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# Physical and structural changes induced by high pressure on corn starch, rice flour and waxy rice flour

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ABSTRACT

The impact of high pressure (HP) processing on corn starch, rice flour and waxy rice flour was investigated as a function of pressure level (400 MPa; 600 MPa), pressure holding time (5 min; 10 min), and temperature (20 °C; 40 °C). Samples were pre-conditioned (final moisture level: 40 g/100 g) before HP treatments. Both the HP treated and the untreated raw materials were evaluated for pasting properties and solvent retention capacity, and investigated by differential scanning calorimetry, X-ray diffractometry and environmental scanning electron microscopy. Different pasting behaviors and solvent retention capacities were evidenced according to the applied pressure. Corn starch presented a slower gelatinization trend when treated at 600 MPa. Corn starch and rice flour treated at 600 MPa showed a higher retention capacity of carbonate and lactic acid solvents, respectively. Differential scanning calorimetry and environmental scanning electron microscopy investigations highlighted that HP affected the starch structure of rice flour and corn starch. Few variations were evidenced in waxy rice flour. These results can assist in advancing the HP processing knowledge, as the possibility to successfully process raw samples in a very high sample-to-water concentration level was evidenced.

*Industrial relevance:* This work investigates the effect of high pressure as a potential technique to modify the processing characteristics of starchy materials without using high temperature. In this case the starches were processed in the powder form - and not as a slurry as in previously reported studies - showing the flexibility of the HP treatment. The relevance for industrial application is the possibility to change the structure of flour starches, and thus modifying the processability of the mentioned products.



## 1. Introduction

High pressure (HP) processing is becoming popular because it increases the shelf life of food and inactivates microorganisms at low temperatures without altering the sensory and nutritional attributes of the products. Moreover, depending on the materials and on the operating conditions applied, it has been proved that HP can modify the functional properties of proteins and inactivate enzymes that may be responsible for shortening the product shelf life (Estrada-Girón, Swanson, & Barbosa-Cánovas, 2005). Furthermore, HP treatment has recently been used to modify the extraction and bioavailability of bioactive compounds, to reduce allergenicity and to retain essential fatty acids (Barba, Terefe, Buckow, Knorr, & Orlien, 2015).

During HP treatments the pressure is isostatically and homogeneously applied to each point of the sample, thus processing time is not a function of its size (Estrada-Girón et al., 2005). This is an advantage in comparison to the traditional thermal processes where processing time depends on product size and geometry (San Martín, Barbosa-Cánovas, & Swanson, 2002). To optimize the HP treatments, many other variables have to be considered. Pressures applied and holding times, for instance, may induce different modifications to the treated products (Bauer & Knorr, 2005; Welti-Chanes et al., 2005). During HP processing, it is also possible to adjust the temperature of the HP chamber, thus combining the high pressure with a traditional heat treatment.

It is well known that HP acts on most food components such as water, proteins and starch. San Martìn et al. (2002) reported that under high pressure the typically tetrahedral arrangement of water molecules is modified to a more compact structure with distorted hydrogen-bond angles. Consequently, the interactions between water and the other food components can be modified by the pressure applied. Angioloni and Collar (2013) studied the effects of HP processing on proteins, evidencing the formation of urea-insoluble complexes,

*Abbreviations:* ANOVA, Analysis of variance; BD, breakdown; BU, Brabender Unit; CS, corn starch; DSC, differential scanning calorimetry; ESEM, environmental scanning electron microscopy; FV, final viscosity; GF, gluten-free; HP, high pressure; LASRC, lactic acid SRC; LSD, least significant differences; MVA, Brabender® Micro-Visco-Amylograph; PT, pasting temperature; Ptime, time necessary to achieve the peak viscosity; PV, peak viscosity; RF, rice flour; SB, setback; SCSRC, sodium carbonate SRC; SEA, starch enzymatic accessibility; SRC, solvent retention capacity; SuSRC, sucrose SRC; T, temperature; *To*, onset temperature; *Tf*, offset temperature; *Tp1*, first peak temperature; *Tp2*, second peak temperature; TS, total starch; WRC, water retention capacity; WRF, waxy rice flour; XRD, X-ray diffraction; $\Delta H$, enthalpy of gelatinization.

