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Investigation on structural and physicochemical modifications of standard maize, waxy maize, wheat and potato starches after DIC treatment

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ABSTRACT

This study reports the impact of the Instantaneous Controlled Pressure Drop (DIC®) treatment on structural, thermal and functional properties of starches from four botanical origins (standard and waxy maize, wheat and potato, SMS, WMS, WTS and PTS respectively). The structural and functional properties of treated starches were studied using differential scanning calorimetry (DSC), wide-angle X-ray diffraction, optical microscopy and rheological measurements. For cereal starches the resulting modifications were almost identical: increase of the gelatinization temperature and decrease of the transition temperature range that were ascribed to enhanced stability (or size) and cohesion (or homogeneity) respectively of starch crystallites. Potato starch exhibited the reverse tendency according to its particular structural organisation. All the starches showed a reduction of the gelatinization enthalpy as the intensity of the processing conditions increased. The DIC® treatment seemed to cause total or partial melting of the less stable starch crystallites at low temperatures. As a result, the gelatinization temperatures (To and Tp) of the DIC-treated starches increased; this could be attributed to the melting of the most stable crystallites which needed higher temperature range. Microscopy observations confirmed the partial or total loss of birefringence of treated starch granules. Relative crystallinity decreased upon DIC® treatment with a larger impact on PTS that became amorphous at 2 bar/12 min. The transition for SMS and WTS from A to Vh-type X-ray diffraction pattern revealed the formation of amylose–lipid complexes induced by the treatment. The Brabender viscosity of cereal starches treated at low pressure and processing time was higher than the one of native starches and was clearly reduced for higher pressure levels. For PTS the Brabender viscosity dramatically decreased for all DIC® conditions. Rheological properties of treated starches showed the same tendency except the WTS, whose viscosity was reinforced by the hydrothermal treatment at 3 bar/0.5 min. The study showed that the different responses observed on treated starches were mainly influenced by DIC® processing conditions and by the botanical origin of the starches.

1. Introduction

Starch is one of the most important biopolymers in processed foods and has many diverse applications in non-food production. Its unique properties largely contribute to the structure and texture of processed products. Native starches require physical, chemical or enzymatic modifications for a wide range of applications, in order to meet the specific needs of industrial processes. Hydrothermal treatments (simultaneous action of heat and moisture) belong to physical modification and differ according to the temperature and moisture content experimented. The two major physical treatments largely cited by the literature that modify the physicochemical properties of starch, without destroying the granules are ANNealing (ANN) (Stute, 1992; Tester, Debon, & Sommerville, 2000; Tester & Morrison, 1990) and Heat Moisture Treatment (HMT) (Collado & Corke, 1999; Gunaratne & Corke, 2007; Gunaratne & Hoover, 2002; Hoover & Manuel, 1996; Jacobs et al., 1998; Kulp & Lorenz, 1981; Tester et al., 2000; Tukomane, Leerapongnum, Shobsngob, & Varavinit, 2007; Vermeylen, Goderis, & Delcour, 2006). These two treatments require different water content, temperature and time conditions.

ANN involves incubation of starch granules in excess of water (>60%, w/w) or at intermediate water content (40–55%, w/w) occurring over a large range of processing times (from 0.5 to 144 h, Jyakody & Hoover, 2008) at temperatures above the glass transition

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temperature (Tg) but below the onset (T_0) temperature of gelatinization (Hoover & Vansanthan, 1994a; Jacobs & Delcour, 1998; Tester et al., 2000). No changes in granule size and shape were found by most of the authors, but a modest molecular reorganization in the internal structure of starch granules (Hoover & Vansanthan, 1994b; Stute, 1992; Waduge, Hoover, Vasanthan, Gao, & Li, 2006). According to some authors, the molecular changes resulted in an increase of the granule stability (Hoover & Vansanthan, 1994a), or the formation of a more organized structure of lower free energy (Blanshard, 1987). The changes of the physicochemical properties of the starches were also analysed in terms of improved crystalline perfection of starch granules (Cooke & Gidley, 1992; Hublin, 1994; Jyakody & Hoover, 2008).

HMT occurs at higher temperatures (90–130 °C) and restricted moisture contents (18–30%, w/w) over processing times varying from 1 h (Lim, Chang, & Chung, 2001) to 16 h (Hoover & Manuel, 1996; Lorenz & Kulp, 1981) or more (16–24 h) (Chung, Hoover, & Liu, 2009; Lawal, 2005; Vermeylen et al., 2006). HMT is known to increase gelatinization temperatures and decrease granular swelling as for the ANN, regardless of the starch origin, but to broaden the gelatinization temperature range unlike ANN (Chung et al., 2009). Application of conventional HMT produce heterogeneous treated starch granules. Maruta et al. (1994) improved the diffusion of steam by the direct contact with the starch layer and by adding a vacuum pressure step before injection of live steam. This additional step intensified the heat and mass transfer into the starch granules. This method was designated by Maruta et al. (1994) as the Reduced Pressurized-Heat Moisture Treatment (RP-HMT). Stapley, Landman, Please, and Fryer (1999) confirmed by NMR imaging experiments, that the moisture content distributions of wheat grains steamed by direct contact are uniform.

