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Resistant starch from plantain (Macho *Musa paradisiaca* L.) and banana (Roatan *Musa sapientum* L.) varieties crosslinked with epichlorohydrin

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Abstract

Resistant starch from plantain (Macho *Musa paradisiaca* L.) and banana (Roatan *Musa sapientum* L.) varieties was chemically modified by crosslinking using epichlorohydrin (EPI). These modified starches were subjected to in vitro digestibility studies using the Englyst method to determine the content of rapidly digestible starch (RDS), slowly digestible starch (SDS) and resistant starch (RS). The thermal stability of these crosslinked starches was evaluated by gelatinization and retrogradation analyses, and their enthalpies were determined using differential scanning calorimetry (DSC). Additionally, their functional properties were evaluated. Chemical modification with EPI significantly increased the RS content in both starch varieties compared to that in native starch. The enthalpy and gelatinization temperature decreased in the EPI-modified starches of both varieties, indicating lower thermal stability during the gelatinization process compared to that of native starch. In general, both varieties of crosslinked plantain starch had lower viscosity (0.43 Pa*s) than did native starch (0.58 Pa*s). The results indicates that this starch crosslinked with EPI constitutes an alternative for use in food for people with health problems such as high cholesterol levels or postprandial insulin concentrations.

Keywords Resistant starch, Chemical modification, Crosslinking, Digestibility, Banana

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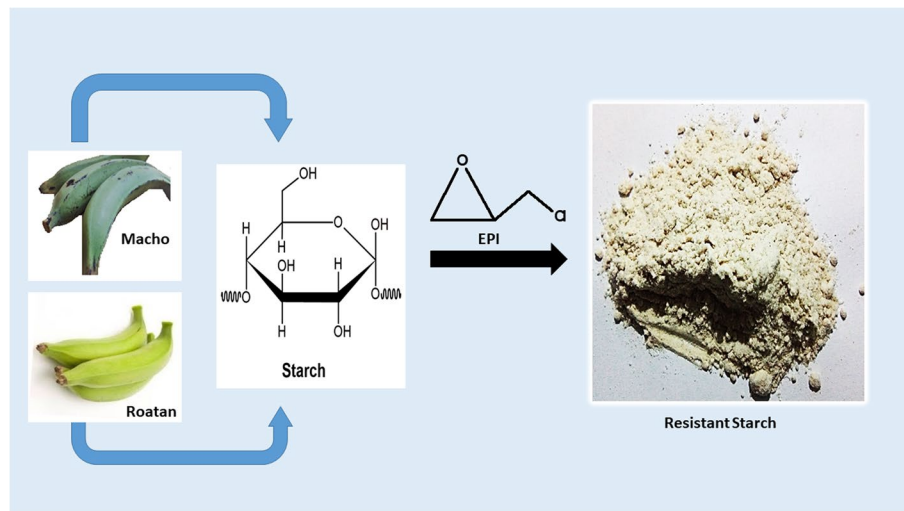
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Graphical Abstract



Introduction

Starch is a polysaccharide in high industrial demand for the development of commercially important products and is an essential raw material in certain industries such as the pharmaceutical and food industries. This polysaccharide has been extracted from various sources, such as cereals, legumes, tubers, roots and a few immature fruits, such as bananas. Banana is the most dynamic tropical fruit in the international market, and the carbohydrates present in the immature physiological state are mainly composed of starch, accounting for up to 80% of the total biomass on a dry basis; this value varies depending on the variety studied, the degree of ripening of the fruit and the extraction method (Bello-Perez et al. 2000; Qamar & Shaikh 2018; Fiallos-Cardenas et al. 2022). Carbohydrates are well known to be the main component of the human diet, and they mainly exert an energetic function (Susanto et al. 2022). However, there are other aspects that have not received sufficient attention and may have positive repercussions on health. These repercussions are due to a fraction of the total starch that resists the attack of digestive enzymes; this fraction is known as resistant starch (RS) (Leonel et al. 2020). This is physiologically defined as the sum of starch and its degradation products that are not absorbed in the small intestine of healthy individuals (Das et al. 2022; Englyst et al. 1992; Zhang et al. 2015). Resistant starch has positive effects on health, such as maintaining the balance of bacteria in the intestinal tract; reducing postprandial glycemia, postprandial insulin concentrations, and cholesterol levels;

and reducing the risk of colon cancer (Bojarczuk et al. 2022). Thus, the current trend is to develop new special products to increase the content of RS. Therefore, various physical and chemical methods have been developed, such as microwave treatment (Das et al. 2022; Englyst et al. 1992), autoclaving (Aparicio-Saguilán et al. 2005; Zhong 2022), extrusion (Gonzalez-Soto et al. 2004; Liu et al. 2023), annealing (Hyun-Jung et al. 2009), enzymatic methods (Mutangi et al. 2009; Das et al. 2022; Das and Baberjee 2022), linearization (Espinoza-Solis et al. 2011) and crosslinking (Woo et al. 2002), with the purpose of increasing the content of resistant starch (RS) in food, modifying the molecular structure of starch and decreasing its digestibility. The magnitude of the resistance of starch is related to the gelatinization capacity of the granule, the type of enzyme, and the degree and type of modification (Boru et al. 2017; Dong-Hyun et al. 2022). Crosslinking is the most widely used alternative to increase RS levels in native starch (Sriprabhom et al. 2023; Zhao et al. 2023). This is because the reducing terminal hemiacetal group on each amylose and amylopectin molecule binds to the crosslinking agent, which decreases its chemical interaction with the hydroxyl groups of water, thus affecting the swelling process of the granules and the gelatinization of starch. Studies have been carried out using epichlorohydrin (EPI) as a crosslinking agent in starch sources such as cassava (*Manihot esculenta* Crantz) (Jyothi et al. 2006), rice (Kittipongpatana et al. 2013), wheat (Šimkovic et al. 1996) and maize (Abid & Abbas 2018). However, there have been no studies using plantain starch as a source in macho and roatan varieties.

