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Effect of the cross-linked reagent type on some morphological, physicochemical and functional characteristics of banana starch (*Musa paradisiaca*)

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ABSTRACT

Cross-linked starches have increased their importance due to their applications such as adsorbents of heavy metals. In this work the effect the reagent used in the chemical modification of banana starch and its impact on some morphological, physicochemical and functional characteristics was evaluated. The reagent used in the cross-linked of starch decreased the fat and protein content, whereas ash level were higher. The morphology of the granules, observed by scanning electron microscopy, was more affected when a blend of sodium trimetaphosphate (STMP)/sodium tripolyphosphate (STPP) and epichlorohydrin (EPI) were used in the modification. The cross-linked starches presented a bimodal distribution and the effect was more conspicuous in those starches modified with STMP/STPP and EPI. The swelling value (60 °C) increased with the cross-linking and the highest value was obtained in those starches modified with STMP/STPP and EPI. However, at higher temperatures the swelling values of cross-linked starches with STMP/STPP and EPI decreased as temperature increased (80 °C), and there after the value was constant. The cross-linked starches with STMP/STPP and EPI showed the lowest solubility values. The cross-linked starch with $POCl_3$ (phosphorous oxychloride) showed a slight decrease in the onset and peak temperatures compared with its native counterpart, but those modified with STMP/STPP and EPI presented an increase in the three transition temperatures, but a decrease in enthalpy value. The results obtained can be used to determine the type of reagent used for cross-linked in order to obtain a starch with specific characteristics.

1. Introduction

Banana is an important crop in the tropical and sub-tropical regions of the world. This fruit is either consumed ripe – due to its high sugar content – or unripe, in several indigenous dishes requiring high starch content. In Mexico and other Latin American countries, banana is mainly consumed ripe. For this reason, large quantities of fruits are lost during commercialization as a consequence of deficient postharvest handling. New economical strategies of banana use are now considered for banana use, such as the production of unripe banana starch due to its high starch content (Juarez-garcia, Agama-Acevedo, Sáyago-Ayerdi, Rodríguez-Ambriz, & Bello-Pérez, 2006; Rodriguez-Ambriz, Islas-Hernandez, Agama-Acevedo, Tovar, & Bello-Perez, 2008).

Starch is perhaps the most important polymeric carbohydrate in terms of its functionality that impart to products in diverse industries. Nowadays, the new product development area in those industries is interesting in searching for starches with improved functional products such as viscosity, solubility, low retrogradation and syneresis tendency, etc. Since some years ago, the tendency is looking for alternative sources to obtain starches exhibiting better physicochemical and functional characteristics. In recent years, substantial progresses have been made in order to obtain starches from these sources, as well as in the study of their functional and physicochemical properties (Hernández-Lauzardo, Méndez-Montealvo, Velásquez, Solorza-Feria, & Bello-Pérez, 2004; Hoover, 2001; Nuñez-Santiago, Bello-Pérez, & Tecante, 2004; Pérez, Lares, & Gónzalez, 1997; Zhao & Whistler, 1994). Utilization of native starches has some drawbacks because the conditions of the process (e.g., temperature, pH, pressure, shear stress, etc.) reduce its use in industrial applications. These shortcomings may be overcome by starch modification using chemical, physical and enzymatic methods (Fleche, 1990). Perhaps, among the most popular methods for starch modification are the chemical procedures. A chemically modified starch is obtained when native starch is treated with specific reactive in order to change some of its properties. This definition includes acetylated, hydroxypropylated and cross-linked starches (Van Der Bij, 1976).

