



Comparative study of the effect of drying temperatures and heat-moisture treatment on the physicochemical and functional properties of corn starch

Paul Malumba^{a,b,*}, Sébastien Janas^a, Olivier Roiseux^a, Georges Sinnaeve^c, Thaddée Masimango^b, Marianne Sindic^a, Claude Deroanne^a, François Béra^a

^a Gembloux Agricultural University, Food Technology Department, Passage des Déportés, 2, 5030 Gembloux, Belgium

^b University of Kinshasa, Agricultural Faculty, BP 14071 Kinshasa 1, Democratic Republic of the Congo

^c Walloon Agricultural Research Centre, Département Qualité des productions agricoles, Chaussée de Namur 24, B-5030 Gembloux, Belgium

ARTICLE INFO

Article history:

Received 18 February 2009

Received in revised form 13 August 2009

Accepted 14 September 2009

Available online 18 September 2009

Keywords:

Starch

Corn

Drying

Heat-moisture treatment

Gelatinization

Pasting

Physicochemical property

Functional property

Swelling

ABSTRACT

This manuscript compares the modifications induced by the heat-moisture treatment of native starch (HMT) and by the hot-air drying of corn on wet-milled starch granules. High temperatures applied during both corn drying and HMT reduced the swelling capacity of granules, increased the starch gelatinization temperatures and decreased their residual enthalpy. Pasting behaviour of pre-treated starch showed a decrease of peak and breakdown viscosity when corn drying and HMT temperatures increased. Microscopic analysis showed that after hydrothermal treatment, starch granules extracted from corn dried at lower temperature swell more significantly than those extracted from corn dried at higher temperature. All these changes suggest the occurring of structural modifications within starch granules during high-temperature pre-treatments. At similar temperatures and initial moisture contents, HMT affected the physicochemical and functional properties of cornstarch more dramatically than hot-air drying. Differences induced by these two treatments were attributed to the availability of water around granules during these two pre-treatment procedures.

© 2009 Elsevier Ltd. All rights reserved.

1. Introduction

Hot-air drying is usually applied to preserve corn kernels by decreasing their water availability. During this process, seeds undergo different alterations. An important consideration when dealing with heated air process is the drying temperature, which depends on the particular end use of grain and the proposed residence time of grain in dryers (Jayas & White, 2003). High temperatures used during drying can impact the wet-milling performance of corn and modify the physicochemical properties of recovered starch granules (Lasseran, 1973; Peplinski, Paulis, Bietz, & Pratt, 1994; Weller, Paulsen, & Steinberg, 1988).

Recently, interest has increased to the effects of high drying temperatures (Altay & Gunasekaran, 2006; Hardacre & Clark, 2006; Haros, Tolaba, & Suarez, 2003; Malumba, Massaux, Deroanne, Masimango, & Béra, 2009) and heat-moisture treatments (Chung, Liu, & Hoover, 2009; Lim, Chang, & Chung, 2001; Takaya,

Sano, & Nishinari, 2000) on the physicochemical and functional properties of wet-milled starch granules (WSG).

Using differential scanning calorimetry (DSC), Haros et al. (2003) concluded that high drying temperatures increase all the transition temperatures of wet-milled starch. As high-temperatures drying have a negative effect on starch–protein separation during the wet-milling, Haros et al. (2003) and Altay and Gunasekaran (2006) assumed that the proteins remaining in cornstarch possibly reduce the entrance of water into the granules during gelatinization, limiting interactions between water and starch components and increasing temperatures of gelatinization by the way.

Even for starch having comparable residual protein content, previous investigation showed that high-temperatures drying reduce the swelling capacities of starch granules and their solubility indexes during gelatinization (Malumba et al., 2009). It is likely that structural changes which possibly occur inside of granules during the drying may affect the pasting characteristics of starch–water system during the subsequent gelatinization. Therefore, changes on physicochemical and functional properties of starch extracted from corn dried at high temperature cannot be exclusively attributed to the residual protein of samples.

When dealing with starch previously submitted to heat-moisture treatments, Lim et al. (2001) and Hoover and Manuel (1996)

* Corresponding author. Address: Gembloux Agricultural University, Food Technology Department, Passage des Déportés, 2, 5030 Gembloux, Belgium. Tel.: +32 81622263; fax: +32 81601767.

E-mail address: paul_malu@yahoo.fr (P. Malumba).

observed some changes on physicochemical and functional properties of cornstarch. It is unknown if those changes are of the same nature and importance as those induced by high-temperatures drying of corn kernels.

The aim of the present research was to study and to compare changes induced by high-temperature drying of corn kernels on physicochemical and functional properties of cornstarch with those induced by heat-moisture treatments of previously extracted starch granules.

2. Materials and methods

2.1. Samples preparation

The Baltimore variety of flint corn was field grown in 2004 at CRA-Wallon Experimental Station (Gembloux, Belgium). The corn was harvested with a moisture content of 32% and immediately shipped in the laboratory where it was stored at -18°C in sealed plastic bag until drying. Before drying, corn was equilibrated to ambient temperature over night. Approximately 700 g of wet corn were dried in the laboratory fluidized-bed dryer with an air velocity of approximately 5.8 m/s.

Experiments were carried out at temperatures between 54 and 130°C in triplicate and wet corn was used as control. For each drying temperature, a specific processing time was chosen in order to obtain final moisture content between 11% and 13%. After drying, kernels were equilibrated at ambient temperature for 10 min and stored in sealed bags at 10°C .

The laboratory wet-milling procedure of Neryng and Reilly (1984) was performed, with the modifications of Haros and Suarez (1997) and Singh and Eckhoff (1996) as previously described by Malumba et al. (2009). Starch yield was calculated on a dry basis as the ratio of the recovered starch to the initial corn from the wet-milling procedure (w/w). Starch recovery was calculated as the ratio of the starch yield to the total weight of starch in native corn, measured using the Ewers method (ISO 10520:1997). The WSG purity was defined as the percentage of starch measured by the Ewers method in a sample of WSG on a dry weight basis. The residual protein in wet-milled starch was determined by the Kjeldahl method, with a 2020 Tecator Digester (Tecator, Sweden) and a 2100 Kjeltel distiller (Tecator, Sweden). Proteins mass was calculated using the general factor 6.25 and reported to the mass of starch used for measurements.

Table 1 summarized the drying parameters and the performance of the wet-milling procedure applied for samples preparation.

2.2. Heat-moisture treatment of native starch

To compare the effect of heat-moisture treatments and drying, the heat-moisture treatment of starch granules extracted from wet corn was carried out between 60 and 130°C in duplicate during the same time as for drying. The moisture levels of starch sam-

ples extracted from undried corn were adjusted to 7.5%, 15% and 30% by adding the appropriate amount of distilled water to the lyophilized WSG and equilibrated for 24 h at 4°C . Eighty grams of mixture were well stirred and sealed in cylindrical cans (0.030 m height and 0.073 m diameter).