Epichlorohydrin is a chlorinated epoxy compound synthesized from dichloropropanol (or allyl chloride) and glycerol and is widely used as a chemical intermediate for the modification of elastomers, crosslinked food starch, surfactants, plasticizers, dyestuffs, pharmaceutical products, oil emulsifiers, etc. Epichlorohydrin has a dual functionality, as both ends of its chemical structure can react and bonds can form between reactive chains (Hirakawa 2014).

On the other hand, studies have reported the use of plantain starch, either in its native state or in a modified state formed during the preparation of cookies (García-Solís et al. 2018; Sanchez-Rivera et al. 2019), tortillas (Aparicio-Saguilán et al. 2013), and pasta (Herlina et al. 2022). In these investigations, the functional, physico-chemical, structural and rheological properties have been reported, providing information about the potential use of this fruit. However, few studies have focused on the chemical modification of the granular structure and its relationship with *in vitro* digestibility.

Therefore, the objective of this work was to carry out chemical modification by crosslinking plantain starch from two varieties (macho and roatan) by testing epichlorohydrin as a crosslinking agent to obtain resistant starch and characterize it.

These banana starches crosslinked with EPI can be used in the modification of synthetic and natural polymers to obtain materials that can compete with conventional nonbiodegradable plastics. Moreover, these starches can be applied in the healthcare industry through the manufacture of industrial foods such as cookies, tortillas and soups.

Materials and methods

Materials

Unripe bananas, macho (*Musa paradisiacal* L.) and roatan (*Musa sapientum* L.), were gifts from the Mundo Nuevo farm located in Tuxtepec, Oaxaca, Mexico. The fruit did not meet the quality requirements for direct commercialization. Enzymes were acquired from Sigma Aldrich Company (St. Louis, MO, USA) and were used to determine digestibility: amyloglucosidase (A7095) from *Aspergillus niger* (300 U/mL), pepsin (P7000) from porcine stomach mucosa (1:10 000 U/mg), pancreatin (P7545) from porcine pancreas (8×U.S.P), and invertase (I4504) grade VII from baker's yeast (401 U/mg). Additionally, guar gum and epichlorohydrin (540072) were purchased from Sigma Aldrich Company (St. Louis, MO, USA).

Isolation of banana starch

To obtain starch from unripe bananas, the methodology reported by Flores–Gorosquera et al. (2004) was used.

After the banana peel was removed, the fruit was ground in an industrial-type blender (Waring Laboratory, model CB 15, USA). To prevent oxidation of the fruit, 3.6 kg of peeled banana was milled with 6 L of 0.3% w/v citric acid solution. The resulting mixture was filtered using an electrical sieve (Retsch, model AS 200, Germany). The following mesh sizes were used: No. 40 (0.425 mm), 100 (0.15 mm), and 270 (0.053 mm). At each step of sieving, the product was washed with sufficient water until the aqueous solution showed no apparent starch residues. At the end of the sieving operation, the starch was allowed to precipitate overnight. Thereafter, the supernatant was decanted, and the starch was washed with distilled water. This process was repeated three times. Finally, the product was dried in a tray dryer (SUSESA) at 40 °C overnight. The powder obtained was sieved through a 100 mesh screen, weighed and stored in a container until use.

Proximal chemical analysis

Proximal chemical analysis was carried out to verify that these compounds did not affect the modification of starch or its properties. The moisture content was determined by gravimetric heating (130 °C for 2 h) using 2–3 g of sample (method 44–19). Ash, protein, and fat were analyzed according to AACC methods 08–01, 46–13, and 30–25, respectively (AACC 2000). These analyses were carried out in triplicate.

Amylose content

The amylose content was determined according to the method described by Hoover and Ratnayake (2002) with some modifications. Twenty milligrams of starch was weighed and dissolved in 8 mL of 90% dimethyl sulfoxide (DMSO) in screw-capped test tubes (added to the tube walls), which were shaken rigorously before being placed in a water bath at 85 °C for 20 min. The samples were allowed to warm, 1 mL of the solution was transferred to a 50 mL volumetric flask, 40 mL of distilled water and 5 mL of I₂/KI solution (0.0025 M I₂ and 0.0065 M KI) were added, and the flask was finally filled with distilled water. The solution was allowed to settle for 15 min before the absorbance was measured at 600 nm in a spectrophotometer (Thermo Scientific, Genesys 10S UV–VIS, USA), which was equilibrated with water and a DMSO-I₂/KI blank solution. To obtain a standard curve, solutions of amylose and amylopectin (1 mg/mL) treated in the same way as the sample were prepared. One milliliter of these solutions with different amylose-amylopectin ratios (0–100%) was transferred to 50 mL flasks, and the process was continued in the same way as for the samples.

Total starch

The total starch content was determined by quantifying the glucose released as a result of enzymatic hydrolysis with amyloglucosidase, which hydrolyzes the α -(1,4) and α -(1,6) glycosidic bonds of the amylose chains and amylopectin, according to the method proposed by Goñi et al. (1997). To do this, 50 mg of sample was dispersed in 3 mL of distilled water and 3 mL of 4 M potassium hydroxide (KOH). The dispersion was stirred for 30 min at room temperature. Subsequently, 3 mL of phosphate buffer and 5.5 mL of 2 M HCl were added, and the pH was adjusted to 4.75. Afterward, 60 μ L of an amyloglucosidase suspension was added. The resulting mixture was incubated in a water bath at 60 °C for 45 min with constant shaking. After this, the mixture was centrifuged at 3000 \times g for 15 min, and the supernatant was collected in a 50 mL volumetric flask. The residue was washed with 10 mL of distilled water. The mixture was subsequently centrifuged, and the supernatant was collected. To determine the amount of glucose released during enzymatic hydrolysis, 50 μ L aliquots were collected from the flask contents and transferred to tubes containing 1 mL of glucose oxidase/peroxidase (GOD-POD) reagent. The tubes were incubated for 10 min at 37 °C, and the samples were subsequently analyzed in a Spectronic Genesys 5 spectrophotometer (Spectronic Instruments, Inc. Rochester, NY, USA) at 510 nm. The samples were analyzed in conjunction with a glucose standard curve determined from a linear regression analysis.

