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Effect of granular disorganization and the water content on the rheological properties of amaranth and achira starch blends

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A B S T R A C T

Blending native starches is a feasible alternative for modifying the functional properties of starch dispersions. Granular interactions between starches lead to desirable properties that can be used for specific applications. Starch blends from amaranth (AmS) and achira (AS) were prepared at different proportions, and the pasting properties, flow curves and low-shear dynamic rheology were evaluated at 5, 7.5 and 10 g/100 g of solids. Granular interactions between starches were promoted when the solid content increased, affecting the formation of pasta. A polynomial model was used to predict the viscosity of the starch blends. The mechanical spectra showed that G′ and G″ had a slight dependence on the frequency. The incorporation of granules of AmS improved the stability of AS gels. Blending AmS and AS modified the rheological properties compared to pastes obtained from pure starches, mainly due to the concentration, size and granule interactions, resulting in low stability of the gels formed.

1. Introduction

During gelatinization, crystalline double helices of starch chains dissociate, resulting in the loss of the maltese cross, disruption of the structure and eventual disintegration of swollen granules (Pérez & Bertoft, 2010).

The rheological behavior of a starch paste is determined by the volume fraction of the swollen particles and shape, deformability, concentration and composition of the continuous phase (Ai & Jane, 2015). After starch gelatinization, amylose is released, promoting the formation of a three-dimensional network and modifying the rheological properties of the starch pastes. In addition, the minor components of starch could have an important effect on the functional properties of starch pastes, i.e., the presence of phosphorus significantly affects gel formation.

In food systems, the rheological properties of starch contribute to its texture, consistency and appearance when it is used as a thickening, gelling, adhesive or stabilizing agent (BeMiller & Whistler, 2009). In general, native starches have low stability under processing conditions or exhibit inadequate functional properties. Structural modifications are used to improve their performance in several industrial applications. An alternative is blending native starches with different structural properties that promote granular interactions and competition for available water. The granular interactions produce functional properties of starch blends that are different from the properties of pure starches. Starch blends are used in several applications, with no need to employ chemical or physical modifications (Lin, Kao, Tsai, & Chang, 2013; Wu, Dai, Gan, Corke, & Zhu, 2016).

Stute and Kern (1994) patented the use of a blend of maize and pea starch for pudding preparations. Replacement of pea starch with maize starch increases the resistance to syneresis and maintains the high gelation capacity of pea starch. In previous research, Fonseca-Florido, Méndez-Montealvo, Velázquez, and Gómez-Aldapa (2016) evaluated the interactions between achira and amaranth starches during the gelatinization process. The authors reported a difference in granule size of up to 50 times between the starches and a shift of 3 °C in the temperature of gelatinization in the blend. Interactions between starch granules from different sources affected the gelatinization of each starch depending on the concentration of solids in the blends. In other work carried out by the same research group, Fonseca-Florido et al. (2017) studied the

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properties of the same starches during the formation of gels at 5 and 40 g/100 g of solids. The textural properties were related to the loss of the granular order observed through analysis of WAXS and SAXS. The starch blends showed less cohesion and hardness than native starches, and the authors explained this behavior as restricted gelatinization of achira starch due to the presence of amaranth starch. In addition, the authors mentioned that a phase transition of crystals from type B to type A at intermediate moisture contents (40 g/100 g) affected the gel properties. Under these conditions, gelatinization was inhibited and the granular morphology was preserved because of the competition for available water.

In this work, the rheological properties of pastes prepared from blending amaranth and achira starches at different proportions were studied. Analyses of pasting properties, flow curves and low-shear dynamic rheology were used to evaluate the effect of the solid concentration on the gelatinization of starch blends.

2. Materials and methods

2.1. Materials and formulation of blends

Achira starch (AS) was obtained directly from the producer Hernando Diaz Burbano (Popayan, Colombia) from the June/2013 batch. Amaranth was acquired in a local market in Queretaro, Mexico from the December/2013 batch, for the subsequent extraction of starch following the method reported by Fonseca-Florido et al. (2016). Native amaranth (AmS) and achira (AS) starches and their blends in proportions of 75% AmS/25% AS (AmS75AS25), 50% AmS/50% AS (AmS50AS50) and 25% AmS/75% AS (AmS25AS75, w/w) were studied.

