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EFFECT OF HYDROTHERMAL TREATMENT ON PHYSICOCHEMICAL PROPERTIES OF WHEAT, WAXY AND STANDARD MAIZE STARCHES

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Standard maize (SMS), waxy maize (WMS) and wheat (WTS) starches were hydrothermally treated at three pressure levels. Effects of D.I.C. processing conditions on thermal characteristics, enzyme susceptibility, pasting and rheological properties were investigated. For treated starches an increase of transition temperatures ($T_o$, $T_p$), a narrowing of width of gelatinization endotherms and a decrease of gelatinization enthalpies ($\Delta H$), were observed. At 3 bar/10 min $\Delta H$ decreased from 11.4 J.g$^{-1}$ to 1.7 J.g$^{-1}$, from 15.5 J.g$^{-1}$ to 2.1 J.g$^{-1}$ and from 9.4 J.g$^{-1}$ to 0 J.g$^{-1}$ for SMS, WMS and WTS, respectively. At same conditions, starches showed a significant increase in enzymatic hydrolysis, yield of saccharification increased from 19% to 44%, from 21% to 59% and from 55% to 79% for SMS, WMS and WTS, respectively. The study suggested that structural modifications influence in-vitro hydrolysis and the access to WMS ultrastructure by enzymes seems to be easier than that of SMS. The rheological behaviour was modified for treated starches: a decrease in the peak viscosity, measured with a viscoamylograph Brabender, and in the apparent viscosity, measured with a controlled stress rheometer, was observed.

Keywords: Starch; D.I.C. hydrothermal treatment; functional properties; Enzyme hydrolysis
1. INTRODUCTION

Starch has many applications in food and non-food industries. For this reason, modifications are often made to native starches to give them specific properties for particular uses. Starch properties can be modified through controlled application of heat and moisture which produces physical modifications within the granules. Annealing and heat-moisture treatment (HMT) cause a physical modification of starches with respect to size, shape or birefringence via controlled application of heat-moisture (Stute, 1992).

In the annealing, starch is suspended in excess water and heated below the gelatinisation temperature, at relatively low values, (40–55 °C) (Stute, 1992). Annealing results in perfection of the crystalline properties that narrow the gelatinization temperature interval by shifting them towards higher values (Hublin, 1994). Annealing does not increase or only moderately the enthalpy of gelatinization (Lawal, 2005).

In the HMT, starch is exposed to higher temperatures (~120 °C), commonly above gelatinization temperature, at very restricted moisture content (18-30%) during 16 h in some cases (Hoover and Manuel, 1996) and shorter in others (Lim et al., 2001). HMT has been shown to alter structure and physicochemical properties of standard maize, waxy maize, amylo maize, potato, wheat (Stute, 1992; Hoover and Manuel, 1996; Lim et al., 2001). The general effects of HMT on starch are the loss of the birefringence, the increase of the gelatinization temperatures and the broadening of the gelatinization temperature range, the increase of water bonding capacities and enzymes susceptibilities, the decrease of swelling and the increase of solubility. These modifications have consequences on functionality of treated starches: the visco graph hot paste consistencies decrease and starch paste became short and shear-stable (Lorenz and Kulp, 1982; Hoover and Manuel, 1996; Gunarante and Hoover, 2002). Hoover and
Vasanthan (1994) and Hoover and Manuel (1996) have shown that the extent of starch chain associations within amorphous regions and the degree of crystalline order are altered during HMT of wheat, oat, normal maize, waxy maize, high amylose maize, potato and lentil starches. The physical properties of heat moisture treated starches depend on the starch origin and treatment conditions used (Hoover and Vasanthan, 1994). Many authors showed that HMT increased the susceptibility of starch to hydrolysis by $\alpha$-amylases (Kulp and Lorenz, 1982; Maruta et al., 1994; Gunaratne and Hoover, 2002) and the extent of the susceptibility varies with botanical source (Colonna and Buléon, 1992; Li et al., 2004; Srichuwong et al., 2005). According to Lorenz and Kulp (1982) the considerable reduction in relative crystallinity of wheat starch caused by HMT resulted in increased enzyme susceptibility. Planchot et al. (1997) cited by Gunaratne and Hoover (2002), have postulated that the fraction of total crystalline material is an important factor defining the rate and extent of $\alpha$-amylase hydrolysis.