Crosslinking with epichlorohydrin

Crosslinking of native plantain starch from two varieties, macho (*Musa paradisiaca* L) and roatan starch (*Musa sapientum* L), with EPI was performed according to a method proposed by Cooreman et al. (1995). In a three-necked flask, 100 g of starch and 100 mL of NaOH (0.082 M) were added. The resulting solution was adjusted to a pH of 12.4, and 0.05 mL of EPI was added. The dispersion was stirred at room temperature for 48 h at a speed of 250 rpm using a mechanical stirrer (Ika brand, Eurostar PWR CVSD model). At the end of the reaction, the dispersion was neutralized to a pH of 6.5 using HCl (1 M). The modified starch was recovered by filtration using a Büchner filter and Whatman No. 4 filter paper and washed 3 times with distilled water. The solid obtained was dried in an oven at 35 °C for 24 h.

Characterization of the chemical and physical properties

Fourier transform infrared (FTIR) spectroscopy

Infrared spectra of the films were recorded at room temperature on a Perkin-Elmer Spectrum 100FT-IR (ATR) spectrometer with a resolution of 4 cm^{-1} and were averaged over 16 scans in the range of 4000–650 cm^{-1} .

Thermal analysis

The thermal properties of the starches were studied using a TA Instruments (model 2010, USA) differential scanning calorimeter. Thermal transitions were determined by the method proposed by Paredes-Lopez et al. (1994). Two milligrams of each sample (dry basis) was weighed and placed in an aluminum pan, and then 7 μ L of deionized water was added. The pan was hermetically sealed and allowed to equilibrate for 1 h before analysis. An empty pan was used as a reference. The sample was subjected to a heating program in the temperature range of 30 to 140 °C at a rate of 10 °C/min. The onset temperature (T_{onset}), peak temperature (T_p), final temperature (T_f) and gelatinization enthalpy (ΔH) were analyzed using TA Instruments software OS/2 version 2.1. Once gelatinized, the samples were stored for 7 days at a constant temperature of 4 °C to determine the retrogradation temperature and enthalpy. After completion of the storage time, the pans were allowed to stand for 1 h at room temperature and then analyzed via DSC under the same conditions described previously.

X-ray diffraction

X-ray diffraction patterns were obtained with a Bruker AXS D8 Advance diffractometer using a CuK α radiation generator with a Ni filter, 30 mA and 40 kV. The diffractograms were collected over the 2θ range of 3 to 40 at a scan rate of 1 deg/min.

Pasting analysis

The viscosity profile of the native and modified starch dispersions was determined using the technique proposed by the AACC (2000). A starch dispersion was prepared at 10% (w/v) total solids on a dry basis, and then 100 ml was taken and transferred to the bowl of a Brabender microviscoamylograph (OHG model). The dispersion was maintained in a heating-cooking-cooling cycle, started at 30 °C and was heated until reaching a temperature of 95 °C. After this temperature was maintained for 10 min, the mixture was cooled to 40 °C, and this temperature was maintained for 10 min. A heating-cooling rate of 2.5 °C/min and a stirring rate of 125 rpm were used throughout the cycle.

Digestibility tests

Starch digestibility properties were determined by applying the method proposed by Englyst et al. (1992). This method is based on enzymatic hydrolysis. Before determining the digestibility of starch, a solution containing the enzymes pancreatin, amyloglucosidase and invertase was prepared. For each experiment, 400 mg of starch, 25 mg of guar gum and 4 mL of distilled water were added to an Erlenmeyer flask with 5 glass beads. The flask

was placed in a boiling water bath for 30 min with constant agitation. After this time, the solution was allowed to cool to room temperature. Then, 5 mL of pepsin was added. Again, the flask was placed in a water bath with constant agitation at 37 °C for 30 min. Afterward, 5 mL of sodium acetate (0.25 M) was added. Subsequently, 2.5 mg of enzyme mixture (prepared initially) was added at intervals of 1 min. Furthermore, tubes with 4 mL of ethanol (80%) were prepared and labeled G20 and G120 minutes for each sample. After 20 min of enzymatic hydrolysis, an aliquot of 0.5 mL was taken and placed in a tube of G20, after which 1 mL of distilled water was added. The tube was agitated by vortexing for 30 s. This procedure was repeated after 120 min of enzymatic hydrolysis (G120). Subsequently, the tubes were centrifuged at 1500×g for 5 min. The amount of released glucose was determined by the glucose oxidase/peroxidase (GOD/POD) method. The following equations were used for determining glucose and the fractions of rapidly digestible, slowly digestible and resistant starch:

$$\% \text{ glucose} = (At \times Vt \times C \times D/As \times Wt) \times 100 \quad (1)$$

$$\text{RDS} = (G20 - FG) \times 0.9 \quad (2)$$

$$\text{SDS} = (G120 - G20) \times 0.9 \quad (3)$$

$$\text{RS} = \text{TS} - (\text{RDS} - \text{SDS}) \quad (4)$$

where:

At = Absorbance of the sample.

Vt = Total volume.

C = Concentration of the standard used.

D = Dilution factor.

As = Absorbance of standard used.

Wt = Sample weight.

RDS = Rapidly digestible starch.

SDS = Slowly digestible starch.

RS = Resistant starch.

Statistical analysis

The results obtained for thermal analysis and the digestibility tests were analyzed using one-way analysis of variance (ANOVA). When the analysis revealed significant differences ($p < 0.05$), the means were compared using Tukey's tests at a level of significance of 0.05. Statistical analyses were performed using the computer SPSS V. 6.0 (software SPSS Institute Inc., Cary, NC, USA).

