricongo starch had granules with diameters ranging from 12.53 to 30.29 μm and length from 24.52 to 55.59 μm. Maiden cultivar presented granules with diameter oscillating between 9.08 and 28.50 μm and length between 17.06 and 54.84 μm. Although FHIA 20 granules presented similarities with the diameters of Maiden and Maricongo (9.54 - 21.41 μm), length was significantly different, ranging from 27.50 to 65.62 μm. Length, diameter, and aspect ratio data appear Table III.

TABLE III
 DIMENSIONS OF PLANTAIN STARCH GRANULES

Parameter	Maricongo	Maiden	FHIA20
Diameter	18.91 ± 4.75 ^a	17.70 ± 4.73 ^a	16.40 ± 3.66 ^a
Length	37.00 ± 7.53 ^a	36.28 ± 8.18 ^a	45.78 ± 12.67 ^b
Aspect Ratio	0.52 ± 0.11 ^a	0.50 ± 0.11 ^a	0.38 ± 0.11 ^b

Values are means ± standard deviation. Means with different letters in the same row differ significantly (p < 0.05).

Comparison of starch diameters showed no significative differences among cultivars. In terms of length, Maricongo and Maiden starch were not significantly different, but FHIA 20 starch had higher length. Observation of starch granules suggested a cylinder morphology. Thus, estimation of aspect ratio allowed to make reasonable comparisons. Maricongo and Maiden had similar dimensions, therefore their aspect ratios were similar. However, FHIA 20 presented higher length values, resulting in a lower aspect ratio. Aspect ratio distribution of each starch is presented in Figs. 3, 4 and 5.

According to the histograms, starch granules from Maricongo (Fig. 3) and Maiden (Fig. 4) had similar aspect ratios, whereas granules from FHIA 20 starch presented a lower aspect ratio. Additionally, Maricongo and Maiden granules had comparable relative frequencies for aspect ratio (0.40 - 0.60). In contrast, aspect ratio of FHIA 20 starch granules mostly ranged from 0.27 and 0.38 (Fig. 5). Thus, Maricongo and Maiden starch had granules which tended to be less elongated than FHIA 20. These differences had an effect in their thermal properties.

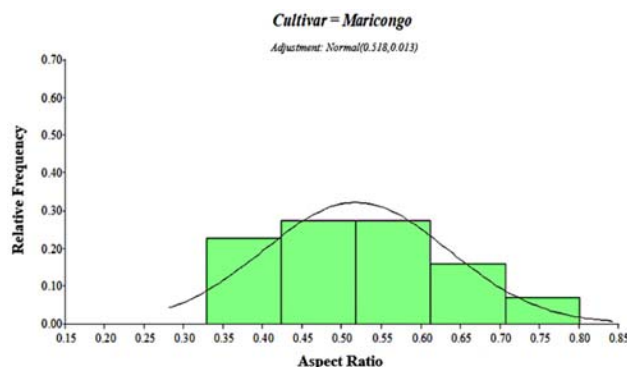


Fig. 3 Aspect Ratio distribution of Maricongo starch granules

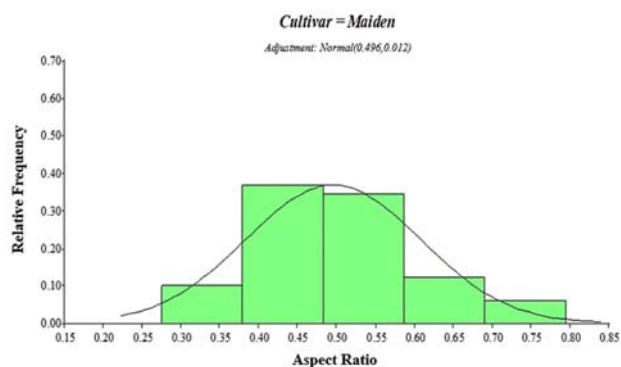


Fig. 4 Aspect Ratio distribution of Maiden starch granules

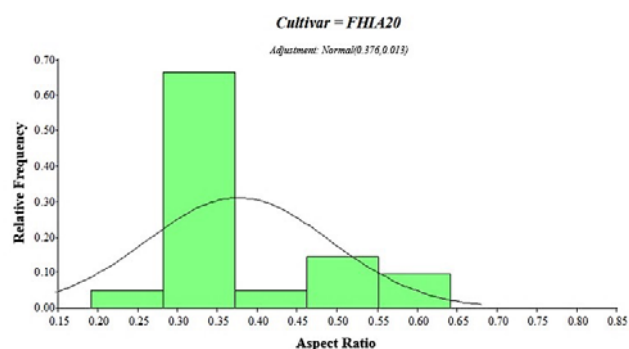


Fig. 5 Aspect Ratio distribution of FHIA 20 starch granules

D. Thermal Properties

According to information in Table IV, temperatures and enthalpy values for each cultivar were in the range reported in the literature for plantain starch [10], [18].

