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STRUCTURAL MODIFICATIONS AND THERMAL TRANSITIONS OF STANDARD  
MAIZE STARCH AFTER D.I.C HYDROTHERMAL TREATMENT

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## Abstract

Standard maize starch was hydrothermally treated by Instantaneous Controlled Pressure Drop (DIC) process at three pressure levels (1, 2 and 3 bar) corresponding to the temperatures of 100, 122 and 135 °C (at 13–27% moisture), respectively. The structural effects of various hydrothermal conditions were examined with differential scanning calorimetry (DSC) and wide-angle X-ray diffraction. In order to understand the changes that occur during DIC treatment, melting endotherms of native maize starch at various moisture contents were determined. The gelatinization temperatures of DIC treated standard maize starch increased with DIC treatment. The transition temperatures ( $T_o$ ,  $T_p$ ) are closely related to the combined effect of pressure and processing time. At approximately 10 min of processing time,  $T_o$  and  $T_p$  were 65.7 and 72.3 °C, 68.8 and 73.6 °C, 74.8 and 79.8 °C for pressure levels of 1, 2 and 3 bar, respectively (against 63.1 and 69.6°C for native starch). DIC treatment narrowed the gelatinization temperature range and decreased gelatinization enthalpy ( $\Delta H$ ), as the severity of processing conditions increased.  $\Delta H$  decreased from 11.4 J.g<sup>-1</sup> (native) to 11.0 (1 bar), 9.0 (2 bar) and 1.7 J.g<sup>-1</sup> (3 bar) for treated maize starch during approximately 10 min. Relative crystallinity of hydrothermally treated starch decreased with increasing DIC conditions. The A-type crystalline pattern was progressively lost (at pressure level  $\geq$  2 bar) and substituted by the  $V_h$ -type X-ray diffraction pattern, corresponding to the formation of amylose-lipid complexes. For severe DIC conditions (pressure level of 3 bar), the substitution was completed. Microscopic observations revealed progressive loss of the birefringence of DIC treated starch granules except at low pressure (1 bar), while the integrity of starch granules was preserved for all the conditions. These modifications that reveal important changes in the crystalline organization of the starch granules are related to their functional properties.

*Keywords:* Standard maize starch; DIC hydrothermal treatment; Thermal transition; X-ray diffraction

## 1. Introduction

Starch is one of the most important natural polymers and its use depends largely on its functional properties. The comprehension of starch phase transitions is extremely important in the food processing operations and the physical properties of food products. Due to the semi-crystalline structure of starch, two phase transitions are likely to occur during the thermal treatment of starch-water systems: the glass transition that concerns the amorphous phase (mainly the branching regions of the amylopectin and most of the amylose chains) and the melting of crystallites (formed by adjacent short chains of amylopectin intertwined into double helices). The melting of crystallites can be detected by X-ray diffraction patterns, and differential scanning calorimetry (Donovan, 1979, Biliaderis, Maurice & Vose, 1980; Hosney, Zeleznak & Lai, 1986; Garcia, Colonna, Lourdin, Buléon, Bizot & Ollivon, 1996; Cruz-Orea, Pitsi, Jamee & Thoen, 2002; Ratnayake & Jackson, 2007). The melting temperatures ( $T_m$ ) of starch-water system strongly depend on the water content. For water content greater than 60% (w/w), the temperature is referred to as starch gelatinization temperature and a single endotherm is observed on the DSC profile. The irreversible changes taking place during gelatinization, namely diffusion of water into the starch granules and swelling of the granules are accompanied by an increase of the viscosity which is responsible for the thickening effect of starch in food products. For lower water contents, multiple transitions occur that reflect melting and recrystallisation processes occurring simultaneously during heating (Biliaderis, Page, Maurice & Juliano, 1986): the transition temperatures referred to as melting temperatures increase and multiple endotherms are formed to the detriment of the former gelatinization endotherm. Concerning the cereal starches, another endotherm appears over the temperature range of 90-120°C, due to the melting of amylose-lipid complexes (Biliaderis, 1991) that may form during gelatinization. These structures give a V-type X-ray diffraction pattern.

The textural properties of starch dispersions are for a major part due to the swelling capacity of starch granules. In the food and non-food industries, starch systems are submitted to intensive heat and shear treatments during sterilisation or homogenisation-mixing respectively; these treatments alter the integrity of starch granules and impair the functional properties of the suspensions. Modified starches have been therefore developed to improve the resistance of starch dispersions to industrial treatments. Nowadays, there is considerable interest in physical modifications, which are considered to be safer than chemical ones especially for food applications with novel functional properties. Physical modifications can be obtained through the controlled application of heat and moisture treatment. Annealing and heat moisture treatments (HMT) (Jacobs, Mischenko, Koch, Eerlingen, Delcour. & Reynaers, 1998; Tester, Debon & Sommerville, 2000; Vermeulen, Goderis & Delcour, 2006; Tukomane, Leerapongnum, Shobsngob & Varavinit, 2007; Kulp & Lorenz, 1981; Hoover & Manuel, 1996; Collado & Corke, 1999; Gunaratne & Hoover, 2002; Gunaratne & Corke, 2007) are the two most usual physical treatments by which the semi-crystalline structure of starch granules are modified without disrupting the granule (Lim, Chang, & Chung, 2001). The differences between these two treatments are the water content and the temperature used. The annealing occurs under large excess of water (50 to 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 (10-16h).

Many studies have been carried out on the structural and physical properties of starches after HMT treatment since the first experimentations conducted by Sair & Fetzer in 1944. The properties of heat moisture treated starches depend on the starch origin (Gunaratne et al., 2002; Hoover & Vasanthan, 1994; Hoover et al., 1996; Kulp et al., 1981; Collado et al., 1999) and treatment conditions used (Takaya & Nishinari, 2000; Collado et al., 1999). Generally the

HMT is known to reduce the water sorption capacity, the swelling capacity of starch granules as well as the viscosity of the starch suspension. The initial temperature of gelatinization ( $T_0$ ) and the temperature of the peak ( $T_p$ ) increase; in the meanwhile, the gelatinization enthalpy decreases and the endotherm of gelatinization is broadened (Sair 1967; Kulp et al., 1981; Stute, 1992; Hoover et al., 1994; Gunaratne et al., 2002; Vermeyleylen et al., 2006). The intensity of the modifications depends on the water content and the temperature/time conditions of the treatment. Buléon & Bertrand (1982) reported an increased susceptibility to hydrolysis that they ascribed to partial gelatinization of starch granules after HMT treatment.

HMT starches have generally been produced on a laboratory scale and many authors have reported that such conditions produce inhomogeneous samples with partially hydrotreated starch granules. For HMT, vapour pressure is often required to assure sufficient heating, but uniform heat distribution and penetration into the starch is not easy to accomplish. Maruta, et al. (1994) improved the conventional method of the HMT by creating a reduced pressure in the vessel containing the starch before the injection of live steam. This method was designated by Maruta et al. (1994) as the reduced-pressurized heat moisture treatment (RP-HMT). The DIC hydrothermal process, developed at a laboratory as well as pilot scale (Rezzoug, Maache-Rezzoug, Mazoyer & Allaf, 2000) some years ago is closer to RP-HMT treatment proposed by Maruta et al. (1994). The difference is that the DIC treatment is followed by an abrupt pressure drop towards vacuum pressure. This step induces a rapid modification of the thermodynamic equilibrium reached during the pressurisation ( $P_1, T_1$ ) 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. The DIC treatment (Instantaneous Controlled Pressure Drop) is a recent process patented and developed in our laboratory (Allaf, Louka, Bouvier, Parent & Forget, 1993) for drying and texturizing food products such as pasta products (Maache-Rezzoug & Allaf, 2005). As for the RP-HMT

process, the instauration of an initial vacuum of 50 mbar before injection of steam at high pressure allows to reduce the resistance of air, thus facilitating the diffusion of steam into the product (Zarguili, Maache-Rezzoug, Loisel & Doublier, 2006). Consequently, the time necessary to reach the steam temperature equilibrium is reduced with homogeneous vapour diffusion and a more effective heat transfer to the starch. In a recent laboratory study, the thickness of the layer of maize starch which can be treated in the DIC equipment to assess uniform heat distribution and homogeneous diffusion of steam into the starch powder has been fixed to 0.5 cm (Zarguili et al., 2006); the time required to reach the equilibrium temperature was 80, 60, 45 and 20 s for processing pressures of 2, 3, 4 and 5 bar, respectively.