The D.I.C. (Détente Instantanée Contôlée: “Instantaneous Controlled pressure Drop”) hydrothermal process, developed in our laboratory some years ago (Zarguili, 2006) is more close to HMT. The major effects observed are almost similar except the gelatinization range temperature where the D.I.C. treatment caused its narrowing (Zarguili, 2006) as observed with annealing (Hublin, 1994). Preliminary studies on SMS and WMS starches (Loisel et al., 2006, Zarguili et al., 2006) showed a partial or total gelatinization of by D.I.C. treated starch, according to processing conditions. The increase of processing time and pressure level induced the narrowing of the gelatinization temperature range, the shift of the characteristics temperatures to higher values and the decrease of gelatinization enthalpy. The occurrence of gelatinization of
treated starches was clearly attested by the increase of median volume diameter in cold water and a loss of birefringence under polarized light. Maruta et al. (1994) observed for HMT treatment that the pressure is often required to ensure a sufficient heating, but it is not easy to achieve a uniform distribution and penetration of heat into the starch layer. These authors improved the conventional method by the introduction of reduced pressure in order to satisfy practical requirements for industrial production. They observed that the combination of reduced pressure during HMT of starch allows homogeneous diffusion of steam and an effective heat transfer to the starch granules.

During D.I.C. treatment, an initial vacuum of 50 mbar was established before introducing steam in processing vessel. As demonstrated by Zarguili et al. (2006), this initial vacuum allows to reduce the resistance of the air and thus to facilitate the diffusion of steam into the product. Consequently, the time necessary to reach the steam equilibrium temperature is reduced (Zarguili, 2006). The originality of D.I.C. method compared to other physical treatments is that the starches are treated at residual moisture content of 13% (dry basis) no hydration step is then used. The conventional methods require previous hydration of starch before the physical treatment. During the D.I.C. treatment, the starch heating 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. Changes of the moisture distribution were measured during the treatment and modelled by Zarguili et al. (2007).

The objective of this study is to understand the physicochemical changes produced on native starches after D.I.C. hydrothermal treatment. Under identical conditions (processing pressure and time), the effects of D.I.C. process on the changes of thermal
transition characteristics, enzyme digestibility, pasting and rheological properties were evaluated on SMS, WMS and WTS starches.
2. MATERIALS AND METHODS

2.1. MATERIALS

SMS, WMS (Waxilys 200) and WTS starches were supplied by Roquette Frères (Lestrem, France). The amylose content was of 27-28% for SMS and WTS and lower than 1% for WMS. The moisture content of these starches was about 12% wet basis.

Fungamyl 800 L, a \( \alpha \)-amylase from *Aspergillus oryzae* was used for starch liquefaction. The enzyme activity was 800 FAU/g (1 Fungal \( \alpha \)-amylase FAU is the amount of enzyme which breaks down 5.26 g of starch per hour according Novozyme’s standard method for the determination of \( \alpha \)-amylase). AMG 300 L, a glucoamylase from *Aspergillus niger* was used for saccharification. The enzyme activity was 300 AGU/ml (1 Novo Amyloglucosidase Unit (AGU) is defined as the amount of enzyme which hydrolyzes 1 micromoles maltose per minute under standardized conditions according Novozymes. The enzymes were gift from Novozymes, Denmark.

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 standard method.

2.2.2. D.I.C. hydrothermal treatment

The equipment and procedure of D.I.C. hydrothermal treatment were largely described in previous studies (Loisel et al., 2006; Zarguili et al., 2006). During the treatment, 22 g of starch (13% dry basis) disposed in circular containers (diameter: 20 cm; height: 5
cm) were placed in the treatment reactor. An initial vacuum of 50 mbar was established. Saturated steam was introduced into the vessel at fixed pressure and maintained for a predetermined 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.

2.2.3. Differential Scanning Calorimetry (DSC)

Thermal characteristics of treated starch were studied by using a Micro DSC III (SETERAM, 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, mix, and then the sample pan was sealed. Sample pan was heated at a rate of 1.2 °C/min from 30 to 110 °C. Thermal transition of starch samples 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 et al. (1987). The degree of gelatinization of treated starch was calculated by the following equation (Marshall et al., 1993). 

$$DG(\%) = \left[ 1 - \frac{\Delta H_t}{\Delta H_{raw}} \right] \times 100,$$

where DG is the degree of gelatinization of D.I.C. treated starch, $\Delta H_t$ and $\Delta H_{raw}$ the gelatinization enthalpy of treated and native starch, respectively.
2.2.4. Enzyme hydrolysis

The dried samples (300 mg) were mixed with 3 ml of citrate phosphate buffer (pH 4.6) in a 5 ml tube. The mixture was treated with enzymes in two steps (a), liquefaction and saccharification, or only in one step of saccharification (b). The first step, liquefaction, was performed at 50 °C with 32 U/l (10 g/l) of Fungamyl 800 L for 120 min. The second step, saccharification, was performed at 65 °C with 1.5 U/l (7 ml/l) of AMG 300 L for 60 min. The saccharification was performed at 65 °C with 1.5 U/l (7 ml/l) of AMG 300 L for 120 min.