DIC® (in french, Détente Instantanée Contrôlée; Instantaneous Controlled Pressure Drop treatment) developed at our laboratory (Maache-Rezzoug & Allaf, 2005; Rezzoug, Maache-Rezzoug, Mazoyer, & Allaf, 2000), is close to RP-HMT treatment. An initial vacuum is applied before the treatment which is performed under high temperature/high steam pressure. The hydrothermal treatment step is then followed by an abrupt pressure drop towards vacuum pressure, instead of slow depression towards atmospheric pressure as for the RP-HMT. This step induces a rapid cooling and the resulting temperature value depends on the vacuum pressure level (Zarguili, Maache-Rezzoug, Loisel, & Doublier, 2006). During the treatment, starch is heated 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, Maache-Rezzoug, Loisel, & Doublier, 2009). Preliminary study on SMS and WMS treated by DIC® at initial moisture content of 12% (Loisel, Maache-Rezzoug, Esneault, & Doublier, 2006), showed a partial gelatinization of treated sample attested by the decrease of the gelatinization enthalpy and the loss of the birefringence under polarized light, as the processing pressure and time increased. No disruption of the starch granules after the treatment could be observed, but the fluidity of the starch dispersions pasted in the Viscograph Brabender considerably increased. DSC and wide-angle X-ray diffraction (Maache-Rezzoug, Zarguili, Loisel, Queveau, & Buléon, 2008) revealed modifications of thermal and structural properties of SMS treated under three pressure levels 1, 2 and 3 bar: i.e. an increase of the gelatinization temperatures (T_o, T_p), a decrease of the gelatinization enthalpy (ΔH) and a narrowing of the gelatinization temperature range as the DIC® processing conditions increased. Loisel et al. (2006) already showed on DIC® treated maize starch, by using response surface methodology, that the steam pressure level and therefore the temperature had a more significant effect than the processing time. These modifications by DIC® treatment seem almost similar to the ones observed on HMT treated starches, except the narrowing of the gelatinization temperature range that was only observed with ANN (Jyakody & Hoover, 2008). It was suggested that the DIC® 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. Maache-Rezzoug et al. (2008) systematically observed the decrease of the relative crystallinity of SMS with increasing DIC® conditions: A-type crystalline pattern progressively vanished (at pressure level ≥2 bar) and was completely substituted, for higher conditions (pressure level of 3 bar), by the V_h-type diffraction pattern, corresponding to the formation of amylose–lipid complexes. These modifications of the crystalline organization of starch granules had consequences on the functional properties of starch suspensions. Maache-Rezzoug, Zarguili, Loisel, and Doublier (2010), showed changes of the cold swelling capacity with large differences depending on botanical origin: SMS being more prone to swell than WMS and WTS showing a dramatic increase at 3 bar for 5 min. For all starches, except for WTS, DIC® treatment yielded an increased fluidity of the pasted suspensions. These structural modifications of DIC® treated starch consequently enhanced their enzymatic hydrolysis (Maache-Rezzoug et al., 2009).

The aim of the present work was to study and to compare the structural, thermal and functional changes induced by DIC® treatment of four starches from different botanical origin: standard maize waxy maize, wheat and potato starches. In order to complete this comparative study, some results reported in this manuscript were already discussed in previous works (Maache-Rezzoug et al., 2009; Maache-Rezzoug et al., 2010; Maache-Rezzoug et al., 2008).

2. Materials and methods

2.1. Materials

Standard maize starch (SMS), waxy maize starch (WMS, Waxilys 200), wheat starch (WTS) and potato starch (PTS) were supplied by Roquette Frères (Lestrem, France). The amylose content was 27–28% for SMS and WTS, lower than 1% for WMS and 23% for PTS. To facilitate the comparison, all starches were conditioned before the treatment at moisture content of 12.5% (wet basis). The initial moisture content of PTS of 16.5% (wet basis) was reduced to 12.5% by air drying at 40 °C.

2.2. Methods

2.2.1. Moisture content

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; Zarguili et al., 2006). During the treatment, starch (12.5%) is placed in the processing vessel (12 L) at atmospheric pressure. An initial vacuum of 50 mbar is 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 bar) and maintained during a determined processing time (Zarguili et al., 2009). 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 and its moisture content is increased. The notation used in the text, for example 2 bar/60 min, means the

DIC® treatment was carried out at the pressure level of 2 bar during 60 min.

2.2.3. *Differential scanning calorimetry (DSC)*

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 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 ΔH 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, and Walke (1987). The residual enthalpy ratio (RE) of the treated starch was also calculated by the following equation $\mathrm{RE}\,(\%) = (\Delta H_t/\Delta H_{\mathrm{raw}}) \times 100$, where ΔH_t is the gelatinization enthalpy of the residual structure after DIC® treated starch and ΔH_{raw} the gelatinization enthalpy of the native starch.

2.2.4. *X-ray diffraction*

Native and DIC® hydrothermal treated starches were equilibrated at 95% relative humidity (RH) using a saturated barium chloride solution, 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 $K_{\alpha 1}$radiation ($\lambda = 0.154$ nm) was selected using a quartz monochromator. A curved position-sensitive detector CPS 120 was used to monitor diffracted intensities in the 0–120°, 2θ range. Diffraction diagrams were all normalised at the same total scattering value, with 2θ ranging from 3° to 30°. The crystallinity ratio was calculated according to the method of Wakelin (Wakelin, Virgin, & Crystal, 1959) using spherolitic crystals and dry extruded potato starch as crystalline and amorphous standards, respectively.

2.2.5. *Brabender viscograph*

DIC® treated starches were heated with demineralised water using a Brabender Viscograph. 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% (w/w) for SMS, WMS, WTS and PTS, respectively. Starch was slurried in demineralized water at room temperature, and 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. The starch concentration was checked by drying the suspensions as previously described (Section 2.2.1). The relevant values obtained from the pasting profile were: start pasting temperature (T_{0B}), temperature of peak viscosity (T_{PB}) and peak viscosity (PV) in Brabender units.

2.2.6. *Rheological measurements*

Flow behaviour 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°). An aliquot of the starch dispersion pasted in the Viscograph Brabender was poured onto the preheated plate of the rheometer at 60 °C, and then covered by a thin layer of paraffin oil on the edge of the sample to avoid evaporation. For flow measurements, an up-down shear scan from 0 to 660 s^{-1} (4 min) was linearly applied, followed by a logarithmic stepwise decrease from 660 to 0.01 s^{-1}, after equilibrium time for each shear rate.

The Herschel–Bulkley model was applied satisfactorily ($R^2 = 0.98$) from the equilibrium curves (not presented), according to the equation $\tau = \tau_0 + k\dot{\gamma}^n$, where τ is the shear stress (Pa), $\dot{\gamma}$ the shear rate (s^{-1}), τ_0 the yield stress (Pa), K the consistency index ($\mathrm{Pa\,s}^n$) and n is the flow behaviour index (dimensionless).

