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Physicochemical and Digestibility Properties of Double-Modified Banana (*Musa paradisiaca* L.) Starches

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ABSTRACT: Banana starch was chemically modified using single (esterification or cross-linking) and dual modification (esterification-cross-linking and cross-linking-esterification), with the objective to increase the slowly digestible starch (SDS) and resistant starch (RS) concentrations. Physicochemical properties and in vitro digestibility were analyzed. The degree of substitution of the esterified samples ranged from 0.006 to 0.020. The X-ray diffraction pattern of the modified samples did not show change; however, an increase in crystallinity level was determined (from 23.79 to 32.76%). The ungelatinized samples had low rapidly digestible starch (RDS) (4.23–9.19%), whereas the modified starches showed an increase in SDS (from 10.79 to 16.79%) and had high RS content (74.07–85.07%). In the cooked samples, the esterified starch increased the SDS content (21.32%), followed by cross-linked starch (15.13%). Dual modified starch (cross-linked-esterified) had the lowest SDS content, but the highest RS amount. The esterified and cross-linked-esterified samples had higher peak viscosity than cross-linked and esterified-cross-linked. This characteristic is due to the fact that in dual modification, the groups introduced in the first modification are replaced by the functional group of the second modification. Temperature and enthalpy of gelatinization decreased in modified starches (from 75.37 to 74.02 °C and from 10.42 to 8.68 J/g, respectively), compared with their unmodified starch (76.15 °C and 11.05 J/g). Cross-linked-esterified starch showed the lowest enthalpy of gelatinization (8.68 J/g). Retrogradation temperature decreased in modified starches compared with unmodified (59.04–57.47 °C), but no significant differences were found among the modified samples.

KEYWORDS: Banana, chemical modification, slowly digestible starch, resistant starch, physicochemical properties

■ INTRODUCTION

The interest in developing functional foods has increased due to demanding foods that can improve the health and well-being of consumers. Functional foods include foods that exert a beneficial effect on human health and/or reduce the risk of chronic disease beyond basic nutritional functions.[1] The beneficial action exercised by functional foods is due to one component or diverse components, which can be present in the food at low concentration. These components are named functional ingredients.[2] For this reason, the food industry is interested in obtaining functional ingredients that can be added to different food products and increase their beneficial action in consumers. Prebiotics are functional food ingredients that are defined as nondigestible substances (indigestible carbohydrates) that exert some biological effect on humans by selective stimulation of growth or bioactivity of beneficial microorganisms either present or therapeutically introduced to the intestine. Lactulose, galactooligosaccharides, fructooligosaccharides, and inulin and its hydrolysates are prebiotics commonly used in human nutrition.[3]

The RS is a fraction of starch that is not hydrolyzed by human digestive enzymes.[4] Several studies have shown that RS has physiological functions similar to those of dietary fiber.[4,5] The RS is fermented in the large intestine by colonic microflora to produce short-chain fatty acids (SCFA), mainly butyrate, which has been linked to colon cancer prevention.[6] In addition, RS

consumption can help reduce the caloric intake, glycemic response, and concentrations of cholesterol and triglycerides.[7]

In this sense, another starch fraction, slowly digestible starch (SDS), has received interest for its beneficial effects.[8−11] The important feature of SDS is that it is digested slowly throughout the entire small intestine, which provides sustained glucose release with a low glycemic index and subsequently a slow and prolonged release of glucose. Therefore, SDS is considered to be beneficial for the dietary management of metabolic disorders[12] of common chronic diseases such as obesity, diabetes, and cardiovascular diseases.[13] For example, the SDS produce satiety and could be incorporated into foodstuffs marketed for weight-loss programs.[10]

Most raw cereal starches have a high proportion of SDS fraction; however, when the starches are gelatinized, the usual result is a decrease or loss of the slow digestion property of native cereal starches.[14] Native starches of cereals have A-type X-ray diffraction patterns in which the crystalline and amorphous regions are arranged concentrically. This structure is digested by a side-by-side mechanism and is the structural basis for the

slow digestion property of native cereal starches. Therefore, there are several studies in which SDS is prepared by chemical, physical, and enzymatic modifications.[10,11,15,16] One method to make SDS has been to modify the molecular structure of starch molecules by including 1-octenyl succinic anhydride (OSA),[10,11] cross-linked,[15] and double-modified starches.[10,11] However, there are few studies of SDS production with noncereal starches.