2.2.5. Determination of reducing equivalents

During the starch hydrolysis samples were withdrawn for analysis of reducing sugars content using 3, 5-dinitrosalicylic acid method (DNS). In all samples, the reaction was stopped by adding 1 volume of water and by heating at 100 °C for 5 min. After centrifugation of the solution at 3000 rpm for 10 min, a 0.5 ml of a diluted supernatant was transferred to a test tube and 0.5 ml of DNS reagent (10 g dinitrosalicylic acid + 200 ml NaOH 2M + 300 g potassium sodium tartrate + qsp 1l distilled water) was added. The tubes were allowed to stand for 10 min in boiling water and cooled to room temperature in ice water. The absorbance of the samples was measured at 550 nm using a spectrophotometer (Shimadzu mini UV 1240). Amount of reducing equivalents was calculated using a glucose standard curve. The starch hydrolysis yield of samples was calculated by:

\[
\text{Starch hydrolyse(%) = } \left( \frac{\text{Reducing sugar expressed as glucose in sample g/l}}{\text{weight of dried starch in sample g/l}} \right) \times 100
\]
2.2.6. Pasting properties using Viscograph Brabender

The processed samples are powdery products that have to be rehydrated for analytical purpose. This was performed using the Brabender Viscograph to obtain a starch paste under repeatable conditions. The starch concentrations were chosen in order to lie within the sensitivity range of the Viscograph: i.e. 6% (w/w) for SMS, 4% (w/w) for WMS and 7% (w/w) for WTS. Starch was slurried in demineralized water at room temperature, and then submitted to gradual heating (1.5 °C/min) from 30 to 96 °C; this temperature was maintained for 10 min and was followed by a cooling step (1.5 °C/min) down to 70 °C before sampling. The moisture content was determined directly after the pasting procedure, to check the starch concentration before rheological measurements. The relevant values obtained from the pasting profile were: onset of the pasting temperature (T₀), temperature of peak viscosity (Tp) and peak viscosity (PV) in Brabender units (100 BU for 25 cmg).

2.2.7. Rheological measurements

Flow behaviour of starch pastes were measured using a controlled stress rheometer (TA Instrument AR1000) with the cone/plate geometry (6 cm/2°). An aliquot of the starch dispersion pasted at 60 °C in the Viscograph Brabender was poured onto the plate of the rheometer preheated at 60 °C, then covered by a layer of paraffin oil to avoid evaporation. For flow measurements, two up-down shear scans from 0.01 to 660 s⁻¹ (4 min each) were linearly applied, followed by a logarithmic stepwise decrease from 660 to 0.01 s⁻¹, after equilibrium for each shear rate, as described by Nayouf et al., 2003. Rheological properties were obtained using Herschel-Bulkley model, according to
equation \( \tau = \tau_0 + k\dot{\gamma}^n \), where \( \tau_0 \) is the yield stress (Pa), \( k \) the consistency index (Pa.s\(^n\)) and \( n \) the flow behaviour index (dimensionless). The Herschel-Bulkley model fitted the data satisfactorily (\( R^2 = 0.98 \)).

2.2.8. Polarised light microscopy

Dilute native and D.I.C. treated standard starch suspensions (1:20) were viewed under polarised light (magnifying 400 X) using a phase contrast microscope equipped with a CCD camera.
3. RESULTS AND DISCUSSION