2.2.7. *Polarised light microscopy*

Dilute native and DIC® treated starches suspensions (1:20) were viewed under polarised light (magnifying 400×) using a Leica microscope equipped with a CCD camera.

3. Results and discussion

3.1. *Differential scanning calorimetry*

Table 1 summarizes DSC data of native and DIC® treated starches (curves not shown). The data clearly show the difference in the transition temperatures (T_o, T_p) and enthalpy of gelatinization (ΔH) between native starches. 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 complex, amylose chains, phosphorus content) and granular architecture (crystalline to amorphous ratio). The highest temperatures of T_o/T_p among native starches are observed for SMS and WMS (63.1/69.6 °C and 65.4/71.3 °C for SMS and WMS, respectively) while native PTS and WTS present lower temperatures of T_o/T_p, (57.7/61.6 °C and 50.4/56.6 °C for PTS and WTS, respectively). The temperature range (R) varied following the order: SMS > WTS > WMS > PTS. A wide temperature range has been ascribed, according to Fredriksson, Silverio, Andersson, Eliasson, and Aman (1998), to a large range of crystals stability. After DIC® treatment T_o and T_p increased with increasing pressure and processing time for all starches excepted for PTS. At pressure level of 2 bar (122 °C) and a processing time of 60 min, T_o/T_p shifted, from 63.1/69.6 °C (native SMS) to 69.4/74.2 °C, from 65.4/71.3 °C (native WMS) to 72.4/77.5 °C and from 50.4/56.6 °C (native WTS) to 62.3/66.4 °C. For PTS, T_o and T_p decreased after DIC® treatment, from 57.7/61.6 °C (native PTS) to 47.3/57.2 °C (1.5 bar/5 min). As PTS was most sensitive to treatment, the processing times associated to applied pressure levels were reduced in order to compare the thermal behaviour of starches. Similar increase in transition temperatures has been reported for HMT treatment of cereal and potato starches (Hoover & Manuel, 1996; Lim et al., 2001). Hoover and Manuel (1996) observed a large increase in transition temperatures of the gelatinization endotherm for standard maize and amylomaize starches, but a small increase in waxy and dull waxy maize starches. These authors attributed the change in transition temperature after HMT to the decrease in the destabilization effect of the amorphous regions on the melting of starch crystallites during gelatinization; this may be due mainly to the formation of amylose–lipid complexes (for SMS and WTS) and interactions between and among amylose chains, rather than to an increase of the crystalline stability. Their results differ from the ones obtained for DIC® treated WMS, for which transition temperatures clearly increased. Consequently, the second explanation may be preferred for WMS and possibly other starches, i.e. an increase of crystallite stability or size, which requires higher temperature to melt after DIC® treatment. Chung et al. (2009) came to the same conclusion for HMT treated SMS.

The temperature range R according to Hublin (1994) is inversely proportional to the degree of cohesion between crystallites; consequently a decrease of R reflects a stronger cohesion between crystallites related to their higher homogeneity (in size and stability). R clearly decreased with the intensity of treatment for cereal starches, whereas for PTS, R reached a maximal value (19.7 °C) at 1.5 bar/5 min and decreased to 5.2 °C at 3 bar/0.5 min. The gela-

Table 1
DSC and X-ray diffractometry characteristics[a] of native and DIC® treated starches at three pressure levels (1, 2 and 3 bar) for various processing time.

Starch/DIC® conditions	Gelatinization					X-ray diffractometry	
	T_o (°C)	T_p (°C)	R (°C)	ΔH (J/g)	RE (%)	Relative cristallinity (%)	X-ray pattern
SMS							
Native	63.1 ± 0.4	69.6 ± 0.5	13.0	11.4	100.0	31	A type
1 bar/60 min	69.4 ± 0.4	75.2 ± 0.6	11.6	9.1	79.8	30	A type
2 bar/60 min	69.4 ± 0.5	74.2 ± 0.5	9.6	9.0	78.9	22	A + V_h
3 bar/0.5 min	70.0 ± 0.8	74.8 ± 0.8	9.6	3.5	30.7	nd	V_h type
3 bar/10min	74.8 ± 0.9	79.8 ± 0.7	10.0	1.7	14.9	nd	V_h type
WMS							
Native	65.4 ± 0.9	71.3 ± 0.9	11.8	15.5	100.0	45	A type
1 bar/60 min	68.2 ± 1.1	73.7 ± 0.9	10.9	14.9	96.1	46	A type
2 bar/60 min	72.4 ± 1.2	77.5 ± 1.1	10.3	10.5	67.7	41	A type
3 bar/0.5 min	66.2 ± 0.2	71.8 ± 0.3	11.2	10.0	64.5	32	A type
3 bar/10min	75.2 ± 0.2	78.9 ± 0.3	7.5	2.1	13.5	10	A type
WTS							
Native	50.4 ± 0.2	56.6 ± 0.2	12.4	9.4	100.0	30.4	A type
1 bar/60 min	53.3 ± 0.7	58.5 ± 0.6	10.4	8.3	88.3	28.3	A type
2 bar/60 min	62.3 ± 0.7	66.4 ± 0.6	8.2	3.2	34.0	14.5	A type
3 bar/0.5 min	–	–	–	0.0	0.0	nd	V_h type
3 bar/10 min	–	–	–	0.0	0.0	nd	V_h type
PTS							
Native	57.7 ± 0.1	61.6 ± 0.1	7.8	14.5	100.0	25	B type
1 bar/30 min	52.0 ± 0.3	58.4 ± 0.3	12.8	8.5	58.6	11.5	B type
1.5 bar/5 min	47.3 ± 0.3	57.2 ± 0.3	19.7	3.8	26.2	6	B type
3 bar/0.5 min	55.3 ± 0.6	57.9 ± 0.7	5.2	1.6	11.0	0	Amorphe type