The heat-moisture treatment procedure was performed at 10 rpm in a rotating batch retort A091 (FMC-Europ N.V., Belgium) equipped with a Siemens Simatic TP25 command pilot and a digital interface Ellab TA 9616 for temperature measurement. Canned starch was rapidly heated from 20°C to the set point temperature by hot water spray.

2.3. Isothermal treatment of samples in excess water

Similar method to that proposed by Okechukwu and Rao (1996) was used for isothermal heating of WSG in excess water. To raise instantaneously the starch granules temperature, 10 g of WSG were sprayed inside of a stainless steel vessel containing 1 L of water previously heated to a predetermined temperature, with a heater system (RCT Basic, IKA, Germany). The sensor PT 1000 controller was placed in direct contact with the stirred water–starch dispersion. The water–starch suspension was stirred at approximately 120 rpm with a pumping downward impeller (A315) placed at the lower part of the vessel (Fig. 1).

At intervals, 20 ml of samples were withdrawn from vessel and mixed with distilled water ice in order to stop any further swelling. Aliquot of the heated water–starch sample was then taken for the size determination of the starch granules.

2.4. Particle size analysis

Particle size distribution was determined at room temperature in water dispersion using a laser scattering analyzer (Malvern Instruments, Ltd., UK) equipped with a Mastersizer 2000 (Ver. 5.22) analysis data station. The swelling of samples was compared by using the median diameter $D(v, 0.5)$ defined as the diameter for which 50% of the particles by volume are larger.

2.5. Thermal analysis of samples

The thermal properties of starch were examined with a 2920 TA Instruments (New Castle, Delaware, USA) with a Refrigerated Cooling Accessory and modulated capability. The cell was purged with 70 ml min^{-1} of dry nitrogen and calibrated for baseline using empty pans and for temperature using two temperature and enthalpy standards (indium, T_{onset} : 156.6°C , ΔH : 28.7 J g^{-1} ; eicosane, T_{onset} : 36.8°C , ΔH : 247.4 J g^{-1}). The empty sample and reference pans were of equal mass. Samples of approximately 4 mg of starch were weighted into aluminium pans. Deionised water was added to obtain 3:1 water:starch ratio. Pans containing the starch–water slurry were hermetically sealed. Measurements were made over a temperature range of 20 – 120°C , with a heating rate of 2°C/min modulated at $\pm 0.5^{\circ}\text{C}$ every 100 s. Gelatinization enthalpy ΔH

Table 1

Drying parameters, starch recovery by the wet-milling procedure, the percentage of residual protein contained in starch yield and the purity of WSG (in dry basis).

Air drying temperature ($^{\circ}\text{C}$)	Drying time (min)	Initial moisture content %	Final moisture content %	Starch recovery (g/100 g starch)	PPS ^a	WSG purity g/100 g
Untreated	Untreated	32.2 ± 0.3	32.2 ± 0.3	90.7 ± 0.5	0.690 ± 0.003	99.2 ± 0.06
60	180	32.2 ± 0.3	12.5 ± 0.2	85.2 ± 0.5	0.690 ± 0.019	98.7 ± 1.01
80	85	32.2 ± 0.3	13.9 ± 0.0	78.2 ± 0.7	0.694 ± 0.001	99.27 ± 1.13
100	50	32.2 ± 0.3	11.4 ± 1.1	66.6 ± 1.1	0.793 ± 0.039	99.4 ± 1.39
130	20	32.2 ± 0.3	14.2 ± 0.4	61.8 ± 0.1	1.268 ± 0.09	95.4 ± 1.30

^a Percentage of residual protein in wet-milled starch.

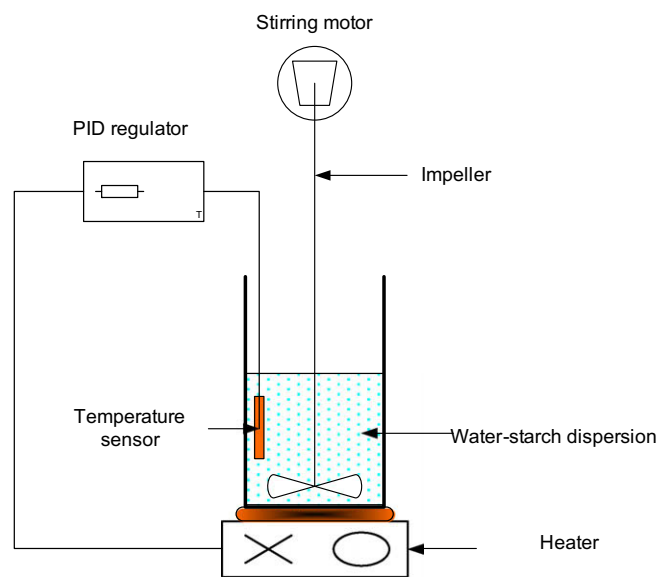


Fig. 1. Heater system used for isothermal treatment of water–starch dispersion.

was calculated by integrating the area of the gelatinization endothermic signal divided by the amount of dry starch used for measurement. The onset temperature and peak temperatures were computed using NV Thermal analysis software (Universal analysis, New Castle, Delaware, USA).

2.6. Pasting behaviour

Pasting properties of starch were measured with a Rapid visco-analyzer (RVA) (Newport Scientific, Australia). Starch (2.27 g on dry basis) was mixed in an aluminium canister containing distilled water to form a starch–water dispersion of 25 g at 20 °C, and placed in an RVA heating block. The suspension was mixed continuously at 160 rpm during measurement. A Thermocline software program controlled the heating and cooling cycles. The programmed cycle was held at 50 °C for 1 min, ramped to 95 °C at the rate of 12 °C/min, held at 95 °C for 5 min, decreased to 50 °C at the rate of 12 °C/min, and held at 50 °C for 1 min. The pasting and final viscosity together with, peak, breakdown and setback of viscosity were recorded and expressed in cP (Centipoise units). Viscosity measurements were performed in water, with addition of 2 mM AgNO₃ to nullify α -amylase effects and facilitate comparisons between samples (Massaux et al., 2008).

2.7. WSG microstructure

Starch obtained after 30 min of isothermal heating in excess water was observed through crossed polarizer, with a Nikon Eclipse E 400 microscope equipped with a CCD-camera (Nikon Co., Tokyo, Japan) and an image processing software (Lucia G, Nikon, Tokyo, Japan).

2.8. Statistical analysis

All analyses were carried out in triplicate. Statistical analyses were performed using Minitab software (version 15, Minitab Inc., State College, PA) for ANOVA. Tukey test ($P < 0.05$) was performed to determine least significant differences (LSD). Quantitative results are presented as mean \pm standard deviation.

3. Results and discussion

3.1. Influence of the pre-treatments temperatures on starch granule size

Without further hydrothermal treatments, median diameter of WSG increased with the pre-treatment temperatures (Fig. 2).

Below 60 °C granules showed sizes closed to those reported by Sandhu, Singh, and Kaur (2004) for native cornstarches (between 13.1 and 13.9 μ m). It is likely that pre-treatments of cornstarch below the onset temperature of gelatinization does not significantly modify the structure of granules. Pre-treatments performed above 80 °C enhanced significantly the size of granules. This swelling behaviour traduces significant changes inside of granules during drying or heat-moisture treatment at high temperature.