The DIC hydrothermal treatment was applied to starches aiming to produce structural modifications and thus modifying their functional properties. A preliminary study on the application of DIC hydrothermal treatment on standard and waxy maize starches (Loisel, Maache-Rezzoug, Esneault & Doublier (2006) showed a partial gelatinization of the treated samples. The occurrence of partial gelatinization was clearly attested by the decrease of the gelatinization enthalpy and the loss of birefringence under polarized light as the pressures and time of the process increased; the greatest effect being obtained for 2.7 to 3 bar during 200 to 300 seconds. The starch granules were not disrupted after the DIC treatment at initial moisture content of starch, but the viscosity of the starch dispersions pasted in the Viscograph Brabender considerably decreased.

The purpose of this study was to investigate the structural and thermal phase transitions induced in a standard maize starch as a result of DIC hydrothermal treatment. The influence of DIC treatment conditions on the thermal transition and structural characteristics in standard maize starch was investigated using DSC, X-Ray diffraction and polarised light microscopy associated with determination of granule size distribution by laser diffraction.

## 2. Materials and methods

### 2.1. Materials

Standard maize starch was supplied by Roquette Frères (Lestrem, France). The moisture content was 12.5% 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.OR (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 (Rezzoug et al., 2000; Loisel et al., 2006; Zarguili et al., 2006). During the treatment, starch (12% wet basis) is placed in the processing vessel. A vacuum of 50 mbar is established. This initial vacuum facilitates the diffusion of steam into product and allows its rapid heating (Zarguili et al., 2006). Saturated steam is then introduced into the vessel at a fixed pressure level (1 to 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 pressurisation 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 that causes an increase in the moisture content. Zarguili, Maache-Rezzoug, Loisel & Doublier (2008) modelled this variation of moisture content through a simple model based on gravimetric data.



### 2.2.3. Differential scanning calorimetry (DSC)

#### 2.2.3.1. Phase transition of standard maize starch at different moisture contents

The phase transitions of the water- maize starch systems were established by using; PYRIS 6 DSC (Perkin-Elmer) for transitions (melting) measured between 100 and 200 °C (heating rate 2 °C/min), and Micro DSC III (Setaram, France) for transitions (gelatinization) measured between 20 and 100 °C (heating rate 1.2 °C/min). Water was added to starch in DSC pans which were allowed to stand for 2h at room temperature for moisture equilibration. A range of 11.5 to 90% moisture content was investigated.

#### 2.2.3.2. Thermal characteristics of DIC treated maize starch

Gelatinization parameters were measured using the Micro DSC III (Setaram, France). Starch samples (800 mg) were placed in a stainless pan; distilled water was added to get a ratio of 1:9 (w/w) starch:water, and then the pan was sealed. The reference pan was filled with water. Pans were heated at a rate of 1.2 °C/min from 30 to 110 °C. Thermal transitions were defined as  $T_o$  (onset temperature),  $T_p$  (peak temperature) and  $\Delta H$  was referred to as the gelatinization enthalpy. The gelatinization temperature range (R) was calculated as  $2(T_p - T_o)$  as described by Krueger, Knutson, Inglett & Walke (1987). The residual enthalpy ratio of the treated starch was also calculated by the following equation  $RE(\%) = \frac{\Delta H_t}{\Delta H_{raw}} \times 100$ , where RE is the residual enthalpy ratio,  $\Delta H_t$  the gelatinization enthalpy of the residual structure after DIC treated starch and  $\Delta H_{raw}$  the gelatinization enthalpy of the native starch.

#### Determination of the amylose-lipid complex

We used DSC Q10 (TA-Instrument, France) for measuring the thermal transition corresponding to the melting of the amylose-lipid complex: 10 mg of starch suspension (1:9

w/w starch:water) were sealed in a stainless pan, and heated from 30 to 130 °C at a heating rate of 2 °C/min.

#### *2.2.4. X-ray diffraction*

Native and DIC-hydrothermal treated maize starches were equilibrated above a saturated barium chloride solution ( $a_w=0.95$ ), and the X-ray diffraction pattern was measured with Inel (France) X-ray equipment at 40 kV and 30 mA. The diagrams of diffraction were recorded according to the method of Debye-Sherrer in transmission for powders. Cu  $K_\alpha$ -radiation ( $\lambda=1.54$  nm) was selected using a quartz monochromator. A curved position-sensitive detector CPS 120 was used to monitor diffracted intensities in the 0–120°,  $2\theta$  range. Diffraction diagrams were all normalised at the same total scattering value, with  $2\theta$  ranging from 3 to 30°. The crystallinity ratio was calculated according to the method of Wakelin (Wakelin, Virgin & Crystal, 1959) using spherulitic crystals and dry extruded potato starch as crystalline and amorphous standards respectively.

#### *2.2.5. Polarised light microscopy*

Dilute native and DIC-hydrothermal standard maize starch suspensions (1:20) were viewed under polarised light (magnifying 400 X) using a Leica microscope equipped with a CCD camera.

#### *2.2.6. 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  $\mu\text{m}$ ). The starch dispersion (6%) was first diluted (1/10) with demineralized water at 20°C before and immediately after the pasting procedure in the Brabender Viscograph then dispersed in the sample dispersion unit (1ml/100ml water). The volume distribution was obtained according to the Mie scattering theory (Loisel et al., 2006). From each distribution,

the median volume diameter  $D(v,0.5)$  and the swelling ratio  $(D/D_0)^3$  were presented; the size dispersion was evaluated using the dispersion index referred to as the span, by the following

$$\text{equation: Span : } \frac{D(v,0.9) - D(v,0.1)}{D(v,0.5)}$$

### 3. Results and discussion

#### *3.1. Phase transitions of starch-water system*

In order to understand the changes that occur during DIC hydrothermal treatment, thermal transitions of native standard maize starch for various water contents were determined by differential scanning calorimetry (Fig. 1). The DSC characteristics are presented on Table 1. In a large excess of water (above 70%) a single endothermic transition is observed for the gelatinization of starch (referred to as G). The peak temperatures and gelatinization enthalpy remain constant: 69.8 °C and 11.5 J.g<sup>-1</sup>, respectively. For intermediate moisture contents, from 70 to 40%, the enthalpy of the first endotherm decreases, from 9.8 to 1.9 J/g (Table 1), although the peak temperature remains constant at about 70 °C. From moisture contents of 35%, a second peak (referred to as M) appears while the first peak of gelatinization is further reduced and completely disappears at a moisture content of 26%. The peak temperature and enthalpy of the second peak (M) increase as the moisture content is reduced: from 140 to 184 °C for moisture contents of 26 to 11.5%, respectively. The presence of multiple melting endotherms at low and intermediate water contents has been reported by many authors: Donovan (1979) for potato starch, Biliaderis et al. (1986) for rice starch, Garcia et al.(1996) for manioc, and Barron, Buléon, Colonna & Della Valle (2000) for smooth pea. Different interpretations have been advanced to explain this phenomenon. In excess of water (above 70%), only one single gelatinization endotherm occurs over a constant temperature range, reflecting the loss of semicrystalline order; the melting of starch crystallites is supposed to be facilitated by the swelling of the amorphous region surrounding the crystallites (Donovan,

1979). At intermediate water contents between 70 and 35%, only part of the crystallites melt which explains the decrease of the gelatinization enthalpy whereas the peak temperature remains constant. At water contents lower than 40% the remaining crystallites melt at higher temperature according to the Flory theory of polymer-diluent interactions. This theory has been successfully applied for water volume fraction lower than 70%; it allows to estimating the melting temperature of the last crystallite as function of the moisture content. The melting term is then preferred to describe the thermal transitions under such conditions of heating at low or intermediate water contents. Biliaderis et al. (1986) however showed that starch, as a semicrystalline polymer, may undergo reorganizations in the amorphous phase and in the remaining crystallites during heating in the calorimeter; this means partial melting followed by recrystallisation processes and subsequent melting during DSC. The results of the DSC characteristics as a function of the moisture content will be used in order to explain the occurrence of the gelatinization process during the DIC treatment.

