EFECTO DE MODIFICACIÓN DE LA TEMPERATURA DE ALGUNAS PROPIEDADES FUNCIONALES DEL ALMIDÓN DE MAÍZ CON ENLACES ENTRECRUZADOS

EFFECT OF THE MODIFICATION TEMPERATURE ON SOME FUNCTIONAL PROPERTIES OF THE CORN STARCH CROSSLINKED

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RESUMEN

La modificación química por entrecruzamiento consiste en introducir grupos fosfatos como puentes o conexiones de entrecruzamiento entre moléculas vecinas en los componentes amiláceos, a fin de producir cambios estructurales y funcionales en el almidón. En este estudio se evaluó el efecto de la temperatura de modificación sobre algunas características funcionales del almidón de maíz; usando el nativo como control. Para ello, se siguió el procedimiento de modificación por entrecruzamiento usado para obtener almidón de grado alimenticio. El procedimiento de la modificación en el almidón de maíz, fue realizado usando pH neutro (6.9±2) y dos temperaturas (122 y 145 °C). Al almidón nativo y los almidones modificados, se les determinaron los índices de absorción de agua, solubilidad y poder de hinchamiento, viscosidad aparente (usando el viscosímetro Brookfiel) y el perfil amilográfico (amilografo Brabender). Los resultados mostraron que las variaciones de la temperatura afectan algunos parámetros de composición; así como, al comportamiento funcional del almidón del maíz, específicamente en las características químicas y reológicas. El asentamiento (*setback*) y la consistencia disminuyeron significativamente ($p \leq 0.05$) y la fragilidad de los gránulos de almidón (*breakdown*) aumentó al compararlos con las propiedades del almidón nativo. También la temperatura alteró la absorción de agua y el poder de hinchamiento. Este efecto de la temperatura se puede interpretar de dos maneras. Primero, debido a que cambia las propiedades funcionales, utilizándolos como diferentes alternativas en la formulación de alimentos o controlándolos para mantener la misma viscosidad en los productos finales.

Palabras clave: *Almidón de maíz, almidón modificado por entrecruzamiento, propiedades reológicas.*

SUMMARY

The chemical modification by cross-linking consists of the introduction of phosphate groups like bridges or crossed connections, among neighboring starch molecules. With this modification, structural and functional changes are produced on the starch. In this study the effect of the temperature on some functional properties of food grade corn starch modified by crosslinked, were evaluated using the native one as control. The process of cross-linking on the corn starch was carried out using a neutral pH

(6.9±2) and two temperatures (122 y 145 °C). The proximate composition, purity, water absorption, solubility and swelling power, apparent viscosity, and the amylographic profile were determined. The results showed that variations of the temperature affect the composition and the functional behavior of the starch of corn, specifically on the chemical and rheological properties of the starches. The setback and consistency were significantly ($p \leq 0.05$) decreased, and the breakdown increased, when they were compared each one. Also the modification of the temperature had altered the water absorption and swelling power. This fact could be interpreted in two ways. First, converting them in promising protagonists in food processing and formulation or controlled in order to maintaining the same viscosity in the final products.

Key words: *Corn starch, cross-linking modified starch, and rheological properties.*

INTRODUCCION

World corn crop is 600 million ton per annum. Nearly 10% is made into starch or starch-derived sweeteners making corn starch the largest starch commodity in the world (Thomas and Atwel, 1999; Perez et al. 2003). Starch is one of nature's major renewable resources and a mainstay of our food and industrial economy.

Corn starches, native and modified, are used in hundreds of food application. Starches modified by cross-linking are widely used in the food industry to overcome undesirable changes in product texture and appearance caused by retrogradation or starch breakdown during processing and storage (Ostergard *et al.*, 1988).

The modification by cross-linking is a technique that involves placing mono or bi functional substituent, such as phosphorous by ester bound along to the starch polymeric backbone (Lim and Seib, 1993). However, has been noted that the functional properties of the cross-linked starch are dependent from control of the parameters of the cross linking process, otherwise its rheological properties could be changed (Light, 1990). The objective of the study was to evaluate the effect of the temperatures used in the protocol of modification by crosslink, on the chemical composition and rheological properties of modified corn starches.

