



## Study of DIC hydrothermal treatment effect on rheological properties of standard maize (SMS), waxy maize (WMS), wheat (WTS) and potato (PTS) starches

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### ABSTRACT

Standard maize (SMS), waxy maize (WMS), wheat (WTS) and potato (PTS) starches were hydrothermally treated by Instantaneous Controlled Pressure Drop (DIC) process at different pressure levels (1, 2 and 3 bar) corresponding to the temperatures of 100, 122 and 136 °C, respectively. The rheological properties and particle size of treated starches under various conditions were compared to the native ones. The results showed for all starches, except for WTS, a reduction of the consistency coefficient and the yield stress ( $\tau_0$ ) with increased intensity of the hydrothermal treatment conditions. Furthermore,  $\tau_0$  vanished for severe treatment conditions. The DIC treatment yielded an increased fluidity and a loss of the conservative modulus of the pastes, as a result of partial gelatinization of starch granules. The extent of the observed effect depended on the botanical origin. Wheat starch exhibited a different behaviour: the consistency coefficient and the conservative modulus being higher for DIC treated starch except for the most severe conditions.

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### 1. Introduction

Starch has many applications in food and non-food industries. As an ingredient, it is extracted from only a few species such as maize, wheat, potato, rice, tapioca and sago. Pregelatinized starches have been widely used for many foods as a major ingredient to provide thickened textures at temperatures below the gelatinization temperature. They are obtained from native or modified starch, by drum drying (Vallous et al., 2002) or by extrusion cooking (Barron et al., 2000). Other processes of physical modification have been explored to improve qualities of the starch such as annealing (Tester et al., 2000; Jayakody and Hoover, 2008) and heat moisture treatment (HMT) (Kulp and Lorenz, 1981; Hoover and Manuel, 1996; Jacobs et al., 1998; Collado and Corke, 1999; Tester et al., 2000; Gunaratne and Hoover, 2002; Vermeylen et al., 2006; Tukomane et al., 2007; Gunaratne and Corke, 2007; Chung et al., 2009). These two latter treatments differ in the water content, temperature and processing time used. Annealing occurs under large excess of water (50–60%) and relatively low temperatures (below the gelatinization temperature), while the HMT is conducted under restricted moisture content (10–30%) and higher temperatures (90–120 °C). Both treatments are applied over large periods of time (10–16 h). The main effects of HMT are loss of birefringence, increased gelatinization temperature, broadened or

unchanged gelatinization temperature range, change in X-ray diffraction patterns, reduced swelling volume and solubility, with consequent changes in functionality (Donovan et al., 1983; Collado and Corke, 1999; Gunaratne and Hoover, 2002). Annealing results in improved perfection of the crystallites within starch granules that narrows the gelatinization temperature interval; consequently, gelatinization temperatures shifted towards higher values (Hublin, 1994; Jacobs et al., 1998; Tester et al., 2000). The enthalpy of gelatinization remains unchanged or is moderately increased depending upon annealing conditions (moisture content and time) and the botanic origin (Karlsson and Eliasson, 2003; Lawal, 2005; Jayakody and Hoover, 2008) in contrast to HMT. The semi-crystalline structure of starch granules is modified by these two usual physical treatments without disrupting the integrity of granule (Lim et al., 2001).

HMT starches have generally been performed at the laboratory scale and many authors have reported that such conditions produce inhomogeneous samples with lumps of gelatinized starch beside heat-moisture treated starch. For this reason, pressure is often required to ensure sufficient heating. To obtain a uniform heat distribution and rapid penetration of steam into the starch granules, Maruta et al. (1994) improved the conventional method by creating a reduced pressure in the vessel before the injection of live steam. This method was designated by these authors as the reduced-pressurized heat moisture treatment (RP-HMT).

The DIC treatment (Instantaneous Controlled Pressure Drop) has been developed at the laboratory as well as the pilot scale

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(Rezzoug et al., 2000), for drying and texturizing of food products such as pasta products (Maache-Rezzoug and Allaf, 2005). As for the RP-HMT process, an initial vacuum is applied before the treatment which is performed under high temperature/high steam pressure; the hydro-treatment step is then followed by an abrupt pressure drop towards vacuum pressure contrary to the RP-HMT treatment. This step induces a rapid modification of the thermodynamic equilibrium reached during the pressurization ( $P_1$ ,  $T_1$ ) towards another equilibrium state ( $P_2$ ,  $T_2$ ). This new state induces a rapid cooling and the resulting temperature value depends on the vacuum pressure level (Zarguili et al., 2009). The originality of the DIC process compared to other hydrothermal treatments is that starch is treated at an initial moisture content of 12.5% (wet basis), no hydration step being then used. During the treatment, the heating of starch is obtained by the absorption of latent heat of steam condensation which causes an increase in the moisture content as the processing time and pressure level increase (Zarguili et al., 2009).