### 3.2. EFFECT OF DIC HYDROTHERMAL TREATMENT

#### 3.2.1. *Thermal transition characteristics*

All the thermal characteristics of DIC treated samples were measured at a water content of 90% for which only one endotherm of gelatinization is expected. The DSC thermograms are presented in Fig. 2: pressure levels varied from 1 bar (Fig.2-a) to 2 bar (Fig.2-b) and 3 bar (Fig.2-c) for different treatment times. Table 2 summarises the transition temperatures: onset ( $T_0$ ), peak ( $T_p$ ), and temperature range (R) calculated as  $2(T_p - T_0)$ , the enthalpies of gelatinization of native and DIC treated maize starch and the residual enthalpy ratio (RE). The DSC parameters of untreated starch were:  $T_0 = 63.1$  °C,  $T_p = 69.6$  °C,  $R = 13$  °C and  $\Delta H = 11.4$  J/g. These values are comparable to the temperatures and enthalpy of gelatinization reported by many authors for standard maize starch (Cooke & Gidley, 1992, Hoover et al., 1996; Lim et al., 2001; Singh, Inouchi & Nishinari, 2006). After the DIC treatment, the

gelatinization endotherms were shifted towards higher temperatures, the effect on  $T_0$  and  $T_p$  being larger for higher pressures and longer times (Fig. 2). The gelatinization temperatures ( $T_0$ ,  $T_p$ ) increased with the increase of processing pressure. At approximately 10 min of processing time,  $T_0$  and  $T_p$  were 65.7/72.3 °C, 68.8/73.6 °C, and 74.8/79.8 °C for pressure levels of 1, 2 and 3 bar, respectively (63.1/69.6 for native starch). Processing time also caused an increase of the transition temperatures. At a fixed pressure of 2 bars,  $T_0$  and  $T_p$  varied from 64.7/70.7 °C, 70.7/75.5 °C, 72.7/77.2°C, to 76.2 /80.3 °C, as the processing times increased from 2, 30 and 60 to 180 min.

The modifications of the transition temperatures are closely related to the combined effect of processing pressure and treatment time. These parameters modify the moisture content of the starch granules during the process, moisture content playing a very important role to induce melting of starch crystallites. Water intake during the DIC treatment is a kinetic phenomenon as was demonstrated by Zarguili et al. (2008). They showed that, for standard maize starch, the moisture content of starch granules increased during the process with processing time, due to the absorption of accumulated steam. Fig. 3 shows the thermal characteristics of DIC treated maize starch at different processing times and moisture contents. The significant modifications of the thermal characteristics started at about 0.5 min at 3 bar, 10 min at 2 bar and 60 min at 1 bar (Fig 3-a and 3-c). The initial moisture content of starch is generally about 11%. During the process, the moisture content reaches the equilibrium after a given time which depends on the level of the processing pressure. At the pressures of 1 and 2 bar, the equilibrium moisture content was 15% and 20% (wet basis) and was reached after 30 and 60 min of processing, respectively. At 3 bar the moisture content was 17% after 20 min of treatment but could not be measured for longer treatment times due to the formation of compact lumps of starch powder. When experiments are performed below the equilibrium conditions, the moisture content (and hence the thermal transitions) depends on the processing

time for a fixed pressure level. All the water contents are below the values for which gelatinization is expected according to the Table 1 (i.e. below 35%). Consequently the transition of starch will be referred to as melting during the DIC process.

Hoover et al. (1996) observed an increase of gelatinization temperatures for standard maize starch after HMT treatment at moisture content of 30% and temperature of 100 °C during 16 hours.  $T_0$  and  $T_p$  of native maize starch increased from 59 and 66 °C to 62 and 71 °C respectively after HMT treatment. After HMT treatment of maize starch (120 °C, 25- 30% of water content and 1 hour) Lim et al. (2001) observed no significant change in  $T_0$  whereas  $T_p$  and  $T_c$  (conclusion temperature) increased substantially. According to Biliaderis et al. (1986) and Gunaratne et al. (2002), the melting temperatures ( $T_0$ ,  $T_p$ ,  $T_c$ ) of the starch crystallites might be controlled indirectly by the swelling or mobility of the surrounding amorphous region. One of the effects of the heat-moisture treatment would be to promote the association between amylose chains and amylose-lipids within the amorphous region (Hoover et al., 1996) thus decreasing the destabilizing effect of the amorphous region upon melting of the starch crystallites.

DIC treatment causes an increase of the transition temperatures as HMT treatment, but has an opposite effect on the gelatinization temperature range ( $R$ ), calculated as  $2(T_p - T_0)$ ;  $R$  decreased from 13 °C for native starch, to 11.6, 9 and 10 °C for DIC treated maize starch at 1 bar/60 min, 2 bar/60 min and 3 bar/10 min, respectively; severe DIC conditions (2 or 3 bar, Fig. 3-b) reducing more the width of the gelatinization endotherms. On contrary, Hoover et al. (1996) and Lim et al. (2001) noted a broadening of the temperature range of about 4-6 °C for standard maize starch. The narrowing of the temperature range after DIC treatment seems similar to the one observed by Stute (1992) after annealing of potato starch. According to Hublin (1994),  $R$  reflects the degree of cohesion between crystallites; when  $R$  decreases a stronger cohesion may exist between crystallites. Fredriksson, Silverio, Andersson, Eliasson

& Aman (1998), Gunaratne et al. (2002) have also suggested that the gelatinization temperature range gives an indication on the quality and heterogeneity (in size or stability) of crystallites. The higher R exhibited by native maize starch (Table 2) can be attributed to its broader range of crystallites stability, and the narrower temperature range exhibited by DIC treated starch suggests the presence of crystallites of more homogenous stability (or more homogenous size). We suppose that the DIC treatment first allowed the fusion of crystallites of low cohesion (or low size), which melt at lower temperature and a reinforcement of the interactions between the remaining crystallites chains. Consequently, the residual structure after treatment might contain crystallites with a greater stability (or greater size).

