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# Modificacion enzimatica de almidon de maiz y sus efectos en la viabilidad de la vitamina c

Enzymatic Modification of Corn Starch and its Effect on the Viability of Vitamin C

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## Abstract:

In the present work, the effect of enzymatic hydrolysis ( $\alpha$ -amylase and amyloglucosidase) at 16 and 20 h on the morphological, physicochemical and structural characteristics of corn starch, and the protective effect of this on ascorbic acid microcapsules was studied. The amylose content increased with respect to the hydrolysis time, observing several perforations, and a reduction in the size of the graph. The thermal properties show lower values of H and the increase in the gelatinization temperatures in the hydrolysed starches. Each starch modified in rubber with rubber was used to encapsulate ascorbic acid. They presented to the mayor the microcapsules formed with hydrolyzed starch at 16 h plus gum arabic, on the small granules and gum arabic (controls).

## Keywords:

Vitamin C, enzymatically hydrolyzed starch, microcapsules, thermal properties

#### **Resumen:**

En el presente trabajo se estudió el efecto de la hidrólisis enzimática ( $\alpha$ -amilasa y amiloglucosidasa) a las 16 y 20 h sobre las características morfológicas, fisicoquímicas y estructurales de almidón de maíz, y el efecto protector de este en microcápsulas de ácido ascórbico. El contenido de amilosa aumentó con respecto al tiempo de hidrólisis, observándose numerosas perforaciones, y una reducción en el tamaño del gránulo. Las propiedades térmicas mostraron menores valores de  $\Delta$ H y el aumento en las temperaturas de gelatinización en los almidones hidrolizados. Cada almidón modificado en mezcla con goma arábiga fue utilizado para encapsular ácido ascórbico. Presentaron mayor estabilidad las microcápsulas formadas con almidón hidrolizado a 16 h más goma arábiga, sobre las de gránulo pequeño y goma arábiga (controles).

#### Palabras Clave:

Vitamina C, almidón hidrolizado enzimáticamente, microcápsulas, propiedades térmicas

## INTRODUCTION

Microencapsulation is a promising approach to protect bioactive compounds sensitive to the environment, reduce reactivity and improve stability, and / or allow a controlled release (Bansode et al., 2010). The published works report the incorporation of several bioactive molecules.

Although many encapsulation techniques have been developed, spray drying is the method commonly used. However, the choice of wall material can be critical, since it affects the encapsulation efficiency and the stability of the resulting microcapsules (Rosenberg et al., 1990). A good choice for a wall material should be based on its physicochemical properties.

In the group of biopolymers, enzymatically modified starches attract a lot of attention due to their great capacity of adsorption by the formed pores. They contain abundant pores from the surface to the center of the granules, which increase the specific surface, acting as excellent natural absorbers (Belingheri et al., 2015).

Vitamin C is a bioactive compound historically known for its nutritional benefits for health. It has wide application as an antioxidant, and providing protection in the sensory and nutritional quality of food (Desai et al., 2006).

The aim of this work is characterize morphologically, physicochemically and structurally the enzymatically modified corn starch and evaluate the stability of the ascorbic acid microcapsules with starch previously modified and characterized in a mixture with gum arabic.

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# MATERIALS AND METHODS

For the modification of the starch, the enzymes  $\alpha$ -amylase and amyloglucosidase (10 U/g starch) were used in acetates buffer at 30 ° C and 380 rpm for 16 and 20 hours. The apparent amylose content was determined by a reaction with I2/KI. The enzymatically modified starches were characterized morphologically by scanning electron microscopy (SEM). The physicochemical properties were obtained by differential scanning calorimetry (DSC) and rapid viscosity analysis (RVA); and the structural, crystallinity and particle size were performed by X-ray diffraction and laser diffraction respectively.

The microcapsules were obtained by spray drying, then they were morphologically characterized by SEM and a stability test was carried out by means of an accelerated aging study (52.5% relative humidity and 55 °C) during 9 weeks of storage. The data were analyzed using an ANOVA with 95% confidence, when there were significant differences, a comparison of means was made with the Tukey test, with  $\alpha \pm 0.05$ .

## **RESULTS AND DISCUSSION**

In the Fig. 1 corn starches enzymatically hydrolyzed are shown, it can be observed how the degree of hydrolysis was increasing according to the time of exposure of the enzymes, having a greater number of pores and eroded surface treatment of 20 hours, with different places of attack. Enzymatic hydrolysis is carried out in different parts of the starch, attacking both  $\alpha$ -1,4 and  $\alpha$ -1,6 bond of amylose and amylopectin, giving rise to smaller glucoses, maltoses and other oligosaccharides and dextrins. Several channels were formed throughout the starch area, as reported by Spinelli et al., (2013). Aggarwal & Dollimore (2000), observed an increase in the size of the pores, when the concentration of amyloglucosidase increased, until a break, giving rise to large irregular holes and a disrupted structure. Jayakody & Hoover (2002) postulated that the presence of pores or channels on the surface of the granules, as in corn starch, facilitates the work of the enzymes towards the interior of the granule, which makes it more susceptible to hydrolysis.