Results and discussion

Physicochemical characterization

Chemical modification of the native starch from two varieties of plantain was carried out by crosslinking with epichlorohydrin. Proximal characterization was carried out before and after the modification, and the results are presented in Table 1.

The starch content in the macho variety was 88.82 ± 0.11 , while that in the roatan variety was 85.86 ± 0.03 . These results indicated that modification by crosslinking was favored in the macho variety. However, this depends on different factors, including the amylose content present in the starch granule. The native plantain starch in the roatan variety had a greater amylose content (38.45 ± 0.39) than that in the macho variety (33.4502 ± 0.51). These values indicated that the modification reaction by crosslinking with EPI was favored in the roatan variety, consistent with the results reported by Páramo-Calderón et al. (2015). This is because the amylose monomeric unit contains three hydroxyl groups in its chemical structure, whereas amylopectin only contains two hydroxyl groups. These functional groups represent the active sites of starch for experimental chemical modifications. Additionally, the hydroxyl group bonded to carbon 6 (C6) is the active site that presents less steric hindrance than the other two active sites (C2, C3) of starch; in amylose, this active site is available, while in amylopectin, it is an $\alpha(1-6)$ branch site. In the literature, a behavior different from that observed in

Table 1 Proximal chemical analysis of native and modified plantain starch

	Macho Native	Macho Modified	Roatan Native	Roatan Modified
Moisture	11.2671 ± 0.43^a	11.2416 ± 0.11^a	10.0671 ± 0.12^a	9.9505 ± 0.03^a
Proteins	0.9902 ± 0.02^a	0.9882 ± 0.01^a	1.0778 ± 0.45^a	1.0741 ± 0.01^a
Lipids	0.5013 ± 0.07^a	0.5012 ± 0.03^a	0.4832 ± 0.03^a	0.4813 ± 0.21^a
Ashes	0.6359 ± 0.02^a	0.6401 ± 0.24^a	0.3063 ± 0.02^a	0.3139 ± 0.14^a
Amylose	33.4502 ± 0.51^a	43.0064 ± 0.73^b	38.4502 ± 0.39^a	45.6284 ± 0.07^b
Amylopectin	66.5498 ± 0.12^c	56.9936 ± 0.12^a	61.5498 ± 0.10^a	54.3716 ± 0.01^b
Total starch	88.8213 ± 0.11^b	87.2841 ± 0.28^a	85.8603 ± 0.03^a	84.9341 ± 0.23^a

Average of three repetitions \pm standard error

Values with the same letter within the same row are not significantly different at $p < 0.05$

this investigation has been reported; the crosslinking of starch with EPI was carried out mainly at the branch points of amylopectin (Kou et al. 2019; Sharma et al. 2023). Furthermore, it has been reported that inter- and intramolecular bonds are formed between amylose and amylopectin molecules (Sharma et al. 2020). Table 1 shows that the amylose content increased in both varieties after modification with EPI. This is because some amylopectin polymer chains experience breakdown or structural arrangement during the crosslinking process, which favors an increase in amylose (Zhao et al. 2023). The amylose content of the macho variety increased by approximately 23%, and that of the roatan variety increased by 15%. These results agree with the decrease in the amylopectin content of the native plantain starches in both varieties with respect to the modified starches, as observed in Table 1. Based on the previous results, the modified roatan variety had fewer hydroxyl groups than did the modified macho variety, for which chemical characterization by infrared spectroscopy was carried out. Figure 1 shows the FTIR spectra of plantain starches before and after modification.

Native plantain starches in both varieties give rise to the characteristic vibration signals of the starches. These vibrations were observed at 3280 cm^{-1} , 2934 cm^{-1} , 1640 cm^{-1} and 994 cm^{-1} , corresponding to the bending vibrations of the free hydroxyl group (-OH) and methylene (-CH₂-) and to the tension vibrations of the associated hydroxyl group (OH) and the ether group -C-O-C-, respectively.

These results agree with those reported by other researchers (Ayo-Omogie et al. 2022; Yang et al. 2022). However, visual comparison of the FTIR spectra of the two banana varieties, native and modified with EPI, revealed no differences between the two spectra. In the FTIR spectra of the modified starches, no new vibration signal was observed. This was due to the vibration signals of the EPI bonded to the polymeric units of the starch overlapping with those of the starch itself. Therefore, the regions of the vibration signals related to chemical modification, the hydroxyl groups and the ether group were determined, and Table 2 presents these results.

From these areas, the relationship between the hydroxyl groups (DH) was determined by Eq. 5.

Table 2 Area ratios of the FTIR vibration signals of the hydroxyl and ether groups

	Area (u ²)			
	Macho Native	Macho Modified	Roatan Native	Roatan Modified
Hydroxyls (-OH, bending vibration)	2444	1614	4384	1486
Hydroxyls (-OH, tension vibration)	171.9	141.8	280.8	146.9
Ether (-C-O-C)	3400	1998	4976	2250
HE	1.391	1.238	1.135	1.514
DH	14.21	11.38	15.61	10.11

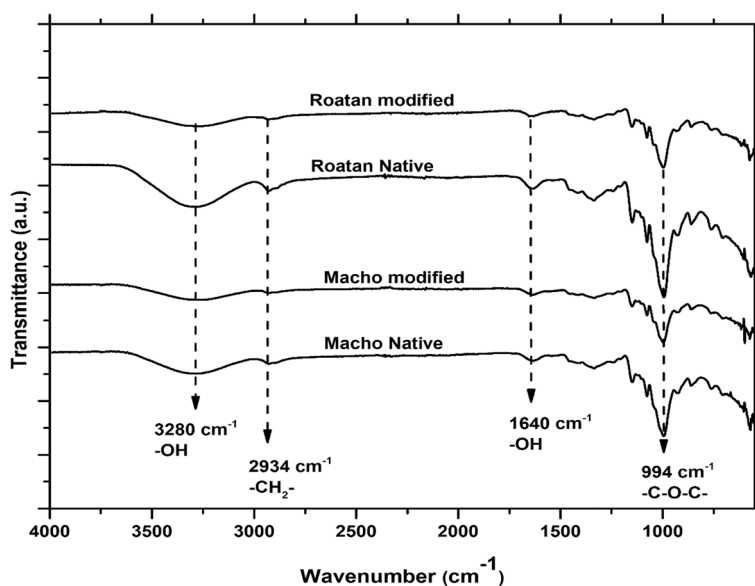


Fig. 1 FTIR spectrum of plantain starch in macho and roatan varieties, before and after its modification

$$DH = \left[\frac{\text{Hydroxyls}(-OH, \text{bending})}{\text{Hydroxyls}(-OH, \text{tension})} \right] \quad (5)$$