The DIC treatment decreased gradually the enthalpy of gelatinization as processing pressure and time increased (Fig. 2) and (Table 2). The gelatinization enthalpy decreased from 11.4 J.g<sup>-1</sup> (native) to 11.0, 9.0 and 1.7 J.g<sup>-1</sup> for treated maize starch at 1, 2 and 3 bar for approximately 10 min. At a fixed pressure level, the enthalpy decreased with processing time (Fig. 3-c); the effect of treatment time being reinforced at high pressure. By considering the residual enthalpy (Table 2), the standard maize starch treated at 1 and 2 bar for 180 min reached a residual enthalpy ratio of 69.3% and 36.8%, whereas 20 min of DIC treatment were sufficient to melt totally starch at 3 bar. The effect of the HMT treatment on the residual enthalpy of standard maize starch depends on the treatment conditions: the gelatinization enthalpy may remain unchanged (Hoover et al., 1996) or decrease (Lim et al., 2001; Miyoshi, 2001; Vermeylen et al., 2006). Loisel et al. (2006) already showed by using response surface methodology that the steam pressure level, and therefore the temperature, had a more significant effect than the processing time; the temperatures associated with the pressure levels were 100 °C, 122 °C and 135 °C for pressures of 1, 2 and 3 bar respectively. Fig. 3-d shows the reduction of enthalpy ( $\Delta H$ ) of residual structure of treated maize starch as function of moisture content for three pressure levels. As already mentioned, the moisture contents at

equilibrium are 15%, 20% and 17% at 1 (100 °C), 2 (122 °C) and 3 bars (135 °C) reached after 30, 60 and 20 min, respectively. For these moisture contents the temperature that have to be reached to initialize the melting processus ( $T_0$ ) according to Table 1 are: 137 °C, 133° C and about 140 °C for 1, 2 and 3 bar respectively: these temperatures did not occur during the DIC process for these pressures. This means that under the moisture and temperature conditions encountered during the DIC process, the melting of the most stable crystallites should not occur; but the melting may concern the smallest or the least cohesive crystallites, or those which have the more defects; the gelatinization process as previously described is also excluded. This indicates that starch reorganization (melting and recrystallisation) within the granule probably took place during the DIC process as was stated from the DSC characteristics, despite low temperatures and moisture contents.

It is also possible that the moisture content may have increased locally to higher values than the ones measured, enhancing thus the thermal transitions. The strong effect of the moisture content (in the range 18-20%) on the reduction of the enthalpy has been clearly attested by Adebowale & Lawal (2003), while Vermeylet et al. (2006) observed that the highest temperatures of treatment and moisture contents of hydrothermally treated potato starch provoked the largest changes on gelatinization enthalpy.

### *3.2.2. Formation of amylose lipid-complexes and X ray diffraction*

Figure 4 shows the DSC thermograms of native and DIC treated starch. These thermograms exhibit two endotherms: the first endotherm, at lower temperature, corresponds to the gelatinization-melting of crystalline lamellae of intact structure of native starch and residual structure of DIC treated starch as previously discussed. The second endotherm at higher temperature corresponds to the disintegration or melting of amylose-lipid complexes. Amylose-lipid complexes are known to present endothermic transitions at temperature above the gelatinization temperature range of starch (Eliasson, 1988); the enthalpy reflects the



relative amount of formed complexes in the sample (Tufvesson, Wahlgren & Eliasson, 2003). The thermal characteristics of amylose-lipid complexes are given in Table 3. For native starch and starch treated under mild DIC conditions (from 1bar/10 min to 2 bar/15 min) the peak temperatures and the enthalpy values of the complex remained constant at 94.7 °C and about 0.2 J/g respectively. From 2 bar and 15 min an increase of the transition temperatures and the enthalpy of melting of the amylose-lipid complex of maize starch clearly appeared; this tendency was reinforced as the DIC conditions, mainly the pressure level/or temperature, progressively increased. Transition temperatures ( $T_0/T_p$ ) increased from 88.5/94.7 °C to 111.3/116.7 °C, while the  $\Delta H$  values increased from 0.2 to 1.7 J.g<sup>-1</sup> for native or mild treated starch to starch treated at 3 bar/15 min, respectively. Lim et al. (2001) also observed an increase of the amylose-lipid complex formation for standard maize starch induced by the HMT treatment (at 120°C, 1 hour and 25 or 30% moisture content). Amylose-lipid complexes rarely exist in native cereal starches but are usually formed upon heating during industrial drying or during gelatinization of starch. According to the transition temperatures and enthalpies values of Table 3, it seems that different kinds of amylose-lipid complexes are encountered during the DIC treatment: from 1bar/10 min to 2 bar/15 min, the complexes induced by the gelatinization of starch during the DSC analysis might prevail, as it occurs for native starch, whereas for higher time/pressure conditions the complexes might be promoted by the HMT treatment. According to Buléon, Colonna, Planchot and Ball (1998) the amylose chains are involved either in isolated inclusion complexes or in crystalline packing arrangements; only this later structure can be detected by X-ray diffraction analysis in the form of Vh-type diffraction diagram. The occurrence of this structure induced by the DIC treatment has to be confirmed by the X-ray diffraction analysis.

Figure 5 shows the X-ray diffraction patterns of native and DIC treated maize starch. An A-type X-ray diffraction pattern with peaks centred at approximately 15°, 17.1°, 18° and 23°

( $2\theta$ ) typical for cereal starches (Zobel, 1964; Imberty, Buléon, Tran & Perez, 1991) is shown for native maize starch. This A-type crystalline pattern was conserved for DIC treated starch at 1 bar for any processing time, and no significant differences in the relative crystallinity value with native starch were observed (Table 3). The reduction in relative crystallinity became significant at a pressure of 2 bar/15 min; the relative crystallinity was 27 and 22% for processing time of 15 and 60 min, respectively. The A-type crystalline pattern was progressively reduced with the increase of processing pressure ( $\geq 2$  bars). New peaks appeared at  $7.5^\circ$ ,  $13^\circ$  and  $19.5^\circ$  ( $2\theta$ ), characteristics of the  $V_h$ -type which revealed the formation of amylose-lipid complexes in starch (Eliasson, 1988; Biliaderis & Galloway, 1989). At severe DIC conditions (3 bar/15 min), the typical peaks of A-type X-ray diffraction pattern were almost replaced by the ones of the  $V_h$ -type pattern. The resolution and intensity of the new peaks attest that amylose-lipid complexes can reorganize in a crystalline packing as a result of the DIC treatment, as suggested before.

The amylose-lipid complex formation is affected by several factors: the more important are the temperature of the process and the water content (Le Bail, Bizot, Ollivon, Keller, Bourgaux & Buléon, 1999). These authors observed a  $V_h$ -type diffraction pattern around 110-115 °C after heating maize starch in excess of water (65% moisture content). They suggested that the important leaching of amylose enables the extra-granular crystallization of amylose and lipid. At low moisture contents, Le Bail et al. (1999) showed that the treatment enhanced the formation of the amylose-lipid complex inside the swollen granules because of the reduction of amylose solubilization. It can be then concluded that the DIC treatment induces the formation of amylose-lipid complexes inside the starch granules, due to the low moisture content (up to 20%) encountered during the process.

### 3.2.3. Structural characteristics

Microscopic observations under polarized light of native and treated maize starch at different pressures are presented in Fig. 6. The native (Fig. 6a) and DIC treated starch at low pressure (1 bar) displayed a clear polarization cross at the hile of the granule (Fig. 6b and 6c), confirming the preservation of the crystallinity. DIC treated starches at 2 bar mainly remained birefringent even for treated sample at 2 bar/60 min (Fig. 6e), for which the absence of polarization cross on some granules started to be observed. At 3 bars/0.5 min the intensity of the birefringence of treated starch slightly decreased but the polarization cross remained clearly for numerous starch granules (Fig. 6f). At the same pressure for higher processing time (15 min), the birefringence of the starch granules totally disappeared (Fig. 6g), this result confirmed the almost total melting of starch (9.6% residual enthalpy ratio) observed by DSC and X ray diffraction. Starch granules were also observed in light microscopy (not presented) that revealed no modification of the size and shape of the DIC treated granules in the dry state. Table 4 presents the size characteristics of starch granules before (in cold water) and after pasting in the Brabender Viscograph (95°C – 20min). As already mentioned by Loisel et al. (2006), the median diameter and the swelling ratio of DIC treated starch increased in cold water, with pressure level and processing time; the size distribution (span) also broadened that might be due for the highest pressure/time conditions to aggregation of starch granules. After pasting the reverse tendency could be observed (except at 1 bar/10 min), that means a progressive disruption of the starch granules as an effect of the DIC treatment. This disruption of starch granules was confirmed by microscopic observations and resulted in a dramatic decrease of the viscosity of the paste (Loisel et al., 2006). The increase of the swelling ratio in cold water may be ascribed to the loss of crystallinity as already discussed that enhances the penetration of water within the starch granules. Upon heating, the decrease of the swelling power has been mentioned by Hoover et al. (1996) and Maruta et al. (1994) on pasted standard maize starch treated by HMT (100°C, 1hour) and RP-HMT (reduced-pressurized

HMT up to 124°C) respectively. Hoover et al. (1996) attributed this decrease to the interaction between amylopectin chains.