[a] T_o: onset temperature; T_p: peak temperature; R: temperature range, calculated as 2 ($T_p - T_o$). 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.

tinization temperature range of treated PTS was broader than the native PTS and other treated starches. This could result in an apparent decrease of T_o and T_p of treated PTS. Hoover and Vansanthan (1994b), Hoover and Manuel (1996) and Lim et al. (2001) noted a broadening of the temperature range for SMS, WTS and PTS and almost no change for WMS by HMT. The narrowing of the temperature range after DIC® treatment seems similar to the one observed by Stute (1992), Fredriksson et al. (1998) and Gunaratne and Hoover (2002) after ANN of PTS, suggesting that the treatment may have improved the homogeneity (in size or stability) of starch crystallites. The narrower temperature range exhibited by DIC® treated starches could be attributed to the fusion of crystallites of low cohesion and a reinforcement of the interactions between the remaining crystallites chains. Consequently, the residual structure after treatment might contain crystallites with a greater stability.

The gelatinization enthalpies (ΔH) of treated starches (Table 1) were largely dependent on the intensity of processing pressure and time. ΔH decreased progressively for all treated starches with increasing processing conditions, as can be observed from the residual enthalpy ratio (RE) with large differences between starches. At 1 bar the most sensitive starch was PTS. At intermediate conditions (2 bar/60 min), WTS exhibited a larger decrease of ΔH compared to SMS and WMS. The gelatinization was completed for WTS at 3 bar/0.5 min, whereas the RE was in the order WMS > SMS > PTS for the other starches. The higher sensitivity of PTS and WTS to DIC® treatment compared to SMS and WMS seemed to be due to the lower gelatinization temperatures of PTS and WTS. The predominant effect of the largest pressure level (3 bar) compared to the processing time had already been observed by Loisel et al. (2006). The gelatinization enthalpy represents the energy absorbed by the melting of the crystalline phase as well as by the swelling of the surrounding amorphous phase, which plays a destabilising effect on the crystallites (Hublin, 1994). According to Cooke and Gidley (1992) ΔH values represent the number of double helices that unravel and melt during gelatinization. The higher ΔH obtained for native PTS 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 (Gunaratne & Hoover, 2002). Consequently, the decrease of ΔH after DIC® treatment suggests that part of the double helices initially present in the crystalline and non-crystalline regions may have disrupted depending on the processing conditions.

HMT is shown to affect diversely the gelatinization enthalpies depending on the botanical origin of starches. For PTS, a decrease of ΔH is generally mentioned by all the authors (Gunaratne & Hoover, 2002; Lim et al., 2001; Vermeylen et al., 2006), while for cereals the effect of HMT vary with the conditions of the treatment. Hoover and Vansanthan (1994b) and Hoover and Manuel (1996) found no change for SMS, WMS and WTS treated by HMT at 100 °C/16 h and 30% of moisture content, whereas a decrease was observed for Lim et al. (2001) and Gunaratne and Corke (2007) for higher temperature (120 °C) and shorter time (1 h) at the same moisture content. The major role of moisture content (and temperature) has been underlined by Vermeylen et al. (2006) on PTS: increasing moisture content during HMT (from 17 to 26%) considerably reduced ΔH. The effect of water on hydrothermal treatment has been largely described in the literature: hydration of starch granule increases the mobility of the amorphous phase (the most vulnerable to water absorption) that in turn causes mobility of the crystalline domains and enhances the melting of crystallites upon treatment (Jyakody & Hoover, 2008).

The evolution of the moisture content of SMS during the DIC® treatment with pressure and processing time has been described by Zarguili et al. (2009), whereby the hydration is caused by the absorption of accumulated steam. The moisture contents at equilibrium are 15 and 20% (wet basis) at 1 bar (100 °C) and 2 bar (122 °C), reached after 30 and 60 min, respectively. At 3 bar the moisture content is 17% for 20 min of treatment. The equilibrium moisture content could not be measured for longer times at this pressure, due to the formation of compact lumps of starch. The different behaviour between SMS and WMS with the treatment can be attributed to their molecular composition, amylose being absent from WMS. It is well known that amylopectin is the support of the crystallites; then the effect of DIC® treatment