The swelling of starch granules is known to begin in the bulk, relatively mobile amorphous fraction, and in the more restrained amorphous region immediately adjacent to the crystalline regions (Hoover & Vasanathan, 1994). High-temperature pre-treatments applied to starch may possibly affect the amorphous region of granules, inducing probably glass transitions, which may modify the water binding capacity and subsequently the swelling behaviour of granules in excess water.

For similar pre-treatment temperatures, changes induced during the corn drying were lower than those induced by the HMT of sample conditioned at 30% and higher than those induced within granules conditioned at 15%. Differences produced by these pre-treatments could be attributed to the availability of water during the heat-treatment procedures.

3.2. Swelling behaviour of starch granules during the isothermal treatments in excess water

During isothermal treatments of starch in excess water, granules' sizes evolved differently according to the temperature applied. Below the gelatinization temperature ($T \leq 60$ °C), granules pre-treated at high temperatures were larger than those pre-treated at lower temperatures. This trend was inverted above 60 °C (onset temperature of gelatinization) (Fig. 3).

The median diameter reached by the granules seems to be closely dependent to the temperatures applied during their hydrothermal treatment in excess water and was modulated by the temperature of pre-treatments applied (Fig. 3).

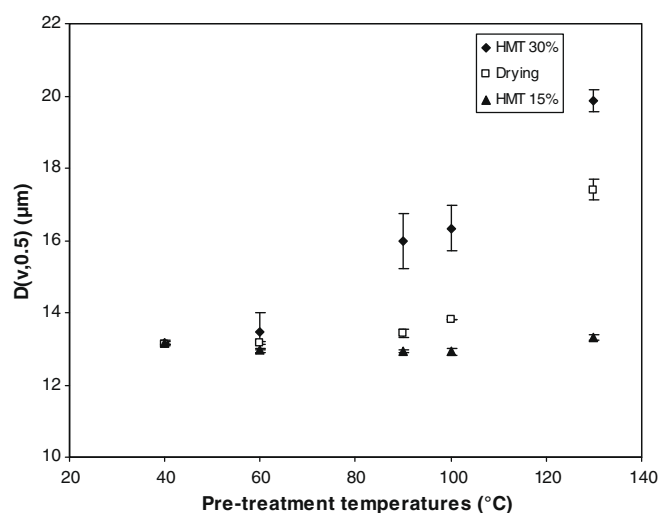


Fig. 2. Influence of pre-treatment temperatures on the corn starch granules size.

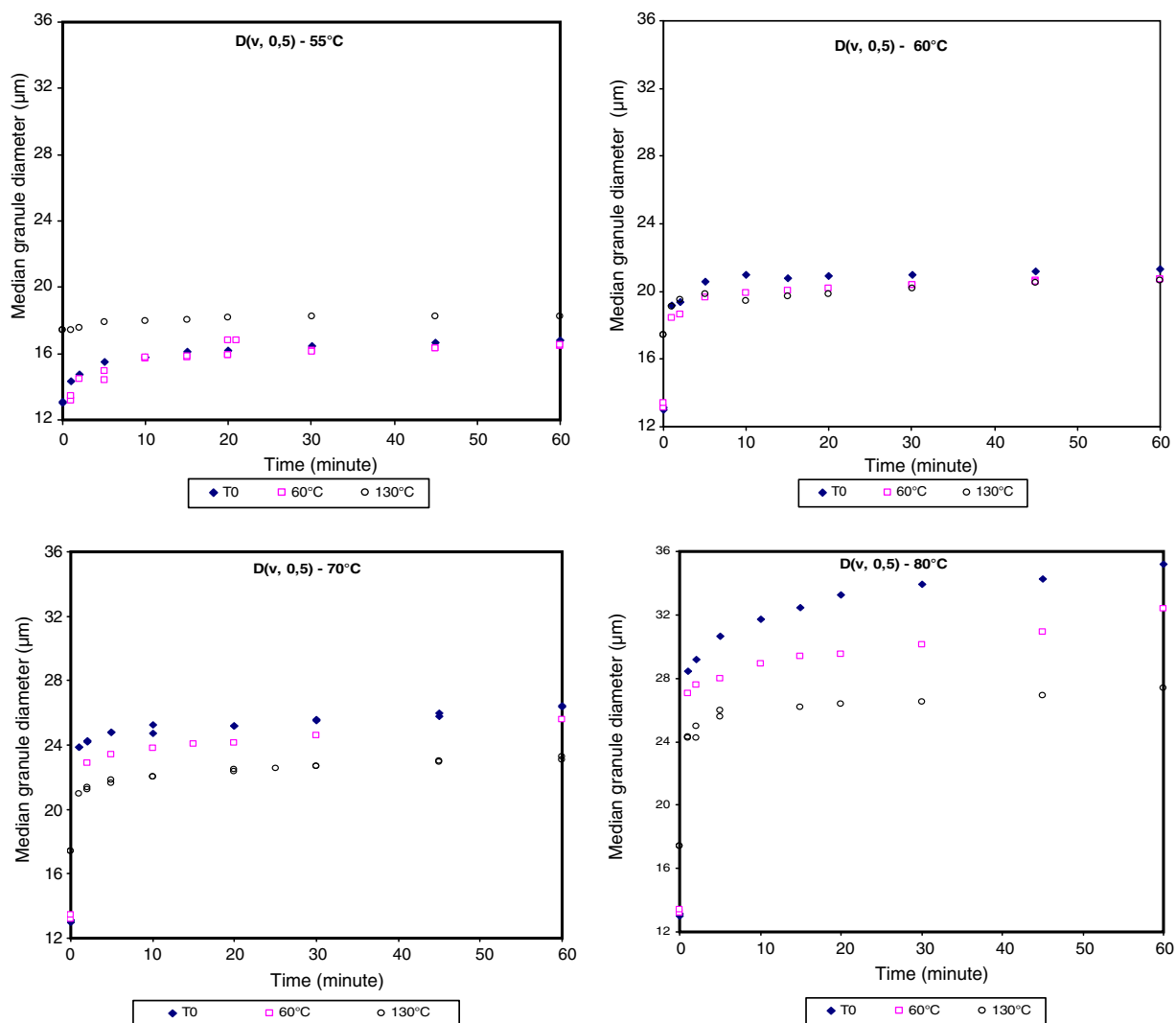


Fig. 3. Median diameter $D(v, 0.5)$ of WSG from undried corn (\blacklozenge T0), corn dried at 60 °C (\square 60 °C) and at 130 °C (\circ 130 °C) isothermally treated at 55; 60; 70; and 80 °C in excess water.