In the determination of the **amylose content**, a statistically significant increase (p < 0.05) can be observed (Fig. 2) as the enzymatic hydrolysis time increased, giving as results 18.34 ± 0.77, 58.94 ± 3.96 and 74.09 ± 2.41 for native starches. hydrolyzed 16 and 20 h respectively. This increase was largely due to the hydrolyzed fractions, glucose and maltose, which formed when the enzymes acted. Chung et al., (2015) observed a high content of amylose in rice after enzymatic hydrolysis with amylolitic

enzymes, he attributes the increase of this polymer to the action of amyloglucosidase.

The **particle size** of the native corn starch and enzymatically hydrolysed for 16 and 20 h time were 15.83, 14.97 and 14.72  $\mu$ m respectively, did not present statistically significant differences (p <0.05); although the tendency was to decrease with hydrolysis time, this change is due to the internal and superficial erosions due to the enzymatic attack of  $\alpha$ -amylase and amyloglucosidase. The results are similar to those reported in the literature (Tester & Karkalas, 2002).

The **X-ray diffraction** patterns of the native and modified starches are shown in Fig. 3. The native corn starches and the modified starches showed a type A diffraction pattern, which is typical of cereals, and is characterized by presence of peaks of greater intensity of diffraction for the angles  $2\theta = 15$ , 17, 18 and 23 °. It can be observed in the diffractogram that the starch that showed the highest crystallinity was the hydrolyzate enzymatically for 20 h, followed by the hydrolyzate of 16 h and with a lower percentage the native with values of 60.77, 40.09 and 28.14% respectively. Authors have postulated that the breaking of the starch chains in the amorphous zones allows an extensive hydrolysis, producing a more crystalline structure (Kainuma & French, 1971).

In **DSC**, the thermal properties of the modified starches showed lower values of  $\Delta$ H and an increase in the temperatura of gelatinization (Table I), showing significant statistical differences (p <0.05) between the hydrolysed starches and the native. The  $\Delta$ H values were 10.5, 7.0 and 9.0 J/g and the gelatinization temperatures of 72.1, 73.3 and 73.2 °C for native starches and hydrolyzed at 16 h and 20 h respectively. The decrease in  $\Delta$ H indicates that porous starches require less energy to promote starch gelatinization, ie the energy needed to unwind the unstable double helices during gelatinization (Sandhu & Singh, 2007).

As for the **microcapsules**, it can be observed that most of the pores are covered on the surface, with a slight agglomeration (Fig. 1). The starch granules have an undefined structure, although with the same tendency as regards the distribution. In Fig. 4, it can be observed how the microcapsules of starch hydrolyzed for 16 hours have a better stability during storage under accelerated aging conditions, conserving 17.6% and 12% of ascorbic acid encapsulated initially in weeks 6 and 8 respectively.

## CONCLUSIONS

Changes were made in the morphological, structural and physicochemical characterization between native and hydrolyzed starches. The microcapsules with hydrolyzed starch for 16 hours showed greater stability during the accelerated aging test compared to the controls. In this study it is concluded that the enzymatic perforation of the starches could be a good alternative to encapsulate bioactive compounds favoring the stability regarding the storage time.

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| Starch | To (°C)                 | Tp (°C)                 | Tc (°C)    | ΔH (J/g)               | Тс-То     |
|--------|-------------------------|-------------------------|------------|------------------------|-----------|
| AMN    | 68.52±0.51 ª            | 72.43±0.36ª             | 77.29±0.43 | 10.30±0.4ª             | 8.77±0.47 |
| AM16H  | 69.42±0.25 <sup>b</sup> | 73.08±0.16 <sup>b</sup> | 78.36±0.33 | 7.83±0.44 <sup>b</sup> | 9.10±0.47 |
| AM20H  | 69.31±0.23 <sup>b</sup> | 73.15±0.25 <sup>b</sup> | 77.7±0.12  | 8.63±0.48 <sup>b</sup> | 8.43±0.34 |

**Table I.** Parameters of thermal profile analysis, measurements made to starch treatments, using differential scanning calorimetry (DSC)<sup>1</sup>.

<sup>1</sup>Data are the means of three repetitions  $\pm$  standard deviation, different superscripts per row represent significant statistical differences (P <0.05). Tp = Peak temperature,  $\Delta$ H = Enthalpy change. AMN = Native corn starch, AM16H = Corn starch enzymatically hydrolyzed for 16 hours, AM20H = Corn starch enzymatically hydrolyzed for 20 hours.