Carbohydrate Polymers 89 (2012) 810–820

Contents lists available at SciVerse ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Role of vacuum steps added before and after steaming treatment of maize starch. Impact on pasting, morphological and rheological properties

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ARTICLE INFO

Article history:
Received 15 January 2012
Received in revised form 13 March 2012
Accepted 5 April 2012
Available online 13 April 2012

Keywords:
Maize starch
Hydrothermal treatments
Vacuum
Granular characteristics
Rheological properties

ABSTRACT

Standard maize starch (SMS) was hydrothermally treated by three processes; DV-HMT (Direct Vapor-Heat Moisture Treatment), RP-HMT (Reduced-Pressurized Heat Moisture Treatment) and DIC (in French: *Détente Instantanée Contrôlée*, instantaneous controlled pressure drop). Impact of processes were studied in order to determine the role of added steps of vacuum before and after treatment of starch by live steam at different pressures (1, 1.5, 2, 2.5 and 3 bar) on morphological, pasting (Brabender) and rheological properties of SMS suspension. The three treatments tend to modify the physical properties of starch on the same way, but the extent of these modifications depends on the process and on the level presure applied. The intensity of modifications follows this order: DIC > RP-HMT > DV-HMT. This was attributed to the presence of the initial vacuum step (DIC and RP-HMT) which intensified the transfer phenomena and to the mechanical effect induced by the abrupt decompression towards vacuum (DIC) leading to weakness of starch granules. The treatments changed the shape and distribution size of granules. The sizes were shifted towards higher values after the treatment due both to the improvement of swelling capacity of granules and to the presence of agglomerates particles of different sizes as confirmed by scanning electron microscopy. The agglomerates glued together by gelatinized granules were favored by the direct contact of starch with steam during the treatments. The results showed for all treatments, a reduction of the consistency coefficient (k) and of the yield stress (τ_0) of starch suspensions with increasing of process intensity. For severe conditions (3 bar), no difference between the treatments was observed; a complete fluidization of starch suspensions (the consistencies were too weak to be detected), τ_0 vanished and the rheological behavior tended to a Newtonian type. Elastic modulus (G'), measured during gelation at 25 °C, decreased dramatically ($G' < 1$ Pa), that revealed the loss of rigidity and disappearance of granular integrity of starch.

1. Introduction

Starch is a renewable biopolymer and one of the most abundant carbohydrates reserve. This biopolymer is used in various industries fields e.g. pharmaceutical, textile, biomass energy, chemical process engineering and especially in food industry. The specific characteristics of starch are of interest for its great nutritional value and thickening properties. Most of applications need hydrothermal transformation to be applied first.

The two hydrothermal treatments largely studied are annealing and Heat-Moisture Treatment (HMT) which modify the physicochemical properties of starch without destroying the granular structure. Annealing involves incubation of starch granules in excess or intermediate water content at a temperature below the onset of gelatinization ranging from 40 to 60 °C (Jacobs & Delcour, 1998). For HMT treatment, starch is exposed to temperatures commonly above the gelatinization temperature (≈120 °C), at very restricted moisture content (18–30%) during 16 hours (Hoover & Manuel, 1996; Lorenz & Kulp, 1981) or shorter (Collado & Corke, 1999; Lim, Chang, & Chung, 2001). HMT starches have generally been performed at the laboratory scale and many authors have reported that such conditions produce inhomogeneous samples. Maruta et al. (1994) observed, for HMT treatment, that pressure is required to ensure an homogeneous diffusion of steam and an effective heat transfer surrounding starch granules. The authors improved the conventional HMT method by introduction of reduced pressure in order to satisfy practical requirements for industrial production. They observed that the combination of

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http://dx.doi.org/10.1016/j.carbpol.2012.04.015

reduced pressure during HMT of starch improved the diffusion of steam and allowed more effective heat transfer.

In this study, we compared three hydrothermal treatments applied to standard maize starch, for which starch powder is directly heated by contact with saturated steam under pressure. The interest of the direct contact between steam and starch is not only the intensification of heat transfer phenomenon but also the transfer of water. The studied hydrothermal treatments were referred as DV-HMT, RP-HMT and DIC. Direct Vapor-Heat Moisture Treatment, termed as DV-HMT treatment by our team in order to differentiate it from the classical methods, consists in heating up the starch powder by saturated steam injected from atmospheric pressure up to processing pressure level. This treatment belongs to HMT according to the definition of Sair & Fetzer (1944): the treatment occurs at low moisture levels (<35%) above the gelatinization temperatures (84–130 °C) and a fixed time (20 min). Contrary to DV-HMT, the Reduced-Pressurized Heat-Moisture-Treatment, designated as RP-HMT by Maruta et al. (1994), is based on an additional step consisting in establishing a vacuum pressure before injection of live steam. The initial vacuum of 50 mbar before injection of steam to high pressure reduces the resistance of the air, and consequently facilitates the diffusion of steam into the product (Bahrani, Loisel, Monteau, Rezzoug, & Maache-Rezzoug, 2011; Zarguili, Maache-Rezzoug, Loisel, & Doublier, 2006). The third treatment, referred as the instantaneous controlled pressure drop treatment (DIC) contains an initial vacuum step as for RP-HMT (Rezzoug, Maache-Rezzoug, Mazoyer, Jeannin, & Allaf, 2000) and an abrupt decompression towards a vacuum, instead of atmospheric pressure as for DV-HMT and RP-HMT. The abrupt decompression induces a rapid modification of the thermodynamic equilibrium reached during the pressurization (P_1, T_1) towards another equilibrium state (P_2, T_2). This transition induces a rapid cooling of material and the resulting temperature value depends on the vacuum pressure level.

Maache-Rezzoug, Zarguili, Loisel, Queveau, and Buléon (2008) observed that the DIC treatment causes structural changes of starch and subsequent changes in the physicochemical properties according to the processing conditions. The major effects observed after treatment are almost similar to classical HMT treatment except that the gelatinization temperature range is narrowed, as observed with annealing (Hublin, 1994; Jayakody & Hoover, 2008). This result suggests that the treatment firstly induced the melting of crystallites of low cohesion (or low stability) which required less energy to melt. Consequently, the residual structure after DIC treatment contained crystallites with a greater stability (or cohesion). Preliminary studies on standard and waxy maize starch (Loisel, Maache-Rezzoug, Esneault, & Doublier, 2006; Zarguili et al., 2006) showed that the thermal properties of DIC treated starch depend on the processing time and the steam pressure level. Increasing of these two parameters induced an increase in the onset (T_{onset}) and in the peak temperature (T_{peak},) of gelatinization as well as a reduction of enthalpy of gelatinization. The occurrence of a partial or total gelatinization was clearly attested by the decrease of enthalpy and a loss of birefringence under polarized light. Maache-Rezzoug et al. (2008) observed a systematic decreasing of the relative crystallinity, measured by X-ray diffractometry, of SMS with increasing DIC conditions: A-type crystalline pattern progressively vanished (at pressure level ≥2 bar) and was completely substituted, for severe 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 some modifications of the cold swelling capacity with large differences depending on the botanical origin: SMS being more prone to swell than waxy maize starch and wheat starch, showing a dramatic increase at 3 bar pressure level and 5 min processing time. For all starches, except for wheat, DIC treatment yielded an increased fluidity of pasted suspensions. These structural modifications could explain an enhancement of their enzymatic hydrolysis (Maache-Rezzoug et al., 2009).