Analysis of the DH native and DH modified values of both varieties of banana starch revealed a decrease in the amount of free hydroxyl groups in the starches modified with EPI (14.21 vs. 11.38 (macho) and 15.61 vs. 10.11 (roatan)). This indicated that chemical modification occurred in the two banana varieties. The amount of plantain starch in the roatan variety decreased up to 35%, while in the macho variety, it decreased up to 20%. These results agree with the decrease in amylopectin of both modified banana varieties with respect to its native starch presented in the proximal analysis (Table 1). On the other hand, the ratio of ether groups to hydroxyl groups (HE) was determined by Eq. 6.

$$HE = \left[\frac{\text{Ether}(-C - O - C-)}{\text{hydroxyls}(-OH, \text{bending})} \right] \quad (6)$$

Analysis of the values of HE native and HE modified of both varieties of plantain starch showed a decrease in the amount of ether groups for the macho variety with respect to the native plantain, by approximately 11%. This was due to loss of the amylopectin structure and an increase in amylose. For the roatan variety, the number of ether groups increased by approximately 33%. Ephycolohydrin interacts with amylose and amylopectin, but this variety (roatan) contains more amylose, resulting in the vibration signals overlapping with the vibration signals of the loss of the amylopectin structure; this is based on studies reported in the literature on the analysis of starch modified by crosslinking (Gieroba et al. 2023).

This finding is consistent with the amylose/amylopectin pattern observed in the proximal blot analysis. Figure 2 shows the mechanism of crosslinking starch with EPI, which occurs in two steps. The first step is the polarization of the hydroxyl group on carbon 6 (C6) with sodium hydroxide to form a water molecule and the sodium salt of the glucose monomer unit. In the second step, the salt of the monomeric unit interacts with the methylene (CH₂) of the epoxide group of the EPI and with the methylene bound to chlorine to form sodium chloride and crosslink the starch chains. This proposed mechanism agrees with the variation of the hydroxyl groups and ether groups in the modified starches with respect to the native starches of both banana varieties obtained from Eqs. 5 and 6.

Therefore, its characterization was also carried out by differential scanning calorimetry and X-ray diffraction because these two techniques are related to the content of these two starch polymers.

X-ray diffraction analysis

The starch of the two varieties of plantain, macho and roatan, was chemically altered by crosslinking with EPI. The X-ray diffraction results for both banana varieties are presented in Fig. 3. The diffractogram of the native plantain starch of the macho variety showed a type B diffraction pattern with peaks at $2\theta=5.2^\circ$, 15° , 17° and 23° (Fig. 3a). The roatan variety of native plantain starch showed a type C diffraction pattern, which is a mixture of the type A and B patterns, with peaks at $2\theta=5.2^\circ$, 15° , 17° , 23° and 26° (Fig. 3b). This finding was similar to the results presented in other investigations (Thanyapanich et al. 2021; Sang-Ho et al. 2002). However, the chemical structure, extent of branching and spatial conformation of amylopectin are dependent on starch biosynthesis. This, in turn, depends on environmental factors such as temperature, humidity, and soil; therefore, the diffraction pattern of these native starches can vary between the same starch source (Taguchi et al. 2023; Yang et al. 2022; Yuyue et al. 2020). Chemical modification by EPI did not significantly affect the diffraction pattern of plantain starch in either the macho variety or the roatan variety.

In the diffractogram, only changes in the intensity of the peaks are observed. For the plantain starch of the macho variety crosslinked with EPI, there was an increase in the intensity of the peaks at $2\theta=5.2^\circ$, 15° , 17° and 23° . This result agrees with what has been reported in the literature (Herlina et al. 2022). This result indicates that chemical modification was carried out on the hydroxyls of the amylose chains and on the hydroxyls of the amorphous regions of amylopectin.

Thermal analysis

The gelatinization temperatures of the native starch and the crosslinked starch of the macho and roatan varieties are shown in the thermogram in Fig. 4. The gelatinization temperature of the cross-linked starch was lower than that of its native counterpart. This is because during chemical modification, the reaction conditions affect the granular structure of both starch sources, leading to a decrease in the gelatinization temperature. Carmona-García et al. (2009) reported that the cross-linking of banana starch (*Musa paradisiaca* L.) with POCl₃ slightly dissociated the granular structure, causing a decrease in the gelatinization temperature.

Table 3 presents the results obtained by DSC. T_p decreased in both varieties. It has been reported that the gelation temperature is not always affected by crosslinking with EPI, whereas ΔH increases with increasing degree of crosslinking (Yeh et al. 1993; Choi & Kerr 2004).

