



Thermal study in the interactions of starches blends: Amaranth and achira



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ABSTRACT

Amaranth starch (AmS) and achira starch (AS) were blended at different proportions to evaluate swelling power (SP), thermal (DSC) and morphological (SEM) properties of the starch blends during gelatinization at two solid contents (5 and 40%) and establish their possible interactions. SP in the blends at 5% solids, was lower than that achieved by the native starches due to water competition, although gelatinization temperatures of the blends were related to the values of the individual starches and their proportion within the blends. Deconvolution of the areas of endothermic peaks, allowed to determinate the contribution of each starch, and established a non-additive effect in excess and limited water conditions. Both starches were affected by water competition and granular interactions, due to the differences in gelatinization temperature, granule size, crystallization, and percentage of amylose of each starch. These results suggest a modification in the swelling and gelatinization process explained by the changes in granules disruption of starches.

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1. Introduction

The starch granules have different sizes and shapes, depending on the botanical source. Its diameter ranges from <1 to 100 μm (Pérez & Bertoft, 2010; Singh, Singh, Kaur, Singh, & Singh, 2003). Granule size plays an important role in the contact when the starches are blended, which influences their physicochemical and functional properties (Puncha-arnon, Pathipanawat, Puttanlek, Rungsardthong, & Uttapap, 2008).

An important characteristic of starches is the X-ray pattern. A type pattern, characteristic of cereals, present dense packing inside the granule (Pérez & Bertoft, 2010; Singh et al., 2003). This structural organization limits the amount of adsorbed water resulting in better stability and higher transition temperatures in the granules (Pérez & Bertoft, 2010; Tester, Karkalas, & Qi, 2004). In the B type pattern, found in tubers and roots, the double helices of amylopectin chains have more space between them. This allows higher water absorption capacity than starches with A type pattern (Pérez & Bertoft, 2010; Tester et al., 2004).

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During the last decade had been done different studies in native starches blends of different botanical source. In some starch blends such as achira and rice, achira and mung bean (Puncha-arnon et al., 2008), potato and barley (Ortega-Ojeda & Eliasson, 2001), potato and amaranth (Gunaratne & Corke, 2007), and yucca and maize (Karam, Ferrero, Martino, Zaritzky, & Grossmann, 2006) there has been reported an overlapping of the corresponding endothermic peaks of each starch, especially when the gelatinization temperatures of the two starches are too close (Karam et al., 2006; Waterschoot, Gomand, Fierens, & Delcour, 2014a), making it difficult to distinguish the contribution of each starch to the gelatinization enthalpy of the blend associated with the loss of the double helices of amylopectin. However, although several studies of thermal properties of starch blends have been reported in literature, it is not clear whether there is or not an additive effect, mainly because it is not easy to evaluate the contribution of each starch to the endothermic peaks in the blend (Fonseca-Florido et al., 2016; Gunaratne & Corke, 2007; Hagenimana, Pu, & Ding, 2005; Novelo-Cen & Betancur-Ancona, 2005; Ortega-Ojeda & Eliasson, 2001; Puncha-arnon et al., 2008).

Two phenomena can take place in starch blends: first, mixing might influence the swelling, gelatinization and gelling properties of each starch; in this case, these properties cannot be predicted

based on the individual response of each starch, so there is no additive effect. In contrast, an additive effect is observed when the properties can be predicted by a linear relationship as the sum of the contributions of each starch (Puncha-arnon et al., 2008; Waterschoot, Gomand, Willebrords, Fierens, & Delcour, 2014b; Yao, Zhang, & Ding, 2003).

In this study, the effect of interactions of starch blends from non-conventional botanical sources as amaranth and achira, both starches have similar fine structure of amylopectin (Kong, Bertoft, Bao, & Corke, 2008; Santacruz, Koch, Svensson, Ruales, & Eliasson, 2002), close gelatinization temperature and different granule size and X-ray pattern diffraction, were evaluated in different proportions during gelatinization at 5 and 40% solid content with the purpose of promoting an increased in water competition. The objective of this work was to determine if there was an additive or non-additive effect in blends based on their swelling power and thermal properties and which starch has a major effect in the gelatinization process of the blends.

2. Materials and methods

2.1. Materials and formulation of blends

Achira starch was acquired from the producer, Hernando Diaz Burbano; batch June/2013 in the city of Popayan, Colombia. Amaranth was purchased from the producer, Luciano Alvarez; batch December/2013, in Queretaro, Mexico, for the subsequent extraction of starch. Native amaranth (AmS) and achira (AS) starches, and their respective blends at different proportions: 75% AmS/25% AS (AmS75AS25), 50% AmS/50% AS (AmS50AS50) y 25% AmS/75% AS (AmS25AS75, w/w) were analyzed, in conditions of water excess (5% solids, w/v) and water restriction (40% solids, w/v).