The aim of this work was to study the morphological, rheological and pasting properties of SMS hydrothermally treated by DV-HMT, RP-HMT and DIC. The impact of such processes was analyzed in order to determine the role of the added steps of vacuum pressure before and after steam treatment, at different pressure levels and at fixed time. In this study, the extent of modifications induced by the three treatments on granule size distribution, pasting properties, flow and viscoelastic behaviors of suspensions were described.

2. Materials and methods

2.1. Raw material

SMS at moisture content of 14% (dry basis) was supplied by Roquette Frères (Lestrem, France).

2.2. Experimental equipment

The experimental setup is composed from: a processing reactor, where the product was treated at high temperature/high steam pressure, a vacuum system which comprises mainly a stainless steel vacuum, a vacuum pump, and a steam generator supplying steam into the reactor (Bahrani et al., 2011).

2.3. Hydrothermal treatments

The hydrothermal treatments, previously described by Bahrani et al. (2011) were performed at a pilot scale during a fixed processing pressure and time of 20 min. SMS powder (5 mm thickness) was placed in an aluminum rectangular container, in the processing reactor at residual moisture content, no hydration step is required (Bahrani et al., 2011; Zarguili et al., 2006), contrary to conventional methods (annealing and HMT) where a hydration step before the treatment is necessary. Five pressure levels were investigated: 1, 1.5, 2, 2.5 and 3 bar, corresponding to saturated steam temperatures of 100, 111, 120, 127 and 133 °C, respectively. For the studied hydrothermal treatments, the principal heating source of starch results from the transfer of steam latent heat of condensation into the starch granules. The starch temperature rises from room temperature to steam equilibrium temperature. The higher the difference in temperature, the higher the quantity of condensed water, which causes an increase of starch moisture content (Zarguili, 2006).

For DV-HMT, saturated steam was injected from atmospheric pressure up to processing pressure level, while for RP-HMT, a reduced pressure was created in the reactor before injection of live steam. As for RP-HMT, an initial vacuum phase is also present for DIC process. The abrupt decompression after heat treatment is performed towards vacuum pressure (50 mbar) for DIC and towards atmospheric pressure for RP-HMT. The presence of initial vacuum pressure for RP-HMT and DIC treatments contribute to accelerate the transfer phenomenon associated with simultaneous heat and mass transfer in the material. Time to reach the equilibrium temperatures of saturated steam was reduced; it was of 41, 33 and 20 s for RP-HMT and DIC processes while it was of 480, 359 and 209 s for DV-HMT, to reach 100 °C (1 bar), 111 °C (1.5 bar) and 120 °C (2 bar), respectively. This significant reduction (10 times) reflects the intensification of heat transfer phenomenon for RP-HMT and DIC processes. According to the processing conditions (initial vacuum, temperature or pressure level), the amount of absorbed water increases rapidly up to equilibrium value of moisture content (Zarguili, Maache-Rezzoug, Loisel, & Doublier, 2009): 0.19, 0.2

and 0.24 (g H_2O/g db) for RP-HMT and DIC and 0.18, 0.19 and 0.2 (g H_2O/g db) for DV-HMT at 100, 110 and 120 °C, respectively.

2.4. Granule size distribution

Granule size distribution was measured at room temperature using a Malvern Master Sizer (Malvern Instruments, Ltd) laser scattering analyser with a 300 mm Fourier cell (range 0.05–879 μm). The pasted starch were diluted (1/10) with demineralized water at 20 °C then dispersed into the sample dispersion unit (1 ml/100 ml water). The volume distribution was obtained according to the Mie scattering theory (Loisel et al., 2006). From each distribution, the median volume diameter ($D_{v,0.5}$) was presented and the swelling ratio was defined as $(D/D_0)^3$, with D and D_0 the median diameters of treated and native starch, respectively.

2.5. Scanning electron microscopy (SEM)

The morphology of the native and treated starch granules was analyzed using a field emission scanning electron microscope (Joel JSM-6400, Japan). A small quantity of each sample was spread directly on double-sided adhesive tape attached to a circular aluminum stub and then were coated with gold under vacuum. The samples were viewed and photographed with a magnification of 500× and 200×.

2.6. Pasting properties

A Brabender Viscograph was employed to measure the pasting properties of starch (6%, w/w). The treated and native starch was slurried in demineralized water at room temperature, then heated from 30 to 96 °C at 1.5 °C min^{-1}, held at 96 °C for 10 min, then cooled at 1.5 °C min^{-1} to 70 °C. Peak viscosity in Brabender units (PV), pasting temperature (T_0), peak temperature (T_P) and the breakdown (BD) corresponding to the difference between peak viscosity and minimum paste viscosity after holding at the maximum temperature, were determined from pasting curves.

2.7. Rheological measurements

Flow behavior and viscoelastic properties of starch pastes were characterized using the cone/plate geometry (6 cm/2°) and all measurements were carried out in a stress-controlled rheometer (TA Instrument AR1000). The starch dispersions at 60 °C were poured onto the preheated plate of the rheometer and covered by a thin layer of paraffin oil on the edge of the sample to prevent from evaporation. Steady shear tests were carried out with two consecutive up-down shear scans from 0 to 600 s^{-1}, followed by a logarithmic descent from 600 to 0.1 s^{-1}, after equilibrium for each shear rate. This last (descending) step was used for describing the fluid behavior.

The dynamic oscillatory tests were carried out at 4% strain (linear viscoelastic range) on a new aliquot, with the following sequence: a mechanical spectrum at 60 °C, then a quenching to 25 °C, followed by a time dependent measurement of the viscoelastic behavior during 10 h at 6.28 rad s^{-1}. The frequency range investigated was from 0.5 to 100 rad s^{-1}.

3. Results and discussion

3.1. Granule size distribution

The size distribution of maize starch granules treated by DV-HMT, RP-HMT and DIC were carried out before (Fig. 1A–C) and after pasting in Brabender Viscograph (Fig. 1A′–C′). The native starch presents a narrow size distribution from 4 to 35 μm with a median diameter in volume ($D_{v,0.5}$) of 13.7 μm (Table 1). Maache-Rezzoug et al. (2010) have reported a similar value for untreated maize starch (12.9 μm) with the same tendency of granule size distribution curve. The size distributions of treated starch before pasting were shifted towards higher sizes with increasing of processing conditions. The enlargement of the distribution follows this order; DV-HMT < RP-HMT < DIC treatment. This enlargement is partially due to the improvement of swelling capacity of starch granules induced by the hydrothermal treatment and to the presence of agglomerates particles which can be explained by the third peak at approximately 300 μm in the distribution curves. Herrera-Gómez, Canónico-Franco, and Ramos (2002) showed defined peaks and shoulders particle size distribution curves of maize starch cooked in limited amount of water, suggesting the existence of a set of aggregate size classes.