However, as shown in Table 3, the gelatinization of ΔH decreased in both varieties. One explanation for this

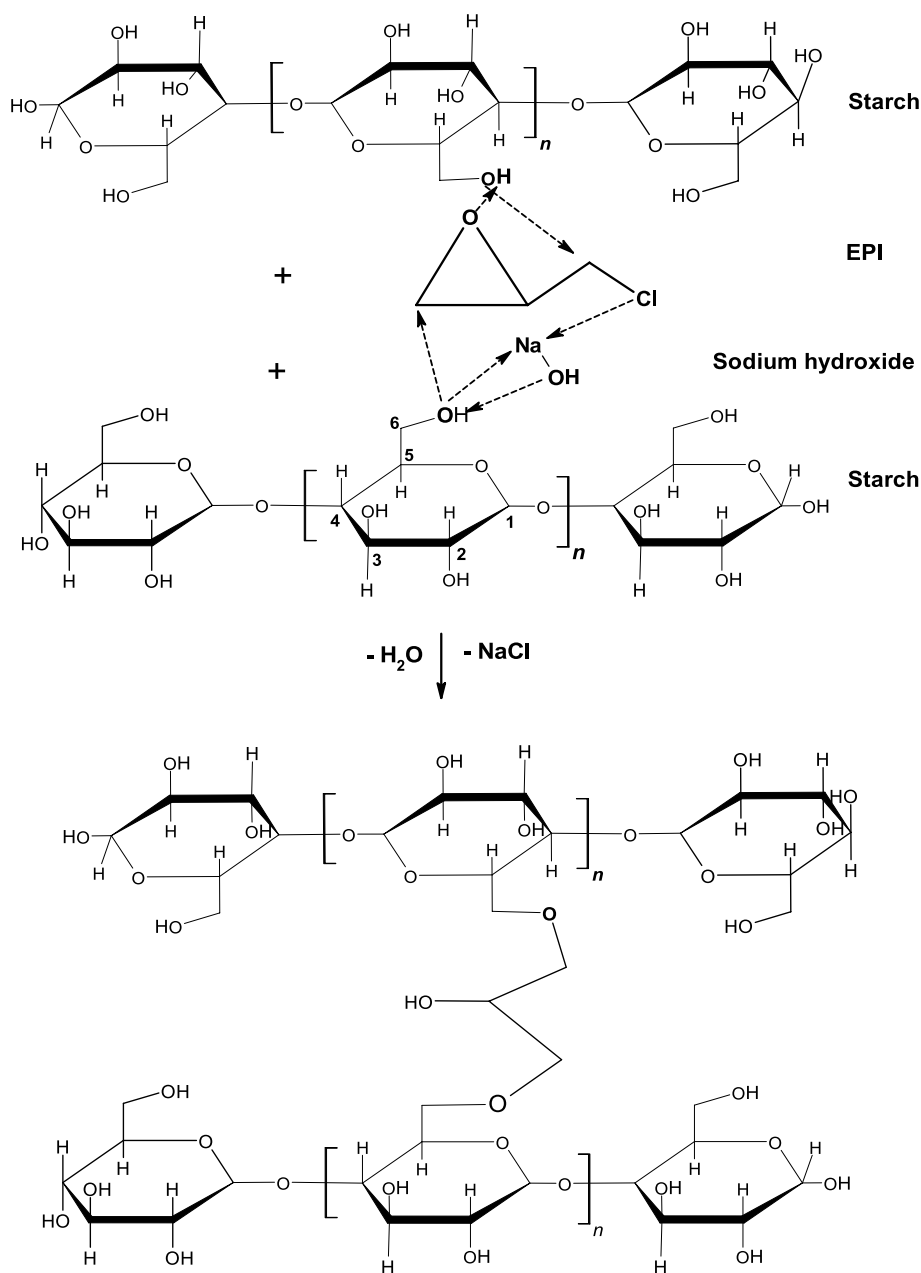


Fig. 2 Crosslinking of starch with EPI

behavior is that the chemical modification in both varieties reduced the number of double helices that are part of the crystalline zone, thus reducing the heat needed for gelation. Chiotelli and Meste reported that the gelatinization enthalpy is indicative of the stability of crystalline regions and indicates the loss of molecular order within the granule (Chiotelli & Meste 2002).

In contrast, a higher gelatinization temperature and lower gelatinization enthalpy (ΔH) were reported in

crosslinked starches in comparison with starch in its native state (Carmona-Garcia et al. 2009).

This indicates that the type of starch source and the concentration of agent used in the chemical modification (crosslinking) process can affect the thermal properties of starch granules in different pathways (Deetae et al. 2008; Wongsagnsup et al. 2014; Woo & Seib 2002).

The temperature and enthalpy of retrogradation of the native and modified starches are shown in Table 4.

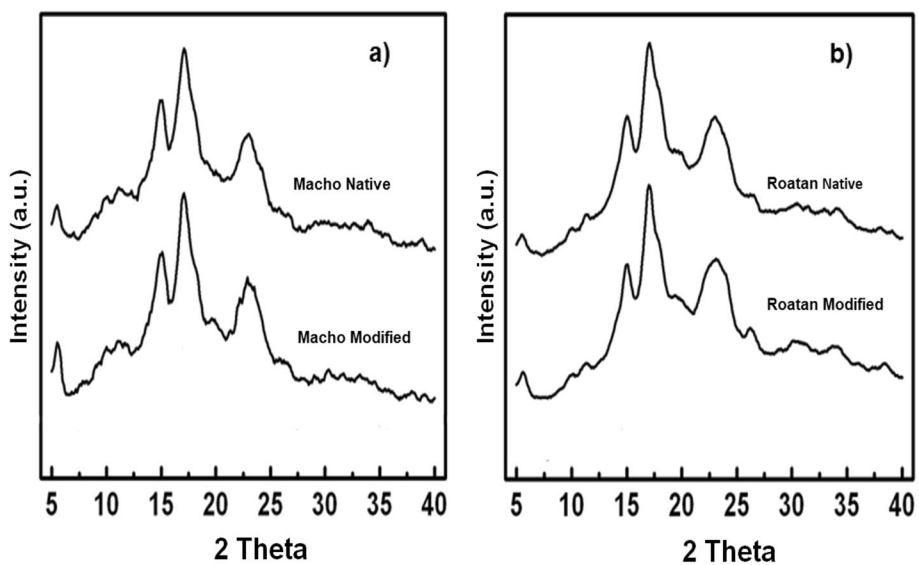


Fig. 3 X-ray diffraction patterns of native starch and modified starch: a macho native and b roatan

