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Starch transitions of different gluten free flour doughs determined by dynamic thermal mechanical analysis and differential scanning calorimetry

R. Moreira*, F. Chenlo, S. Arufe

Departamento de Enxeñaría Química, Escola Técnica Superior de Enxeñaría, Universidade de Santiago de Compostela, Campus Vida, 15782 Santiago de Compostela, Spain

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ABSTRACT

Gluten-free flour doughs (three from different maize varieties and one from chestnut fruit) processed at the same consistency level (1.10 ± 0.07 N m) with different water absorption were used to determine the starch transitions by means of two different experimental techniques, differential scanning calorimetry (DSC) and dynamic thermal mechanical analysis (DMTA). The ranges of temperatures of gelatinization (G), amylopectin melting (M1), amylose–lipid complexes melting (M2) and amylose melting (M3) for all tested flour doughs were determined by both experimental techniques with acceptable agreement between them. The starch transitions in DMTA were determined by means of the elastic modulus (G, M1 and M2) or damping factor (G, M3) evolution with temperature. The temperatures and enthalpies of the transitions depended on water content, the nature and characteristics (mainly damaged starch) of the starch and the presence of other compounds (mainly lipid and sugars) in the flour doughs.

1. Introduction

Gluten-free products based on starchy foods are in increasing demand due to the growing number of people diagnosed with coeliac disease. The research on the transformations experienced by food materials during thermal processes is essential to estimate and control the final product properties. The use of traditional and global starch source like maize or alternative and local source like chestnut is necessary to increase the supply of products with high quality to a growing market.

The main component of maize and chestnut is the starch. Starch is present in form of granules with crystalline and amorphous structures. Physicochemical properties and thermal behaviour of starch depend on the amorphous/crystalline ratio and the arrangement of the structure in the granule (Tahir, Ellis, & Butterworth, 2010). Chemically, starch is constituted by two carbohydrate polymers, amylose (linear) and amylopectin (branched) (French, 1984) with different behaviour during thermal processing and also depending on the water content.

Differential scanning calorimetry (DSC) is the most common method to study the thermal behaviour of isolated starches for determining temperature of transitions and the corresponding enthalpies (Eliasson, 1980). Particularly, gelatinization of different starch is well studied in the bibliography by its importance in starch processing for food and non-food purposes. At high water content one broad endothermic peak, G, by the swelling of the amorphous region and subsequent melting of crystallites is observed, but at intermediate water content, this transition is partially postponed to higher temperatures resulting M1 transition (Jang & Pyun, 1996). Other thermal transitions, due to biopolymer interactions, can be determined at higher temperatures as the reversible dissociation of lipid–amylose complexes in the range from 100 to 120 °C (Liu, Yu, Xie, & Chen, 2006; Torres, Moreira, Chenlo, & Morel, 2013) and also melting amylose above 140 °C (Jang & Pyun, 1996). These transitions also depend on water content of the sample.

Nevertheless, some endothermic peaks associated to the thermal transitions are very weak and consequently their determination and evaluation is troublesome. This fact is pronounced in samples with high water content because the limited dry mass amount and DSC is not sensitive to changes affecting to mechanical properties of the material (Warren, Royall, Butterworth, & Ellis, 2012).

The study of the starch transitions in cereal doughs like maize and chestnuts flour doughs is more complex than the study of isolated starch from different sources. The presence of other biopolymers in a relevant proportion like proteins and lipids

* Corresponding author. Tel.: +34 851816759.
E-mail address: ramon.moreira@usc.es (R. Moreira).

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together with the particle size of the flour affect significantly the water absorption of the samples to achieve a determined consistency. At these conditions, doughs can be submitted to different industrial thermal processes involving operations such as baking, extrusion of flour based products and the material properties depend on starch gelatinization and other transitions promoted by high temperatures. The chemical, physical and viscoelastic properties of the final starchy products depend mainly on the extension of water–starch and water–biopolymers interactions developed during processing.

Dynamic thermo-mechanical analysis (DMTA) is an experimental method in which a sinusoidal force is applied to the sample at fixed angular frequency measuring the stress and strain inside the linear viscoelasticity region (LVR) at constant heating/cooling rate. This analysis was employed by other authors to evaluate the starch gelatinization due to strong structural changes takes place during the plasticizing process promoted by water (Bogracheva, Wang, Wang, & Hedley, 2002). In fact, gelatinization temperatures range can be clearly observed by peaks of the storage modulus, G', complex viscosity, G^* or $\tan\delta$ (Chanvrier, Appelqvist, Li, Morell, & Lillford, 2013; Moreira, Chenlo, & Torres, 2011).

The experimental determinations of the phase transitions at high temperatures (above 100 °C) of flour doughs by using DMTA or DSC methods may lead to different results, beyond the physical fundamentals of each technique, by the fact of the water evaporation. Water during DSC is evaporated generating an overpressure inside the sealed pan and equilibrium between sample and surrounding is achieved. In DMTA experiments, water is also removed by evaporation and sample dries. Both methods are interesting because DSC analysis can be useful to understand the crumb formation and DMTA tests can be related to the crust generation (Rouille, Chiron, Colonna, Della Valle, & Lourdin, 2010; Vanin, Michon, Trystram, & Lucas, 2010). Furthermore, the water content effect on the determination of the transitions by both methods can be also evaluated.