A progressive increase of $D_{v,0.5}$ was observed with increasing of processing pressure: $D_{v,0.5}$ varies from 15.5 to 21.7 μm for treated starch by DV-HMT at 1 and 2.5 bar, from 15.90 to 17.7 μm and from 16.3 to 22.7 μm for treated starch by RP-HMT and DIC at 1 and 2 bar, respectively. The values of $D_{v,0.5}$ and the shape of the size distribution curves at 3 bar for DV-HMT and from 2.5 bar for RP-HMT and DIC (Table 1 and Fig. 1, before pasting), confirmed the presence of aggregates particles formed at strong processing conditions. The mechanism of aggregates formation of maize starch granules during cooking with limited amount of water was studied by Herrera-Gómez, Canónico-Franco, and Ramos (2005). The authors showed that these limited conditions induced formation of aggregates of different sizes which are held together by gelatinized granules that show no Maltese cross. During the three treatments, increasing of pressure level has as consequence the partial or total fusion of starch granules (calorimetric results not showed).

Maache-Rezzoug et al. (2008) showed a partial or total gelatinization of SMS treated by DIC, attested by the decreasing of gelatinization enthalpy and the loss of birefringence under polarized light, as the processing pressure and time increased. The extent of gelatinization also depends on the moisture content of starch granules during the treatment. Water tends to reinforce the mobility of amylose chains, thus promoting the destabilization effect of the amorphous region. The number of melted granules had a direct impact on the size of formed aggregates. At low pressure levels (lower or equal to 2 bar) the fraction of gelatinized granules is low and small aggregates can be formed. As the fraction of gelatinized granules is low, consequently the number of particles glued to the gelatinized granules is limited. Beyond 2 bar, the gelatinized fraction increases and more complex aggregates can be formed, especially for starch treated by DIC at 3 bar, where a total fusion of granules was observed.

Scanning electron micrographs of native and treated SMS at pressure of 1.5 and 3 bar (Fig. 2) showed spherical granules with regular shape for native granules (Fig. 2A). SMS treated by DV-HMT (Fig. 2B), RP-HMT (Fig. 2C) and DIC (Fig. 2D) at 1.5 bar also exhibited an individual spherical granules or irregular form, mainly for DIC treatment. According to Herrera-Gómez et al. (2002) the spherical shape suggests that the granule is not gelatinized while an irregular shape indicates that the granule has been gelatinized, at least partially. Fig. 2B′, Fig. 2C′ and Fig. 2D′, corresponding to starch treated at 3 bar by DV-HMT, RP-HMT and DIC, respectively, showed aggregates with different sizes formed by particles of irregular shape. The largest aggregates were observed for DIC treated starch.

Herrera-Gómez et al. (2005) defined 5 aggregate classes depending on the cooking degree of maize starch. According to this classification, class 1 corresponds to a fully gelatinized granule surrounded only by a limited number of partially or non-gelatinized granules. Class 2 is composed of aggregates of larger sizes which correspond to class 1 aggregates glued together. Beyond this class, the number of gelatinized granules increases. Class 4, is defined by

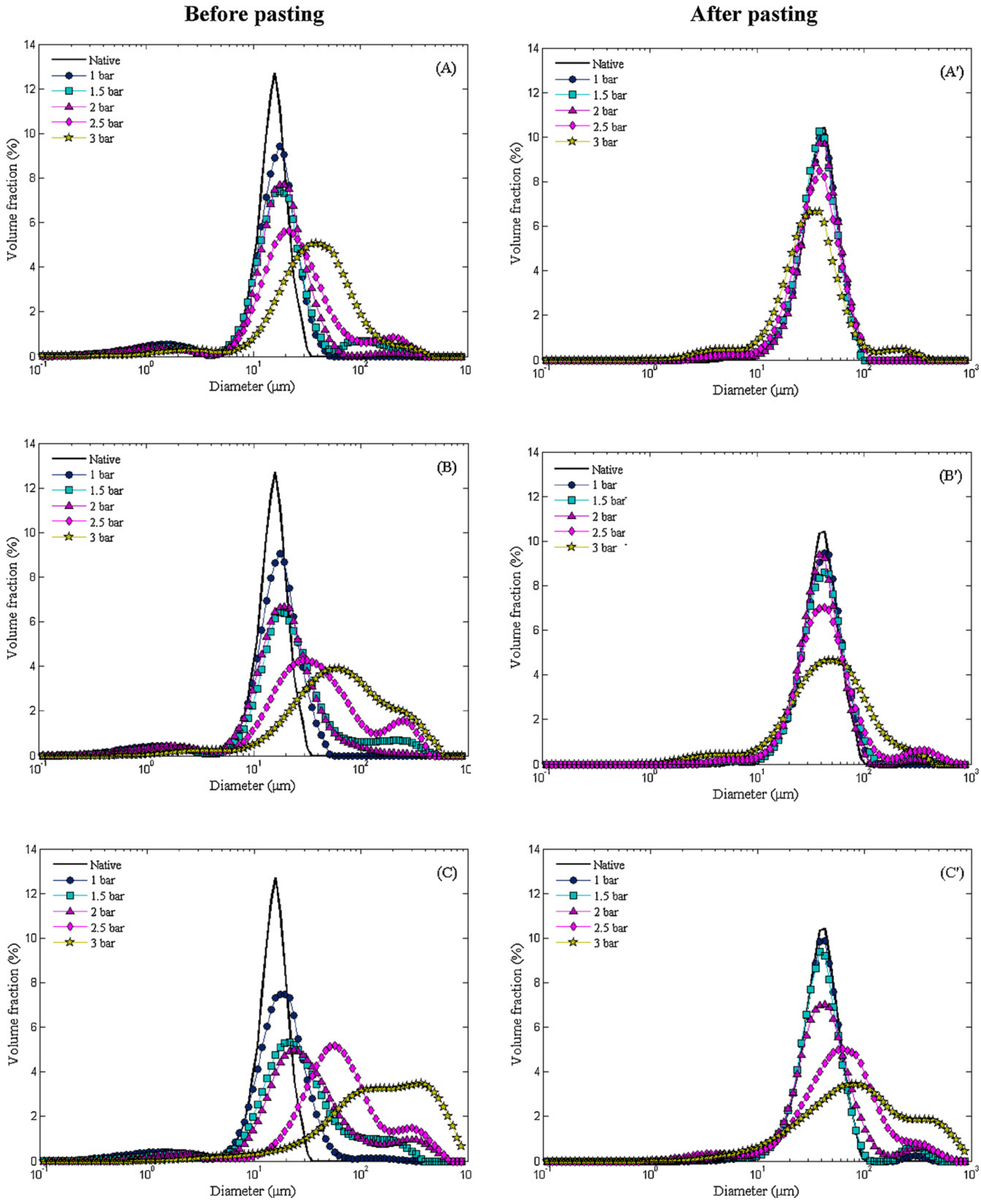

Fig. 1. Size distribution of native and DV-HMT, RP-HMT and DIC treated SMS before (A, B and C) and after (A′, B′, C′) pasting in the Brabender Viscograph, respectively.

aggregates ranging between 70 and 220 μm formed by granules completely gelatinized. According to this classification, the presence of the single particles at low conditions as for the native starch (Table 1 and Fig. 2), correspond to class 0. At intermediate and high conditions for DV-HMT (2.5 and 3 bar) and intermediate for RP-HMT (2.5 bar) and DIC (2 bar) the starch treated can be classified in class 1 aggregates. The granules treated by RP-HMT and DIC at 3 and 2.5 bar, respectively, are formed by aggregates of larger sizes, corresponding to class 2. The starch treated by DIC at 3 bar consists of aggregates representative of class 4.