2.2. Phosphorus content

Phosphorus content was measured using a standard method (995.11; AOAC 2012). Samples were dried and incinerated to remove organic matter, and the inorganic residue was solubilized using hydrochloric acid. A color reaction was carried out based on the formation of a blue complex between phosphate and sodium molybdate [$(MoO_2\ _4MoO_3)_2\ H_3PO_4$] in the presence of ascorbic acid as a reducing agent. Analyses were carried out in triplicate for each starch, and the phosphorus content was calculated using equation (1).

$$Phosphorus\ (g/100\ g) = 100 \times [(V_2/V_1) \times P]/W \quad (1)$$

where V_1 = volume of the solution used in the color reaction (mL), V_2 = volume of the volumetric flask containing incinerated sample (mL), P = amount of phosphorus in the standard curve corresponding to sample absorbance (mg), and W = amount of sample weighed (mg).

2.3. Pasting properties

The pasting profile of the starch dispersion of AmS and AS and their blends at concentrations of 7.5 and 10 g/100 g solids were measured by the rotational test in a rheometer (Anton Paar, model Physica MCR 101) using sandblasted parallel plates with a diameter of 25 mm and a gap of 1000 μm. The test was run at a heating or cooling rate of 5 K/min and a shear rate of 50 1/s. Mineral oil was used to cover the parallel plates to avoid water evaporation during the test. The rheometer was programmed for running time sweeps of the heating cycles from 25 to 90 °C, then held at 90 °C for 1 min before cooling to 25 °C. The tests were carried out in triplicate.

2.4. Determination of flow curves

The flow curves at 5, 7.5, and 10 g/100 g of solids were determined using the same equipment and geometry as the pasting properties. Once the pastes were prepared, at the final temperature (25 °C), two up-down cycles from 0.03 to 100 s^{-1} were applied. The power law equation was used to describe the flow curves (Eq. (2)).

$$\sigma = K\dot{\gamma}^n \quad (2)$$

where σ is the shear stress (Pa), K is the consistency index (Pa.s), γ is shear rate (s^{-1}) and n is flow behavior index (dimensionless) (Rao, 1999). The tests were performed in triplicate.

2.5. Dynamic rheological measurement

Starch dispersions with 5, 7.5 and 10 g/100 g of solids were prepared using distilled water. The viscoelastic properties were measured by oscillatory tests using the same rheometer and geometry as described in the pasting properties. During the test, a heating or cooling rate of 5 K/min, and a constant strain of 0.5% were used. The parallel plates were covered with mineral oil to avoid water evaporation during the test. The linear viscoelastic region (LVR) was determined using deformation sweeps at 25 °C, and all tests were run at a frequency value of 1 Hz. Once the LVR was found, the rheometer was programmed for running a frequency sweep (50–0.5 Hz) with a constant strain value of 3%. The storage modulus (G', Pa) and loss modulus (G", Pa) were evaluated for each test. The tests were performed in triplicate.

2.6. Statistical analysis

The results were analyzed by one-way analysis of variance (ANOVA) using Origin software (Version 8.0) with a 95% confidence level. Tukey's test was used to compare means ($p \leq 0.05$). To describe the effect of the proportion of each starch and the solid content on the viscosity of the starch pastes, a second-order polynomial model was applied to the experimental data (Eq. (3))

$$y_i = b_{0i} + b_{1i}\,x_1 + b_{2i}\,x_2 + b_{3i}\,x_1\,x_2 + b_{4i}\,x_1^2 + b_{5i}\,x_2^2 \quad (3)$$

where x_1 and x_2 are the code variables for amaranth content and solid concentration, respectively, and b_{0i}, b_{1i} … b_{5i} are regression coefficients. The R^2 and the critical F-value parameters were estimated to determine if the model was adequate for describing the experimental data.

3. Results and discussion

3.1. Phosphorus content

Phosphorus is one of the minor components that significantly affects the functional properties of starch (Singh, Singh, Kaur, Sodhi, & Gill, 2003). Achira starch (AS) had a phosphorus content of 0.048 ± 0.003 g/100 g, which is similar to the concentration reported by other authors [0.05–0.08 g/100 g, Moorthy, Vimala, and Mukherjee (2002), 0.037–0.039 g/kg, Thitipraphunkul, Uttapap, Piyachomkwan, and Takeda (2003)]. In AS, phosphorus is found in the form of an esterified phosphate monoester bound covalently to amylopectin, contributing to viscosity, clarity of the suspensions, freeze-thaw stability and water absorption capacity (Singh et al., 2003; Thitipraphunkul et al., 2003; Waterschoot, Gomand, & Delcour, 2016). In the amaranth starch (AmS), the phosphorus content was 0.366 ± 0.001 g/100 g and was associated with free phospholipids, which are usually found in starch granules in cereals