MATERIALS AND METHODS

Native corn starch was provided by INDELMA C.A., Cagua, estado Aragua, Venezuela. The corn starch was chemically modified at laboratory scale, from the commercial one. The general principles for preparation of the food grade starch are described below .

Phosphate starch.

The native corn starch was crosslinked with Na3 $(PO)_3$ using two temperature (122, 145ºC) and neutral pH (6.9 2), to produce an starch with low D.S., Paschall (1964). To prepare the reticulated starch, a mixture of 12.6 g of Sodium Tripolyphosphate ($Na_5P_3O_{10}$) is dissolved in 167 ml of water (commercial Sodium Tripolyphosphate is suitable) and 100 g of starch is dispersed in the solution. The slurry is then filtered with suction on a fitted glass funnel. The filter cake is crumbled and dried overnight at 40-45 ºC in a forced-draft air oven. The starch-salt mixture is powdered in a waring blender and dried at 65 ºC for 90 min, in a forced-draft air oven. The dried mixture is transferred to a 1-liter stainless-steel beaker. The beaker is placed in a preheated oil-bath (180 and 190ºC) and heated for 20-25 minutes with sufficient agitation (with a half-moon stirrer) to give continuous movement to the entire mass. The starch temperature should reach 122 or 145 ºC after 20 min. The mixture is cooled, and dissolved in 200 ml of distilled water, and then recovered on a Büchner funnel. The filter cake is washed with three 200 ml portions of distilled water. The product is crumbled and air-dried.

Proximate Composition and purity of Corn Starches

Native and modified starches were analyzed for moisture, ash, crude protein (%N x 6.25), crude fiber Smith (1967), and fatty materials using the method described by Schoch (1964). Purity, expressed as a total starch percentage was calculated as: 100-(moisture+ crude protein + ash, +crude fiber +fatty materials).

Qualitative Syneresis of starch gels

A starch water suspension was prepared with 60 g of starch (14 % of moisture) in a total volume of 500 ml; the suspension was heated from 30 to 95C. The slurry was cooled and stored overnight for 24 h at refrigeration temperature (3-4C).The water lixiviation was established with a positive symbol (+) and the absent of water lixiviation as negative (-).

Brabender Viscoamylograph (BV) Gelatinization profile

Gelatinization profile was measured in an 8 % aqueous suspension of the sample, using the method described in AACC, 2003. The following parameters: initial gelatinization temperature, peak viscosity, viscosities (at 95°C, 50°C and holding time), breakdown, and setback and consistency index, were calculated from the corresponding plots. Bhattachary, K.*et al.*, 1979, and Zhuo *et al.*, 1998.

Apparent Viscosity Measurement of Corn Starches

The apparent viscosity was determined using a Brookfield Viscosimeter (model LVT, spindle No. 4 at 6,12,30,60 rpm, in the three starch suspensions using the solution heated in the amylograph this determination was done with N° 4 spindle at two temperatures; 50 and 30°C, Whistler and Paschall (1967).

Functional Properties of Corn Starches

Water absorption, swelling power and solubility of these starches were measured by a combination of the methods of Anderson 1982 and Schoch 1964 described by González and Pérez (2002).

Statistical Evaluation of Analytical Data

Data collected for the three lots of each starch were analyzed by one-way ANOVA followed by Duncan test, using the Statgraphics Program (Statically Graphics Educational, Version 6.0 1992. Manugiststics, inc. and Statistical Graphics Corp., USA).

RESULTS AND DISCUSSION

Composition and purity of Corn Native and Modified Starches

The composition and purity of starches is showed in Table 1. The moisture content of the native and modified using the lowest temperature corn starches were similar between them, and higher than those of the corn starch modified at 145 C. Crude protein contents were significantly decreased, and the crude fiber were increased ($p \leq 0.05$) by the temperature changes. Due to the incorporation of the phosphates and sodium groups, the ash content of both corn starches modified was higher ($p \leq 0.05$) than native counterpart, similar results are reported by Yung-Ho and Chen-Yi, (1992). The fatty materials were not affected by the temperature changes.

