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Acetylation of normal and waxy maize starches as encapsulating agents for maize anthocyanins microencapsulation

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ABSTRACT

Encapsulation by spray drying of purple maize anthocyanins was carried out using encapsulating agents produced from maize starch derivatives. Normal and waxy maize starches were hydrolyzed with hydrochloric acid and were esterified with acetic anhydride before extrusion process. The influence of different derivative starches as encapsulating agents were investigated regarding the morphology (SEM), encapsulation efficiency (EE), adsorption isotherms and anthocyanins retention (AR) after 30 days of storage at different a_w (0.11–0.94) at 40 °C. SEM images showed spherical microparticles with rough surfaces. The values of EE were higher in starch derivatives with respect to hydrolyzed native normal and waxy maize starches. After storage, microparticles produced with acetylated normal maize starch had the highest AR in the range of 0.11–0.75 a_w. It was found that the experimental data were well represented by means of the GAB and Peleg models.

Keywords: Encapsulation; Spray drying; Maize anthocyanins; Hydrolyzed starch; Acetylation; Storage stability

1. Introduction

Mexican purple maize is used mainly to prepare “atole”, a traditional hot beverage. Because of its intense purple color, purple maize represents an important source of anthocyanins. Recently, interest in the potential use of anthocyanins from purple maize (*Zea mays* L.) as natural colorant has increased. Anthocyanins not only impart color to foods that contain them, but also they have been related to antioxidant, vasoprotective, anti-inflammatory, anticarcinogenic, antiobesity and antidiabetic effects (Bishayee et al., 2011; Rojo et al., 2012; Shih et al., 2010). Their stability depends on factors such as their molecular structure, pH, temperature, light intensity, presence of copigments, metal ions, enzymes, oxygen, ascorbic acid, sugars, among others (Bakowska-Barczak and Kolodziejczyk, 2011). Unlike synthetic colorants, anthocyanins present low toxicity (Bagchi et al., 2006), however, their incorporation into processed food matrices are limited since anthocyanins degraded dramatically at the pH level of above 6.0 under high temperatures (100 to 121 °C) (Sui et al., 2014), and light

Abbreviations: EE, encapsulation efficiency; SEM, scanning electron microscopy; AR, anthocyanins retention; DS, degree of substitution; EP, encapsulation productivity; N, hydrolyzed normal maize starch; W, hydrolyzed waxy maize starch; NA, acetylated normal maize starch; WA, acetylated waxy maize starch; MN, microparticles of normal maize starch; MW, microparticles of waxy maize starch; MNA, microparticles of acetylated normal maize starch; MWA, microparticles of acetylated waxy maize starch; TAC, total anthocyanins content; SAC, superficial anthocyanins content; PME, purple maize extract; PALF, pericarp and aleurone layer fractions, k, k_1, k_2, n_1, n_2; C, isotherm models parameters.

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accelerates degradation of anthocyanins (Aramwit et al., 2010). There are several mechanisms for stabilizing anthocyanins. The most popular one is encapsulation by spray drying (Cavalcanti et al., 2011). Spray drying is a process which consists of the conversion of feed from a fluid state into a dried particulate form by spraying the feed into a gaseous drying medium (Cal and Sollohub, 2010). The encapsulating agent acts as a physical barrier against the effects of oxygen, water, light, and inhibits chemical and enzymatic degradation (Wang et al., 2009). The utilization of microparticles instead of anthocyanins extracts can increase their stability in an isotonic soft drink (Burin et al., 2011), enriched ice creams (Çam et al., 2014) and cookies (Davidov-Pardo et al., 2012). The kinetics of release of anthocyanins encapsulated with starch derivatives depends on the type and modification of starch, the processes of hydration and swelling of the modified starch which forms the matrix of microparticles, being the main controlled factor.

The selection of an adequate encapsulating agent is important for the stability of the anthocyanins. Several encapsulating agents used in microencapsulation include: gums, polysaccharides, lipids, proteins, fibers and mixtures of them (Davidov-Pardo et al., 2013). For anthocyanins microencapsulation, starches from various sources have been tried. These include maize, yucca and potato, which have been used because they are abundant in nature and are cheaper than gums (Cai and Corke, 2000; Robert et al., 2010; Tonon et al., 2010). Native starches increase their performance by means of modification (also called derivatization). Among the modifications, we have cross-linked starches with sodium tripolyphosphate (Verdalet-Guzmán et al., 2013), hydroxypropylated starches (Kshirsagar and Singhal, 2008). Hydrolyzed starches, such as, maltodextrins, cyclodextrins and dextrins, resulting from the action of acids or specific enzymes on starches (Spada et al., 2013) and hydrolyzed and esterified starches with octenyl succinic anhydride (OSAn), the last have been used as encapsulating materials due to they form a fine and stable emulsion (Bangs and Reineccius, 1988; Thirathumthavorn and Charoenrein, 2006).