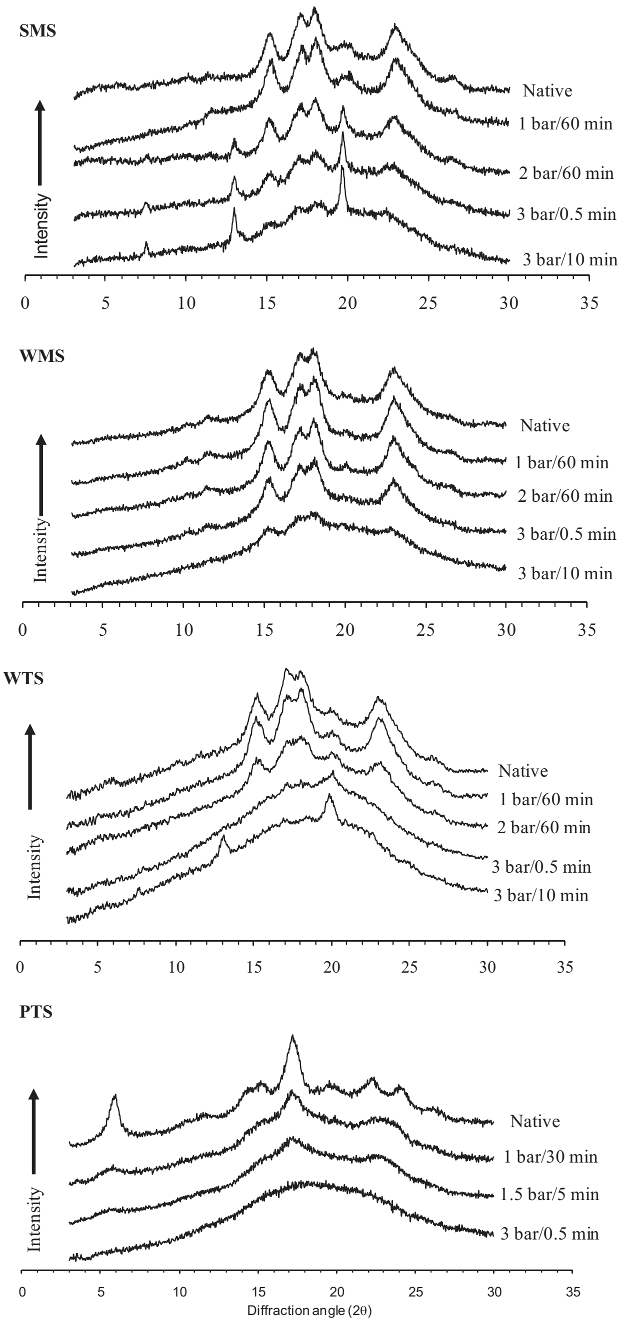

Fig. 1. X-ray diffraction patterns of native and DIC® treated SMS, WMS, WTS and PTS starches at different processing conditions.

has to be examined on the basis of the cristallinity pattern of starch.

3.2. X ray diffraction

Fig. 1 shows the X-ray diffraction patterns of native and DIC® treated SMS, WMS, PTS and WTS starches. The values of relative crystallinity and the type of X-ray pattern are presented in Table 1. Native SMS, WMS and WTS displayed the typical A-type X-ray diffraction pattern of cereal starches (Imberty, Buléon, Tran, & Perez, 1991; Zobel, 1964), characterized by diffraction peaks at: 15°, 17,1°, 18° and 23° (2θ), while PTS starch displayed a B-type diffraction pattern with peaks centered at: 5.6°, 15°, 17°, 22° and 24° (2θ). After treatment, the crystallinity of all starches decreased with increasing pressure and processing time, with differences according to botanical origin. At 1 bar, the relative crystallinity of the cereal starches was almost unchanged, whereas it decreased deeply for PTS; from 25% for the native one to 11.5 and 6% for samples treated at 1 bar/30 min and 1.5 bar/5 min, respectively. The B-type diffraction pattern of PTS was retained, but the peaks were attenuated with increasing conditions of the treatment. Beyond these conditions, the structure of PTS starch became amorphous. For cereal starches, the effect of DIC® treatment became significant at the pressure of 2 bar, for which the relative crystallinity started to decrease as well as the intensity of the peaks characterizing the A-type diffraction pattern. From this pressure, the crystalline X-ray diffraction pattern of the cereals developed differently according to their amylose content. For WMS, the A-type pattern was conserved, but the intensity of the peaks was reduced progressively from 2 bar/60 min to 3 bar/10 min along with the relative crystallinity varying from 41 to 10%, respectively. SMS and WTS on the contrary presented a change from A- to Vh-type with the emerging of new peaks at 7.5°, 13° and 19.5° (2θ) at 2 bar/60 min for SMS and 3 bar/0.5 min for WTS. SMS starch behaved differently from WTS as the A-type and the Vh-type diffraction patterns coexisted at 2 bar/60 min. At 3 bar/0.5 min the A-type diffraction pattern completely vanished to the benefit of the V_h-type for both starches. This X-ray diffraction pattern corresponds to the formation of amylose–lipid complexes during DIC® treatment. Evidence of this formation inside the starch granules was demonstrated in a previous study on SMS (Maache-Rezzoug et al., 2008) and can be also put forward for WTS.

HMT has been reported in the literature to decrease the overall crystallinity of starches. For PTS, several researchers found a transition from B- to A-type pattern (Hoover & Vasanthan, 1994; Stute, 1992; Vermeylen et al., 2006), while Lim et al. (2001) only observed a decrease in peak intensity on the diffractograms for the following conditions: 25 and 30% (moisture contents), 120 °C for 1 h. The DIC® conditions seem to have a stronger impact on the crystalline organisation of the PTS granules, leading to a complete disorganisation of the structure. Lim et al. (2001) observed on SMS HMT-treated that the A-type X-ray diffraction pattern was maintained, with a small decrease of the peak intensity of the X-ray diffractograms for the highest moisture content (30%) and Chung et al. (2009) observed a slight decrease of relative crystallinity (from 28.6 to 27.9%).

These results seem to reveal that the DIC® treatment modifies the starch organisation to a greater extent than HMT. The decrease of relative crystallinity considered along with the large reduction in gelatinization enthalpy could be attributed to the partial or complete (for PTS) disruption of amylopectin crystallites. The formation of amylose–lipid complexes has also been mentioned on HMT treatment of SMS (Hoover & Vansanthan, 1994b; Lim et al., 2001) and has been associated to a restriction of starch swelling.

3.3. Structural characteristics

The polarized light micrographs of DIC® treated SMS, WMS, WTS and PTS at 1 bar and 3 bar are presented in Fig. 2. The micrographs showed the persistence of the polarization cross related to the crystalline order, for SMS and WMS starches treated at 1 bar/60 min (Fig. 2a and b). For these starches, no change of the structure could be observed compared to the native starches (not shown), since their relative crystallinity remained almost constant (30% for SMS and 48% for WMS, Table 1). On the opposite, the polarisation crosses became less contrasted for WTS and particularly faded out for PTS according to the decrease of their relative crystallinity: from 30 to 28% for WTS and 25 to 11.5% for PTS, related to native and treated starch respectively. At 3 bar/10 min, the polarization cross almost disappeared for SMS and WTS (Fig. 2a′ and 2c′), completely vanished for PTS (Fig. 2d′), but remained still distinct for WMS (Fig. 2b′).

Table 2
Pasting and rheological properties of native and DIC® treated SMS, WMS, WTS and PTS at three pressure levels (1, 2 and 3 bar) for various processing time.