#### 4. Conclusion

This study demonstrates that the DIC hydrothermal process of starch leads to modifications that are in most cases in agreement with on the ones observed with HMT treatment: the gelatinization of standard maize starch treated by DIC occurs at higher temperatures and requires lower enthalpy compared to untreated starch. But on the opposite, a narrower gelatinization temperature range (R) is observed for DIC treated maize starch that can be compared to the one reported with the annealing treatment. This result suggests that the treatment firstly allows the melting of most fragile crystallites (of lowest cohesion) or the smallest ones which require less energy to melt. Consequently, the residual structure contains crystallites with a greater stability or size, as well as greater homogeneity (of stability or size). This new organization is linked with the formation of crystalline arrangements of amylose-lipid complexes inside the starch granules owing to the enhanced mobility of amylose chains during the treatment. All the modifications of the crystalline structure are enhanced by the temperature and moisture content encountered during the DIC treatment (related to pressure and time of treatment). It is worth noting that the starch reorganization of the structure occurs without any swelling of starch granules and leaching of amylose during the treatment; except may be for the highest conditions of the treatment for which the starch granules become sticky. All these structural modifications result in a progressive decrease of the melting enthalpy of starch with the intensity of the treatment. This may be related to the greater accessibility to water observed during swelling in cold water and consequently to an increase of the susceptibility to further physical or enzymatic treatment of the starch suspensions.

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## Figures captions

Figure 1. DSC thermograms of native standard maize starch at different moisture contents (% wb). The volumic fraction of water is given in parentheses.

Figure 2. DSC thermograms for native and DIC treated standard maize starch at pressure levels of 1(a), 2 (b) and 3 bar (c) for various treatment times.

Figure 3. Thermal characteristics of DIC treated maize starch versus processing time at various pressure levels of 1, 2 and 3 bar: (a) peak temperature ( $T_p$ ), (b) temperature range of gelatinization, (c) gelatinization enthalpy ( $\Delta H_g$ ). (d) gelatinization enthalpy ( $\Delta H_g$ ) versus moisture content.

Figure 4. DSC thermograms of native and DIC treated maize starch with the amylose-lipids complex.

Figure 5. X-ray diffraction patterns of native and DIC treated standard maize starch at different processing conditions.

Figure 6. Microscopic observations in polarized light of native standard maize starch (a) and DIC treated maize starch at 1 bar/10 min (b), 1 bar/60 min (c), 2 bar/15 min (d), 2 bar/60 min (e), 3 bar/ 0.5 min (f), 3 bar/15 min (g).

**Fig.1.**

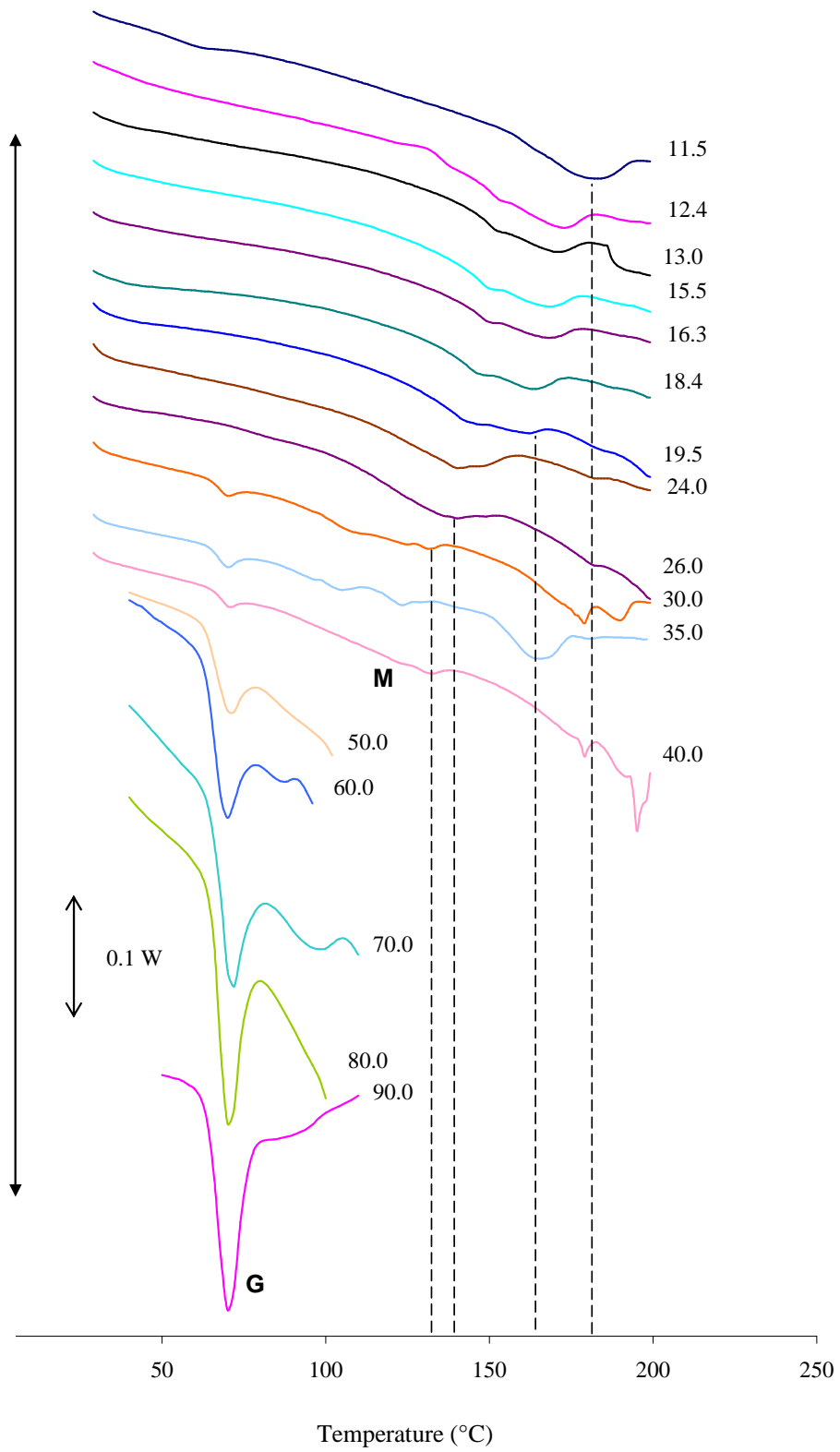
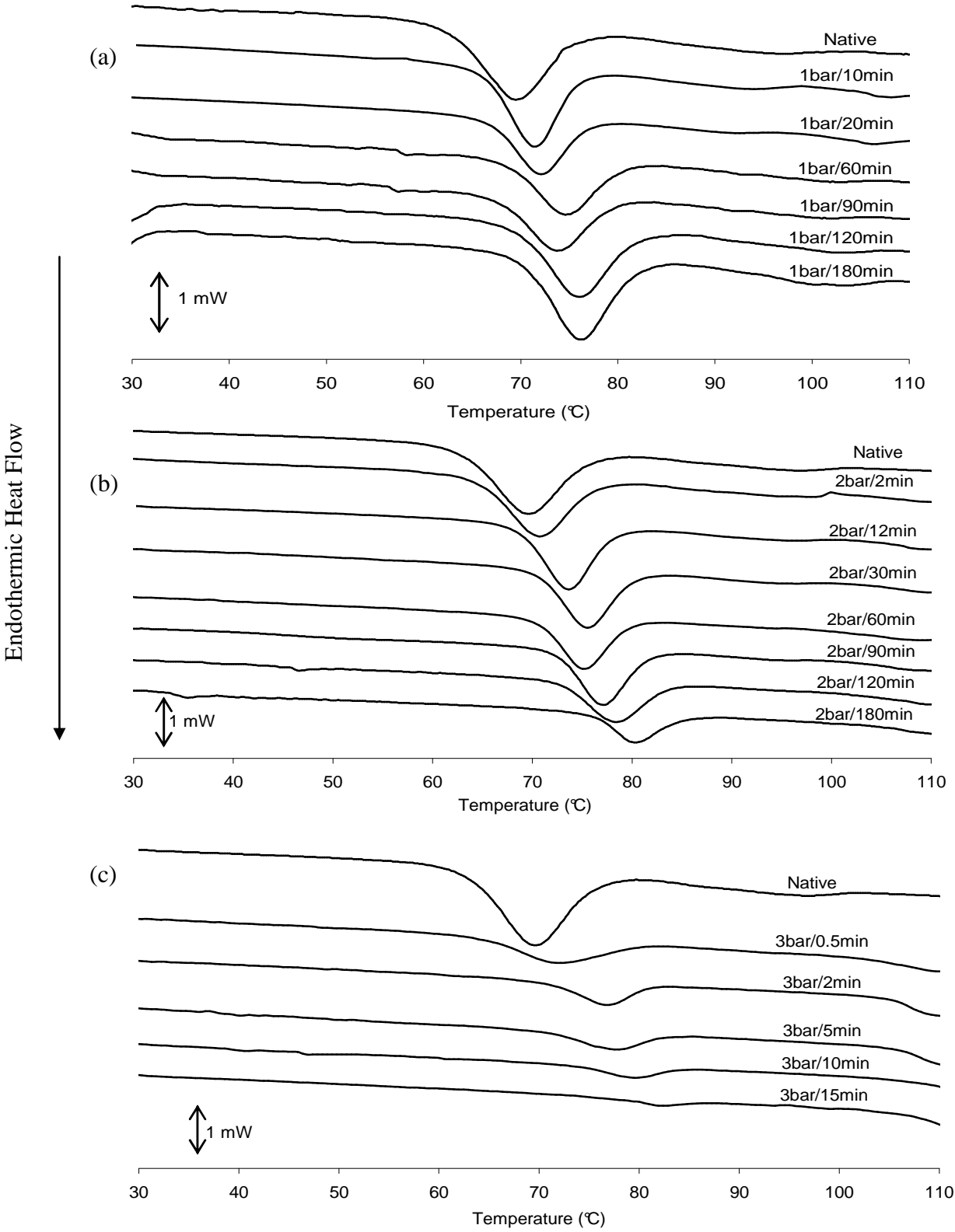