The granule size measurements after pasting by Brabender showed that the treated starch slightly affected by the

Table 1
Brabender and particle size characteristics of native, DV-HMT, RP-HMT and DIC treated SMS.

Sample	Particle size analysis				Pasting properties			
	Before pasting		After pasting		T_0 (°C)	T_P (°C)	PV (BU)	BD (BU)
	$D_{v,0.5}$ (μm)	$(D/D_0)^3$	$D_{v,0.5}$ (μm)	$(D/D_0)^3$				
Native	$13.73^{\pm 1.10}$	1.00	$36.16^{\pm 0.13}$	1	$81.6^{\pm 0.4}$	$94.1^{\pm 0.06}$	$888^{\pm 8.4}$	$208^{\pm 1.1}$
DV-HMT								
1 bar	$15.50^{\pm 0.07}$	1.44	$36.81^{\pm 0.06}$	1.05	84.8	94.80	918	168
1.5 bar	$16.47^{\pm 0.06}$	1.73	$35.50^{\pm 0.31}$	0.95	86.0	95.80	738	98
2 bar	$16.88^{\pm 0.12}$	1.86	$36.60^{\pm 0.07}$	1.04	87.0	96.00	555	57
2.5 bar	$21.70^{\pm 0.16}$	3.95	$34.84^{\pm 0.50}$	0.89	87.5	97.50	212	–
3 bar	$36.20^{\pm 0.45}$	18.33	$29.50^{\pm 0.83}$	0.54	–	–	30	–
RP-HMT								
1 bar	$15.90^{\pm 0.14}$	1.55	$38.92^{\pm 0.15}$	1.25	85.5	95.00	893	173
1.5 bar	$17.30^{\pm 0.07}$	2.00	$37.55^{\pm 0.60}$	1.12	86.4	95.70	717	91
2 bar	$17.77^{\pm 0.49}$	2.17	$37.21^{\pm 0.13}$	1.09	87.3	97.00	472	31
2.5 bar	$33.74^{\pm 0.53}$	14.84	$39.17^{\pm 0.07}$	1.27	–	–	30	–
3 bar	$60.63^{\pm 0.15}$	86.11	$43.89^{\pm 0.78}$	1.79	–	–	30	–
1 bar	$16.37^{\pm 0.10}$	1.69	$36.85^{\pm 0.11}$	1.06	86.0	95.50	885	150
1.5 bar	$19.90^{\pm 0.30}$	3.04	$37.05^{\pm 0.16}$	1.08	88.5	97.00	321	3
2 bar	$22.70^{\pm 0.60}$	4.52	$38.42^{\pm 0.15}$	1.20	90.0	98.70	175	–
2.5 bar	$56.38^{\pm 0.84}$	69.24	$54.98^{\pm 0.80}$	3.52	–	–	30	–
3 bar	$138.30^{\pm 3.80}$	1022.01	$82.23^{\pm 1.70}$	11.76	–	–	30	–

$D_{v,0.5}$: median volume diameter; $(D/D_0)^3$: swelling ratio with D_0 the median diameters of native starch; T_0: initial pasting temperature; T_P: temperature of peak viscosity; PV: peak viscosity; BD: breakdown viscosity corresponding to the difference between the peak and the minimum viscosity after holding at the maximum temperature. BU: Brabender Units. The particle size values are means of triplicate determinations ± standard deviation. For the pasting properties three replications were performed on native starch for the determination of standard deviation.

three hydrothermal treatments presents a morphological behavior almost similar to that of native starch. From Fig. 1A′–C′, it can be seen that the size distributions of starch treated by DV-HMT at 1, 1.5, 2 and 2.5 bar, by RP-HMT at 1, 1.5 and 2 bar as well as by DIC at 1 and 1.5 bar are superimposed. The distributions of particles size were comprised between 10 and 100 μm, with a mean diameter in volume ($D_{v,0.5}$) equal to 36.16 μm for native starch. This value is in agreement with those obtained for a maize starch by other authors (Nayouf, Loisel, & Doublier, 2003; Tecante & Doublier, 1999). The class 1 agglomerates formed during the three treatments and observed before pasting were disintegrated during cooking by Brabender. The agitation caused the gradual disappearance of the aggregates in favor of single swelled particles; consequently the values of $D_{v,0.5}$ are identical to that of native starch. These modifications can be ascribed to concomitant processes of swelling and destruction of aggregates during pasting by Brabender. It has to be noted that the granule size dispersion during heating revealed not only the heterogeneity of granules size and capacity of swelling of starch but it also revealed the intensity of modifications of granular structure after hydrotreatment. At high processing pressures (3 bar for RP-HMT and 2.5 and 3 bar for DIC), the granular structure disappeared and the measurements were carried out on stable aggregates formed by fully gelatinized particles or fragments.

3.2. Pasting properties

Typical Brabender Viscograph curves of native, DV-HMT, RP-HMT and DIC treated SMS are presented in Fig. 3 and the pasting parameters in Table 1. With the Brabender Viscograph, the viscosity is measured in arbitrary units (BU) during heating, shearing and cooling of starch paste.

At 1 bar, the curves of DV-HMT treated starch only exhibited higher values than the native one during the holding step at 95 °C. The viscosity development during heating of granules has been attributed to amount and extent of amylose leaching, granular swelling and the extent of friction between swollen granules (Jacobs, Eerlingen, Clauwaert, & Delcour, 1995). The higher viscosity values of treated starch at low pressure level (1 bar) could be attributed to the development of granular swelling. At 1.5 and 2 bar, the viscosity of all treated starch decreased compared to that of native one, according to extent of the treatment. Moreover, the presence of a viscosity plateau suggests that the integrity of starch granules was maintained during heating. At higher pressure (2.5 and 3 bar) the viscosity of heated starch suspensions reduced until it become very fluid: a complete fluidization of the suspension (not measurable in Brabender Viscograph) was achieved at 3 bar for DV-HMT and 2.5 and 3 bar for RP-HMT and DIC treatments. This fluidization may be attributed to the disruption of starch granules.

Four relevant parameters were determined from Brabender viscograms; for native starch, the swelling onset temperature or pasting temperature (T_0) was 81.6 °C and reached a maximum (T_P) of 94.1 °C with a peak viscosity (PV) of 888 BU and Breakdown Value (BV) of 208 BU. The three hydrothermal treatments modified the characteristic parameters of starch suspensions. The pasting temperatures were higher and viscosities values (PV and BV) lower than the ones observed for native starch, when the treatment conditions increased (pressure level >1 bar). Similar results were observed by Maache-Rezzoug et al. (2009) and Loisel et al. (2006) for DIC treatment and by Chung, Hoover, and Liu (2009) and Hoover and Manuel (1996) for HMT treatment.