Starch source/DIC® conditions	Pasting properties			Rheological properties (60 °C)			
	T_{oB} (°C)	T_{PB} (°C)	PV (BU)[e]	τ_o (Pa)	K (Pa s^n)	n	η (mPa s) at 600 s^{-1}
SMS[a]							
Native	82.5	97.5	835	2.28	1.39	0.57	92.6
1 bar/60 min	82.5	97.5	920	0.68	0.72	0.58	50.1
2 bar/60 min	–	–	0	0.00	0.04	0.91	22.5
3 bar/0.5 min	–	–	0	0.00	0.02	0.93	12.8
3 bar/10 min	–	–	0	0.00	0.001	0.99	0.94
WMS[b]							
Native	72.5	83.0	640	0.70	0.88	0.53	44.7
1 bar/60 min	77.5	87.5	675	0.71	0.81	0.52	38.8
2 bar/60 min	82.0	90.0	448	0.31	0.26	0.62	23.4
3 bar/0.5 min	77.5	85.0	670	0.32	0.35	0.56	21.5
3 bar/10 min	81.0	88.5	490	0.17	0.27	0.59	19.9
WTS[c]							
Native	80.0	97.5	562	0.95	0.44	0.78	109.3
1 bar/60 min	80.0	97.5	600	0.87	0.75	0.70	111.5
2 bar/60 min	82.5	97.5	523	1.00	0.87	0.72	146.8
3 bar/0.5 min	85	97.5	570	1.48	2.85	0.57	184.5
3 bar/10 min	70	97.5	385	0.00	0.03	0.88	13.9
PTS[d]							
Native	67.5	97.5	705	0.77	1.28	0.57	83.1
1 bar/30 min	–	–	0	0.02	0.15	0.71	23.5
1.5 bar/5 min	–	–	0	0.00	0.02	0.89	9.9
3 bar/0.5 min	–	–	0	–	–	–	–

[a] 6% (w/w) aqueous SMS suspension; [b] 4% (w/w) aqueous WMS suspension; [c] 7% (w/w) aqueous WTS suspension; [d] 2% (w/w) aqueous PTS suspension. T_o: onset of the pasting temperature. T_p: temperature of peak viscosity. PV, peak viscosity. [e] UB, Units Brabender. τ_0: yield stress. K: consistency index. n: flow behaviour index (K and n were determined from Herschel–Bulkley model); η apparent viscosity measured at a shear rate of 600 s^{-1} at 60 °C.

These views confirmed that the loss of crystallinity upon DIC® treatment varied on a very different way according to the botanical origin of starches.

3.4. Pasting properties

Typical Brabender Viscograph curves of native and DIC® treated starches are shown in Fig. 3 and the pasting parameters are summarized in Table 2. It is difficult to compare the Brabender viscosities of starches, due to the differences in concentration of starch suspensions. WTS and WMS starches were less affected by DIC® treatment than SMS and PTS starches regarding the Brabender viscosities. The starch suspension of treated PTS was very fluid its Brabender viscosity could not be measured. This result is in agreement with previous studies on PTS treated by HMT (Hoover & Vansanthan, 1994b; Svegmark et al., 2002). For cereal starches, the peak viscosity (PV) of SMS, WMS and WTS increased for samples treated at 1 bar/60 min compared to the native ones (Table 2). At 3 bar/0.5 min, the Brabender viscosity remained the same as that of the native WMS and WTS, while there was no viscosity developed from SMS suspension (nor for pressures larger than 1 bar); this may be explained by the disruption of starch granules leading to extremely fluid suspensions. At 2 bar/60 min and 3 bar/10 min, PV decreased for WMS from 640 BU (native) to 448 and 490 BU, respectively. For WTS, under the same conditions, PV decreased from 562 BU (native) to 523 and 385 BU, respectively. WTS exhibited, at 3 bar/10 min, higher viscosity than the native one, before and upon heating in Brabender, with a viscosity of about 170 BU in cold water; this was explained by the swelling of pregelatinized WTS, induced by the treatment.

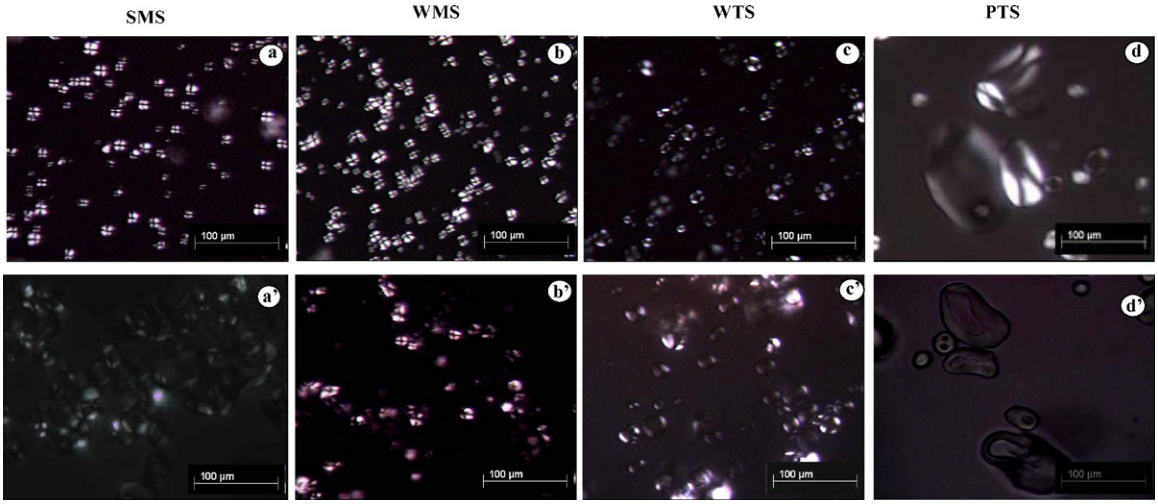

Fig. 2. Microscopic observations in polarized light of DIC® treated SMS (a and a′), WMS (b and b′) and WTS (c and c′) at 1 bar/60 min and 3 bar/10 min, respectively, and PTS treated at 1 bar/30 min (d) and 3 bar/0.5 min (d′).