Fig. 2.



**Fig. 3.**

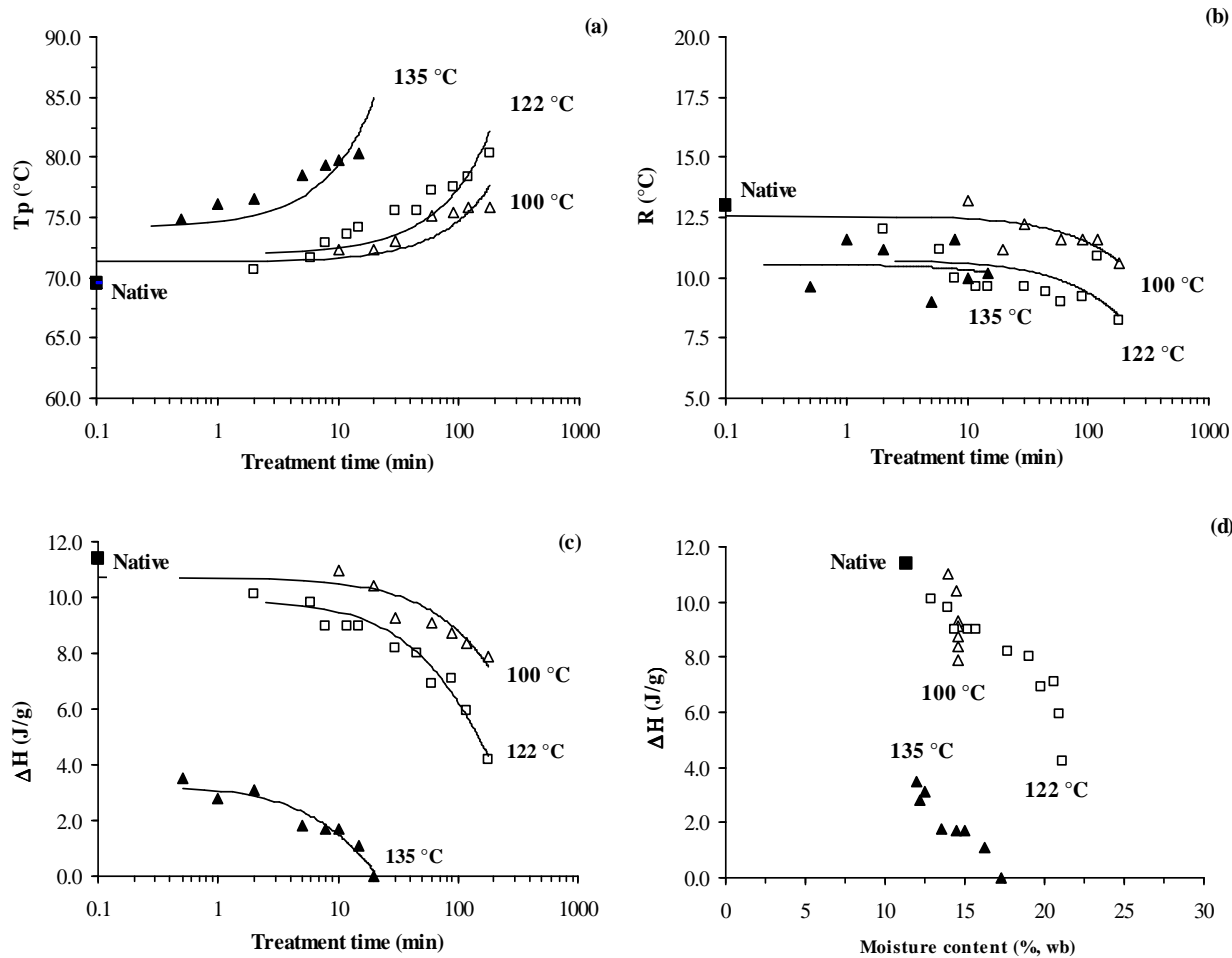


Fig. 4.