Native banana starch is resistant to digestion because it exhibits a B-type X-ray diffraction pattern.[14,17] Therefore, it is regarded as the natural source with the highest RS level, but like the SDS fraction, when the granules are gelatinized, the RS fraction decreases or is lost. There are diverse studies concerning the chemical modification of banana starch to increase the RS fraction.[18−20] The single chemical modifications of banana starch are cross-linking, acetylation, litnerization, and oxidation;[18−22] dual modification (oxidation and acetylation) of banana starch was utilized to elaborate films.[23,24] The objective of this work was to evaluate the effects of the double chemical modification of banana starch on its physicochemical and digestibility characteristics.

■ MATERIALS AND METHODS

Starch Isolation. Unripe bananas (*Musa paradisiaca* L.) were purchased at a local market in Cuautla, Morelos State, Mexico, and starch was isolated using a pilot-scale procedure proposed by Flores-Gorosquera et al.[25] Skin color and size were the parameters used for cutting of the fruit in stage 2.[26] The fruit was peeled, cut into 5−6 cm cubes (100 kg total weight), immediately submerged in aqueous citric acid solution (0.5 g/L), and then macerated at low speed in a Waring blender (10 kg of fruit to 10 L of solution) for 2 min. The homogenate was consecutively sieved through screens (40, 100, 200, and 325 U.S. mesh) until the wash water (distilled) was clear. The starch sediments were dried in a spray-dryer (Niro Atomizer model P-6.3, Copenhagen, Denmark), with a feeding temperature of 130−150 °C, a solids concentration in the feeding line of 300−400 g/kg, and an air outlet temperature of 70−80 °C. The powder was ground to pass a U.S. 100 sieve and stored at room temperature (25 °C) in a glass container.

Cross-Linking with Epichlorohydrin (ECH). Starch was cross-linked using the methodology of Cooreman et al.[27] Banana starch (100 g, dry wt) was suspended in 0.082 M NaOH (100 mL) with stirring. The pH of the slurry was adjusted to 12.4, and ECH [0.05% (50 μL) of the weight of starch] was added. The slurry was stirred at room temperature for 48 h. After the pH of the slurry had been neutralized to 6.5 using 1 M HCl, the suspension was filtered through a Buchner filter and washed three times with distilled water (300 mL). The resulting starch was dried at 40 °C.

Esterification with Octenylsuccinic Anhydride (OSA). Starch was esterified using the methodology of Han and BeMiller.[10] Starch (100 g, dry wt) was dispersed in distilled water (225 mL) with stirring. The pH of the slurry was adjusted to 8.5−9.0 with 1 M NaOH. 2-Octen-1-ylsuccinic anhydride [0.60 g (0.6 mL), 3.0% of the weight of starch] was added, and agitation was continued at room temperature ($\approx$20 °C) while the pH was maintained at 8.5. After 6 h, the starch slurry was neutralized to pH 7.0 with 1 M HCl. The modified starch was collected by centrifugation, washed three times with water and once with acetone, and dried at 40 °C.

Dual Modification. The starches were double modified in two ways, the first by cross-linking followed by esterification, as described above, and the second by first esterifying the starch and then cross-linking it.