3.1. Thermal properties

The effect of D.I.C. hydrothermal treatment on gelatinization temperatures [onset (To), peak (Tp), and temperature range (R)] and gelatinization enthalpy (ΔH) of treated starches (SMS, WMS and WTS) were studied. The obtained values were compared with those of native starches. The native starches displayed differences in gelatinization temperatures and enthalpy changes, as indicated by DSC analysis (Table 1). To, Tp, R and ΔH of SMS and SWS were higher than corresponding values for wheat. To, Tp and ΔH of the native starches followed the order: WMS>SMS>WTS. To and Tp were of 65.4 and 71.3.4 °C for WMS, of 63.1 and 69.6 °C for SMS, of 50.4 and 56.6 °C for WTS. According to Gunaratne and Hoover (2002), the differences in gelatinization temperatures among starches can be attributed to the interplay of three factors: molecular structure of amylopectin (unit chain length, extent of branching), starch composition (amylose to amylopectin ratio, amount of lipid complexed, amylose chains, phosphorous content) and granular architecture (crystalline to amorphous ratio). Amylopectin plays a major role in starch granule crystallinity, the presence of amylose lowers the melting temperature of crystalline regions and the energy for starting gelatinization (Flipse et al., 1996). That explains the high gelatinization temperatures and enthalpy values of WMS, which contains mainly amylopectin. Whereas Noda et al. (1998) attributed the influenced of DSC parameters to the molecular architecture of crystalline region, which corresponds to the distribution of amylopectin short chains and not to the proportion of crystalline region which corresponds to the amylose to amylopectin ratio. The gelatinization temperatures ranges (R) of native starches (Table 1), calculated as 2 (Tp – To) were 13 °C, 11.8 °C and 6.2 °C for SMS, WMS and WTS,
respectively. Fredriksson et al. (1998) reported that wide temperature range implied a large amount of crystals with varied stability. Cooke and Gidley (1992) have shown that $\Delta H$ is due mainly to the disruption of the double helices rather than the longer range disruption of crystallinity. Gunaratne and Hoover (2002) postulated that the higher $\Delta H$ values could be attributed to the presence of higher number of double helices and/or weaker interaction between adjacent amylopectin double helices within the crystalline domains of the native granules. The higher gelatinization parameters of WMS suggest that the chains forming the doubles helices are longer with greater interchain association than those of WTS.

For all starches, D.I.C. hydrothermal treatment increased $T_o$ and $T_p$, but decreased $R$ and $\Delta H$ (Table 1). $T_o$ and $T_p$ increased with increasing pressure level and processing time and shifted to higher values (Fig. 1). At 2 bar ($122 \, ^\circ C$) and processing time of 90 min, $T_o - T_p$ shifted from 63.1 - 69.6 $^\circ C$ (native SMS) to 72.9 - 77.5 $^\circ C$, from 65.4 – 71.3 $^\circ C$ (native WMS) to 73.1 - 77.8 $^\circ C$ and from 50.4 - 56.6 $^\circ C$ (native WTS) to 65.2 - 68.0 $^\circ C$.

At the same D.I.C. conditions (1 bar/90 min), the increase in $T_o$ (6.5 $^\circ C$) and $T_p$ (5.8 $^\circ C$) for SMS was equivalent to that observed for WTS [$T_o$ (7.2 $^\circ C$) and $T_p$ (4.9 $^\circ C$)], whereas this increase was lower for WMS [$T_o$ (2.6 $^\circ C$) and $T_p$ (2.4 $^\circ C$)]. Similar increases have been reported on HMT of cereal starches (Lim et al., 2001; Hoover and Manuel, 1996; Hoover and Vasanthan, 1994). Lim et al. (2001) observed an increase in $T_o$ and $T_p$ from 62.6 and 66.9 $^\circ C$ for native maize to 63.4 and 76.7 $^\circ C$, after HMT (120$^\circ C$ during 1 hour and 30% of water content). Hoover and Manuel (1996) observed a large increase in $T_o$, $T_p$ and $T_c$ for standard maize and amylo maize V starches, but a small increase in waxy and Dull waxy maize starches. According to these authors, the change in transition temperature following HMT is probably influenced by the decrease...
in the destabilization effect of the amorphous regions when the starch crystallites melt, due to the formation of amylose-lipid complexes and interactions between and among amylose chains.

As discussed previously, the gelatinization temperature range (R) gives an indication of the quality and heterogeneity of crystallites (Fredriksson et al., 1998; Gunaratne and Hoover, 2002), R reflects the size and crystallites perfection. Many researchers have already showed the broadening of the gelatinization temperature of starches after HMT treatment (Hoover and Manuel, 1996; Lim et al., 2001; Adebowal et al., 2005), and this broadening depends on botanical source. An inverse tendency was observed with D.I.C. treated starches, a narrowing of the gelatinization temperature range for the three starches, as observed with annealed starches (Hublin, 1994). A greater decrease in gelatinization range was observed in SMS and WTS compared to WMS (Table 1). According to Hublin (1994), the temperature range reflects the degree of cohesion between crystallites, when R decreases a stronger cohesion exists between crystallites. The narrower temperature range exhibited by D.I.C. treated starches suggests the presence of crystallites of homogenous stability. We suppose that the D.I.C. treatment allowed first the fusion of crystallites of low cohesion, which required less energy to melt and a reinforcement of the interactions between the remaining crystallites chains. Therefore, the residual structure after treatment contains a greater homogeneity of crystallites.