Gelatinization profile

Except for the viscosity at 50 ºC, the overall viscosities of the both modified starches were lightly increased, being most conspicuous when was used the high temperature. It can be noted the initial gelatinization temperature (IGT) did not was affected. However, the setback and consistency were significantly decreased ($p \leq 0.05$) and the breakdown increased, when they were compared with the native counterpart (Table 2).

Apparent Viscosity

As can be noted all of the starches have a pseudo-plastic behavior. The behaviors of the overall viscosity of the native starch, and in both modified starches (at 50 ºC) are agreed with the results shown by the amylogram (BV). However, when they are measured at 30 ºC their overall viscosities are increased. These changes in viscosities are due to the changes in the molecular level of the starch by the connections of the phosphate, when, they are compared to the native counterpart. But when they are compared between them, the changes in viscosity are due to the effect of the temperature on the connection of the phosphate to the molecules (Figure 1).

Syneresis of starch gels

Table 1, report the results of the syneresis of starches. The three starches have negative syneresis. Indeed, it is strengthens by the strong associative forces inside their granules, as was pointed out before.

Table 1. Proximate composition, purity, and syneresis* of the Corn Starches

Parameter	Native	Modified (1) pH 6.9 ± 2/145 °C	Modified (2) pH 6.9 ± 2/122°C
Moisture (%)	11.47^{a}	6.87^{b}	10.45^{a}
Crude Protein** (%)	0.83^{a}	0.18^{b}	0.28^{b}
Fatty material (%)	0 .52^{a}	0.62^{a}	0.75^{a}
Crude fibre (%)	0.53^{a}	0.98^{b}	1.21^{b}
Ash (%)	0.02^{a}	0.98^{b}	0.73^{b}
Purity	97.90	97.24	97.03
Syneresis	-	-	-

(: dry basis, except moisture) (**: % N x 6.25). The mean values from n=9, in the same row followed by the same letter are not statistically different at a 5% significance level.*

Table 2. Gelatinization profile of Corn Starches (Amylograph Brabender)

Parameter (U.B.)	Native	Modified (1) pH 6.9 ± 2/145 °C	Modified (2) pH 6.9 ± 2/122 °C
I.G.T. °C	78^{a}	78,6 ^{a}	78 ^{a}
Peak Viscosity	380^{a}	658^{b}	650^{b}
Viscosity 95 °C	360^{a}	480^{b}	360^{a}
Viscosity 50 °C	760^{a}	550^{b}	730^{a}
Breakdown	80^{a}	358^{b}	290^{c}
Setback	400^{a}	300^{b}	370^{a}
Consistency	320^{a}	-58^{b}	-290^{c}

The mean values (n=9) in the same row followed by the same letter are not statistically different at a 5% significance level. IGT= Initial gelatinization temperature.