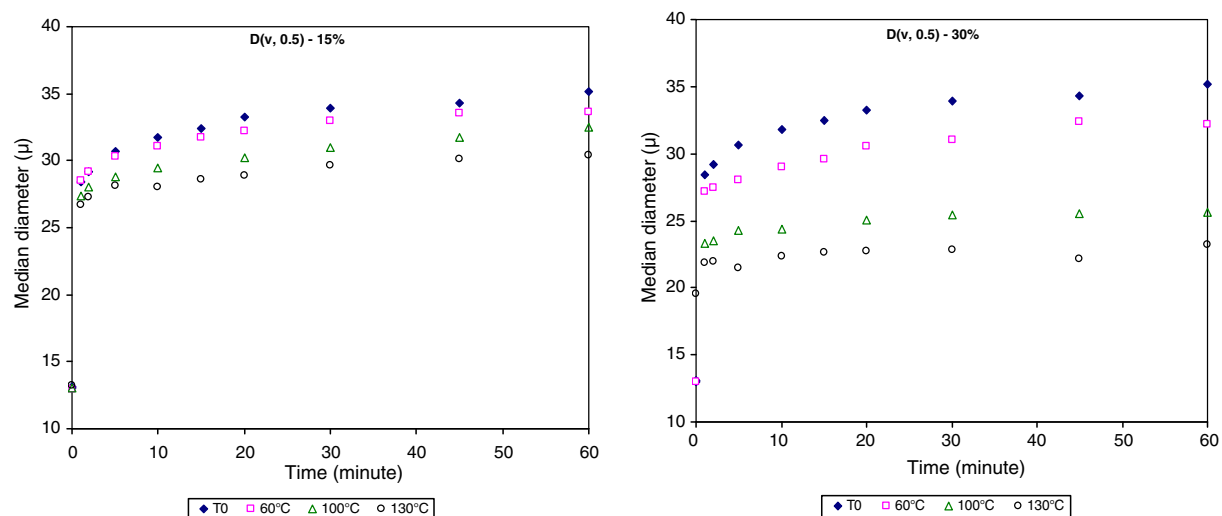


Fig. 4. Diameters of WSG from undried corn conditioned at 15% (left) and 30% (right) of moisture content, without heat-treatment (\blacklozenge T0), Heated at 60 °C (\square), 100 °C (\triangle) and 130 °C (\circ), as measured during their isothermal treatment in excess of water at 80 °C.

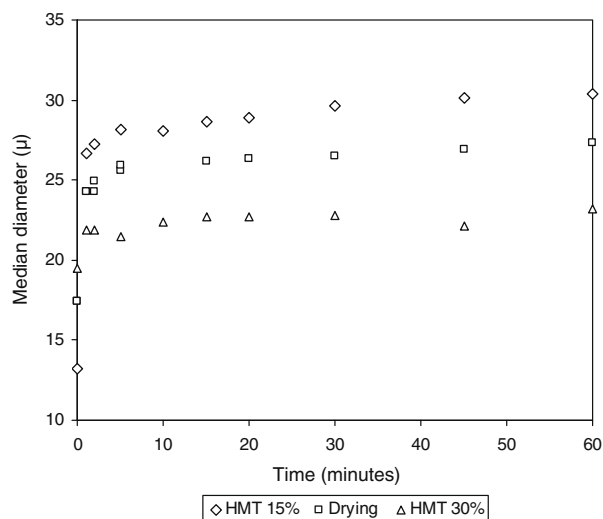


Fig. 5. Swelling behaviour of starch granules extracted from corn dried at 130 °C (□) and those of native wet-milled starch pre-treated at 130 °C with 15% (◇) and 30% (Δ) moisture content during the isothermal treatment in excess water at 80 °C.

As previously observed by several authors (Olayinka, Adebo-wale, & Olu-owolabi, 2008; Hoover and Manuel (1996), Gunaratne & Hoover, 2002; Hoover & Vasanthan, 1994; Kulp & Lorenz, 1981; Lorenz & Kulp, 1981, 1982), high temperatures applied during the heat pre-treatments (drying or HMT) decreased the swelling capacity of starch granules during gelatinization.

Kugimiya, Donovan, and Wong (1980) and Zhong and Sun (2005) have shown that cornstarch heated with intermediate moisture content underwent a series of thermal transitions including melting of crystals, melting of the amylose–lipid complexes and glass transition. The extent of these transitions could explain the restriction of the swelling capacity of starch granules extracted from corn dried at high temperature or heat-treated at high temperature with intermediate moisture content.

Fig. 4 shows that the heat-moisture treatment of samples with a high moisture content restricted significantly the swelling capaci-

ties of WSG. This fact illustrates the fundamental importance of moisture content in the modification of physicochemical properties of starch during their heat pre-treatment.

The comparison of the swelling capacity of starch granules extracted from corn dried at various temperatures and that of native starch heated with 15% and 30% moisture content shows the intermediate swelling behaviour of dried corn kernels (Fig. 5).

The decrease of the swelling capacity of starch granules was amplified when granules were pre-treated with high moisture content. This fact explains the intermediate swelling behaviour of starch extracted from corn kernels harvested at approximately 32% and dried until 12% moisture content, in comparison to the swelling behaviour of starch granules heat-treated at 15% and 30% of moisture content. Indeed, during drying, the corn kernels moisture content decreases progressively and restricts the effect of heat-treatment on the swelling behaviour of embedded corn-starch, while the moisture content around granules was constant all over the heat-moisture treatment.

3.3. Thermal characteristics of starch pre-treated in different conditions

Thermal transitions of starch (in excess water) extracted from corn dried at various temperatures and those of starch previously heated at different temperatures with 30% moisture content are shown in Figs. 6 and 7.

Fig. 6 shows that the gelatinization endotherms of wet-milled starch shifted slightly to higher temperatures when corn kernels were dried above 80 °C.

A more marked tendency to the increase of transition temperatures with increased pre-treatment temperatures were observed by examining starch submitted to HMT at various temperatures with 30% moisture (Fig. 7).

Moreover, gelatinization enthalpies of starches decreased when pre-treatment temperatures increased, indicating a pre-gelatinization occurred before thermal analysis. These results are consistent with studies Lim et al. (2001) whom observed a decrease of the gelatinization's enthalpies of cornstarch pre-treated at 120 °C with 25% moisture content.