Maltodextrins are considered as good anthocyanins protectors during the spray drying process because they present high solubility and low viscosity at high concentrations of solids (Cai and Corke, 2000; Ersus and Yurdagel, 2007; Robert et al., 2010; Tonon et al., 2010). However, maltodextrins are hygroscopic, and the encapsulated anthocyanins are susceptible to be degraded to a colorless structure (chalcone) because of the hydration of their main structure (flavilium cation) (Brouillard and Delaporte, 1977). Anthocyanins from Corozo (*Bactris guineensis*) encapsulated with maltodextrins were largely affected by the environment's humidity (>76%) (Osorio et al., 2010). On the other hand, starches modified by acid hydrolysis have shown good encapsulating properties (Palma-Rodriguez et al., 2013; Spada et al., 2012). For increasing the stability of the encapsulated anthocyanins, it is desirable to have low moisture absorption. One approach to overcome high hygroscopicity of the starch is the substitution of hydroxyl groups by acetyl groups.

"Acetylated starch is synthesized by the reaction of native or hydrolyzed starch with acetic anhydride in an aqueous medium in the presence of sodium hydroxide as catalyst" (Katerinopoulou et al., 2014). The acetyl groups introduced into the starch chains confer emulsificant properties to the starch molecules and provide water resistance. Moreover, it was proved that a posterior hydrolysis of the modified starches show a higher surface activity and less viscosity than the modified starches themselves (Konował et al., 2012; Murúa-Pagola et al., 2009). Acetylated starches are used for manufacturing food products, biodegradable films and for controlled drug release (Singh and Nath, 2013). The use of acetylated starch as encapsulating agent improved encapsulation efficiency of gallic acid with respect to the native starch, but it did not affect the release of gallic acid profile Robert et al. (2012).

To our best knowledge, there exist few works reporting the use of acetylated starches as encapsulating agents. Moreover, no publications devoted to the encapsulation of anthocyanins by means of acetylated starches exist. The aim of the present work was the preparation and characterization of encapsulated anthocyanins produced by starch derivatives. In order to assess the effect of the starch type on the structure and performance of the obtained microparticles, normal and waxy maize starches were used. Starches from the two maize types were subjected to a chain of chemical modifications that included: acid hydrolysis, esterification with acetic anhydride and posterior hydrolysis by extrusion. These modified starches were compared with respect to starches subjected only to acid hydrolysis. For evaluating the efficacy of encapsulating agents the following characteristics were assessed: anthocyanins microencapsulation efficiency and anthocyanins retention after 30 days of storage at water activities from 0.11 to 0.84 at 40 °C. Finally, the equilibrium moisture content of both hydrolyzed and acetylated starches, was determined by means of adsorption isotherms of microparticles prepared with them. The mathematical models used for describing adsorption isotherms were GAB and PELEG.

2. Materials and methods

2.1. *Chemicals and plant material*

The grains of purple maize (*Zea mays* L. race Cónico) were collected at San Juan Ixtenco, Tlaxcala, México. This purple maize race has intense purplish-red kernels with pigments located at the pericarp and aleurone layers of the seed. Normal and waxy maize starches were donated from CPIngredients (San Juan del Rio, Querétaro, México). Analytical grade salts: NaOH, LiCl, CH_3CO_2K, KCl, K_2CO_3, $Mg(NO_3)_2$, NaCl, KCl, BaCl; solvents: methanol (analytical and HPLC grade), water (HPLC grade), acetic anhydride (analytical grade) and acids (hydrochloric, acetic and formic) were purchased from J. T. Baker (USA).

Anthocyanins standards: delphinidin-3-glucoside (Df-3-glu), cyanidin-3-glucoside (Cy-3-glu), cyanidin-3-rutinoside (Cy-3-ru), pelargonidin-3-glucoside (Pg-3-glu), peonidin-3-glucoside (Pn-3-glu) and malvidin-3-glucoside (Mv-3-glu) were purchased from Extrasynthese (Lyon Nord, Genay Cedex, France).

2.2. *Anthocyanins extract preparation*

Maize grains were equilibrated at 16% moisture content. The pericarp and aleurone layers fractions (PALF) were mechanically removed in a Strong Scott Barley Pearler operated on a batch basis. 20 g of grains were loaded into pearler during 1 min. The dehulled grains were then released and passed through a sieve to remove broken grains and then reintroduced into the mill for another 2 min. This procedure was repeated 3 times to produce cumulative extraction levels of approximately 16% db. The removed PALF was milled in a hammer mill (model 200, Pulvex México) and sieved in a mesh