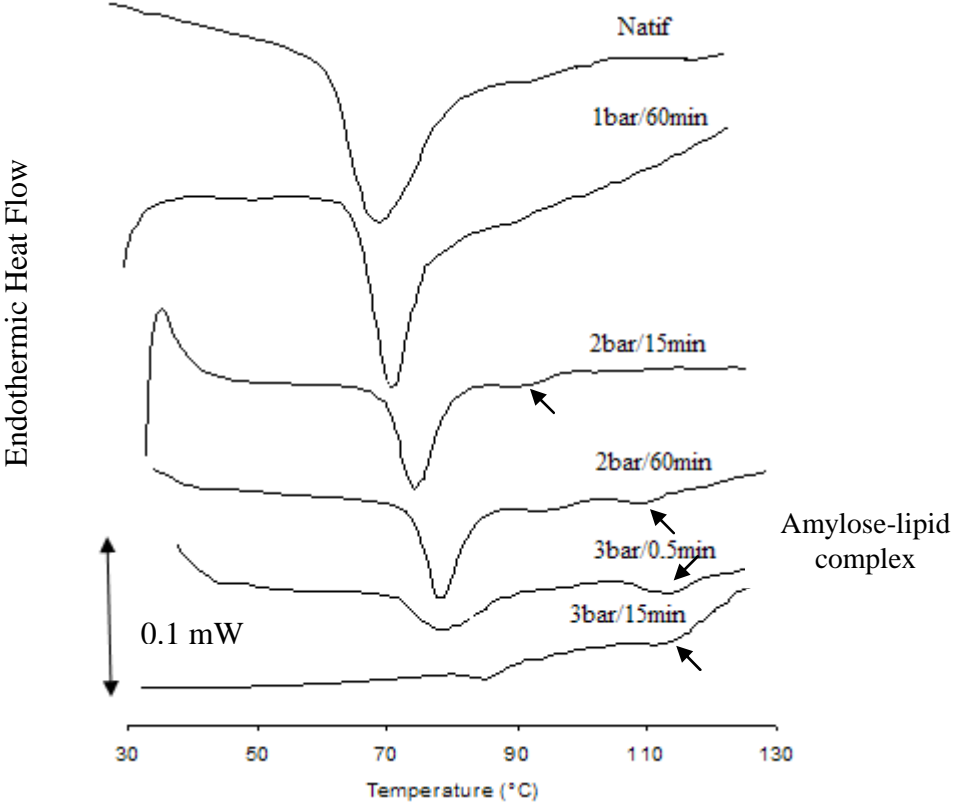


Fig. 5.

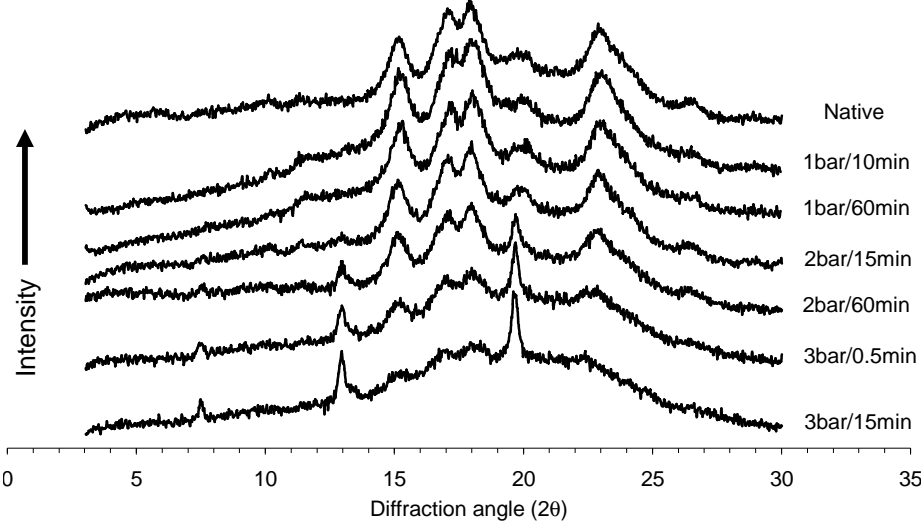


Fig. 6.

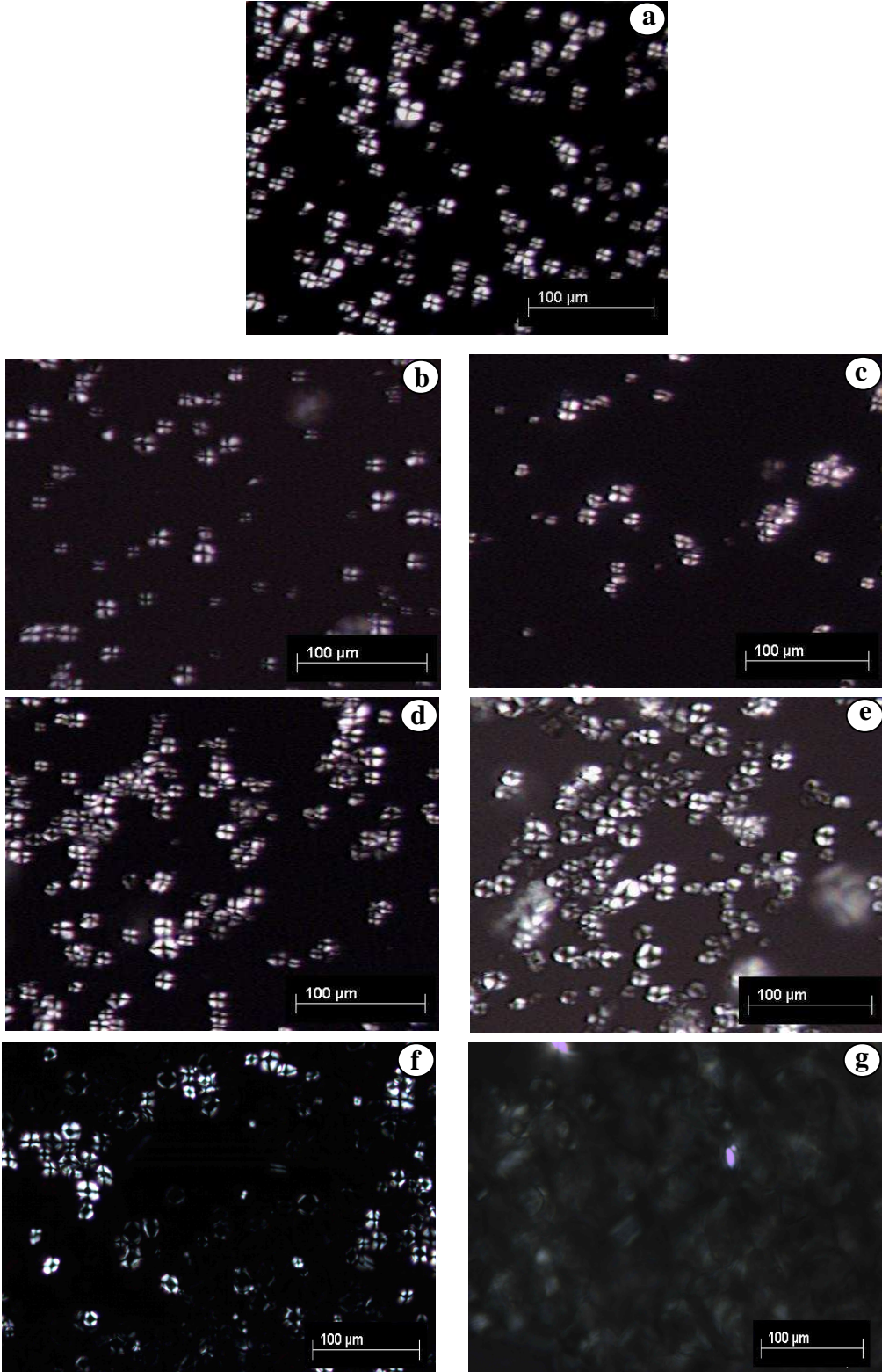




Table 1. DSC characteristics of native maize starch heated at different water contents.