TABLE IV
THERMAL PROPERTIES OF PLANTAIN STARCHES

Parameter	Maricongo	Maiden	FHIA20
Onset Temperature (To in °C)	68.94 ± 0.21 ^a	67.92 ± 0.34 ^b	66.27 ± 0.11 ^c
Peak Temperature (Tp in °C)	73.07 ± 0.28 ^a	72.04 ± 0.74 ^a	69.84 ± 0.08 ^b
End temperature (Te in °C)	79.69 ± 0.70 ^a	77.40 ± 0.19 ^b	87.95 ± 0.59 ^c
Enthalpy change (ΔH in J/g)	11.45 ± 0.37 ^a	5.89 ± 0.65 ^b	17.03 ± 0.33 ^c

Values are means ± standard deviation. Means with different letters in the same row differ significantly ($p < 0.05$)

Onset temperatures were similar among cultivars. Peak temperature, the temperature of greatest starch hydration, were similar for Maricongo and Maiden, but FHIA exhibited a lower value (Fig. 6). Likewise, end temperatures for Maricongo and Maiden were similar, while FHIA 20 presented a noticeable higher end temperature. Despite differences, end temperatures fall within the range reported by Chávez-Salazar et al. [10]

The loss of molecular order in granule starches is reflected by the enthalpy change (ΔH). Subsequently, starch crystallites melted, as consequence of the heating process [35]. Enthalpy values of Maricongo and Maiden starches were within the range

reported in previous plantain works (i.e., 8.04 to 9.47 J/g) [10], [18]. Maiden starch had the lowest enthalpy value, followed by Maricongo, and FHIA 20, (5.89, 11.45 and 17.03 J/g, respectively).

The final gelatinization temperature of FHIA 20 starch was higher as well as the transition enthalpy, which indicates that the starch of this cultivar needs more heat to carry out the transition from crystalline to gelatinized starch compared to the other starches. These values can relate with what was observed in the SEM micrographs (Fig. 2), where FHIA 20 starch presented the greater granules. Therefore, it could be inferred that FHIA 20 starch granule will require more heat to be totally gelatinized.

Integrating these results with data in the literature, it has been evidenced that plantain starch granules have an ample gelatinization range, a greater heterogeneity in the granule size distribution and different arrangement of the components of starch.

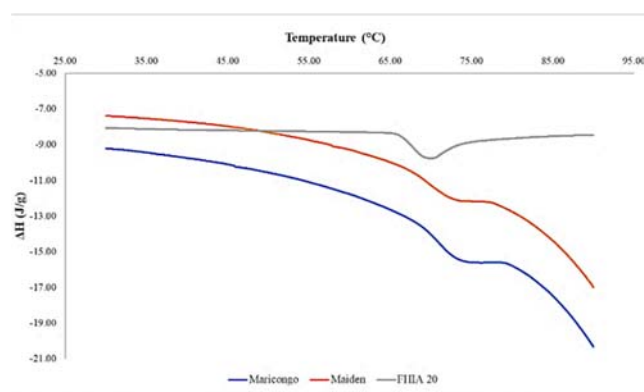


Fig. 6 Thermograms of Maricongo, Maiden and FHIA 20 starches

IV. CONCLUSION

Maricongo, Maiden and FHIA 20 cultivars were not significantly different in terms of starch content, which confirmed the potential use of this fruit as starch source for food industry. Amylose content was significantly lower in FHIA 20 starch compared to Maiden and Maricongo.

Regarding of size distribution and morphology, FHIA 20 starch showed more tendency to elongated granules, which influenced its thermal properties, resulting in a higher final temperature of gelatinization. Maiden and Maricongo starches did not show differences in morphology and aspect ratio as well as thermal behavior.

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