According to Watcharatewinkul, Puttanlek, Rungsardthong, and Uttapap (2009), cited by Zavareze and Dias (2011), increasing of paste temperature and decreasing of peak viscosity, final viscosity, and breakdown of canna starch treated by HMT (15, 18, 20, 22, and 25% moisture/100 °C/16 h) are due to associations between the chains in the amorphous region of the granule as well to changes in crystallinity during hydrothermal treatment. As the forces of the intragranular bonds are reinforced, the starch requires more heat for structural disintegration and paste formation. Olayinka, Adebowale, and Olu-Owolabi (2008) reported that the pasting properties of HMT sorghum starch depend on the intensity of the treatment conditions; as the moisture level and paste temperature increased and peak viscosity declined.

The variation of peak viscosity (PV) as a function of processing pressure (Fig. 4A) could be divided into three parts depending on the intensification of heat transfer due to the presence of initial vacuum for DIC and RP-HMT treatments and also on the mechanical effect induced by the final release of pressure towards vacuum for DIC treatment. At low pressure conditions (1 bar), an increase of viscosity for starch treated by DV-HMT and almost no change

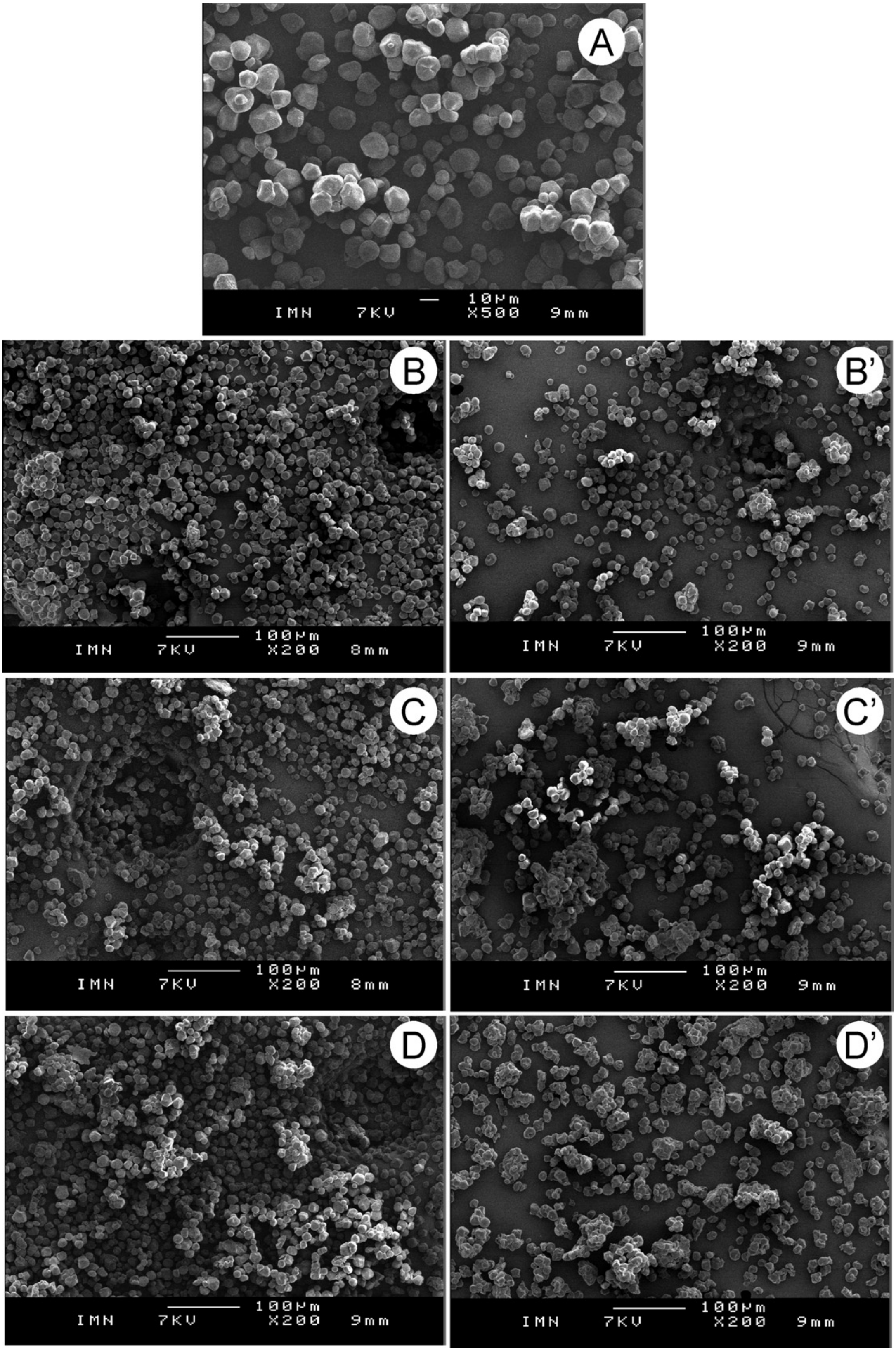

Fig. 2. Scanning electron micrographs of native (A, magnification 500×) and treated SMMS at 1.5 bar by DV-HMT (B), RP-HMT (C) and DIC (D) and treated starch at 3 bar by DV-HMT (B′), RP-HMT (C′) and DIC (D′). Magnification 200×.

for RP-HMT and DIC treated starch compared to the native one were observed. The difference between DV-HMT and RP-HMT is due only to the presence of vacuum step before steam injection for RP-HMT. The less intense heat conditions of DV-HMT seem to promote the swelling capacity of granules that remained intact. The swollen granules embedded within the amylose network could be more resistant to shear during pasting. The comparison between RP-HMT and DIC treatment (Fig. 4A) shows that the mechanical