Moisture content (%, w <sub>b</sub> )	Melting			Gelatinization		
	T <sub>o</sub> (°C)	T <sub>p</sub> (°C)	ΔH <sub>m</sub> (J.g <sup>-1</sup> )	T <sub>o</sub> (°C)	T <sub>p</sub> (°C)	ΔH <sub>g</sub> (J.g <sup>-1</sup> )
11.5	154.8	183.7	10.1	-	-	0.0
12.4	134.4	173.0	10.6	-	-	0.0
13.0	141.5	171.0	6.4	-	-	0.0
15.5	137.3	164.6	8.6	-	-	0.0
16.3	140.6	168.9	7.3	-	-	0.0
18.4	138.4	166.0	7.5	-	-	0.0
19.5	132.9	162.1	6.1	-	-	0.0
24.0	116.7	140.5	7.6	-	-	0.0
26.0	116.7	140.4	6.6	-	-	0.0
30.0	98.9	131.8	4.5	61.5	66.2	0.5
35.0	85.0	123.5	2.5	61.4	67.0	1.3
40.0	-	-	0.0	63.2	69.9	1.9
50.0	-	-	0.0	64.0	70.3	5.7
60.0	-	-	0.0	65.5	72.6	8.1
70.0	-	-	0.0	65.7	70.5	9.8
80.0	-	-	0.0	66.0	69.8	11.5
90.0	-	-	0.0	65.9	69.6	11.4

Values are means of triplicate determinations: T<sub>o</sub>: onset temperature; T<sub>p</sub>: peak temperature, ΔH<sub>g</sub>: enthalpy of gelatinization and, ΔH<sub>m</sub>: enthalpy of melting.

Table 2. Thermal characteristics<sup>a</sup> of native and DIC treated maize starch at various steam pressures level and processing time.

Sample		Transition temperatures				
DIC treatment <sup>b</sup>	Moisture content (% w <sub>b</sub> )	T <sub>o</sub> (°C)	T <sub>p</sub> (°C)	R (°C)	ΔH (J/g)	RE (%)
Native	11.4	63.1±0.4 <sup>c</sup>	69.6±0.5	13.0	11.4	100.0
1 bar/10 min	13.9	65.7±0.5	72.3±0.4	13.2	11.0	96.5
1/20	14.4	66.8±0.2	72.4±0.4	11.2	10.4	91.2
1/30	14.6	67.0±0.2	73.1±0.3	12.2	9.3	81.6
1/60	14.6	69.4±0.4	75.2±0.6	11.6	9.1	79.8
1/90	14.6	69.6±0.2	75.4±0.4	11.6	8.7	76.3
1/120	14.6	70.1±0.5	75.9±0.7	11.6	8.4	73.7
1/180	14.6	70.6±0.2	75.9±0.4	10.6	7.9	69.3
2 bar/2 min	12.9	64.7±0.4	70.7±0.6	12.0	10.1	88.6
2/12	15.2	68.8±0.3	73.6±0.5	9.6	9.0	78.9
2/30	17.8	70.7±0.6	75.5±0.7	9.6	8.2	71.9
2/60	19.8	72.7±0.5	77.2±0.4	9.0	6.9	60.5
2/90	20.6	72.9±0.6	77.5±0.8	9.2	7.1	62.3
2/120	20.9	73.0±0.5	78.4±0.6	10.9	6.0	52.6
2/180	21.2	76.2±0.7	80.3±0.6	8.2	4.2	36.8
3 bar/0.5 min	12.0	70.0±0.8	74.8±0.8	9.6	3.5	30.7
3/2	12.5	71.0±1.1	76.6±0.9	11.2	3.1	27.2
3/5	13.6	74.0±0.8	78.5±1.0	9.0	1.8	15.8
3/10	15.0	74.8±0.9	79.8±0.7	10.0	1.7	14.9
3/15	16.2	75.2±0.9	80.3±0.8	10.2	1.1	9.6
3/20	17.3	-	-	-	0.0	0

<sup>a</sup> T<sub>o</sub>: onset temperature; T<sub>p</sub>: peak temperature; R: temperature range, calculated as 2 (T<sub>p</sub> – T<sub>o</sub>),

<sup>b</sup> DIC treatment at pressure level of 1, 2 and 3 bar at various processing time.

Values are means of triplicate determinations ± standard deviation. ΔH: enthalpy of gelatinization; 0.5 J/g is the mean absolute error (three repetitions) of ΔH. RE (%): residual enthalpy ratio.

Table 3. DSC characteristics<sup>a</sup> of starch gelatinization and amylose-lipid complex in native and DIC treated maize starch at various processing time and pressure levels of 1, 2 and 3 bar.

Sample	Gelatinization				Amylose-lipid complex			X-Ray Diffractometry	
	T <sub>o</sub> (°C)	T <sub>p</sub> (°C)	R(°C)	ΔH (J/g)	T <sub>o</sub> (°C)	T <sub>p</sub> (°C)	ΔH(J/g)	Relative crystallinity (%)	X-ray pattern
Native	63.1±0.4	69.6±0.5	13.0	11.4	88.5±0.2	94.7±0.6	0.18	31	A type
1bar/10min	65.7±0.5	72.3±0.4	13.2	11.0	88.5±0.2	94.5±0.4	0.18	31	A type
1bar/60min	69.4±0.4	75.2±0.6	11.6	9.1	88.1±0.3	94.5±0.5	0.20	30	A type
2bar/15min	69.4±0.5	74.2±0.5	9.6	9.0	88.5±0.3	94.3±0.3	0.37	27	A type
2bar/60min	72.7±0.5	77.2±0.4	9.0	6.9	103.5±0.5	109.9±0.3	0.92	22	A + V <sub>h</sub>
3bar/0.5min	70.0±0.8	74.8±0.8	9.6	3.5	104.9±0.2	109.9±0.3	1.0	Nd	V <sub>h</sub> -type
3bar/15min	75.2±0.9	80.3±0.8	10.2	1.1	111.3±0.3	116.7±0.5	1.7	Nd	V <sub>h</sub> -type

<sup>a</sup> T<sub>o</sub>: onset temperature; T<sub>p</sub>: peak temperature; R: temperature range, calculated as 2 (T<sub>p</sub> – T<sub>o</sub>),  
ΔH: enthalpy of gelatinization or melting of the complex

Nd : not determined

Table 4. Size characteristics of starch granules for native and DIC treated standard maize starch before and after pasting in the Brabender;

Sample DIC treatment <sup>b</sup>	Before pasting			After pasting		
	D(v,0.5) ( $\mu\text{m}$ )	$(D/D_0)^3$	span	D(v,0.5) ( $\mu\text{m}$ )	$(D/D_0)^3$	span
Native	12.9	1	1.37	41.1	1	1.31
1 bar/10 min	19.6	3.50	1.51	53.8	2.19	1.68
1/30	19.3	3.35	1.62	40.0	0.92	1.31
1/60	19.3	3.35	1.47	39.3	0.87	1.21
1/90	19.4	3.40	1.54	36.0	0.67	1.05
1/120	19.2	3.29	1.64	35.1	0.62	1.05
1/180	21.7	4.76	1.91	36.6	0.71	1.07
2 bar/2 min	15.7	1.80	1.42	31.2	0.44	1.06
2/12	19.4	3.40	1.67	32.4	0.49	1.35
2/30	25.8	8	2.69	26.7	0.27	1.13
2/60	27.7	9.90	2.43	23.8	0.19	1.3
3 bar/0.5 min	39.6	28.9	2.70	25.2	0.23	1.25
3/5	61.0	105.7	2.45	29.6	0.37	1.76
3/10	60.4	102.6	2.33	36.7	0.71	2.53

D(v, 0.5): median diameter;  $(D/D_0)^3$ : swelling ratio; span:  $[(D(v,0.9)-D(v,0.1))/D(v,0.5)]$

Values are means of triplicate determinations