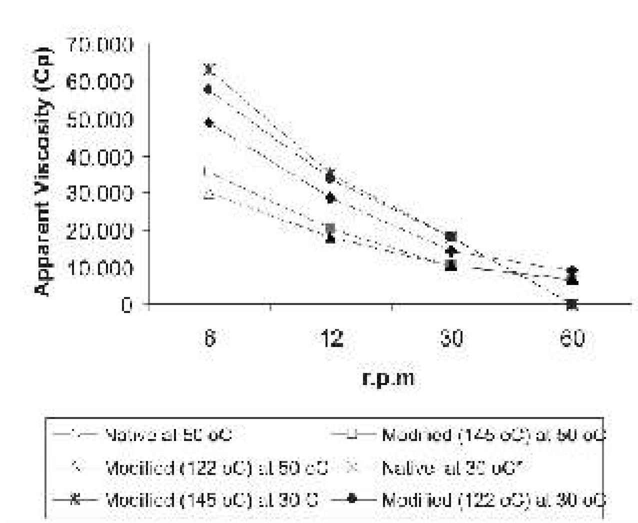

Figure 1. Apparent Viscosity (centipoises) of Corn Starches

Functional Properties of Corn Native and Modified Starches

The effects of temperature on water absorption, solubility and swelling power of these starches are shown in Figure 2 (A, B and C). As can be seen, the modification alters the three parameters. Water absorption and swelling power are the most effected by temperature, observing that the starch modified at 122 ºC absorb most water, than the starch modified at 145 ºC. While, the behavior observed for swelling power has been contrary. Solubility of the starches are affected by the modification at the initial stages

(65 through 80 ºC), reaching same values, as the native one at final stages (80 through 95 ºC); similar tendency is reported by Hugh, cited by Whistler and Paschal, (1964). These parameters' tendency could reflect differences in strength and nature of intra granular bonding, which is a direct result of variations in crystalline and amorphous regions inside the starch granules.

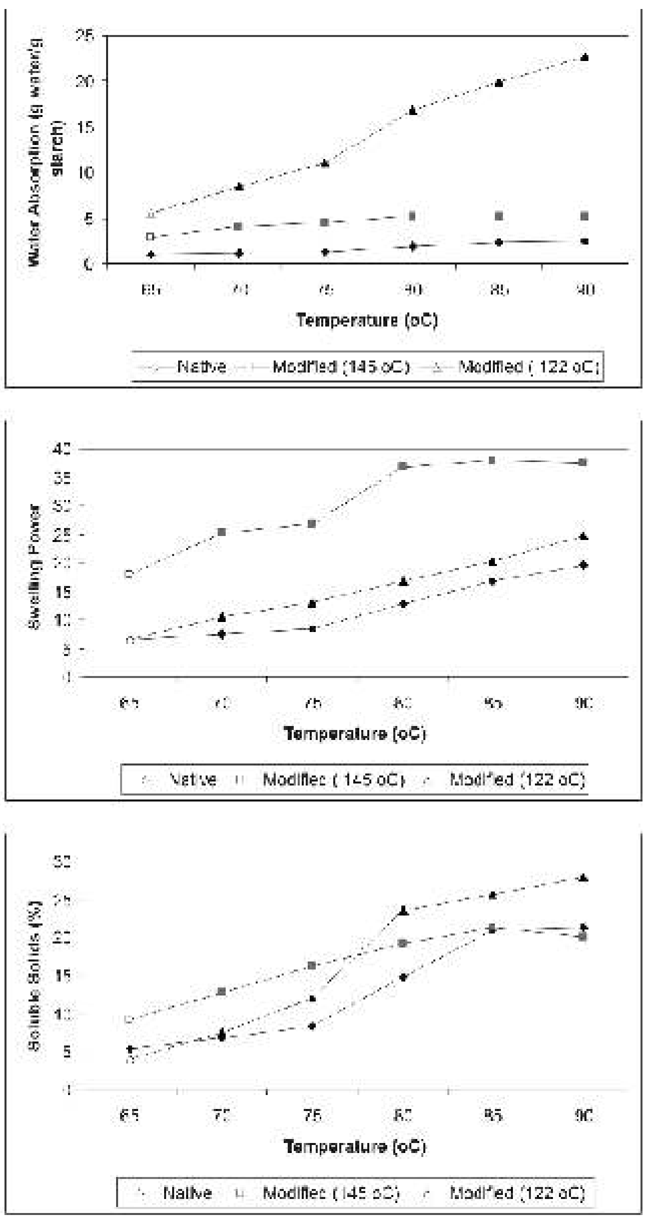

Figure 2. Water Absorption (A), Solubility (B) and Swelling Power (C) of native and Corn Starches.

CONCLUSIONS

Changes in modification temperatures affect notably the chemical and rheological properties of the corn starches. This fact could be interpreted in two ways. First, converting them in promising protagonists in food processing and formulation or considered in order to maintaining the same viscosity in the final products.

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