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Cross-linked starch plays a major role in the manufacture of foods in order to thicken, stabilize and provide texture (Rogol, 1986; Thomas & Atwell, 1999; Wurzburg & Szymanski, 1970). Recently, this modified starch was used as adsorbent of heavy metals in waste water (Kim & Lim, 1999; Kweon, Choi, Kim, & Lim, 2001). The invention of cross-linked starch stemmed from the need for starch granules that are tough enough to resist disintegration when cooked with water. To avoid a thick pasty mass, Felton and Schopmeyer (1940) designed an inexpensive process to chemically treat native starch with acid chlorides including phosphorous oxychloride ($POCl_3$) in water. Other researchers followed suit with novel chemical approaches to cross-linking starch using other reagents such as epichlorohydrin (EPI) or sodium trimetaphosphate (STMP) (Hofreiter, Mehltretter, Bennie, & Hammerstrand, 1960; Konigsburg, 1950). Lim and Seib (1993) investigated the preparation of starch phosphates and reported that a mixture of phosphate salts (sodium trimetaphosphate (STMP) and sodium tripolyphosphate (STPP) gave better results than using STMP alone to prepare di-starch phosphate (cross-linking starches). Important factors in the cross-linking reaction include chemical composition of reagent, reagent concentration, pH, reaction time and temperature (Lim & Seib, 1993; Rutengerg, 1980).

The objective of this study was to evaluate the effect of the reagent type in the cross-linking of banana starch on some morphological, physicochemical and functional characteristics.

2. Materials and methods

2.1. Starch isolation

Unripe bananas (*Musa paradisiaca* L.) were purchased at the local market of Cuautla, Morelos State, Mexico and starch was isolated by the procedure described by Flores-Gorosquera et al. (2004).

2.2. Chemical starch modification

The native banana starch was modified with three cross-linked reagents. Cross-linked starch ($POCl_3$) was prepared using the methodology of Felton and Schopmeyer (1940). Banana starch (100 g, dry basis) was dispersed in distilled water 300 ml) and the slurry was adjusted to pH 11.0 with a 1 N NaOH solution. The cross-linking concentrate agent, $POCl_3$ (1 ml) was added drop wise over a 10 min, while maintaining the pH at 1.0 with the NaOH solution. The starch dispersion was stirred for 1 h at room temperature, and then filtered through Whatman No. 41 filter paper, washed with water and dried at 40 °C for 24 h.

Cross-linked starch with sodium trimetaphosphate (STMP) and sodium tripolyphosphate (STPP) was prepared using the methodology of Seib and Woo (1999). In brief, banana starch (50 g), water (70 ml), STMP (5.96 g), (STPP, 0.6 g) and sodium sulfate (5.0 g) were mixed in a round-bottom flask. The mixture was adjusted to pH 11.5 by adding 25 ml 1.0 M sodium hydroxide (i.e., approx. 2.0% sodium hydroxide, starch basis). The slurry was stirred continuously, warmed up to 45 °C, and held at this temperature for 3 h. The slurry was neutralized to pH 6.5 with 1.0 M hydrochloric acid. The modified starch preparation was collected by centrifugation, washed with water (7×, 150 ml) and dried at 40 °C.

Cross-linked starch (epichlorohydrin) was prepared using the methodology of Tare and Chaudhari (1987). Banana starch (100 g), water (150 ml), sodium chloride (1.5 g) and epichlorohydrin (5.5 ml) were mixed. Afterwards, a potassium hydroxide solution (6 g of potassium hydroxide on 40 ml of water) was added slowly over a 30 min time period. The starch dispersion was stirred and water (50 ml) and epichlorohydrin (2 ml) were added. The slurry was stirred for 18 h at room temperature and then filtered through Whatman No. 41 filter paper, washed with water and dried at 40 °C.

2.3. Chemical composition of native and cross-linked banana starch

Moisture content was determined by gravimetric heating (130 ± 2 °C for 2 h) using a 2–3 g sample. Ash, protein and fat were analyzed according to AACC[12] methods 08–01, 46–13 and 30–25, respectively (AACC, 2000). Phosphorus content was assessed in the modified starch following the methodology of Smith and Caruso (1964).

2.4. Scanning electron microscopy

For SEM studies, the samples were fixed to a conductive double glued tape of copper; which was covered with a 20 nm of thick coal layer. It was deposited under a vacuum using an evaporator in a JEOL JSMP 100 (Japan) electron microscope. Later on, samples were covered in the ionizer metals JEOL with a 50 nm thickness gold layer. A film piece was mounted on aluminum stubs using a double-sided tape and then coated with a gold layer (40–50 nm), allowing surface and cross-section visualization. All samples were examined using an accelerating voltage of 5 kV.