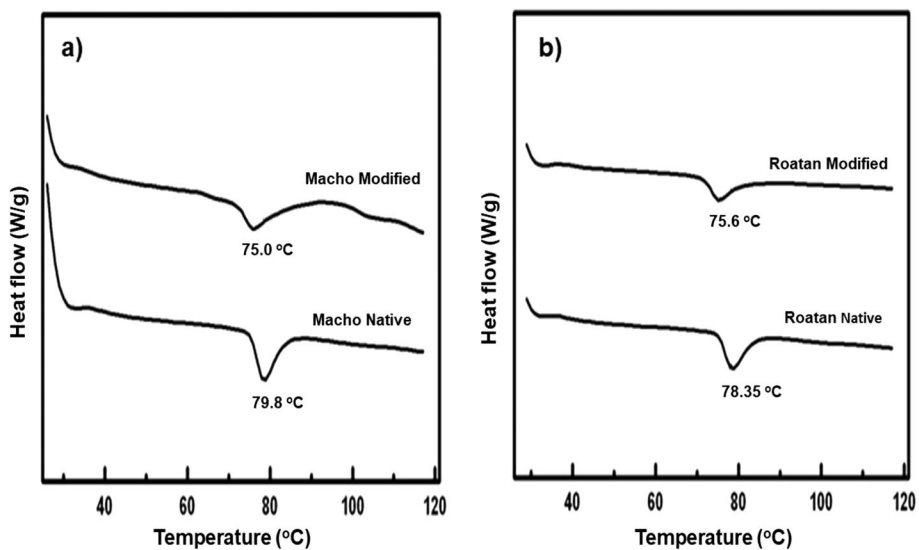


Fig. 4 Gelatinization temperature of native and modified starch

Table 3 Gelatinization properties of native and modified banana starch

Sample	Ti (°C)	Tp (°C)	Tf (°C)	ΔH (J/g)
Macho Native	74.0679 ± 0.13 ^a	79.8276 ± 0.15 ^a	85.9505 ± 0.13 ^a	11.0176 ± 0.05 ^a
Macho EPI	71.0398 ± 0.05 ^c	75.0428 ± 0.10 ^c	80.0741 ± 0.03 ^c	9.3456 ± 0.35 ^c
Roatan Native	75.0306 ± 0.02 ^d	78.3503 ± 0.06 ^a	86.1531 ± 0.14 ^a	11.0324 ± 0.01 ^a
Roatan EPI	71.4502 ± 0.11 ^c	75.6265 ± 0.13 ^c	81.6223 ± 0.09 ^c	9.0193 ± 0.06 ^c

Mean of three repetitions ± standard error

The same letters in the same column indicate that there are no significant differences (α = 0.05)

Ti Start temperature, Tp Average temperature (gelatinization temperature), Tf Final temperature, ΔH Gelatinization enthalpy

Table 4 Retrogradation properties of native and modified plantain starch after 7 days of storage at 4 °C

Sample	Ti (°C)	Tp (°C)	Tf (°C)	ΔH (J/g)
Macho Native	44.0679 ± 0.13 ^c	54.8276 ± 0.15 ^c	75.9552 ± 0.13 ^c	2.0134 ± 0.05 ^a
Macho EPI	42.8932 ± 0.13 ^b	63.4781 ± 0.09 ^e	67.4093 ± 0.19 ^d	5.3458 ± 0.09 ^b
Roatan Native	45.0306 ± 0.05 ^d	58.6503 ± 0.23 ^b	76.1531 ± 0.10 ^c	2.0334 ± 0.31 ^a
Roatan EPI	41.7432 ± 0.17 ^c	61.3280 ± 0.19 ^d	68.5238 ± 0.14 ^e	6.0123 ± 0.12 ^c

Mean of three repetitions ± standard error

The same letters in the same column indicate that there are no significant differences ($\alpha=0.05$)

Ti Start temperature, Tp Average temperature (gelatinization temperature), Tf Final temperature, ΔH Gelatinization enthalpy

The retrogradation temperature increased after 7 days, independent of the variety of plantain starch. Similar behavior has been observed for rice starches modified with various degrees of crosslinking with sodium trimetaphosphate (TMFS) (Chatakanonda et al. 2000). The enthalpy of retrogradation more than doubled for both varieties of banana starch. Apparently, the heat released by amylopectin molecules to reassociate and crystallize (retrogradation) is greater when they are crosslinked since the mobility of amylopectin chains is restricted by crosslinking, thus slowing their reassociation and releasing more heat (ΔH). In addition, the formation of new crystals as a result of crosslinking requires more energy to recrystallize.

Pasting profile

The viscosity profile of plantain starch in the roatan and macho varieties was significantly modified by EPI (Fig. 5).

The viscosity of plantain starch decreases in both varieties because the crosslinked starch chains increase its resistance to heat, inhibiting the swelling of the starch granules and consequently reducing the viscosity (Yussof et al. 2013).

This also coincides with what has been reported in strongly crosslinked starches where viscosity is reduced. This is because the functional properties after starch modification are affected, thus reducing the quantity of heat in the system (Nabeshima & Grossmann 2001; Shin et al. 2003; Tharanathan 2005).

On the other hand, during the cooling stage from 90 to 25 °C, the viscosity of both banana starch sources did not increase significantly compared to that of their native counterparts. This is because the amylose chains that are part of the amorphous zones within the starch granules were stabilized by crosslinking, inhibiting their reorganization or retrogradation.

However, the viscosity differed depending on the variety of plantain, while for the macho variety crosslinked with EPI, the viscosity was relatively low (0.43 Pa*s) compared to that of roatan plantain starch (0.58 Pa*s).