Degree of Substitution (DS). The DS of OSA starches was determined by titration following the methodology of Song et al.[28] The OSA starch sample (5 g, dry weight) was accurately weighed and dispersed by stirring for 30 min in 25 mL of 2.5 M HCl−isopropyl

alcohol solution. One hundred milliliters of 90% (v/v) aqueous isopropyl alcohol solution was added and the slurry stirred for an additional 10 min. The suspension was filtered through a glass filter, and the residue was washed with 90% isopropyl alcohol solution until no Cl$^-$ could be detected (using 0.1 M AgNO$_3$ solution). The starch was redispersed in 300 mL of distilled water, and then the dispersion was heated in a boiling water bath for 20 min. The starch solution was titrated with 0.1 M standard NaOH solution, using phenolphthalein as indicator. A control sample was simultaneously titrated with unmodified starch as a sample. The DS was calculated utilizing the equation

$$DS = \frac{0.162 \times (A \times M)/W}{1 - [0.210 \times (A \times M)/W]}$$

where A is the titration volume of NaOH solution (mL), M is the molarity of NaOH solution, and W is the dry weight (g) of the OSA starch; 0.162 and 0.210 are the fractions of molecular weight of anhydroglucose and octenylsuccinic anhydride, respectively.

X-ray Diffraction Analysis. X-ray diffraction patterns were obtained using a Advance D8 diffractometer from Bruker (Coventry, U.K.) at 35 kV with Cu Kα radiation (154.2 pm). The samples were scanned in the angular range of 3−37° (2θ). The crystallinity percentage (%C) was determined from the diffractogram by calculation of the area corresponding to the crystalline peaks (A_p; from the difference between the area under the curve and the area of the amorphous halo), the total area under the curve (A_t), and the instrumental noise (N) according to the following equation:[29]

$$\%C = \frac{A_p}{(A_t - N)}$$

Pasting Characteristics. The pasting characteristics of the modified and unmodified starches were determined with a Rapid Visco-Analyzer (model 4, Newport Scientific Pty, Ltd., Warriewood, NSW, Australia) using standard profile 2 (method 61.02).[30] Starch (3.65 g, dry basis) and distilled water (25.35 g) were added to the aluminum sample container. The equipment was programmed to a cycle of heating−cooking−cooling, starting at 50−90 °C, and cooling to 50 °C at a heating rate of 8 °C/min and a speed of 160 rpm.

Differential Scanning Calorimetry (DSC). The thermal properties of starches, such as temperature and enthalpy of gelatinization, were measured using a differential scanning calorimeter (DSC, TA Instrument, model 2010, New Castle, NJ) previously calibrated with indium. A 2 mg sample (dry basis) was weighed in an aluminum pan, and 7 μL of deionized water was added. The pan was sealed tightly and then allowed to stand for 1 h before the analysis was performed. An empty aluminum pan was used as reference. The sample was subjected to a heating program over a range of temperature from 10 to 120 °C and a heating rate of 10 °C/min. After scanning, the gelatinized samples were stored at 4 °C for 7 days and rescanned from 20 to 120 °C at a rate of 10 °C/min. The characteristics of the transitions, including onset (T_o), peak (T_p), and conclusion (T_c) temperatures of gelatinization and the enthalpy of gelatinization (ΔH_g) and retrogradation (ΔH_r), were obtained directly from the analysis with the software TA Instruments, OS/2 version.[31]

Starch Digestibility. The digestion property was analyzed by using the Englyst assay.[8] Starch samples (800 mg) and water (8 mL) were added to 125 mL Erlenmeyer flasks and heated in a boiling water bath for 20 min. After heating, 5 glass beads (15 mm diameter) (for mechanical disruption of the physical structure of the sample), guar gum (50 mg, for keeping the sample in suspension and preventing excess disruption of the sample by the glass beads), and 10 mL of pepsin/hydrochloric acid solution were added. The samples were incubated at 37 °C for 30 min. Then 10 mL of 0.25 M sodium acetate was added, and the samples were agitated gently to disperse the contents. The water