2.5. Particle size

Particle size distribution was run in quadruplicate at room temperature using a Malvern Master-Sizer 2000 (Malvern Instruments, Ltd. Worcestershire, UK) laser diffraction analyzer with a Fourier cell (0.02–2000 μm) and the Hydro SM Small Volume Sample Dispersion Unit (SVSDU) with a capacity of 50–120 μL. The instrument outputs a volume distribution as the fundamental measurement as well as median D [υ, 0.5]. Laser diffraction requires media of different refractive indices, in this study were used a 1.330 y 1.335 for water and starch, respectively.

2.6. 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, USA) previously calibrated with indium. Two milligram sample (dry basis) was weighed on an aluminum pan, adding 7 μL of deionized water. The pan was sealed tightly and then it was allowed to stand for 1 h before carrying out the analysis. An empty aluminum pan was used as a 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. The gelatinization or peak temperature (T_p) and the transition enthalpy (ΔH), were obtained directly from the analysis with the software TA Instruments, OS/2 version.

2.7. Swelling and solubility

Swelling power (SP) and solubility (S) were measured according to a modified method of Schoch (1964). A 0.4 g (dry basis) ground sample was mixed with 40 ml of water and put in a centrifuge tube using a vortex mixer. After heating for 30 min. in a water bath at 60, 70, 80 and 90 °C, the heated solution was centrifuged at 3000*g* during 10 min. The SP and S were determined as: SP = weight of sediment/weight of dry sample solids; S = (weight of dissolved solids in supernatant/weight of dry sample solids in the original sample) × 100.

2.8. Statistical analysis

One-way analysis of variance (ANOVA) at a significance level of 5% ($\alpha = 0.05$) was applied using the statistical program Sigma-stat, version 2.1 (Walpole, Myers, & Myers, 1999), when statistical differences were found, the Tukey test of multiple comparison was applied.

3. Results and discussion

3.1. Effect of the reagent type in the cross-linked

In the cross-linked reaction with $POCl_3$ under alkaline condition the hydrophilic phosphorus group reacts immediately with the OH of the starch, producing a di-starch phosphate. It was reported that cross-linked starches could have approximately 1 cross-linked bond between 100 and 3000 glucose units (Wurzburg, 1986). In the other hand, when the cross-linked is produced by STMP, due to the presence of a ring in its structure, a bimolecular reaction is necessary, however the same di-starch phosphate is produced (Hirsch & Kokini, 2002). Both cross-linked reagents, $POCl_3$ and STMP, produce the same structure in the starch granules, but with STMP the number of phosphate groups incorporated in the starch is higher and these are introduced in the inner of the granule, the cross-linked with $POCl_3$ is carried out only in the surface of the granule. This pattern was corroborated by the determination of phosphate groups. The banana starch modified with $POCl_3$ had lower level (0.010%) than STMP (0.214%). In previous studies, phosphorus content was evaluated in cross-linked wheat starch and the highest concentration reported was of 0.023% (Van Hung & Morita, 2005). The phosphorus content is a value that indirectly tests the cross-linked degree, because when high amount of this element is found, higher cross-linked was carried out. In the same sense, other report determined indirectly the cross-linked level in rice starch using the pasting profile.

Table 1
Chemical composition of native and cross-linked banana starch (*Musa paradisiaca* L.) with diverse reagents*.

Starch	Moisture (%)	Ash (%)	Protein (%)	Fat (%)
Native	6.72 ± 0.3^{a}	0.27 ± 0.02^{a}	0.98 ± 0.05^{a}	0.82 ± 0.05^{a}
Cross-linked ($POCl_3$)	1.24 ± 0.1^{b}	0.44 ± 0.03^{a}	0.76 ± 0.03^{b}	0.78 ± 0.08^{a}
Cross-linked (STMP)	3.29 ± 0.4^{c}	2.08 ± 0.18^{b}	0.86 ± 0.03^{c}	0.32 ± 0.02^{b}
Cross-linked (EPI)	3.22 ± 0.3^{c}	0.55 ± 0.03^{a}	0.75 ± 0.04^{b}	0.38 ± 0.04^{b}

Means superscripted by the same letter are not significantly different ($P \leqslant 0.05$).
* Mean values of three measurements ± standard error.