The gelatinization enthalpies of treated starches (Tables 1) showed that the ΔH values depend on the intensity of D.I.C. conditions. The gelatinization enthalpies decreased progressively for the three types of starches with increasing pressure level and processing time. The extent of the decrease after treatment followed the order:
WMS>SMS>WTS. At processing pressure of 2 bar and 90 min, the gelatinization enthalpies decrease for WTS from 9.4 (native) to 0.1 J.g⁻¹, for SMS from 11.4 (native) to 7.1 J.g⁻¹ and for WMS from 15.5 (native) to 11.2 J.g⁻¹. By considering gelatinization degree, we noted after D.I.C. treatment (2 bar and 90 min) a partial gelatinization of 98.9%, 37.7% and 27.7%, for WTS, SMS and WMS, respectively. Vermeylen et al., 2006 observed on potato starch the decrease of gelatinisation enthalpy with more severe HMT conditions, but effects of moisture content are considerable only at higher temperature, between 90 and 120 °C. According to Gunaratne and Hoover (2002), the decrease in ΔH on HMT suggest that some of the double helices present in crystalline and non crystalline regions of the granule could be disrupted under the conditions prevailing during treatment. Thus, few double helices would unravel and melt during gelatinization of HMT treated starches.

We already showed on standard maize starch (Zarguili et al., 2007) that during D.I.C. treatment the moisture content of starch granules increases as pressure and processing time increase, due to the absorption of accumulated steam. The initial moisture content of starch (13%, base dries) is different from the real moisture content present during the treatment. This increase reaches an equilibrium value after a given time which depends on the level of processing pressure. At the pressure of 1 and 2 bar, the equilibrium moisture content was 17% and 26% (dry basis) and reached after 30 and 60 min of D.I.C. treatment, respectively. However, for pressure level of 3 bar the measure of equilibrium moisture content (beyond 60 min) could not be taken because of the formation of a compact lump making measurement difficult. From this study, at 3 bar and 10 min, the moisture content uptake was 18% (dry basis).
3.2. ENZYME DIGESTIBILITY

In a first reaction, the enzyme digestibility of native WMS was compared to the digestibility of two WMS treated by D.I.C. This digestibility was carried out in two steps. The first step, liquefaction, was performed with Fungamyl 800 L for 120 min. The second step, saccharification, was performed with AMG 300 L for 60 min. The kinetics of liquefaction and saccharification (not showed) of WMS treated by D.I.C. at 1 bar with a processing time of 90 min are very similar to those obtained from native WMS. These results suggest that the low D.I.C. conditions (1 bar/90 min) do not have a significant effect on the enzymatic hydrolysis. It is important to note that the yield of liquefaction is very low, only 10% obtained after 2 hours.

On the other hand, we observe that kinetics of liquefaction and saccharification but also hydrolysis yields of WMS hydrotreated at 3 bar with a processing time of 10 min is strongly improved. The liquefaction with Fungamyl involved the production of maltose syrup with a little production of glucose syrup. Very fast is the rate, with a hydrolysis yield around of 40% obtained in less of 10 min. The saccharification with AMG involved the production of glucose syrup, is observed by TLC analysis (Fig 2). After 1 hour of saccharification, a yield of hydrolysis of 80% is obtained. These first experimentations demonstrate that the high D.I.C. conditions (3 bar/10 min) have a big effect on rates and yields of liquefaction and saccharification.

A similar effect was observed with saccharification without preliminary liquefaction (results not showed.). A hydrolysis yield of 70% is obtained after 60 min using WMS treated by D.I.C. at 3 bar/10 min, while a hydrolysis yield near of 55% is obtained after 130 min with WMS native.
The effects of D.I.C. process on the enzymatic hydrolysis of WMS were compared to those obtained on SMS and WTS starches. Saccharification alone with AMG was carried out (Fig. 3), we observe that in all starches the kinetics of saccharification is more efficient from treated starches than native starches. The more pronounced increase in hydrolysis was observed for all starches when severe D.I.C. conditions were applied (pressure level \( \geq 3 \) bar, table 1). The hydrolysis yield after 30 min of the three native starches was increased after D.I.C. treatment at 3 bar for 10 min following the order: WMS (39%), SMS (24%) and WTS (21%).

The increase in the susceptibility towards enzymatic hydrolysis after treatment suggests a strong link with the structural modifications induced by the heat treatment. The increase of starch hydrolysis is concomitant with the decrease of the gelatinization enthalpy. That was observed in precedent experimentations (Table 1). In a recent work we showed that the D.I.C. treatment decreased the relative crystallinity of hydrothermally treated starches as the severity of processing conditions increased (Zarguili, 2006). The increase in the accessibility of starches to enzyme attack after HMT has been also reported by several researchers (Gunaratne and Hoover, 2002).