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bath was adjusted to a stroke speed of 160 strokes/min, and 5 mL of enzymes blend (pancreatin, 1 g, P1750, Sigma, St. Louis, MO; invertase, 3000 units, I4504, Sigma; amyloglucosidase, 140 units, A7095, Sigma) was added to the sample at intervals of 1 min. After 20 min, 0.5 mL of the sample was removed and added to a tube containing 20 mL of 66% ethanol solution. After 100 min of hydrolysis, the same procedure was carried out. The glucose content was determined using glucose oxidase peroxidase assay (ELITech glucose PAP SL, Siemens Healthcare Diagnostic, S. de R.L. de C.V., Mexico, D.F.), and the Englyst method was used to determine fractions of RDS, SDS, and RS. Each sample was analyzed in triplicate.

Statistical Analysis. Experiments were arranged in a completely randomized design. Results are presented as mean ± standard error of mean (SEM) of three separate determinations. A commercial software program (SigmaPlot for Windows version 11.0, Germany) was used to evaluate, by one-way analysis of variance, significant differences in the means of measured parameters. Statistically significant differences ($p < 0.05$) among means were evaluated using the Tukey mean-comparison procedure.

■ RESULTS AND DISCUSSION

Total Starch and Degree of Substitution. Total starch was determined after extensive hydrolysis of starch, and no statistical difference was shown between the unmodified starch and those chemically modified (Table 1). This pattern is due to the low DS

Table 1. Total Starch, Degree of Substitution, and Crystallinity Level of Unmodified and Chemically Modified Banana Starches[a]

sample	total starch (%)	degree of substitution[b]	crystallinity (%)
unmodified	82.34 ± 1.36 a	ND[c]	23.79 ± 0.22 a
cross-linked	81.36 ± 0.79 a	ND[d]	30.34 ± 0.32 c
esterified	80.95 ± 1.57 a	0.016 ± 0.001 a	32.76 ± 0.19 d
esterified−cross-linked	79.98 ± 1.39 a	0.006 ± 0.001 b	28.47 ± 0.03 b
cross-linked−esterified	81.29 ± 0.75 a	0.020 ± 0.000 c	31.84 ± 0.72 d

[a] Means of three replicates ± standard error. Different letters in the same column indicate significant differences (α = 0.05). [b] Degree of substitution of OSA starch (only starches modified with octenylsuccinic anhydride). [c] ND, not detected. [d] ND, not determined.

determined in the modified samples. DS of esterified sample was higher than those determined in the esterified and cross-linked samples, but lower than those of the cross-linked and esterified starches (Table 1). The reason for this is because when starch is esterified only, minor disorganization of the structure is caused by the modification; however, when it is esterified and thereafter cross-linked, the groups introduced in the first modification are replaced, decreasing the DS of the starch. However, when the first modification was cross-linking, the starch was more susceptible to the introduction of new chemical groups of the second modification, increasing the DS. This pattern could be because disarrangement of starch components structure during the first chemical modification facilitates the introduction of substituents of the second modification. Han and BeMiller[10] carried out esterification with OSA, esterification and cross-linking, and cross-linking and esterification, but they did not determine the DS.