It was mentioned that introduction of covalent bonds (by phosphate groups), causes that starch granules are joined, producing low molecular mobility and consequently the gelatinization is carried out at higher temperature (depending on the cross-linked level) (Chatakanonda, Varanit, & Chinachoti, 2000).

A multifunctional reaction might be produced with epichlorohydrin (EPI), because one or two EPI molecules can be consumed to produce only one cross-linked (glycerol bond). The cross-linked with EPI is not homogeneous and the joints are located principally in the crystalline areas of the starch granules (Jane, Radosavljevic, & Seib, 1992; Shiftan, Ravanelle, Alexandre Mateescu, & Marchessault, 2000). The mechanism of cross-linked using STMP and EPI is that both reagents penetrate in the inner of the starch granule and the cross-linked is distributed in higher volumes into the granule. This generate that the modification, present higher influence of the physicochemical and functional properties of the polysaccharide (Hirsch & Kokini, 2002). When EPI is used the cross-linked level can not be related with the phosphorus content, then the pasting profile (using a Brabender viscoamylograph) was determine to calculated a degree of cross-linking, because when the cross-linking

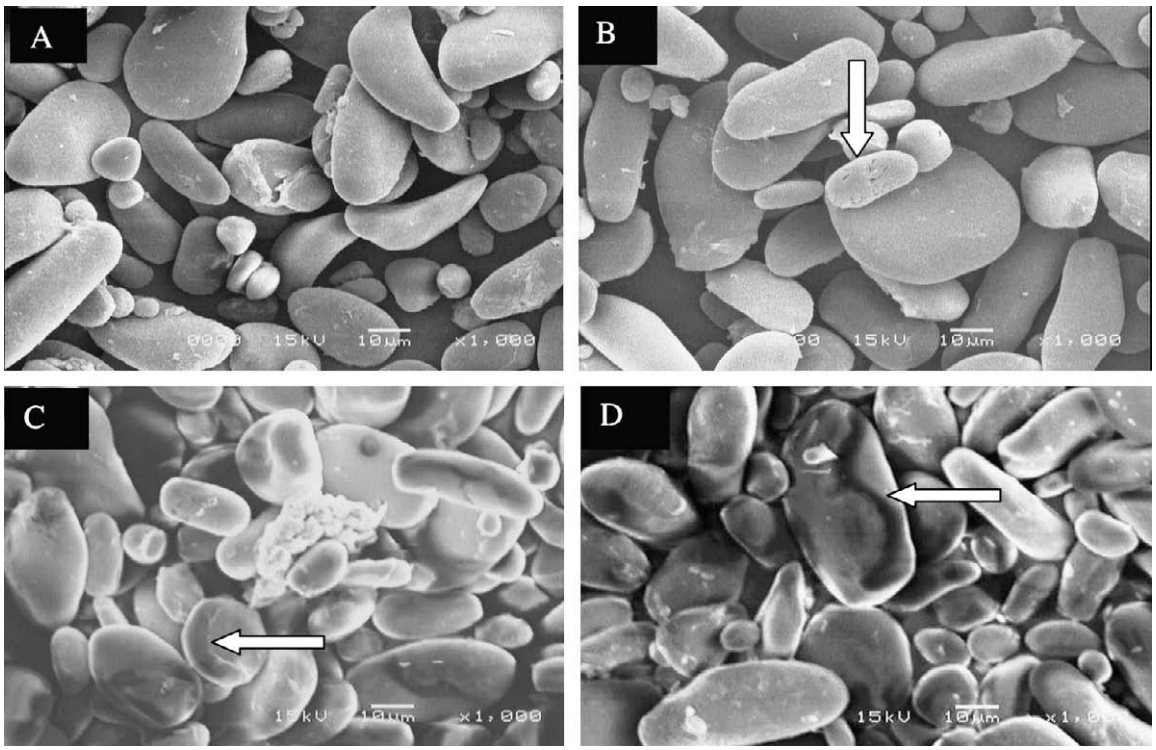

Fig. 1. Scanning electron micrographs of starch granules of native (A), cross-linked starch ($POCl_3$) (B), cross-linked starch (STMP/STPP) (C) and cross-linked starch (EPI) (D).