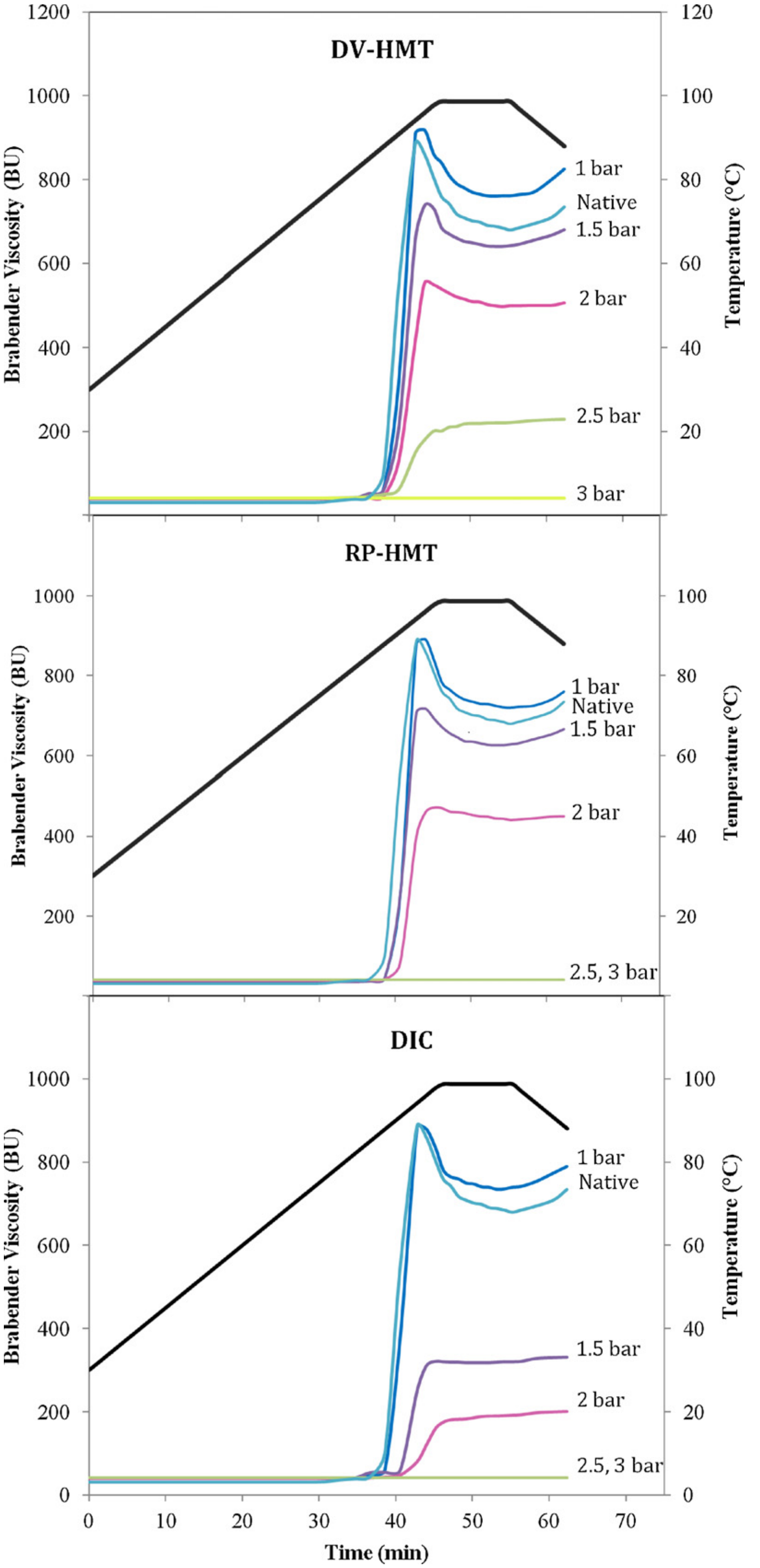

Fig. 3. Pasting profiles of suspension (6%, w/w) of native and DV-HMT, RP-HMT and DIC treated SMS, measured by Brabender Viscograph.

effect induced by the pressure drop during DIC treatment is negligible. The release of pressure from 1 bar to 50 mbar is not sufficient to have a significant effect. Conversely, at intermediate processing conditions (1.5 and 2 bar) this effect became significant, as indicated by the difference in PV values which was more important. In the same time, the thermal effect became negligible (DV-HMT compared to RP-HMT). The abrupt decompression towards vacuum makes the granules more fragile and thus more sensitive to the heating and shearing applied during the pasting procedure, leading to lowering of viscosity. At intense conditions (2.5 and 3 bar) a

Table 2
Herschel–Bulkley and viscoelastic parameters of native, DV-HMT, RP-HMT and DIC treated SMS suspensions.

Sample	Rheological properties (60 °C)				Viscoelastic properties (60 °C)		
	τ_0 (Pa)	K (Pa s^n)	n	$\dot{\gamma}=600\ \mathrm{s}^{-1}$	ω = 6.3 (rad s^{-1})		
				η (mPa)	G' (Pa)	G'' (Pa)	tan δ
Native	$3.23^{\pm0.2}$	$2.59^{\pm0.3}$	$0.59^{\pm0.01}$	$193^{\pm2.7}$	$94.1^{\pm7.2}$	$18.79^{\pm0.78}$	$0.19^{\pm0.01}$
DV-HMT							
1 bar	5.63	2.96	0.58	211	117	17	0.14
1.5 bar	2.4	1.58	0.62	143	99.9	13.3	0.13
2 bar	1.22	1.02	0.6	81.00	66.1	9.24	0.12
2.5 bar	0.00	0.83	0.63	77.8	1.21	1.53	1.26
3 bar	0.00	0.009	0.95	6.5	0.00	0.06	–
RP-HMT							
1 bar	5.3	3.13	0.57	208.8	133.4	18.14	0.14
1.5 bar	3.69	2.09	0.59	157.9	110.7	14.1	0.12
2 bar	0.69	1.14	0.6	89.4	25.2	7.21	0.28
2.5 bar	0.00	0.014	0.94	9.5	0.00	0.11	–
3 bar	0.00	0.01	0.92	6.00	0.13	0.47	–
DIC							
1 bar	4.60	3.05	0.57	202.5	124.5	18.08	0.14
1.5 bar	0.55	0.49	0.71	77.6	114.3	26.17	0.23
2 bar	0.00	0.23	0.68	29.7	30.1	7.43	0.25
2.5 bar	0.00	0.00	1.08	–	0.00	0.24	–
3 bar	0.00	0.00	0.96	–	–	–	–

6% (w/w) SMS suspension; τ_0: yield stress; K: consistency index; n: flow behavior index (τ_0, K and n were determined from Herschel–Bulkley model); η: apparent viscosity measured at a shear rate of 600 s^{-1} at 60 °C. Five replications were performed on native starch for the determination of standard deviation.

dramatic decrease of PV were observed for all treatments. A complete fluidization of the suspensions was obtained, due to the disruption of starch granules. For 3 bar, no difference between the three treatments was observed.

3.3. Rheological properties

The majority of equilibrium flow curves (not showed), of shear stress versus shear rate of native and treated starch dispersions, after two consecutive up-down shear cycles to eliminate the thixotropic phenomenon, present the typical shear thinning behavior with a yield stress of starch pasted suspensions. Herschel–Bulkley model was found to fit satisfactory the flow curves of treated starch at low and intermediate conditions, according to Eq. (1):

$$\tau = \tau_0 + k\dot{\gamma}^n \tag{1}$$

where τ is the shear stress (Pa), $\dot{\gamma}$ the shear rate (s^{-1}), τ_0 the yield stress (Pa), k the consistency index (Pa s^n) and n is the flow behavior index (dimensionless). The model parameters (τ_0, k and n) and the apparent viscosity (η) calculated for a shear rate of 600 s^{-1} are given in Table 2. A shear-thinning behavior ($n < 1$) with a yield stress was observed, for native and treated starch in low and intermediate conditions up to 2 bar for DV-HMT and RP-HMT and only 1.5 bar for DIC treatment. For higher pressures, the rheological behavior of treated starch first remained shear-thinning but the yield stress disappeared, while at 3 bar for DV-HMT and 2.5 and 3 bar for the two other treatments, the starch suspensions tended towards a Newtonian fluid with behavior index of nearly one. In this case, the thixotropic behavior (not shown) completely disappeared. Many authors have showed that the starch suspensions exhibit a time-dependant shear-thinning behavior that may be thixotropic (Doublier, 1981; Nguyen, Jensen, and Kristensen, 1998) or antithixotropic (Bagley & Christianson, 1982; Tattiyakul & Rao, 2000).