X-ray Diffraction Study of Unmodified and Chemically Modified Banana Starch. The unmodified and chemically modified banana starches showed a B-type X-ray diffraction pattern (Figure 1). These diffraction patterns arise from the crystallites that are formed by clusters of double helices of amylopectin chains. Although all patterns were from the A polymorph, the degree of crystallinity changed somewhat (to as much as 36% from the initial value of 23%) as a consequence of the chemical treatments. This is consistent with the reactions taking place in the amorphous regions between crystallites.[28,32,33] All of the modified starches showed a higher crystallinity percentage; however, esterification increased the crystallinity level in banana starch, and a similar percentage was determined in banana starch with dual modification when esterification was carried out in the second step, when the groups introduced in the second modification are conserved in the starch (Table 1). High crystallinity can be related to a higher amount of short chains[34] that are produced during the chemical modification, because starch molecules in the amorphous lamella and a portion of the crystalline lamella were degraded during the reaction as was reported in oxidized starches.[35] This crystallinity level can be important in the starch digestibility.[10]
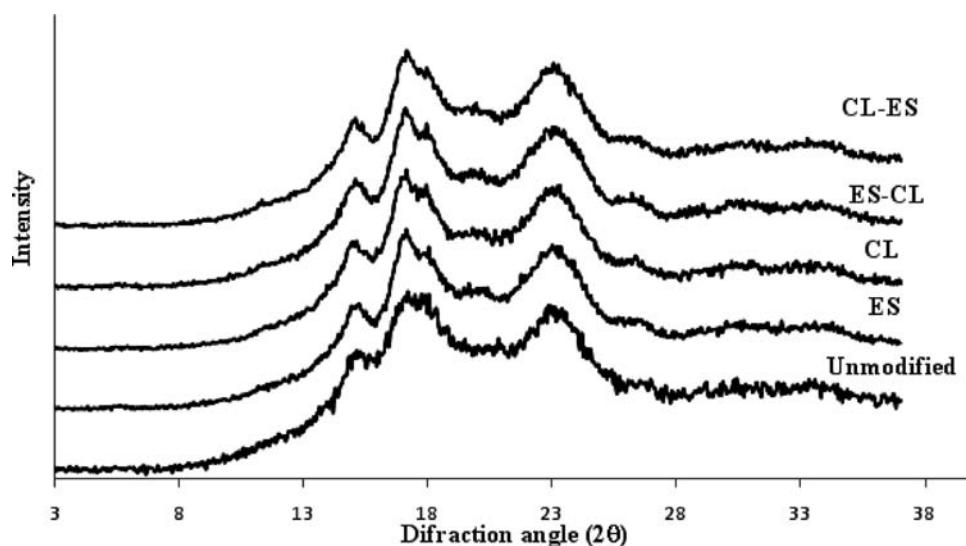

Figure 1. X-ray diffraction patterns of the unmodified and chemically modified banana starches: esterified (ES), cross-linked (CL), esterified−cross-linked (ES-CL), and cross-linked−esterified (CL-ES).

Table 2. Englyst Test Results of Unmodified and Chemically Modified Banana Starches[a,b]

sample	RDS	SDS	RS[c]
unmodified	4.23 ± 0.11 a	10.79 ± 0.33 a	85.07 ± 0.85 d
cross-linked	9.19 ± 0.61 c	16.79 ± 1.34 d	74.01 ± 1.06 a
esterified	5.75 ± 0.12 b	11.63 ± 0.34 b	82.61 ± 0.96 c
esterified−cross-linked	5.62 ± 0.23 b	13.72 ± 0.70 c	80.66 ± 1.05 b
cross-linked−esterified	4.60 ± 0.34 a	12.77 ± 0.90 c	80.63 ± 0.83 b

[a] Means of three replicates ± standard error. Different letters in the same column indicate significant differences (α = 0.05). RDS, rapidly digested starch; SDS, slowly digested starch; RS, resistant starch (%). [b] Samples without gelatinization before analysis. [c] RS was calculated as 100 − (RDS + SDS), assuming sample as 100% starch.

Table 3. Englyst Test Results of Cooked Unmodified and Chemically Modified Banana Starches[a,b]

sample	RDS	SDS	RS[c]
unmodified	65.75 ± 0.62 c	12.75 ± 1.86 b	21.49 ± 1.61 a
cross-linked	65.40 ± 0.99 c	15.13 ± 0.81 c	19.45 ± 0.80 a
esterified	53.69 ± 0.80 a	21.32 ± 1.00 d	24.99 ± 1.23 b
esterified−cross-linked	61.35 ± 1.55 b	13.15 ± 0.96 b	25.49 ± 1.18 b
cross-linked−esterified	61.25 ± 0.69 b	9.61 ± 0.38 a	29.14 ± 0.57 c

[a] Means of three replicates ± standard error. Different letters in the same column indicate significant differences (α = 0.05). RDS, rapidly digested starch ; SDS, slowly digested starch; RS, resistant starch (%). [b] Samples cooked in a boiling water (20 min), cooled, and assayed. [c] RS was calculated as 100 − (RDS + SDS), assuming sample as 100% starch.