increased the peak viscosity decreased (Chatakanonda et al., 2000; Kaur, Singh, & Singh, 2006). However, it is important mentioned that independently of the reagent used in the cross-linked reaction, covalent bonds are produced and more important is the number of cross-linked bonds introduced in the starch.

3.2. Chemical composition

Moisture content of cross-linked banana starch decreased up to 100% compared with its native sample (Table 1). This pattern is related to the reaction between the OH groups of glucose units of starch and the bi- or poly-functional chemical reagent used in this chemical modification, decreasing the possibility of reaction between OH of starch chains and the water molecules and consequently the join of water to this polymer. The effect was more notorious in the sample with phosphorous oxychloride ($POCl_3$) that might be explained by the reaction sub-products because with $POCl_3$, since sodium chloride is produced and this has the possibility to join water molecules that are eliminated during the purification step of the cross-linked starch. Ash level increased in the cross-linked starch in the order: $POCl_3$ < epichlorohydrin (EPI) < sodium trimetaphosphate (STMP). This pattern is due to the introduction of some phosphate groups in the amylopectin molecule during the modification process as was reported in potato starch that naturally contains this kind of groups. The highest ash content was determined in the sample modified with STMP. That might be due to the sub-products of the reaction contain Na and P, that might be retained in the modified starch, thus increasing the ash amount. The protein content in the cross-linked starches decreased respect to native sample. This effect is due to partial solubilization of the proteins with the reagents used in the chemical modification. The lowest protein value was found in the samples modified with $POCl_3$ and EPI, followed by STMP/STPP. Fat levels had a similar pattern because in general the cross-linked starches showed a lower value than its native counterpart. They had the order: STMP/STPP < EPI < $POCl_3$. The reagent type used in the modification plays an important role in the proximal composition and the polarity of the solvent might be implicates in this pattern. These results might be important in the functionality of these cross-linked starches when applied to diverse systems.

3.3. Scanning electron microscopy

The appearance of starch granules after modification was studied using SEM (Fig. 1). The native sample (Fig. 1A) and modified with $POCl_3$ (Fig. 1B) had similar morphology, where only some granules showed exo-erosion (see arrow). This pattern is related to a low degree modification obtained with this reagent type. When STMP/STPP (Fig. 1C) and EPI (Fig. 1D) were used, diverse large granules (mainly) showed black zones on the surface (see arrows) along the longitudinal axis, indicating a slight fragmentation and the formation of a deep groove (Singh, Kaur, & McCarthy, 2007). These characteristics in the surface of cross-linked banana starch granules indicate different degree of modification and consequently different physicochemical and functional properties.

3.4. Granule size distribution

Due to the changes in the granule size produced by the chemical treatment, the granule size distribution was tested in the cross-linked banana starches (Fig. 2). The native starch exhibited a modal distribution (between 11.4 and 138 μm) with an average size of 50 μm. The cross-linked starch with $POCl_3$ showed a bimodal distribution with a principal peak where the average size was lower than its native counterpart, and a second small peak was presented up to 140 μm. The second peak is due to granule aggregation, due to partial amylose lixiviation during the chemical modification. This pattern was more evident when the modification was carried out with STMP/STPP and EPI, because the principal peak showed an average size higher than the native sample and the peak at higher size was more evident (see arrow). The higher granules aggregation in these cross-linked starches are due to the higher granule disorganization and amylose lixiviation than in the starch modified with $POCl_3$ as it was showed by the enthalpy of gelatinization.