The aim of this work is to determine the starch transitions of several gluten-free flour doughs (three from different maize varieties and one from chestnut fruit) processed at the same consistency level with different water absorption by two different experimental techniques (DSC and DMTA) in order to establish comparisons between the results obtained with both tested methods. Results on starch transitions are discussed in relation to chemical and physical properties of flours and doughs also experimentally determined.

2. Materials and methods

2.1. Materials

Maize (0.40 ± 0.05 kg water/kg dry solid, dry basis (d.b.)) and chestnut (1.29 ± 0.13 d.b.) flours obtained from 3 different types of Spanish maize kernels, white (WM, *Rebordanes* variety), yellow (YM, *Sarreaus* variety) and purple (PM, *Meiro* variety) and chestnuts (CH, *Castanea sativa* Mill.), acquired in a local market were employed as raw material.

2.2. Methods

2.2.1. Flour processing

Chestnut fruits, previously selected, dehulled, peeled and cut in cubes using a laboratory blender (Waring, Model HGBTWT, USA) and maize kernels were air-dried in a pilot-scale tray dryer (Angelantoni Challenge 250, Italy) at 45 °C with air velocity of 2 m/s, relative humidity of 30% and 5–6 kg/m^2 of load density. Drying was carried out until a moisture content of the sample of 11% d.b. was achieved. Final dry solid was determined gravimetrically after sample drying by using a vacuum oven (Heareus Vacutherm 5250 VT6025) at 70 °C and 0.15 atm of absolute pressure to dry up to constant weight (AOAC, 1995). Dried particles were milled using an ultra-centrifugal mill (ZM200 Retsch GmbH) with an internal sieve of 200 μm. The flours obtained were placed in a desiccator with a saturated solution of $Mg(NO_3)_2$, prepared according to recommendations (Greenspan, 1977) to obtain a constant relative humidity of surrounding air of 54% at 25 °C, until equilibrium between samples and surrounding air was reached. Equilibrated flours achieved constant moisture content (8–10%, d.b.). Flours were then storage at 4 °C in vacuum sealed bags until its utilization.

2.2.2. Physicochemical characterization

The average particle size of the obtained flours was determined by sieving employing standard sieves of 40, 63, 80, 125, 200 and 250 μm (Standard ISO-3310.1, Cisa Cedacería Industrial, Spain). Average particle diameter by mass (D_w) was calculated considering the average particle size, D_{pi} (μm), of each mass fraction, $w_{i\,(\%)}$.

Starch characterization was carried out by means of total starch (TS, % g starch/g dry flour) and damaged starch (DS, % g damaged starch/g dry flour). TS was measured as total starch in flour without previous gelatinization using a “Total Start Assay Kit” whose method was approved by the American Association of Cereal Chemists (AACC, 2000). DS was determined as the starch fraction that is thermal or mechanically damaged, using a “Starch Damage Kit” (ICC, 1996).

The starch extraction from maize and chestnut flours was carried out according to the method of Singh and Singh (2001) with minor modifications. Maize and chestnut powder (10 g) was added into 100 ml of distilled water with 0.5% (w/w) of sodium sulphite. The slurry was filtered through a 63 μm sieve. The residue on the sieve was washed with distilled water for three times. The filtrate was precipitated over night at 4 °C. Then, the supernatant was discarded and the starch was washed with distilled water and precipitated again for two times. The starch was collected and dried at 40 °C up to constant weight. The amylose/amylopectin ratio was determined according to the procedure previously established in bibliography (McGrance, Cornell, & Rix, 1998). All these tests were made at least in duplicate.

Lipid content of flours was determined following ISO standards (ISO, 1982). Total fibre content of flours was evaluated by means of a standard enzymatic-gravimetric method according to AOAC (AOAC, 1996). Flours protein amount was established by Kjeldahl method (AOAC, 1996). Sugar content was determined by HPLC according to the AACC standard method (AACC, 1994). The assays were performed at least in triplicate.

2.2.3. Dough processing

Doughs were obtained using Mixolab® apparatus (Mixolab® Chopin Technologies, France). The protocol utilized (ICC, 2008) consisted of flour and water mixing at constant temperature (30 °C) and mixing rate (80 rpm) until the torque produced by dough (consistency) of 1.10 ± 0.07 N m, the same consistency reached by wheat flours in industrial dough elaboration, was achieved. At this consistency, the dough mixing properties like water absorption (WA), development (DT) and stability time (ST) were determined. The WA (% d.b.) is defined as the amount of water needed to obtain a dough with the desired consistency. The DT and ST are defined as the time to reach the maximum torque and the time at which the torque produced by dough is kept at 1.10 ± 0.07 N m, respectively. More details about the Mixolab® protocol and the characteristic parameters were previously reported (Moreira, Chenlo, Torres, & Prieto, 2010).

2.2.4. Differential scanning calorimetry (DSC)

DSC studies of flour dough samples at the same water content of doughs studied by DMTA were prepared using the same method