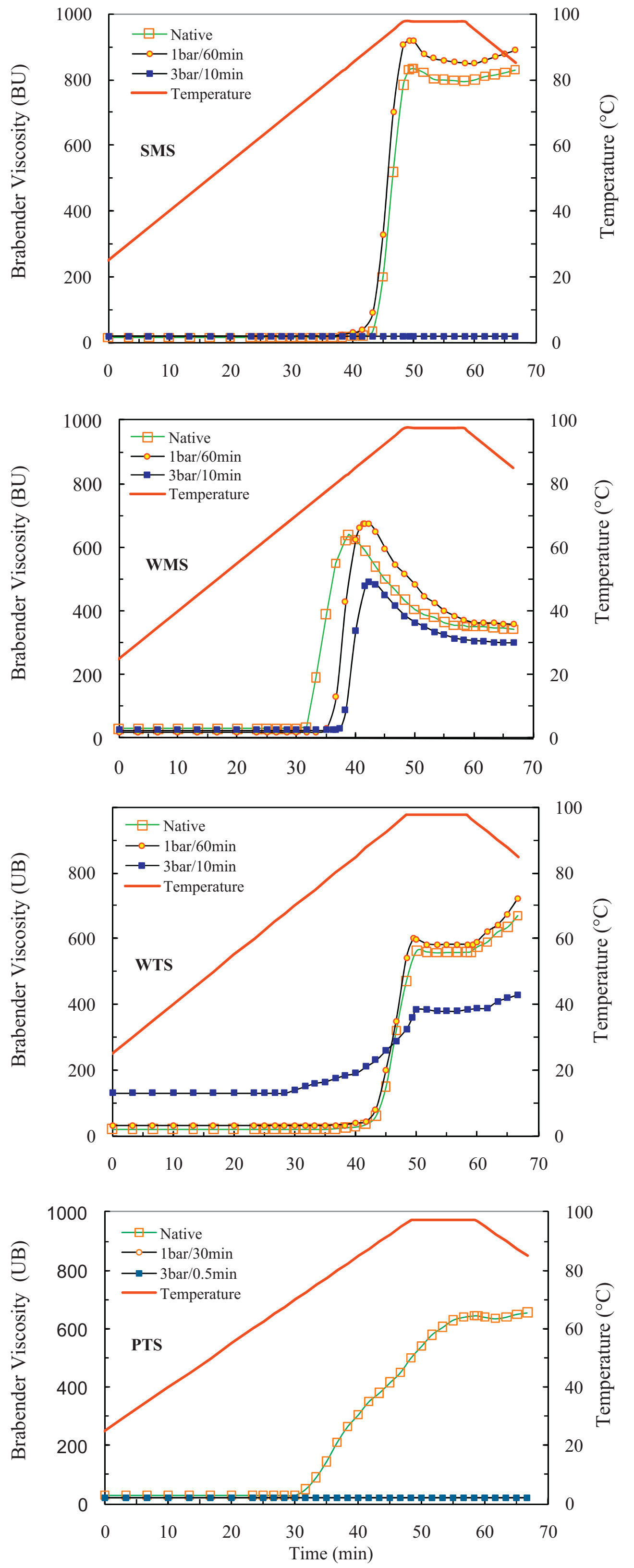

Fig. 3. Brabender curves of native and DIC® treated SMS (a), WMS (b), WTS (c) and PTS (d) starches at different processing conditions.

Concerning the pasting temperatures (T_{OB} and T_{PB}), no change was observed for SMS treated at 1 bar, in contrast to WMS, for which T_{OB} and T_{PB} increased with the intensity of processing pressure and time. T_{PB} for WTS, was not modified by the treatment, while T_{OB} increased at 2 bar/60 min and 3 bar/0.5 min, and then decreased at 3 bar/10 min. Many authors have observed an increase of the pasting temperatures after HMT treatment and a reduction of the peak viscosity for standard maize, amylomaize (Hoover & Manuel, 1996), potato (Hoover & Vansanthan, 1994b; Kulp & Lorenz, 1981), lentil, oat (Hoover & Vansanthan, 1994b) and cassava starches (Abraham, 1993). However, pasting properties of waxy maize starch seemed to be unaffected by HMT (Hoover & Manuel, 1996). According to the literature for cereal starches, the decrease of viscosity could be explained by a decrease of the swelling factor of starch granules (expressed as the volume of swollen granules reported to the volume of dry starch after pasting) due to enhancement of inter and intramolecular hydrogen bonds between the amylose chains and the formation of amylose–lipid complex after HMT treatment.

As a conclusion, we observed for DIC® treatment, an increase of the Brabender viscosity for cereal starches at 1 bar, probably related to enhanced swelling of starch granules; for higher conditions, SMS was fluidized, while the viscosity progressively decreased with the processing time and pressure for WMS and WTS. At 3 bar/0.5 min, the Brabender behaviour was almost unchanged compared to native starches for these two starches, indicating the predominant effect of the time over pressure in that particular case. These overall results seem to indicate that DIC® treatment affected the viscosity of starch suspensions more than the usual HMT. WTS revealed an outstanding behaviour that was noted by Hoover and Vansanthan (1994b): these authors found an increase of the Brabender viscosity under mild HMT treatment (100 °C, 16 h, 30% moisture content) for WTS, which seems to agree with our results, although no cold swelling could be detected.

3.5. Rheological properties

Fig. 4 presents the flow curves measured at 60 °C of starch suspensions of native and DIC® treated SMS and WTS (flow curves of WMS and PTS are presented in Maache-Rezzoug et al., 2010). The flow curves present a non-Newtonian shear thinning behaviour with or without a yield stress, as described by Doublier (1981), except the ones treated at 2 bar/60 min and 3 bar/10 min for SMS, 3 bar/10 min for WTS and at 1.5 bar/5 min for PTS (Maache-Rezzoug et al., 2010), which tend to a Newtonian behaviour. We observed the persistence of the thixotropic behaviour of starch suspensions, which may result from a disruption of starch granules aggregates under shearing, except for Newtonian suspensions.