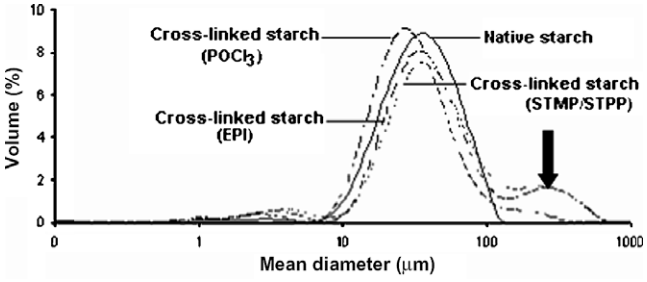

Fig. 2. Particle size distribution of native and cross-linked banana starches.

3.5. Effect of temperature on swelling and solubility

The Fig. 3 shows the swelling and solubility behaviour of native and cross-linked starches. At the lowest temperature of the

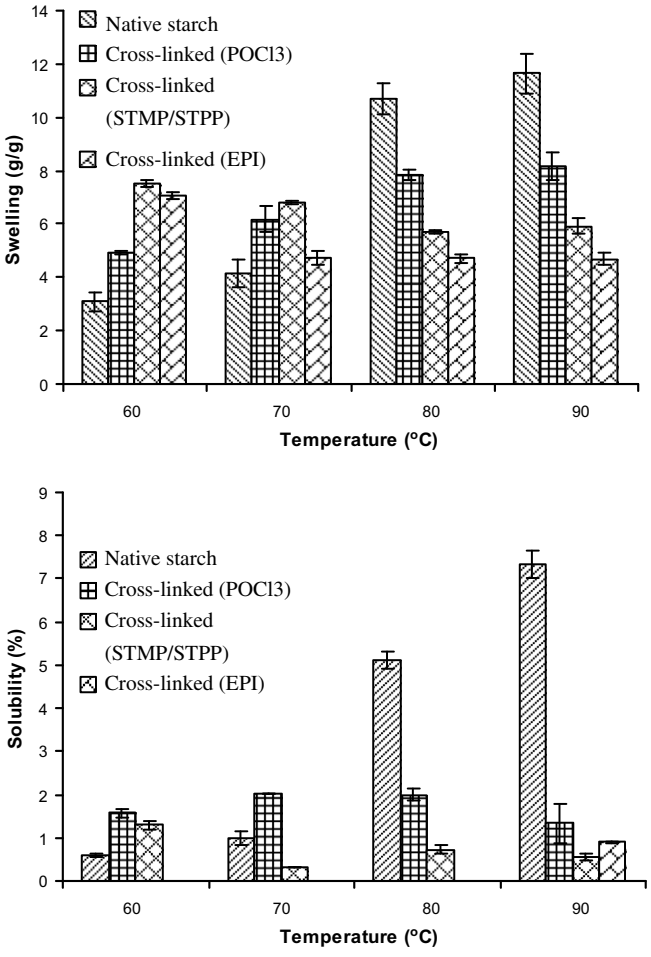

Fig. 3. Effect of temperature on swelling (up) and solubility (down) of native and cross-linked starches.

Table 2
Gelatinization characteristics (T_o, T_p, T_c and enthalpy) of native and cross-linked banana starch*.

Starch	T_o (°C)	T_p (°C)	T_c (°C)	ΔH (J/g)
Native	72.35 ± 0.18[a]	78.44 ± 0.19[a]	89.21 ± 0.8[a]	12.68 ± 0.29[a]
Cross-linked ($POCl_3$)	70.86 ± 0.23[b]	77.02 ± 0.28[b]	87.53 ± 0.20[b]	12.61 ± 0.50[a]
Cross-linked (STMP/STPP)	78.04 ± 0.09[c]	83.40 ± 0.34[c]	98.37 ± 0.89[c]	11.05 ± 0.55[b]
Cross-linked (EPI)	83.89 ± 0.50[d]	90.14 ± 0.31[d]	102.72 ± 0.39[d]	10.40 ± 0.46[b]

Means superscripted by the same letter are not significantly different ($P \leqslant .05$).
* Mean values of three measurements ± standard error.