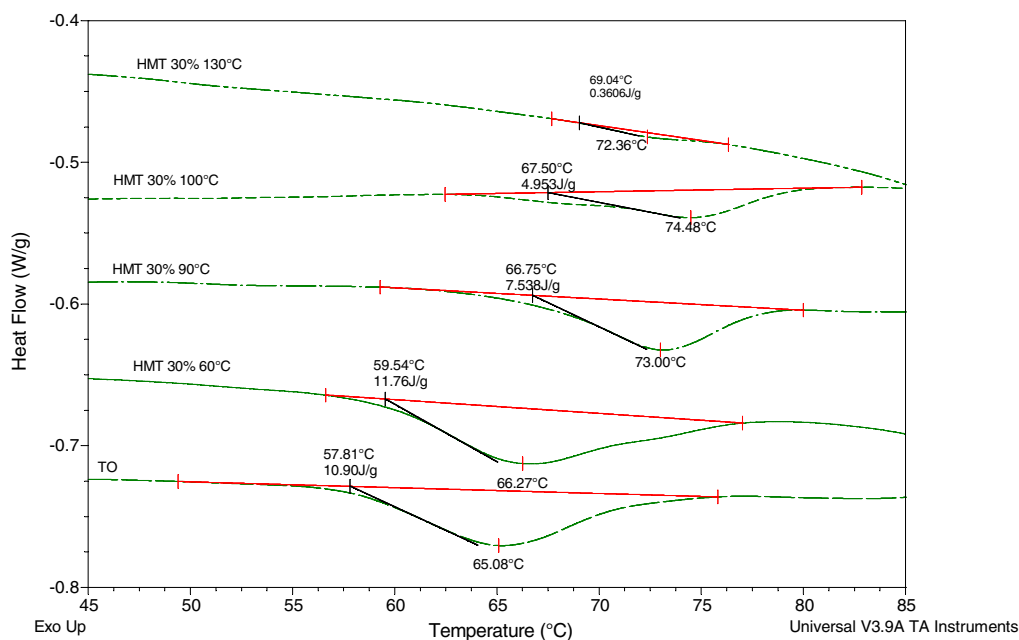


Fig. 6. Thermograms of WSG extracted from wet-kernel (T0) and corn kernels dried at 60, 80, 100 and 130 °C (vertical axe presents the scale of heat flow at w/g).

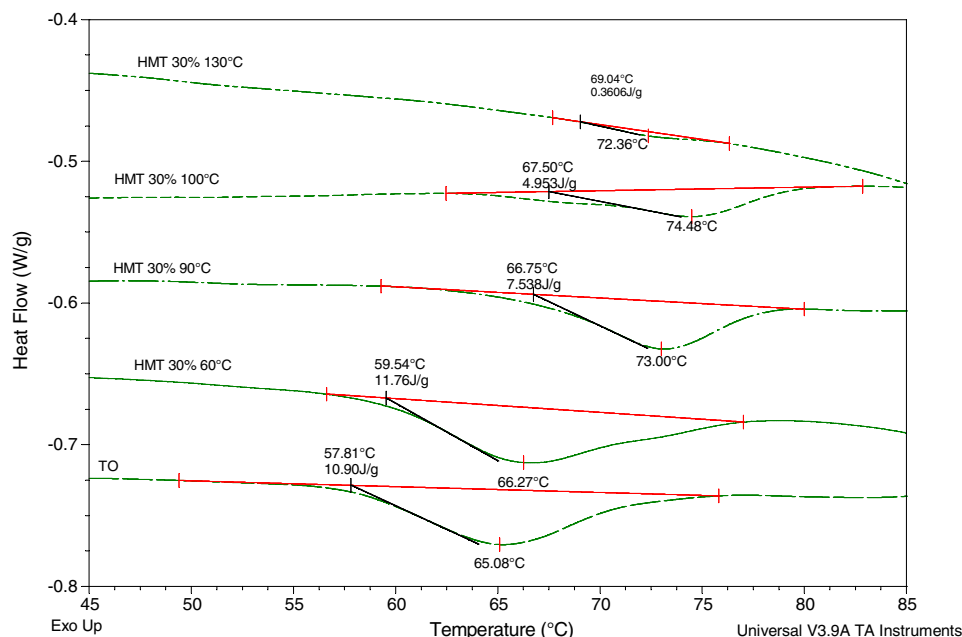


Fig. 7. Thermograms traces of starches conditioned at 30% of moisture content and then heat-moisture treated at different temperatures.

Ji, Ao, Han, Jane, and BeMiller (2004) hypothesised that the onset temperature of gelatinization would be a measure of the perfection of starch crystallites, less perfect crystallites showing lower gelatinization onset temperatures. Assuming this hypothesis Altay and Gunasekaran (2006) postulated that the remained ungelatinised granules after pre-treatments could have more perfect structure than starch granules gelatinized during the pre-treatments.

To verify the effect of moisture content on the thermal properties of starch, three groups of native starch conditioned at 7.5%, 15% and 30% moisture were submitted to the HMT at 100 °C and analyzed (Fig. 8).

Below 15% moisture content no perceptible change was observed in the thermogram. Low moisture content appears as a limiting factor of gelatinization of starch. This fact may explain the lower change observed with starch extracted from corn dried at high temperature in comparison with changes induced by the heat-moisture treatment of samples conditioned at 30% for equivalent temperatures.

3.4. Influence of the pre-treatment temperatures on the pasting behaviour of starches

Pasting behaviour measured by rapid visco-analyzer shows that the peak and breakdown viscosity, decrease significantly when

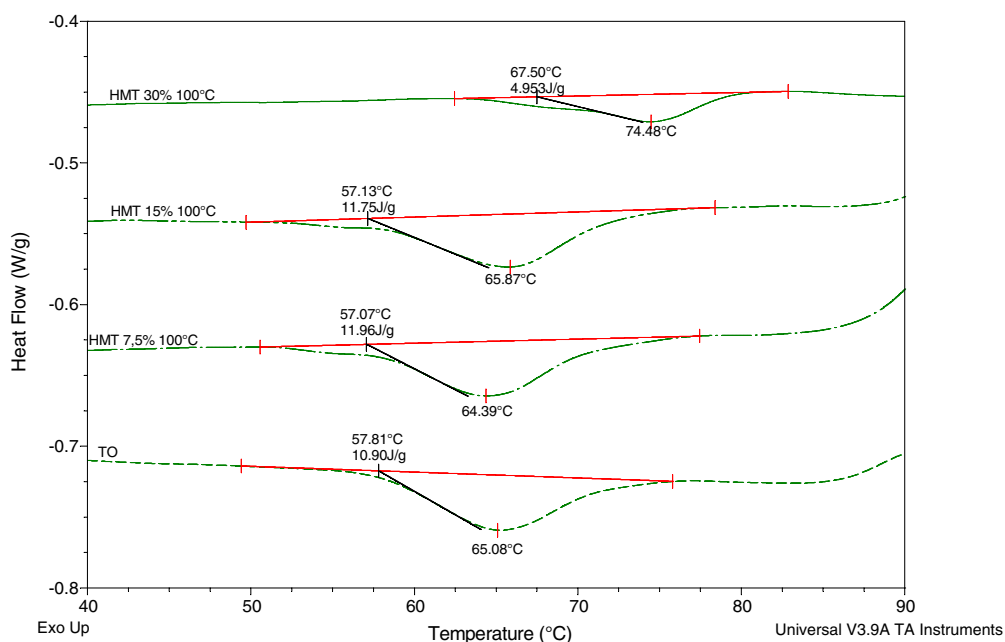


Fig. 8. Thermograms of starch samples conditioned at various moisture contents and then submitted to HMT at 100 °C as observed by DSC analysis in excess water (TO: native corn starch used as control).

both the drying and HMT temperatures increased (Fig. 9a and b) while final viscosities (Fig. 9c) raised significantly before to drop for starch from corn dried with hot-air above 90 °C.

Similar phenomena were observed by Mistry, Wu, Eckhoff, and Litchfield (1993) with starch extracted from corn kernels dried with hot-air and by Hoover and Manuel (1996) with cornstarch submitted to heat-moisture treatment at high temperature.