The major effects observed after DIC treatment are almost similar to HMT treatment except that the gelatinization temperature range is narrowed as observed with annealing (Hublin, 1994; Jayakody and Hoover, 2008). This result suggests that the treatment firstly induced the melting of crystallites of low cohesion (low stability) which required less energy to melt. Consequently, the residual structure after the DIC treatment contained crystallites with a greater stability (cohesion) (Maache-Rezzoug et al., 2008). Preliminary studies on standard and waxy maize starches (Loisel et al., 2006; Zarguili et al., 2006) showed that the thermal properties of DIC treated starch depend on the processing time and the steam pressure level. Increasing these two parameters induces an increase in the onset ( $T_{\text{onset}}$ ) and in the peak ( $T_{\text{peak}}$ ) temperatures of gelatinization and a reduction in gelatinization enthalpy. The occurrence of a partial or total gelatinization was clearly attested by the decrease of enthalpy and a loss of birefringence under polarized light. The X-ray diffraction pattern confirmed the partial or total loss of the crystalline structure of native starch depending on the conditions of the DIC treatment: the relative crystallinity of hydrothermally treated maize starch decreased and the polymorphic type changed. The A-type crystalline pattern was progressively lost with the increase of processing pressure ( $\geq 2$  bar), and was substituted by the  $V_h$ -type X-ray diffraction pattern, corresponding to the formation of amylose–lipid complexes. At severe DIC conditions (pressure level of 3 bar), the typical peaks of A-type X-ray diffraction pattern were substituted completely by the ones of the  $V_h$ -type pattern (Maache-Rezzoug et al., 2008).

The objective of the present study was to describe the rheological properties of hydrothermally treated starches in the DIC process in relation to starch granules properties (size and size distribution, swelling behaviour). This study was based on rheological measurements (viscosity and viscoelasticity). These effects were investigated on starches of different origins: standard maize (SMS), waxy maize (WMS), wheat (WTS) and potato (PTS); identical treatments conditions (processing pressure and time) were applied, except for PTS. Lower pressure/time conditions were applied to potato starch due to its higher sensitivity to hydrothermal treatment.

## 2. Materials and methods

### 2.1. Materials

Standard maize starch (SMS), waxy maize starch (WMS, Waxi-lys 200), wheat starch (WTS) and potato starch (PTS) were supplied by Roquette Frères (Lestrem, France). The moisture content of these starches during the treatment was about 12% wet basis.

### 2.2. Methods

#### 2.2.1. Moisture content

The starch moisture content was determined by air oven at 105 °C during 24 h, according to the A.F.N.O.R (NF V03-707, 2000) standard method and related to the wet basis (% wb).

#### 2.2.2. DIC hydrothermal treatment

The equipment and procedure of DIC hydrothermal treatment were largely described in previous studies (Zarguili et al., 2006). During the treatment 22 g of starch (12.5%, wet basis), disposed in circular containers of 12 cm of diameter and a thickness of 0.5 cm were placed in the processing vessel (12 L). An initial vacuum of 50 mbar was established. As demonstrated by Zarguili (2006), this initial vacuum allows the air resistance to be reduced and thus facilitates the diffusion of steam into the product, consequently a rapid heating is obtained. Saturated steam is introduced into the vessel at a fixed pressure level (1–3 bars) and maintained during a determined processing time. In this study the processing pressure was fixed at 1 bar (100 °C), 2 bar (122 °C) and 3 bar (135 °C). The pressurization is followed by an abrupt decompression towards vacuum (50 mbar). After the vacuum phase, atmospheric air is injected to return to atmospheric pressure for sample recovery. During the treatment, starch is heated by the absorption of latent heat of vapour condensation and its moisture content is increased.

#### 2.2.3. Pasting procedure using the Brabender Viscograph

The DIC treated starches were pasted with demineralised water using a Brabender Viscograph in order to obtain starch pastes under repeatable conditions. The starch concentrations were chosen to lie within the sensitivity range of the Viscograph, depending on the botanical origin of starches. The concentrations used were 6%, 4%, 7% and 2% for SMS, WMS, WTS and PTS, respectively. The suspension was heated at 1.5 °C/min from 50 to 95 °C, then kept for 20 min at the plateau temperature and subsequently cooled down to 70 °C at 1.5 °C/min before immediate characterisation. The starch concentration was checked by drying the suspensions as previously described (Section 2.2.1).

#### 2.2.4. Granule size distribution

Granule size determination was carried out at room temperature using a Malvern Master Sizer (Malvern Instruments, Ltd.) laser scattering analyser with a 300 mm Fourier cell (range 0.05–879 µm). The starch dispersion was first diluted (1/10) with demineralised water at 20 °C before and immediately after the pasting procedure in the Brabender Viscograph, and then dispersed into the sample dispersion unit (1/100 ml water). The measure was repeated three times. The volume distribution was obtained according to the Mie scattering theory (Loisel et al., 2006). From each distribution, the median volume diameter ( $D_{V,0.5}$ ) was presented and the swelling ratio was defined as  $(D/D_0)^3$ , with  $D$  and  $D_0$  the median diameters of treated and native starch, respectively (Nayouf et al., 2003); the size distribution was evaluated using the dispersion index referred to as the span, by the following equation:

$$\text{Span} = \frac{D(v, 0.9) - D(v, 0.1)}{D(v, 0.5)} \quad (1)$$

#### 2.2.5. Rheological properties

Flow behaviour and viscoelastic properties of starch pastes were measured at 60 °C (to avoid retrogradation) using a controlled stress rheometer (TA Instrument AR1000) with the cone/plate geometry (6 cm/2°). The starch dispersions at 60 °C were

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