Digestion Properties of Unmodified and Chemically Modified Banana Starch. The digestion properties of unmodified and chemically modified banana starch are shown in Table 2 (ungelatinized samples). In general, all samples had low rapidly digestible starch (RDS) content. The esterified and esterified−cross-linked banana starches had RDS (5.75 and 5.62%, respectively) similar to their unmodified and cross-linked−esterified counterparts (4.23 and 4.60%, respectively), and these values were lower than the other ungelatinized chemically modified banana starch.[36] Cross-linked banana starch had the highest RDS level (9.19%), compared with the other samples, but also it showed the highest slowly digestible starch (SDS) content of the modified banana starches. The chemically modified banana starches had higher SDS (11.63−16.79%) than their unmodified counterpart (10.79%), a pattern that agrees with single and dual modifications carried out in waxy corn starch.[10] The fraction of resistant starch (RS) was high for all samples (79−85%), indicating that unripe banana has a high RS content.[37,38]

The cooked unmodified and chemically modified banana starches before the Englyst test (Table 3) showed that in general RDS increased when compared with the ungelatinized samples. Esterified banana starch showed the lowest RDS (53.69%) followed by the dual-modified banana starch (61.25−61.35%). Esterified waxy corn, normal corn, tapioca, and potato starches had lower content RDS than their unmodified counterparts,[10] a pattern inverse to that determined here. Esterified banana starch had the highest SDS (21.32%) content followed by cross-linked banana starch (15.13%); however, the dual-modified banana starch had similar or lower SDS levels than its unmodified counterpart, showing that the banana starch cross-linked−esterified had the lowest SDS content (9.61%), and the pattern did not agree with the SDS value determined in the esterified banana starch. Cross-linked−esterified dual-modified banana starch had lower SDS and high RS contents. Cross-linked−esterified banana starch had the highest RS content and esterified and esterified−cross-linked presented similar RS value. Cross-linked banana starch had the lowest RS amount, showing that this chemical modification produces a structure that is more accessible than the other modification. These results agree partially with the pattern determined in waxy corn starch, in which the starch esterified with OSA had a higher RS (22.1%) content than the cross-linked sample (12.9%).[10] It was reported that esterification with OSA produces high content of SDS and high RS amount, which depends on the botanical starch source,[10] reducing the enzymatic degradation of starch[39,40] and thus decreasing the glycemic response.[39] However, the combination of esterification and cross-linking and vice versa decreases the SDS content in comparison with cross-linking and/or esterification alone.[10] The study of uncooked and cooked starches can give more information of the digestibility properties of the samples and consequently the possible applications in foods with or without heat treatment during their preparation.