The rheological parameters according to Herschel–Bulkley or power law model (with or without yield stress, respectively) are presented in Table 2. A progressive decrease could be noted of yield stress (τ_0) and consistency index (K) as pressure and time increase, except for WTS for which these parameters clearly increased at 2 bar/60 min and 3 bar/0.5 min. No yield stress was obtained for DIC® treated PTS because of its low consistency, as for SMS treated at 2 and 3 bar and for WTS at 3 bar/10 min. The apparent viscosity (η) of starch suspensions, measured at a shear rate of 600 s^{-1}, highlighted the effect of DIC® conditions on the rheological properties of starch suspensions: i.e. a decrease of viscosity for SMS and WMS for higher conditions, with a greater susceptibility for SMS and a complete fluidification for PTS. These results confirm the low viscosities obtained by Brabender Viscograph in these conditions. WTS had a specific behaviour, showing a great viscosity at 2 bar/60 min and 3 bar/0.5 min after pasting. According to Doublier, Llamas, and Le Meur (1987), the starch suspensions are made of three fractions: (a) soluble macromolecules (amylose), (b) finely dispersed particles (amylopectin) obtained after

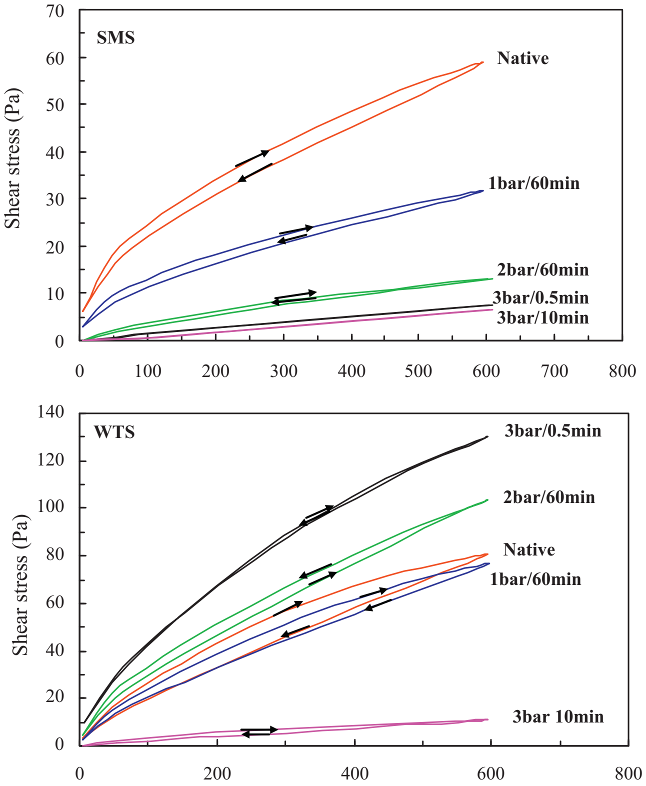

Fig. 4. Flow curves of native and DIC® treated starches dispersions measured at 60 °C after pasting in Viscograph Brabender, with starch concentration of 6 and 7% for SMS and WTS, respectively.

disruption of swollen starch granules as a result of heating and shearing, and (c) solid particles corresponding to complete or fragments of swollen granules. The rheological behaviour of starch suspensions is known to be the result of two major characteristics: the viscosity of the continuous phase composed mostly of amylose, and the volume fraction of the dispersed phase. In the range of concentrations used in this work, the volume fraction is near the unity: the suspension can then be described as a packing of swollen starch granules, the overall behaviour being governed by the dispersed phase, as no gelification of the amylose occurs at the measurement temperature (60 °C) (Doublier et al., 1987). In previous studies, some authorss (Doublier et al., 1987; Tester et al., 2000), observed that the ratio amylose/amylopectin plays an important role in the process of swelling of cereal starch granules, concluding that the higher the percentage of amylopectin, the more the starch granules tend to swell; the combination with amylose making the starch granules more resistant to this phenomenon. González-Reyes, Méndez-Montealvo, Solorza-Feria, Toro-Vazquez, and Bello-Pérez (2003) also showed that starches presenting higher crystallinity level are more prone to swell. The fluidization of starch suspensions, but mostly SMS and PTS, under DIC® treatment, could then be related to a decrease of the volume fraction of starch granules, as a result of their rupture; WMS and WTS granules being more resistant to this phenomenon.

4. Summary and conclusion

The objective of this work was to study and to compare the modification of structural, thermal and functional characteristics under DIC® treatment of starches from four botanical origins: standard maize (SMS), waxy maize (WMS) wheat (WTS) and potato (PTS) starches. The DIC® treatment seemed to cause partial or complete gelatinization of the studied starches, due to the melting of the less stable crystalline structure. As a result, the gelatinization temperatures (T_o and T_p) of the most stable crystalline remnants were increased. This effect is different from the ANN and HMT for which the heat treatment is carried out at temperatures below the gelatinization temperature of starch, and the increase in the gelatinization temperature is due to the rearrangement of starch crystallites. The modifications of the crystalline structure are enhanced by temperature and moisture content encountered during the DIC® treatment (related to pressure and time of treatment). We observed for SMS and WTS the formation of amylose–lipid complexes at 2 bar/60 min and 3 bar/0.5 min, respectively, without any leaching of amylose. These structural modifications contributed to an increase of the pasting temperatures, measured by the Brabender Viscograph, especially for WMS, that seemed to be the most resistant starch. The viscosity of WTS suspensions increased at 2 bar/60 min and 3 bar/0.5 min compared to the native one, but considerably decreased for longer time of the treatment, as for the other starches. An outstanding cold-swelling behaviour was found for WTS at 3 bar/10 min. On the contrary, the viscosity of PTS was dramatically reduced even at low pressures. The DIC® treatment affected the functional properties of starches on a different way from the HMT treatment described in the literature, and with variable consequences according to the time and pressure conditions and the botanical origin of starch.

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