According to the above, the differences found in the viscosity profiles of both starch varieties (roatan and macho) are attributed to the structural differences and amylose-amylopectin ratio of both starches since amylose interacts with amylopectin during the process of

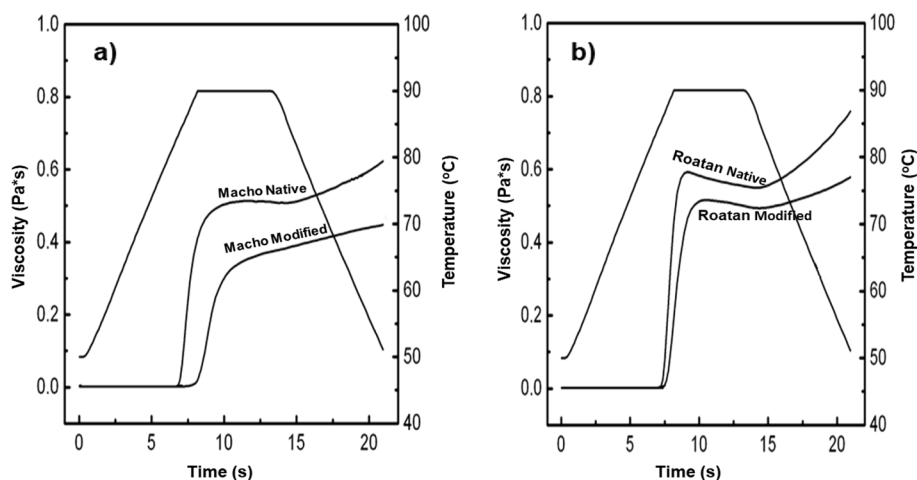


Fig. 5 Pasting of plantain starches: macho (a) roatan (b)

swelling (Cooreman et al. 1995; Eliasson 1985; Morris 1990; Tester & Morrison 1990).

In vitro digestibility tests

The digestibility properties of the plantain starches of the macho and roatan varieties, native and crosslinked, are shown in Table 5.

The results showed a significant decrease in RDS in both varieties when crossed, regardless of the variety. This is expected since crosslinking generates networks of starch molecules that are difficult to hydrolyze with enzymes. However, the largest decrease in the RDS was in the roatan variety (RDS=8.02%).

However, that result is related to crosslinking. It does not necessarily establish that the crosslinked starch tends to be entirely resistant to starch (RS) since other fractions that only retard digestion, such as SDS, can be formed.

Based on the results in Table 5, the addition of the roatan variety increased the amount of SDS. The macho variety decreased from $10.11 \pm 0.12\%$ to $5.65 \pm 0.04\%$ as a result of EPI.

The resistant starch (RS) content increased considerably, from 26.06 ± 0.32 to 82.25 ± 0.63 for the macho variety and from $28.00 \pm 0.35\%$ to $73.07 \pm 0.25\%$ for the roatan variety.

This result indicates that the RS content increased more than twofold in the modified starches. Crosslinking of these starches by EPI produces a stabilizing effect on the granular structure of starch, with a tendency to reduce enzymatic susceptibility (Jyothi et al. 2006). The stabilization of starch granules depends both on interactions with the crosslinking agent and on the source and variety of starch.

Because amylopectin undergoes structural rearrangement due to crosslinking, it may cause slow degradation or, otherwise, high resistance to enzymatic degradation. The type of crosslinking agent combined with the starch variety influences the formation of crosslinked structures and, therefore, the digestibility. Furthermore,

structural differences (length of amylopectin chains or degree of amylopectin branching) between the macho and roatan varieties can affect digestibility. The results are consistent with the X-ray patterns (Fig. 2) and with the viscosity profiles (Fig. 4).

Conclusions

Effective crosslinking of the macho and roatan varieties was carried out with EPI. Crosslinking occurred preferentially in the amorphous zones of the starch granules, which stabilized the granular structure of the starch, favoring the content of slowly digestible starch (SDS) and resistant starch (RS) and modifying the thermal behavior of the gelatinization process from $75\text{ }^\circ\text{C}$ to $79.8\text{ }^\circ\text{C}$ for the macho variety and $75.6\text{ }^\circ\text{C}$ to $78.35\text{ }^\circ\text{C}$ for the roatan variety. The highest RS content was obtained with EPI in the macho variety ($82.25 \pm 0.63\%$ vs. $73.07 \pm 0.25\%$). This behavior was also shown in the viscosity profiles.

The effects were attributed to the structural differences between the starch of the plantain variety macho and the variety roatan (length of amylopectin chains or the degree of branching in amylopectin). Crosslinking with EPI is an alternative method for producing functional ingredients and is of interest to the food industry. Crosslinking of banana starch with EPI can be applied as an alternative method for producing functional ingredients in foods commonly used in the diets of people with health problems and for carrying out comparative studies with other foods; moreover, studies in the area of polymeric materials can be carried out to obtain composites.

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Code availability

Not applicable.

Authors' contributions

ARH and APS designed and performed the experiments, analyzed the results and wrote the manuscript; DEPC, LAVL and FNMA performed the physico-chemical characterization, pasting profile, and in vitro digestibility tests; AAC, MAGM and MVZ obtained the FTIR spectra and performed the thermal analysis, X-ray diffraction experiments and data analysis.

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Declarations

Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Table 5 Digestibility of native and modified plantain starch

Sample	RDS (%)	SDS (%)	RS (%)
Macho Native	63.83 ± 0.11^e	10.11 ± 0.12^b	26.06 ± 0.32^a
Macho EPI	12.10 ± 0.15^c	5.65 ± 0.04^a	82.25 ± 0.63^e
Roatan Native	58.18 ± 0.29^d	13.79 ± 0.30^d	28.00 ± 0.35^b
Roatan EPI	8.02 ± 0.11^a	18.29 ± 0.33^e	73.07 ± 0.25^c

Mean of three repetitions \pm standard error

The same letters in the same column indicate that there are no significant differences ($\alpha=0.05$)

ADR Rapidly digestible starch, SDS Slowly digestible starch, RS Resistant starch; RS was calculated as $100 - (\text{RDS} + \text{SDS})$, assuming the sample was 100% starch

Competing interests

Not applicable.

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