2.1.1. Amaranth starch extraction

The method reported by Wang and Wang (2001) was used, with modifications reported by Wang and Wang (2004). Amaranth grains (250 g) were soaked in 1250 mL of 0.1% NaOH for 18 h. After this time, the grains were ground in a home blender (Model BPST02-B00, professional series, Oster) at maximum speed for 2 min. The suspension was sieved through U.S. mesh size 100 (0.150 mm) and 200 (0.075 mm). Residues were washed with distilled water until the obtained liquid was transparent indicating no starch residues. The suspension was centrifuged (Centra GP8R, International Equipment Company, Inc., Needham Heights, MA) at 5000 rpm for 15 min and the supernatant was discarded. The starch was neutralized with 1.0 M HCl to a pH of 6.5, before washing with distilled water three times and recovered by centrifugation at each stage using the conditions previously mentioned. Finally, the starch was dried in a CE5F SHEL LAB Forced Air Oven (Sheldon Mfg. Inc, Cornelius, OR) at 40 °C for 24 h; afterwards it was ground and stored in plastic vials until further analysis.

2.2. Amylose and amylopectin content

For amylose and amylopectin determination, amylose/amylopectin assay procedure by Megazyme, K-AMYL 07/11 (Megazyme International Ireland Ltd., Ireland) was used, following the method described by Gibson, Solah, and McCleary (1997).

2.3. X-ray diffraction

X-ray diffraction patterns of the native starches, amaranth (AmS) and achira (AS) were obtained using a XRD diffractometer (Equinox 2000, Inel, NH, USA), with a potential difference of 35 kV

and a density current of 15 mA, with monochromatic copper radiation, CuK α with $\lambda = 1.5406$. Data were collected in the 2θ angle from 4 to 80° at 0.1 s⁻¹ and 5 s per angular step. In the diffractograms, the areas corresponding to the crystalline and amorphous regions were determined using the Fytk software (Version 0.9.8). The crystallinity was determined according to the method described by Hermans and Weidinger (1948).

2.4. Scanning electron microscopy (SEM)

Native starches, AmS and AS were analyzed in a scanning electron microscope (JEOL JSM-6300, JEOL Ltd., Akishima, Tokyo). The completely dried samples were deposited on a sample holder with electrically conductive carbon double-sided tape, subsequently coated with gold. Samples were observed at 15 A and 20 KV. To determine the size distribution of the granules, the mean of 20 measurements was reported for both native starches.

2.5. Swelling power

Swelling power (SP) was determined by triplicate, following the methodology reported by Muñoz, Pedreschi, Leiva, and Aguilera (2015) with modifications. 0.5 g of each sample was placed into 50 mL centrifuge tubes, 10 mL of distilled water was added and stirred on a Vortex for 30 s before heating at 60, 70, 80 and 90 °C in a water bath for 30 min. The tubes were cooled in an ice water bath until they reached room temperature and then centrifuged at 6000 rpm for 30 min (Hermle Z300, Labnet International Inc., Edison, NJ). The supernatant was decanted and dried for 24 h in a CE5F SHEL LAB forced air oven (Sheldon Mfg. Inc.) and the sediment was weighed (W_s). The weight of the dry supernatant was measured (W_1). The swelling power (SP) was obtained from the water solubility index (WSI) calculated as follows:

$$WSI = \frac{W_1}{0.5} \times 100 \quad (1)$$

$$SP = \frac{W_s}{0.5 (100 - WSI)} \quad (2)$$

2.6. Thermal properties

A differential scanning calorimeter, model 822E (Mettler-Toledo) was used to determine onset (T_o), peak (T_p) and end (T_e) temperature and gelatinization enthalpy (ΔH) of native starches, amaranth (AmS), achira (AS), and their blends. Samples were weighed in a ratio of 1:19 (starch:water) for 5% solids and a ratio of 1:1.5 (starch/water) for 40% solids. Samples were placed in standard 40 μ L aluminum crucibles (Mettler Toledo) and distilled water was added using a Hamilton microsyringe. The crucibles were hermetically sealed and heated at 5 °C/min from 25 to 95 °C.

To evaluate morphological changes undergone by native starches and their blends, at 5 or 40% solids during the gelatinization process, the samples were heated using an 822E differential scanning calorimeter (Mettler-Toledo, Schwerzenbach, Switzerland) using a heating rate of 5 °C/min, to reach the desired temperature (40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95 and 100 °C). Samples were then cooled and lyophilized (Freezone 4.5 Freeze Dry System, Labconco Corp., Kansas City, MO). Subsequently, samples were analyzed by SEM using the previously described conditions (Toro-Vazquez et al., 2003).

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