Pasting Characteristics of Unmodified and Chemical Modified Banana Starch. Cross-linking of starch restricted its swelling when heating. Diverse reagents are used for cross-linking such as phosphorus oxychloride (POCl$_3$), sodium trimetaphosfate (STMP), and epicholohydrin (ECH). STMP and ECH could penetrate into the inner region of the starch granules, and the cross-links were distributed within the granules.[41,42] The reaction with STMP forms distarch phosphate; however, the reaction with ECH forms mono- or distarch glycerols depending on the conditions, such as starch concentration, temperature, and starch state. In neutral conditions, cross-linked banana starch showed lower peak viscosity when the modification was carried out with ECH than with POCl$_3$, showing higher restriction to swelling.[43] A similar pattern was shown here because cross-linked banana starch had the lowest peak viscosity followed by esterified−cross-linked, where a slight increase in peak viscosity was found in this sample, but the second modification predominated in this characteristic (Figure 2), which is in agreement with the low DS of OSA groups present in this sample (Table 1). An increase in the peak viscosity, compared with the unmodified starch, was found in banana starch esterified with OSA and when esterification was the second modification (cross-linked−esterification). It was reported that esterification with OSA produces disorganization of starch components in the granule, allowing the granules to swell to a greater degree than its unmodified counterpart.[44] A similar pattern in the peak viscosity of waxy corn, normal corn, and tapioca starches esterified with OSA compared with their unmodified counterpart was found, but esterified potato starch and its unmodified sample had a similar peak viscosity value.[10] The botanical source plays an important role in the physicochemical properties of chemical modified starches.

Thermal Properties. The single and dual modification of banana starch decreased the temperatures and enthalpy of gelatinization (Table 4). The effect was minor in the cross-linked starch, similar to that determined in cross-linked banana starch with diverse reagents.[43] The enthalpy of gelatinization decreased in higher amount in the esterified and double-modified banana starch compared with its unmodified (11.05 J/g) counterpart. However, no statistical difference was found in the esterified and esterified−cross-linked banana starches. The cross-linked−esterified banana starch had the lowest enthalpy of gelatinization
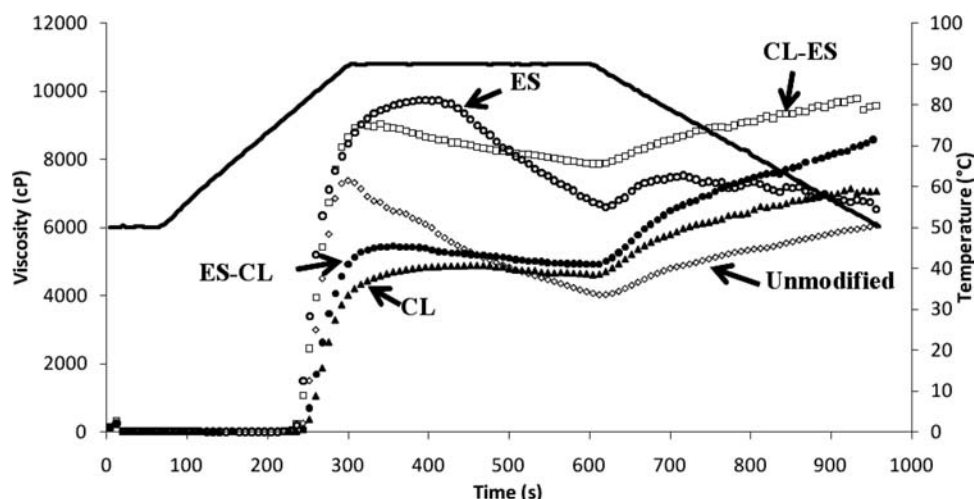
Figure 2. Rapid Visco Analyzer pasting curves of unmodified and chemically modified banana starches: esterified (ES), cross-linked (CL), esterified−cross-linked (ES-CL), and cross-linked−esterified (CL-ES).

Table 4. Gelatinization Properties of Unmodified and Chemically Modified Banana Starches[a]

sample	T_o (°C)	T_p (°C)	T_c (°C)	ΔH (J/g)
unmodified	70.38 ± 0.14 b	76.15 ± 0.14 c	85.92 ± 0.27 c	11.05 ± 0.021 d
cross-linked	70.00 ± 0.12 b	75.30 ± 0.23 b	84.65 ± 0.29 b	10.42 ± 0.26 c
esterified	68.81 ± 0.03 a	74.50 ± 0.18 a	84.21 ± 0.37 b	9.68 ± 0.06 b
esterified−cross-linked	69.90 ± 0.25 b	75.37 ± 0.15 b	83.79 ± 0.22 ba	9.45 ± 0.18 b
cross-linked−esterified	68.52 ± 0.35 a	74.02 ± 0.25 a	82.51 ± 0.52 a	8.68 ± 0.20 a

[a] Means of three replicates ± standard error. Different letters in the same column indicate significant differences (α = 0.05). T_o, onset temperature; T_p, peak temperature; T_c, conclusion temperature; ΔH, gelatinization enthalpy.