As seen from Table 2, the yield stress (τ_0), the consistency index (k) and consequently the apparent viscosity (η) at a shear rate of 600 s^{-1}, first increased for all treated starch at 1 bar compared to the native one and then decreased significantly for higher pressures.

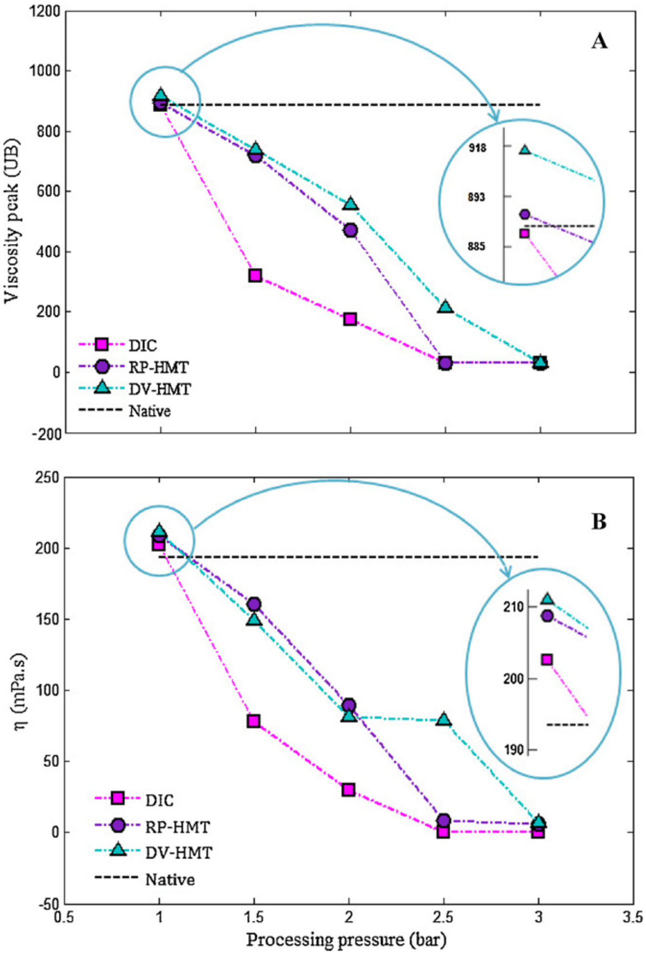

Fig. 4. Variation of peak viscosity (A) and apparent viscosity (B), measured at a shear rate of $\dot{\gamma} = 600\ \mathrm{s}^{-1}$ and temperature of 60 °C, as a function of processing pressure for DV-HMT, RP-HMT and DIC treatments.

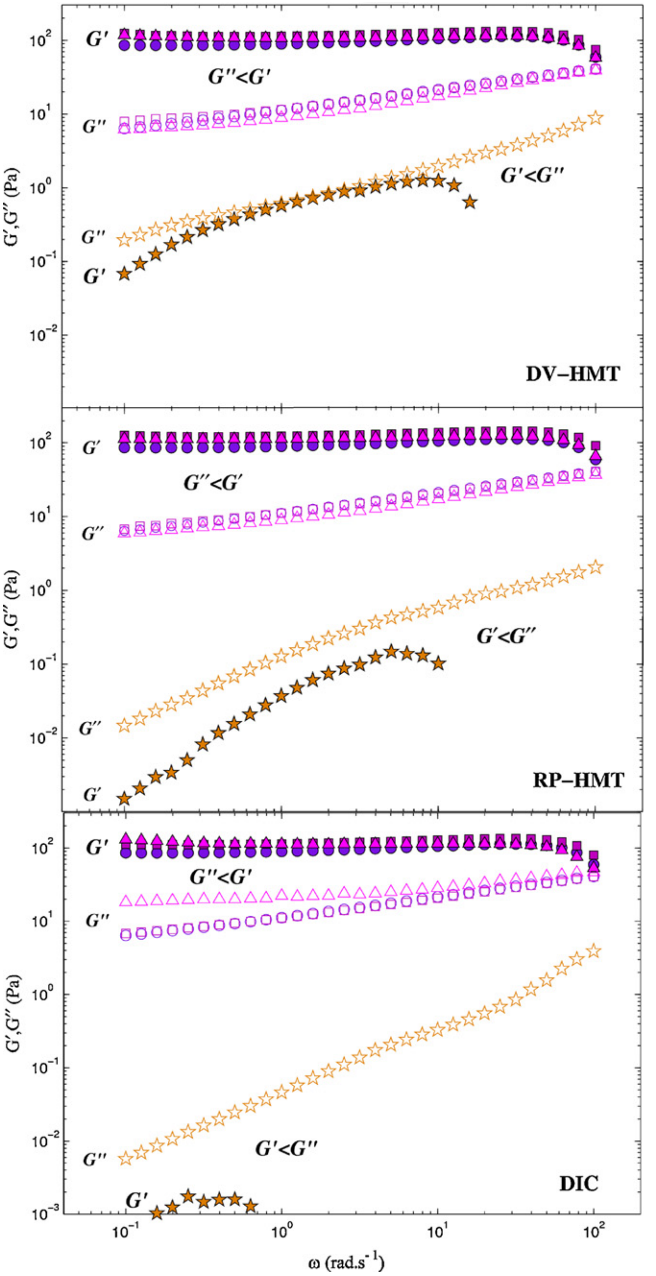

Fig. 5. Mechanical spectra of SMS suspension measured at 60 °C and shear strain of 4% of native (circle) and treated starch suspensions at 1 bar (square), 1.5 bar (triangle) and 2.5 bar (star). G' (solid), G'' (hollow) symbols.