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disulfide bonds and/or other strong protein aggregates in chickpea, green pea and soybean batters treated at pressures higher than 200 MPa. The same authors also concluded that HP can be used to improve the breadmaking functionality of chickpea, green pea and soybean batters. In addition, Yamazaki and Sasagawa (1998) reported that, in the presence of a sufficient amount of water, a continuous increase of pressure up to 600 MPa caused a partial swelling of the rice starch granules, even if no thermal treatment was applied. Le Bail et al. (2013) highlighted starch gelatinization in broad bean, tapioca and pea starch dispersions following HP treatments at 500 MPa for 20 min at 20 and 40 °C, whereas potato starch suspensions were not affected.

The gelatinization–retrogradation process is one of the principal events that control the texture and quality of starch-containing foods, as evidenced by Lii, Shao, and Tseng (1995), and it is one of the most complex transformations that a food can undergo in the presence of water when thermally treated. This phenomenon is even more critical in gluten-free (GF) baked products, as they usually contain a large amount of starch. Normally, at atmospheric pressure, gelatinization takes place by heating starch in the presence of a sufficient amount of water: the crystalline structure is disrupted, granules swell, and amylose leaches out into the water phase, increasing the viscosity of the system; upon cooling, starch re-organizes itself. If starch concentration is high enough, the leached-out amylose and the swollen granules convert themselves into an elastic gel (Cappa, Lucisano, & Mariotti, 2013b). Starch retrogradation is a crucial phenomenon in many food processes: it is desirable in GF pasta production, as it is useful for giving rigidity to cooked pasta, and for reducing both the stickiness of the pasta surface and the loss of soluble materials into the cooking water (Lucisano, Cappa, Fongaro, & Mariotti, 2012); on the other hand, it should be delayed in GF bread production, as it is strongly involved in bread staling (Cappa, Lucisano, & Mariotti, 2013a; Mariotti, Pagani, & Lucisano, 2013).

Different techniques have been used to study the gelatinization/retrogradation properties of starches and flours, such as differential scanning calorimetry (DSC), X-ray diffractometry, nuclear magnetic resonance spectroscopy, vibrational spectroscopy (*e.g.* Raman spectroscopy) and Fourier transform infra-red spectroscopy (Karim, Norziah, & Seow, 2000). Information on the tendency of a given starch to gelatinize and retrograde can also be obtained from its pasting behavior by evaluating changes in viscosity of a starch suspension during heating and cooling cycles (Bhattacharya, Erazo-Castrejon, Doehlert, & McMullen, 2002; Limpisut & Jindal, 2002; Mariotti, Zardi, Pagani & Lucisano, 2005; Mariotti, Sinelli, Catenacci, Pagani, & Lucisano, 2009; Shuey & Tipples, 1980). Solvent retention capacity (SRC) evaluation, an-easy-to-apply and useful method originally designed to predict wheat flour functionalities (Duyvejonck, Lagrain, Pareyt, Courtin, & Delcour, 2011; Xiao, Park, Chung, Caley, & Seib, 2006), could also be used to evidence starch and protein properties in gluten-free bread mixtures (Mariotti, Lucisano, Pagani, & Ng, 2016).