Table 5. Retrogradation Properties of Unmodified and Chemically Modified Banana Starches after Storage at 4 °C for 7 Days[a]

sample	T_o (°C)	T_p (°C)	T_c (°C)	ΔH (J/g)
unmodified	44.37 ± 1.38 a	59.04 ± 0.16 b	68.17 ± 0.90 ab	4.19 ± 0.09 b
cross-linked	45.44 ± 0.94 a	57.94 ± 1.07 a	68.30 ± 0.90 ab	3.97 ± 0.36 b
esterified	43.56 ± 0.90 a	57.47 ± 0.78 a	67.23 ± 0.65 a	4.19 ± 0.09 b
esterified−cross-linked	43.31 ± 1.07 a	58.48 ± 0.35 a	69.14 ± 0.38 b	4.61 ± 0.13 c
cross-linked−esterified	44.37 ± 0.83 a	57.6 ± 0.81 a	68.07 ± 0.53 a	3.32 ± 0.04 a

[a] Means of three replicates ± standard error. Different letters in the same column indicate significant differences (α = 0.05). T_o, onset temperature; T_p, peak temperature; T_c, conclusion temperature; ΔH, retrogradation enthalpy.

(8.68 J/g). A decrease of 20% in the enthalpy of gelatinization of esterified waxy corn starch compared with its unmodified sample was reported, due to the internal linkages of starch components that are weakened by the introduction of a hydrophobic alkenyl group,[45] producing discontinuity in the double helices of amylopectin chains and minor enthalpy during the phase transition. This agrees with the lowest enthalpy of gelatinization value assessed in the cross-linked−esterified banana starch and with the lowest SDS and RS contents in the cooked sample.

The retrogradation properties of unmodified and chemically modified banana starches are shown in Table 5. Temperatures associated with this phase transition were similar in the starches studied, and a similar pattern was found in the enthalpy for unmodified and banana starch with a single chemical modification. However, esterified−cross-linked banana starch had the highest enthalpy value, and consequently the highest retrogradation, and the cross-linked−esterified starch had the lowest

enthalpy value. The presence of other chemical groups in the structure of cross-linked−esterified starch provokes minor reassociation of starch chains and consequently low retrogradation; this pattern is in agreement with the high DS (0.020) determined in cross-linked−esterified banana starch. Slight variation was found in the retrogradation enthalpy of the cross-linked banana starch with different reagents, because a slight decrease in this parameter was assessed compared with its unmodified counterpart, and there was no difference among the cross-linked ones.[44]

In conclusion, the chemical modifications (esterification and cross-linking) changed the digestibility and physicochemical properties of banana starch. Banana starch esterified with OSA had increased SDS content and cross-linked with ECH to a lesser extent; however, dual-modified banana starches showed decreased SDS but increased RS content. The highest SDS content was obtained with the single esterification. Esterified and cross-linked starches showed X-ray diffraction patterns similar to that

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of their unmodified counterpart, but had higher crystallinity level. The chemical modifications altered the structural order in banana starch, resulting in decreased temperature and enthalpy of gelatinization and retrogradation. Moreover, in the dual-modified starches the characteristics of the second modification predominated. In the pasting characteristics the esterified and cross-linked—esterified starches showed higher peak viscosity, whereas cross-linked and esterified—cross-linked samples had lower peak viscosity. Chemical modifications can be used to tailor digestibility properties of starch.

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