test (60 °C) the swelling value increased proportionally with the cross-linking and the highest value was obtained in those starches modified with STMP/STPP and EPI. These results indicate that cross-linked banana starch with STMP/STPP and EPI altered the granule structure (as was observed in the SEM study) and the water penetrates easily. When temperature increased the native and the cross-linked starch with $POCl_3$ raised their swelling value, whereas that of the modified starch with STMP/STPP and EPI decreased. The higher disorganization of starch components in the cross-linked with STMP/STPP and EPI provoked that the starch granules were more prone to the temperature, producing amylose lixiviation and a minor amount of water retained. At higher temperature (80 °C) native starch presented an important increase in swelling value but at (90 °C) swelling did not change; similar pattern was showed by the cross-linked starch with $POCl_3$. For those cross-linked starches with STMP/STPP and EPI an inverse pattern was obtained, because the swelling values decreased as temperature increased (80 °C), but thereafter the value was constant. This pattern is in agreement with the modification of starch granule, since it has been reported than cross-linking inhibited swelling of granules after gelatinization, resulting in a paste and not a gel after subsequent cooling (Chatakanonda et al., 2000).

The solubility of native starch increased with temperature (Fig. 3), a pattern that agrees with its swelling behaviour. These results are due to the lixiviation of amylose from starch granules and to high temperatures the external long chains of amylopectin also contribute to those solubility values. The cross-linked starch with $POCl_3$ presented a slight increased in the solubility value between the sample tested to 60 and 70 °C. However, when temperature increased, the values did not change perhaps due to the stabilization of the granule after the cross-linking reaction. This effect was more notorious in the cross-linked starches with STMP/STPP and EPI, because the lowest solubility values were found in those samples. These results are important when the banana cross-linked starches are applied in systems where heating or high process temperatures are required.

3.6. Thermal properties

The native banana starch had a gelatinization peak temperature of 78.44 °C with gelatinization enthalpy of 12.68 J/g (Table 2). This single transition corresponds to the dissociation of the amylose and amylopectin molecules within the starch granules and leaching out of amylose to the continuous phase (Fujita, Lida, & Fujiyama, 1992; Liu, Leliévre, & Ayoung, 1991; Russel & Juliano, 1983). The cross-linked starch with $POCl_3$ showed a slight decrease in the three temperatures: onset (T_o), peak (T_p) and end (T_e) compared to its native counterpart (Table 2), but the enthalpy values were not different ($\alpha = 0.05$). This pattern might be related with a slight disorganization of starch granules during the modification due to the reagent used. Choi and Kerr (2004) reported that cross-linked starches prepared using a relatively low concentration of the $POCl_3$ had gelatinization parameters similar to its native counterpart, while those cross-linked starches prepared using higher reagent concentration showed higher T_p and ΔH values. The thermal parameters for $POCl_3$ cross-linked starch is related with the lower cross-linking level tested with the phosphorus content (0.010%) more than the chemical characteristics of the bond introduced in the modification, because covalent bonds are produced independently of the reagent used.

The modified starches with STMP/STPP and EPI present an increase in the three transition temperature, but a slight decrease in enthalpy value (Table 2). The results confirmed that the introduction of phosphate groups (STMP/STPP) (0.214%) and glycerol bond (EPI) into starch tightened the molecular organization in the starch molecules, thus gelatinization is carry out at a higher temperature. In general, it was reported that the gelatinization enthalpy was not affected by cross-linking (Chatakanonda et al., 2000), suggesting that complete melting of crystalline regions occurred in cross-linked banana starch with both reagents.

4. Conclusions

The cross-linked modify the chemical composition of banana starch and differences were showed among the cross-linked starches with the different reagents used. The cross-linked with STMP/STPP and EPI showed a higher effect on the banana starch granule and a bimodal distribution with a small peak up to 140 μm was detected. The swelling and solubility values were affected by the cross-linked reaction with lower values of these parameters with STMP/STPP and EPI. The stabilization of the granules during this reaction is responsible of this pattern. The higher temperature and slightly lower enthalpy of gelatinization of cross-linked starches with STMP/STPP and EPI is in agreement with the stabilization due to the reaction and melting of crystalline regions.

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