3.3. Pasting properties

Typical Brabender Viscograph curves of native and D.I.C. treated starches are shown in Fig. 2, of SMS, WMS and WTS. The pasting properties of analysed starches are summarized in table 2. It is difficult to compare the pasting values of starches because of the differences in starch concentrations used during measurements. The starch concentrations were chosen in order to lie within the sensitivity range of the Viscograph: i.e. 6% for SMS, 4% (w/w) for WMS and 7% for WTS.
No change in pasting temperature was observed for D.I.C. SMS at 1 bar. The peak occurring at 97.5 °C and the onset of the pasting temperature at 82.5 °C for native and SMS treated at 1 bar for 90 min (Table 2). The PV increased from 835 UB (native) to 870 UB for SMS treated for 90 min and 1 bar. At severe D.I.C. conditions (2 bar for 90 min and 3 bar for 10 min), starch produced a very soft gel which was not measurable under the experimental conditions. While the pasting temperature of WMS increased following D.I.C. treatment. The PV decreases with increase of the intensity of D.I.C. conditions (processing pressure and time). However, at same pressure, processing time seems to reduce viscosity (result not given). D.I.C. treatment decreased $T_o$ of WTS, from 80 °C for native starch to 70 °C for D.I.C. WTS at 3 bar for 10 min. The $T_p$ remained unchanged after D.I.C. treatment. At the same D.I.C. condition (1 bar and 90 min) like SMS, PV of D.I.C. WTS was higher than native starch. WTS treated at 3 bar for 10 min showed a cold swelling behaviour with a rapid rehydration traduced by a Brabender viscosity of about 180 UB (Fig. 4). This cold viscosity is explained by a partial solubilization of WTS already pregelatinized following D.I.C. treatment. Compared to SMS and WTS starches, the final viscosity of WMS, that is virtually free of amylose, is lower. This is probably related to the differences of amylose leaching and its contribution to the setback viscosity. It well known that when gelatinized starch paste is subject to cooling the extent of viscosity increase is mainly governed by the rapid reassociation of linear amylose chains by formation of gel matrix.

Many authors have been observed that HMT increased pasting temperature characteristics and decreased of Brabender pasting viscosity at 95 °C after 30 min holding time for standard maize, amylomaize (Hoover and Manuel, 1996), potato (Hoover and Vasanthan, 1994) and lentil, oat (Hoover and Vasanthan, 1994). However,
for waxy maize starch heated in conventional oven, pasting properties seemed to be unaffected (Hoover and Manuel, 1996). According these authors, the decrease of viscosity could be explained by the increase of inter and intramolecular hydrogen bonds due to the association of the amylose chains and the formation of the complex amylose-lipid after hydrothermal treatment. Recent work showed by the X-ray diffraction pattern of SMS D.I.C. treated at 2 bar for 60 min and 3 bar for 0.5 and 15 min the partial loss (treatment at 2 bar) or total (treatment at 3 bar) of the crystalline structure and the presence of a crystalline amylose-lipid complex formed during D.I.C. treatment (Zarguili, 2006). Eliasson (1985) reported that amylose-lipid complex inhibits the swelling of starch. Tester and Morrison (1990) reported also that amylopectin contributes to swelling, whereas the amylose and lipids inhibits swelling.

3.4. Flow properties

The flow properties of native and D.I.C. SMS, WMS and WTS starch dispersions were studied in the shear rate range of 0.01-660 s⁻¹ and the results are presented in Table 2. All the curves (not shown) exhibited a non-newtonian shear thinning behaviour with or without a yield stress. The shear-thinning behaviour appear clearly ($n < 1$), except for the SMS suspensions treated at 2 bar for 90 min and 3 bar for 10 min, whose rheological behaviour is rather newtonian ($n = 1$, $\tau_o = 0$). For all treated starches, one observed the decrease of yield stress ($\tau_o$), consistency index ($k$), and apparent viscosity ($\eta$) with the increase in processing pressure and time. For SMS treated at 2 and 3 bar, no yield stress was measured (Table 2). A drastic reduction in the apparent viscosity was observed, with values close to those of water. These results confirm those obtained by the Viscograph Brabender at the same D.I.C. conditions. Contrary to the SMS, the flow
behaviour index of WMS remained unchanged after D.I.C. treatment, n was almost constant and its value is approximately equal to that of the native starch (0.53).