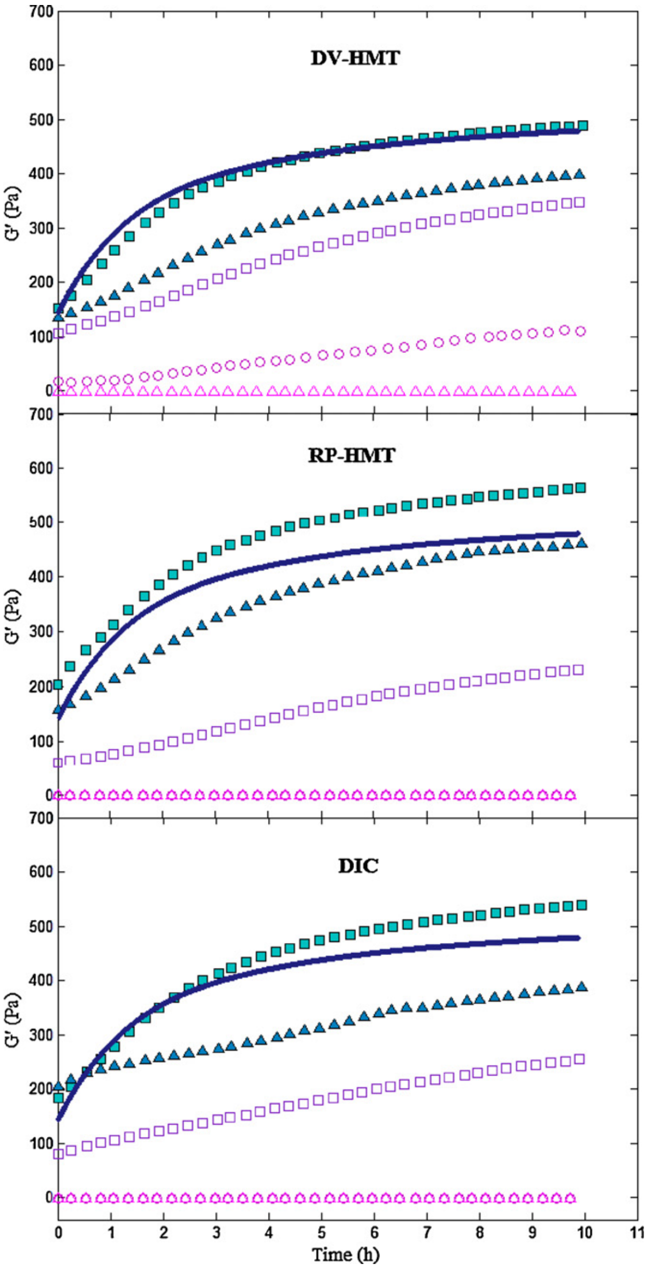

Fig. 6. Evolution of elastic modulus (G') of suspensions during gelation at 25 °C of native (line) and treated SMS at 1 bar (solid square), 1.5 bar (solid triangle), 2 bar (hollow square), 2.5 bar (hollow circle) and 3 bar (solid triangle).

The influence of all treatments at different processing pressures on apparent viscosity (Fig. 4B) seems to follow the same tendency as for PV measured by Brabender (Fig. 4A). At low conditions the rheological measurements, carried out at 60 °C, contribute to better discriminating between the treatments by comparison with Brabender measurements, which were carried out at higher temperatures (96 °C). From Fig. 4B, η decreased significantly with the treatment intensity and the difference between the treatments disappeared at 3 bar. A complete fluidization of the suspensions can be explained by the disruption of granular structure during the treatments confirmed by microscopic observations (Fig. 2B′–D′). Many authors showed that the apparent viscosity of starch suspensions decreases as the conditions of the hydrothermal treatment become more intense, as was illustrated by annealing (Jacobs & Delcour, 1998), HMT (Chung et al., 2009; Hoover & Manuel, 1996), nixtamalization (Méndez-Montealvo, Sánchez-Rivera, Paredes-López, & Bello-Pérez, 2006; Méndez-Montealvo, García-Suárez, Paredes-López, & Bello-Pérez, 2008) and DIC treatments (Loisel et al., 2006; Maache-Rezzoug et al., 2009).

The viscoelastic behavior of native and treated starch dispersions illustrated in Fig. 5, were performed at 60 °C to avoid retrogradation of amylose, was analyzed through the variations of storage modulus (G') and loss modulus (G'') as a function of frequency. The native and all treated starch dispersions at low and intermediate conditions have the properties of a weak gel. The elastic modulus is significantly higher than the viscous modulus (between $G' > 4G''$ and $G' > 7G''$ depending on processing conditions) and both are practically independent of frequency. For the intense conditions, the viscoelastic behavior is typical of dilute solutions ($G'' > G'$) and the two modulus varied with the oscillation frequency. The values of G', G'' and the tangent of loss angle (tan δ)

calculated for a frequency of 6.3 rad s^{-1} are summarized in Table 2. G' decreased for all treated starch as the process conditions became more intense.

The aging tests were performed over a long period of time (10 h) and a temperature of 25 °C for a frequency of 6.3 rad s^{-1} in order to measure the gelation of amylose which is mainly localized in the continuous phase (Fig. 6). For native and treated starch dispersions, the occurrence of gelation of amylose is attested by increasing of G' indicating the creation of network structure, at low and intermediate conditions (pressure level < 2 bar). The change of rheological properties corresponds to molecules reassociated in an ordered structure. This process is referred to as retrogradation (Atwell, Hood, Lineback, Varriano-Marston, & Zobel, 1988), consists of two main mechanisms: aggregation and crystallization of amylose and the development of gel structure, while the second mechanism is related to the development of crystallinity in the polymer-rich regions (amylopectine) for creation of network structure (Miles, Morris, & Ring, 1984). At 2.5 and 3 bar for RP-HMT and DIC treatments and 3 bar for DV-HMT, no gelation of amylose was detected. Decreasing of G' could be mainly linked to the lower ability of amylose to form a gel in the continuous phase (Loisel et al., 2006), the helical chains that have to be formed upon cooling were not aggregated and hence did not form a three-dimensional network.

According to Doublier, Llamas, and Le Meur (1987), the rheological behavior of pasted starch suspensions results from its biphasic structure. The dispersed phase consists of swollen granules (mainly amylopectin) and is characterized by the volume fraction and rigidity of starch granules resulting from the pasting conditions. The continuous phase is composed from soluble macromolecules (amylose) that have diffused out of the starch granules upon pasting. The changes that occur during hydrotreatment and pasting greatly affect the rheological properties of the starch suspension. The storage modulus indirectly measures the rigidity of the swollen granules. The decrease of G' for treated starch induced by treatment intensity may reflect either a loss of rigidity of starch granules and, at severe conditions (3 bar), the disappearance of granular integrity. Lu, Duh, Lin, and Chang (2008) showed during gelation at 25 °C of starch gel that the low G' revealed a weaker granular integrity.

4. Conclusion

The study showed a marked dependence on the particles sizes distribution according to the treatment and processing conditions. The size distributions of treated starch were shifted towards higher sizes with increasing of processing conditions, following this order; DV-HMT < RP-HMT < DIC. The enlargement is due to the improvement of swelling capacity of starch granules at low and intermediate processing conditions but also to the presence of agglomerates particles at severe conditions (pressure > 2 bar). The number of gelatinized granules during the treatment had a direct impact on the size of formed aggregates. The results confirm that granule properties play an important role on pasting and rheological properties of starch suspension.

The modifications of pasting and rheological properties was satisfactorily divided into three parts according to the pressure level: low (1 bar), intermediate (1.5 and 2 bar) and intense conditions (2.5–3 bar) with varied effects due to the specificity of each treatment: intensification of heat transfer due to the initial vacuum, for RP-HMT and DIC treatments, and mechanical effect induced by the final vacuum for DIC. For intermediate conditions, the mechanical effect of DIC treatment is predominant compared to RP-HMT and DV-HMT. Consequently, the structure of the granules becomes fragile making it more sensitive to heating and shearing upon pasting. For severe conditions, the heating effect becomes so important that the mechanical effect was masked, whereas at 3 bar no difference between the treatments was observed. This can be explained by the partial (DV-HMT) or total melting of starch granules (RP-HMT and DIC). At this condition a complete fluidization of suspensions and the decrease of G' measured during gelation were observed, revealing the loss of rigidity and integrity of starch granules.

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