The peak's height of viscosity reflects the ability of granules to swell freely before their physical breakdown. Normally, starch

granules that able to swell to a high degree are also less resistant to breakdown on cooking and exhibit a significant decrease of viscosity after reaching the peak of viscosity during the heating process (Singh, Singh, Kaur, Sodhi, & Gill, 2003). By decreasing the peak and breakdown viscosity during the pasting procedure and the swelling capacity of starch granules during their gelatinization, high pre-treatments temperature confers to starch granules a resistance which prevents their breakdown.

Singh et al. (2003) postulated that differences in the breakdown susceptibility of starches may be attributed to the granule's rigidity and to their lipid content.

The onset temperature of pasting increased significantly when both corn drying and heat-moisture pre-treatments' temperatures increased (Table 2). The increase observed here may be compared with the increase of onset temperature observed by DSC analysis.

3.5. Microscopic characterization of WSG isothermally treated in excess water

Without anymore hydrothermal treatment, the microscopic analysis under polarized light showed that wet-milled starch extracted from wet corn or from corn dried at lower temperature presents a granular shape with differentiable semi-crystalline maltose cross. Starch extracted from corn dried at higher temperature presented larger granules in which maltose cross were less clearly differentiable (Fig. 10). After hydrothermal treatment, starch granules extracted from corn dried at lower temperature swell more significantly than those extracted from corn dried at higher temperature. This suggests the occurring of structural change within starch granules during the drying at high temperatures. The granular structure of wet-milled starch from corn dried at lower temperatures was more readily destroyed during the hydrothermal treatments.

Even at 80 °C, the swollen granules from corn dried at 130 °C well conserved their globular morphology. The low deformability of WSG at high temperatures confirmed that the thermal rigidity of WSG was improved by high drying temperature.

The structure of starch granule is thought to be hierarchically organised on four length scales: molecular scale, lamellar structure, growth rings and the whole granule morphology (French, 1984). The crystalline regions consist of double helices of amylopectine arranged in a specific crystalline morphology. The lamellae are alternating regions of amorphous and crystalline material. Waigh, Gidley, Komanshek, and Donald (2000a, 2000b) have presented a theory and some experimental evidence which allow to consider that starch has many physical properties in common with a chiral side-chain liquid-crystalline polymer. In this theory the lamellar structure of granule consist on alternating regions of amorphous and crystalline material due to the antagonistic effect of entropy of amorphous backbone and ordering of double helices of amylopectine. Within this model, the amylopectine is regarded as a side-chain liquid-crystalline polymer, in which the double helical clusters represent the rigid mesogen units which confer liquid-crystalline ordering on the molecule. In the crystals, the mes-

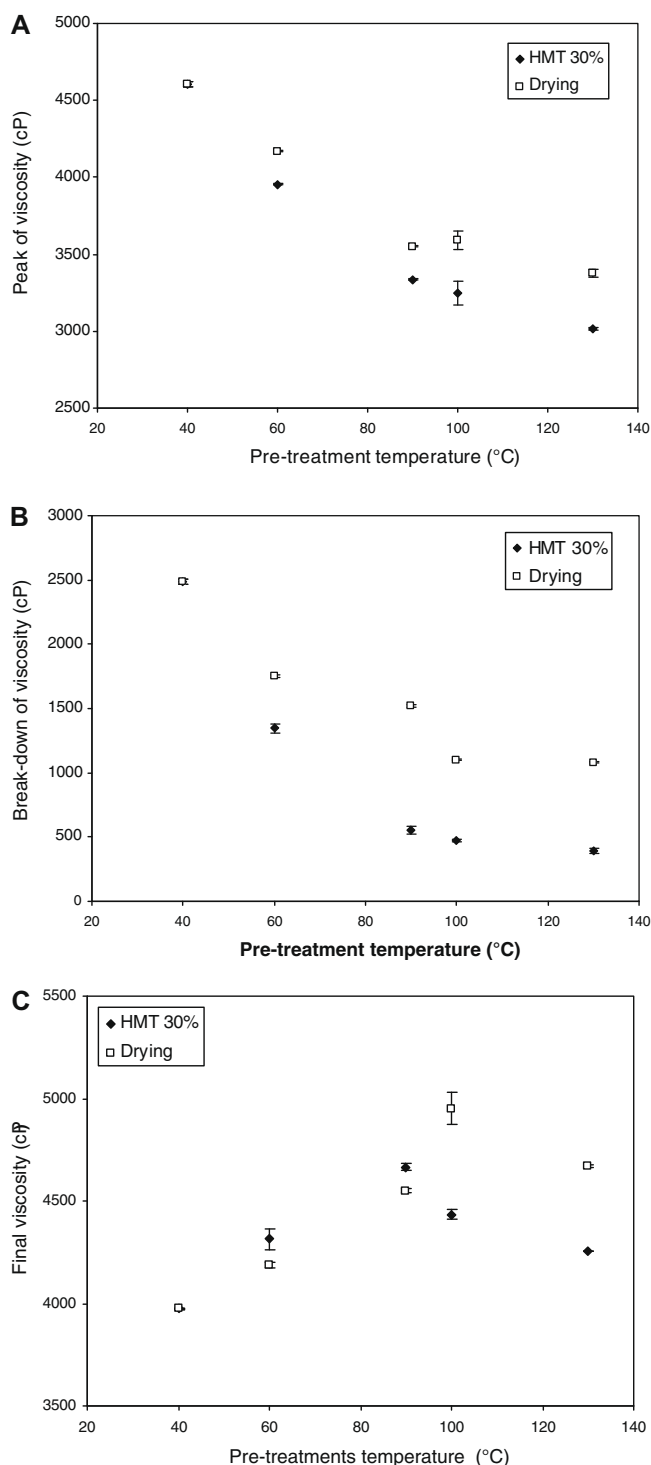


Fig. 9. Pasting characteristics of wet-milled starch according the corn drying (□) and the heat-moisture treatment (■) temperature.

Table 2
Influence of the pre-treatment on the pasting temperatures (peak) of WSG.

Sample	Pasting temperature (°C)	
	Corn drying	HMT at 30%
70	71.45 ± 0.64a	71.45 ± 0.64a
60	78.95 ± 0.00b	78.30 ± 3.33b
90	77.82 ± 0.60b	86.27 ± 1.37c
100	85.10 ± 0.63d	85.85 ± 0.56c
130	78.20 ± 0.00c	85.87 ± 0.53c