The variation of viscosity deduced using the Herschel-Bulkley model for the three starches at various D.I.C. conditions, agrees overall with pasting viscosity values measured by Brabender. The reduction in viscosity after D.I.C. treatment is mainly allotted to the reduction in swelling capacity of treated starches. The rheological behavior of starch suspensions is known to be the result of a combination of two major factors: the continuous phase and the volume fraction of dispersed phase. In the range of concentrations used in this work (Loisel et al., 2006), the volume fraction appears to be close to unity: the suspension can then be described as a packing of swollen starch granules, the overall behavior being governed by the dispersed phase (Doublier et al., 1987).

3.5. MICROSCOPIC OBSERVATIONS

The polarized light microscope images (not shown) of D.I.C. treated SMS, WMS and WTS starches showed that the starch granules size did not appear to have changed. At 1 and 2 bar for 90 min of processing time, about half of the starch granules exhibited birefringence with a few swollen granules. The gradual loss of birefringence observed using microscopy is also reflected in the result obtained by DSC measurements (Table 1). We observed that the cross polarization is still clear on a significant number of granules of treated SMS and WMS. The degree of gelatinization calculated for these starches were of 23.7 - 37.7% and 2.6 - 27.7%, respectively. For WTS treated at pressure of 2 bar and 90 min a few starch granules exhibited birefringence with little swelling. The DSC measurements indicated that the starch granules were almost completely gelatinized (98.9%). At 3 bar and 10 min, all starch granules of WST lost
their birefringence. Whereas for SMS and WMS some intact granules are visible, this confirms the DSC results, where the gelatinization degrees of the residual structure at this condition, were of 85.1 and 86.5%, respectively.

4. CONCLUSIONS

This study has shown that the D.I.C. treated starches gelatinise at higher temperatures and over narrower temperature ranges than native starches. Moreover, gelatinization enthalpies decreased progressively for the three treated starches with increasing pressure level and processing time. The extent of the decrease followed this order: WMS>SMS>WTS. The similar enzymatic behaviour was observed on D.I.C. treated starches. For all starches the kinetics of saccharification was more efficient from treated than native starches. The enzymatic susceptibility of starches is directly related to the structural modifications produced by the hydrotraitement. The considerable reduction in relative crystallinity caused by the D.I.C. treatment had as consequence the increase of the enzymes susceptibility.


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model to describe the change of moisture distribution in maize starch during D.I.C.
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Table 1. DSC characteristics of native and D.I.C. treated starches, of SMS, WMS and WTS starches, at various steam pressures level and processing time. Hydrolysis yield after 30 min of saccharification with AMG.

<table>
<thead>
<tr>
<th>Starch source</th>
<th>D.I.C. treatment</th>
<th>Gelatinization parameters</th>
<th>Hydrolysis yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$T_o$ ($^\circ$C)</td>
<td>$T_p$ ($^\circ$C)</td>
</tr>
<tr>
<td>SMS</td>
<td>Native</td>
<td>63.1 ± 0.4</td>
<td>69.6 ± 0.5</td>
</tr>
<tr>
<td></td>
<td>1 bar/90 min</td>
<td>69.6 ± 0.2</td>
<td>75.4 ± 0.4</td>
</tr>
<tr>
<td></td>
<td>2/ bar/90 min</td>
<td>72.9 ± 0.6</td>
<td>77.5 ± 0.8</td>
</tr>
<tr>
<td></td>
<td>3 bar/10 min</td>
<td>74.8 ± 0.9</td>
<td>79.8 ± 0.7</td>
</tr>
<tr>
<td>WMS</td>
<td>Native</td>
<td>65.4 ± 0.9</td>
<td>71.3 ± 0.9</td>
</tr>
<tr>
<td></td>
<td>1 bar/90 min</td>
<td>68.0 ± 0.7</td>
<td>73.7 ± 0.6</td>
</tr>
<tr>
<td></td>
<td>2 bar/90 min</td>
<td>73.1 ± 0.9</td>
<td>77.8 ± 0.8</td>
</tr>
<tr>
<td></td>
<td>3 bar/10 min</td>
<td>75.2 ± 0.2</td>
<td>77.9 ± 0.3</td>
</tr>
<tr>
<td>WTS</td>
<td>Native</td>
<td>50.4 ± 0.2</td>
<td>56.6 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>1 bar/90 min</td>
<td>57.6 ± 0.5</td>
<td>61.5 ± 0.5</td>
</tr>
<tr>
<td></td>
<td>2 bar/90 min</td>
<td>65.2 ± 0.3</td>
<td>68.0 ± 0.3</td>
</tr>
<tr>
<td></td>
<td>3 bar/10 min</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

$T_o$: onset temperature; $T_p$: peak temperature. Temperature values are means of triplicate determinations ± standard deviation. R: temperature range calculated as 2 ($T_p - T_o$). $\Delta H$: enthalpy of gelatinization with the mean absolute error (three repetitions) of 0.5 J/g. DG: degree of gelatinization. nd: not determined.
Table 2. Pasting and rheological characteristics of native and D.I.C. treated starches at pressure of 1, 2 and 3 bar for two processing time.