In this study, HP treatments were applied to corn starch (CS), rice flour (RF) and waxy rice flour (WRF), three raw materials commonly used in gluten-free baked products, in order to investigate potential induced physical and structural changes at temperature below the gelatinization temperature at atmospheric pressure. Unlike most other works performed on the same type of materials (Błaszczak, Valverde, & Fornal, 2005; Katleen, Vallons, & Arendt, 2009), in this study a very high sample-to-water concentration level was used. This condition provided for shorter and less costly drying treatments of the materials after HP processing and for macromolecular changes different from the ones induced by HP treatment at lower sample-to-water concentration level. Three different variables were considered during HP processing: pressure (400 MPa or 600 MPa), pressure holding time (5 min or 10 min), and temperature (20 °C or 40 °C). Comparisons with the untreated raw materials were performed to evidence the effects of the HP processes.

## 2. Materials and methods

### 2.1. Raw materials

Corn starch was donated by Roquette America Inc. (Iowa, USA), while rice flour and waxy rice flour were provided by Beneo-Remy NV (Leuven-Wijgmaal, Belgium).

### 2.2. Chemical composition of the raw materials

The moisture content of the raw materials was determined according to the approved method of the AACC 44–40 (2000). The total nitrogen content was evaluated by thermal conductivity measurement after organic combustion with a LECO FP-528 instrument (LECO Corporation, St. Joseph, MI, USA), using helium as carrier gas; the protein content was then calculated adopting 5.95 as a conversion factor. The amounts of total starch (TS) and the starch enzymatic accessibility (SEA) were determined using the "Total Starch Assay Kit" and the "Starch Damage Assay Kit," respectively (Megazyme International Ireland Ltd., Bray Business Park, Bray, Co., Wicklow, Ireland). The amylose content was assessed by the UNI-ISO 6647 Method (1991) and expressed as the proportion by weight of amylose (g/100 g db). All determinations were made at least in duplicate ($n \geq 2$).

### 2.3. Sample preparation and high pressure processing

Each raw material was mixed with water to obtain a final moisture level of 40 g/100 g, and kept at 15 ± 1 °C for 1 h. The samples were then packed twice in polyethylene thermo-sealed bags (0.1 mm thick; Consolidated Plastics, Twinsburg, OH, USA) to isolate them from the pressure transmitting fluid (10% oil - Hydrolubic 123-B; Houghton International Valley Forge, Pennsylvania, USA - in water). After this, HP was applied through an indirect compression system, using a 2 L capacity warm isostatic press (Engineered Pressure Systems Inc., Haverhill, MA, USA). The selected pressures, 400 MPa and 600 MPa, were applied and maintained for the desired treatment time (5 min and 10 min), then released. The selected temperatures of the treatment chamber (20 °C and 40 °C), both below the gelatinization temperature of the raw materials at atmospheric pressure, were reached by means of an electric resistance heating band. All of the above-mentioned conditions were defined and selected after a number of preliminary trials (*data not shown*). The HP treatments were applied to two independent batches for each type of sample.

After the HP treatment, the samples (24 in total) were dried in a vacuum oven (mod. 1410 VWR, USA) at 67 kPa and 35 °C, until a final moisture content of 14 g/100 g was reached. The dried samples were then crushed with a mortar in order to obtain dispersible powders having a particle size lower than ≤500 μm.

In addition, untreated samples (CS40, corn starch; RF40, rice flour; WRF40, waxy rice flour) were prepared to evaluate the potential changes to macromolecules induced only by the hydration/dehydration process alone; with this purpose, each raw material was mixed with water to obtain a final moisture level of 40 g/100 g, and subsequently dried to a moisture content of about 14 g/100 g, before being crushed and analyzed as the HP-treated samples. In total, 30 samples were investigated: 3 raw materials, 3 untreated samples (but submitted to the hydration/dehydration process), and 24 samples treated under the different HP processing conditions.

### 2.4. Characterization of the untreated and HP treated samples

#### 2.4.1. Solvent retention capacity

The solvent retention capacity of the samples was evaluated in accordance with the approved method of the AACC 56–11 (2000) designed for wheat flour, with some minor modifications: 1.5 g of sample was weighed in a calibrated 15 mL centrifuge tube with a conical