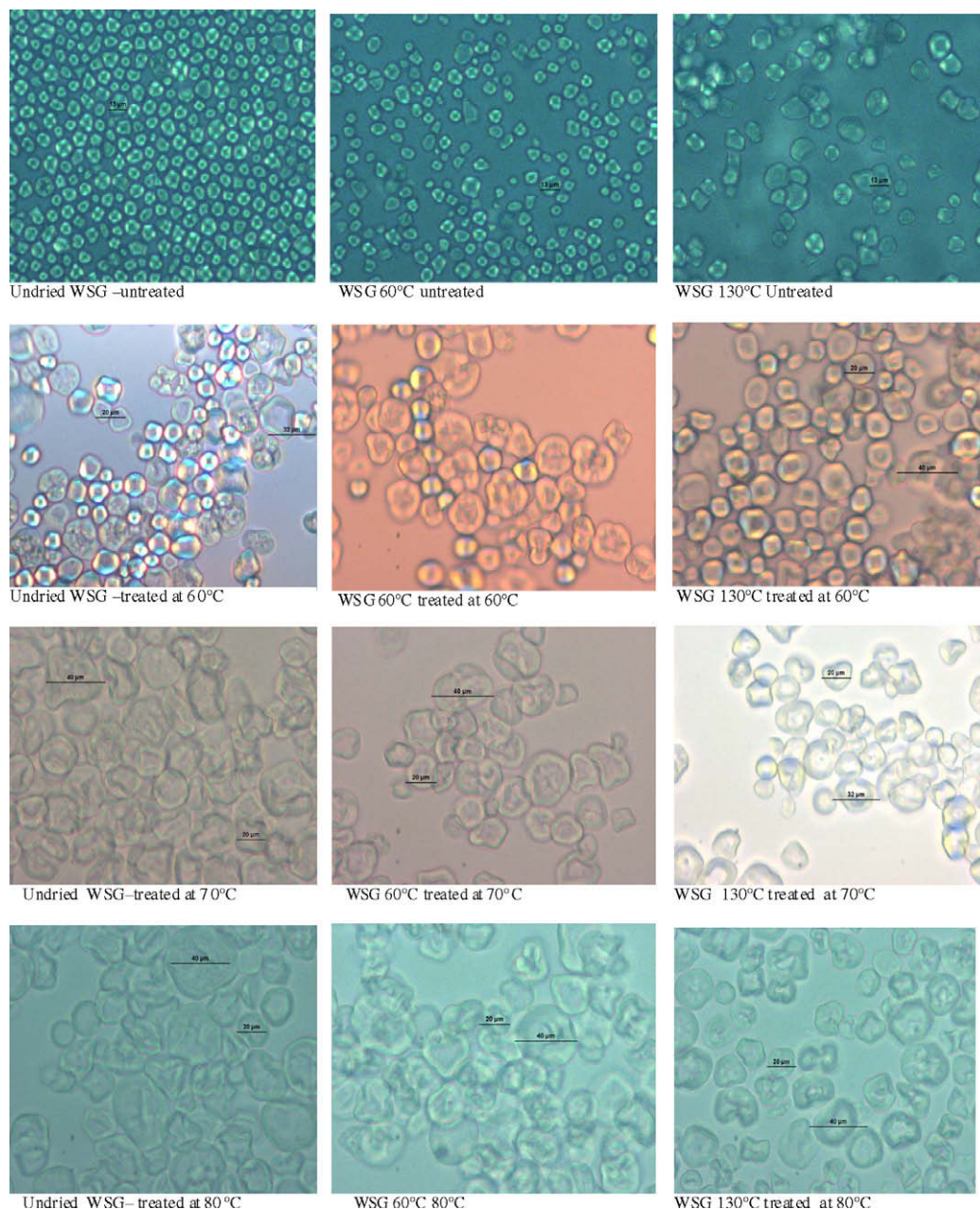


Fig. 10. Microscopic images under polarized light of WSG from undried and corn dried at 60 and 130 °C, without anymore treatment (untreated) and after 30 min of hydrothermal treatment at 60, 70 and 80 °C.

ogens are supposed aligned, and there are long range correlations between neighbouring lamellar crystals which can take smectic or nematic configuration depending to the availability of water or the heat-treatment (Donald, Kato, Perry, & Waigh, 2001).

In accordance with this theory it is postulated that during the heat-treatment of starch in limiting water availability upon separation of some amylopectine double helices from their lamellar crystallites (the crystalline smectic–nematic or smectic/isotropic phase transition), a true helix-coil transition occurs. The balance of these two processes is determined by the amount of water in the system for plasticisation of the amorphous backbone, and spacers, and for dissociation of the double helices in the coil state. The rigidity observed during further isothermal treatment of pre-treated starch in excess water could be justified, at least partially, by postulating that during the heat pre-treatment some smectic/nematic or smectic/isotropic phase transitions and double helice-

coil transitions occurred inside of the granule, allowing the re-assembly of free ends of amylopectine helices with part of amylopectine other than their original helix duplex partner, forming junctions and creating more general amorphous hydrogen bonded associations which stabilise the structure.

Several studies concerning the effect of heat-moisture treatment on thermal characteristic or swelling behaviour of starch showed that the rigidity induced after pre-treatment of the granule is more important in cornstarch rich in amylose rather than waxy starch (Hoover & Manuel, 1996; Tester, Debon, & Sommerville, 2000; Tsai, Li, & Lii, 1997). The liquid–crystalline model approach alone cannot explain this phenomenon since this theory concerns especially the crystalline region of granules where the amounts of free amylose are limited. Donald et al. (2001) stated that, during the heat-treatment the role of amylose appears to be to promote the loss of regularity in the packing of amylopectine, presumably

by entangling with the unwinding amylopectine side chains. Glass transitions occurring in amorphous region, rich in free amylose chain, probably play a fundamental role in inducing granular rigidity observed after heat-moisture treatment of cornstarch. One possible way in which it could do this is by increasing the motions of amylose chains which increase the formation of entanglements with neighbouring chains, including with unwound chains from helix-coil transition of amylopectine, acting as temporary cross-links, thereby conferring more rigidity on crystals.

Differences between the swelling capacities of samples pre-treated with different moisture contents can then be justified by the plasticization effect of water on the balance of transition induced inside of granule structure during the pre-treatment and by the junctions created between polymers present inside of the system. More experimental evidence from small and wide angle X-ray scattering, ¹³C-CP/MAS-NMR and modulated differential scanning calorimetric study are still needed to accurately elucidate the structural basis of this phenomenon.

4. Conclusion

High temperatures applied during the corn drying and the heat-moisture treatments of native starch granules increased the thermal resistance of WSG, reduced their swelling capacity during subsequent hydrothermal treatment, increased their gelatinization temperatures, decreased their residual enthalpy, and changed their pasting behaviour in excess water. For samples having similar residual protein content, the swelling rate and the pasting characteristics of starch are closely dependent on temperature and moisture content during the pre-treatment. This suggests that changes observed during the gelatinization of wet-milled starch granules cannot be attributed only to the residual protein of samples. Modifications in granules structure during the pre-treatment participate contribute certainly on the evolution of physicochemical and functional properties of wet-milled starch granules. For similar pre-treatment temperatures and initial moisture content, HMT affects more dramatically the physicochemical and functional properties of cornstarch than did hot-air drying of corn. It is likely that difference observed by comparing the corn drying effects and those of heat-moisture treatment of previously extracted granules starch may be attributed to availability of water inside of granules structure, which conferred different level of rigidity to starch granules during their pre-treatment by creating junctions between polymer chains. However, more experimental evidence is still needed to accurately elucidate the structural basis of this phenomenon.