<table>
<thead>
<tr>
<th>Starch source</th>
<th>D.I.C. treatment</th>
<th>Pasting properties</th>
<th>Rheological properties</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$T_o$(°C)</td>
<td>$T_p$(°C)</td>
</tr>
<tr>
<td>SMS$^a$</td>
<td>native</td>
<td>82.5</td>
<td>97.5</td>
</tr>
<tr>
<td></td>
<td>1 bar/90 min</td>
<td>82.5</td>
<td>97.5</td>
</tr>
<tr>
<td></td>
<td>2 bar/90 min</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>3 bar/10 min</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>WMS$^b$</td>
<td>native</td>
<td>72.5</td>
<td>83.0</td>
</tr>
<tr>
<td></td>
<td>1 bar/90 min</td>
<td>77.5</td>
<td>88.5</td>
</tr>
<tr>
<td></td>
<td>2 bar/90 min</td>
<td>82.0</td>
<td>90.0</td>
</tr>
<tr>
<td></td>
<td>3 bar/10 min</td>
<td>81.0</td>
<td>88.5</td>
</tr>
<tr>
<td>WTS$^c$</td>
<td>native</td>
<td>80.0</td>
<td>97.5</td>
</tr>
<tr>
<td></td>
<td>1 bar/90 min</td>
<td>77.5</td>
<td>97.5</td>
</tr>
<tr>
<td></td>
<td>2 bar/90 min</td>
<td>75.0</td>
<td>97.5</td>
</tr>
<tr>
<td></td>
<td>3 bar/10 min</td>
<td>70.0</td>
<td>97.5</td>
</tr>
</tbody>
</table>

$^a$ 6% (w/w) aqueous standard maize starch suspension; $^b$ 4% (w/w) aqueous waxy maize starch suspension; $^c$ 7% (w/w) aqueous wheat starch suspension; $T_o$: onset of the pasting temperature; $PV$, peak viscosity. $^d$ UB, Units Brabender. $\tau_0$ : yield stress; $K$ : consistency index; $n$ : flow behaviour index ($K$ and $n$ were determined from Herschel-Bulkley model); $\eta$: apparent viscosity measured for shear rate of 1s$^{-1}$. 

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Figure captions

Fig. 1. Differential scanning calorimetry curves of native and DIC treated standard maize (SMS), waxy maize (WMS) and wheat (WTS) starches at processing time of 90 and 10 min and pressure level of 1 (100°C), 2 (122°C) and 3 bar (135°C).

Fig. 2. TLC analysis of WMS hydrolysis. Native WMS after 20 min of Liquefaction (A), treated WMS at 3 bar/10 min after 20 min of Liquefaction (B), native WMS after 120 min of Liquefaction and 60 min of saccharification (C) treated WMS at 3 bar/10 min after 120 min of Liquefaction and 60 min of saccharification (D).

Fig. 3. Time course of several starches hydrolysis by AMG. WMS native (●), WMS treated by DIC at 3 bar/10 min (○), WTS native (■), WTS treated by DIC at 3 bar/10 min (□), SMS native (▲) and SMS treated by DIC at 3 bar/10 min (△).

Fig. 4. Brabender curves of native and DIC treated SMS, WMS and WTS.
Fig. 1

**SMS**

- Native
- 1 bar/90 min
- 2 bar/90 min
- 3 bar/10 min

**WMS**

- Native
- 1 bar/90 min
- 2 bar/90 min
- 3 bar/10 min

**WTS**

- Native
- 1 bar/90 min
- 2 bar/90 min
- 3 bar/10 min
Fig. 2

A B C D

glucose
maltose
Fig. 4

![Graph of Brabender Viscosity vs. Time and Temperature for SMS, WMS, and WTS samples under different conditions.]

- **SMS**: Shows a significant increase in Brabender Viscosity with temperature, indicating a possible gelation process.
- **WMS**: Exhibits a lower Brabender Viscosity compared to SMS, with a temperature effect also visible but less pronounced.
- **WTS**: Displays a distinct peak in Brabender Viscosity at a certain temperature, followed by a sharp decline, suggesting a phase transition.

The graphs are labeled with conditions such as 'Native', '1bar/90min', '2bar/90min', '3bar/10min', and 'Temperature', which help in understanding the experimental setup and results.