Acknowledgements

The financial support to Mr. Malumba was supplied by the "Cooperation Univeritaire au Développement, CUD" an instance of Belgium cooperation. The authors are grateful to Mrs. Lefebvre Florence and Mr. Delimme Guy, Jacquet Nicolas and Maniet Guillaume for their technical assistance.

References

Altay, F., & Gunasekaran, S. (2006). Influence of drying temperature, water content, and heating rate on gelatinization of corn starches. *Journal of Agricultural and Food Chemistry*, 54, 4235–4245.

Chung, H.-J., Liu, Q., & Hoover, R. (2009). Impact of annealing and heat-moisture treatment on rapidly digestible, slowly digestible and resistant starch levels in native and gelatinized corn, pea and lentil starches. *Carbohydrate Polymers*, 73(3), 436–447.

Donald, A. M., Kato, L., Perry, P. A., & Waigh, T. A. (2001). Scattering studies of the internal structure of starch granules. *Starch/Stärke*, 53, 504–512.

French, D. (1984). Organisation of starch granules. In R. L. Whistler, J. N. Bemiller, & E. F. Paschall (Eds.), *Starch: Chemistry and technology* (2nd ed., pp. 183–247). London, UK: Academic Press, Inc.

Gunaratne, A., & Hoover, R. (2002). Effect of heat-moisture treatment on the structure and physicochemical properties of tuber and root starches. *Carbohydrate Polymers*, 49, 425–437.

Hardacre, A. K., & Clark, S. M. (2006). The effect of hybrid and growing environment on the rheological properties of starch and flour from maize (*Zea mays* L.) grain dried at four temperatures. *International Journal of Food Science and Technology*, 41(2), 144–150.

Haros, M., Tolaba, M.-P., & Suarez, C. (2003). Influence of corn drying on its quality for the wet-milling process. *Journal of Food Engineering*, 60, 177–184.

Haros, M., & Suarez, C. (1997). Effect of drying, initial moisture and variety in corn wet-milling. *Journal of Food Engineering*, 34, 473–481.

Hoover, R., & Manuel, H. (1996). The effect of heat-moisture treatment on the structure and physicochemical properties of normal maize, waxy maize, dull waxy maize and amylo maize V starches. *Journal of Cereal Science*, 23, 153–162.

Hoover, R., & Vasanathan, T. (1994). Effect of heat-moisture treatment on the structure and physicochemical properties of cereal, legume, and tuber starches. *Carbohydrate Research*, 252, 33–53.

Jayas, D. S., & White, N. D. G. (2003). Storage and drying of grain in Canada: Low cost approaches. *Food Control*, 14, 255–261.

Ji, Y., Ao, Z., Han, J.-A., Jane, J.-L., & BeMiller, J. N. (2004). Waxy maize starch subpopulations with different gelatinization temperatures. *Carbohydrate Polymers*, 57, 177–190.

Kugimiya, M., Donovan, J. W., & Wong, R. Y. (1980). Phase transitions of amylose-lipid complexes in starches: A calorimetric study. *Starch/Stärke*, 32(8), 265–270.

Kulp, K., & Lorenz, K. (1981). Heat-moisture treatment of starches. I. Physicochemical properties. *Cereal Chemistry*, 58(1), 46–48.

Lorenz, K., & Kulp, K. (1981). Heat-moisture treatment of starches. II. Functional properties and baking potential. *Cereal Chemistry*, 58(1), 49–52.

Lorenz, K., & Kulp, K. (1982). Cereal- and root starch modification by heat-moisture treatment. I. Physico-chemical properties. *Starch/Stärke*, 34(2), 50–54.

Lasseran, J. C. (1973). Incidence of drying and storing conditions of corn (maize) on its quality for starch industry. *Starch/Stärke*, 25(8), 257–262.

Lim, S.-T., Chang, E.-H., & Chung, H.-J. (2001). Thermal transition characteristics of heat-moisture treated corn and potato starches. *Carbohydrate Polymers*, 46, 107–115.

Malumba, P., Massaux, C., Deroanne, C., Masimango, T., & Béra, F. (2009). Influence of drying temperature on functional properties of wet-milled starch granules. *Carbohydrate Polymers*, 75, 299–306.

Massaux, C., Sindic, M., Lenartz, J., Sinnaeve, G., Bodson, B., Falisse, A., et al. (2008). Variations in physicochemical and functional properties of starches extracted from European soft wheat (*Triticum aestivum* L.): The importance to preserve the varietal identity. *Carbohydrate Polymers*, 71, 32–41.

Mistry, A. H., Wu, X., Eckhoff, S. R., & Litchfield, J. B. (1993). Wet-milling characteristics of high-temperature, high-humidity maize. *Cereal Chemistry*, 70(3), 360–361.

Nerying, A., & Reilly, P. J. (1984). Laboratory wet-milling of ensiled corn kernels. *Cereal Chemistry*, 61(1), 8–14.

Okechukwu, P. E., & Rao, M. A. (1996). Kinetics of cowpea starch gelatinization based on granule swelling. *Starch/Stärke*, 48(2), 43–47.

Olayinka, O., Adebawale, K. O., & Olu-owolabi, B. I. (2008). Effect of heat-moisture treatment on physicochemical properties of white sorghum starch. *Food Hydrocolloids*, 22, 225–230.

Peplinski, A. J., Paulis, J. W., Bietz, J. A., & Pratt, R. C. (1994). Drying of high-moisture corn: Changes in properties and physical quality. *Cereal Chemistry*, 71(2), 129–133.

Sandhu, K. S., Singh, N., & Kaur, M. (2004). Characteristics of the different corn types and their grain fractions: Physicochemical, thermal, morphological, and rheological properties of starches. *Journal of Food Engineering*, 64, 119–127.

Singh, N., Singh, J., Kaur, L., Sodhi, N. S., & Gill, B. S. (2003). Morphological, thermal and rheological properties of starches from different botanical sources. *Food Chemistry*, 8, 219–231.

Singh, N., & Eckhoff, S. R. (1996). Wet-milling of corn – A review of laboratory-scale and pilot plant-scale procedures. *Cereal Chemistry*, 73(2), 659–667.

Takaya, T., Sano, C., & Nishinari, K. (2000). Thermal studies on the gelatinization and retrogradation of heat-moisture treated starch. *Carbohydrate Polymers*, 41, 97–100.

Tester, R. F., Debon, S. J. J., & Sommerville, M. D. (2000). Annealing of maize starch. *Carbohydrate Polymers*, 42, 287–299.

Tsai, M., Li, C., & Li, C. (1997). Effect of granular structures on the pasting behaviors of starches. *Cereal Chemistry*, 74(6), 750–757.

Waigh, T. A., Gidley, M. J., Komanshek, B. U., & Donald, A. M. (2000a). The phase transitions in starch during gelatinization: A liquid-crystalline approach. *Carbohydrate Research*, 328, 165–176.

Waigh, T. A., Kato, L., Donald, A. M., Gidley, M. J., Clarke, C. J., & Riekell, C. (2000b). Side-chain liquid-crystalline model for starch. *Starch/Stärke*, 52, 450–460.

Weller, C., Paulsen, M. R., & Steinberg, M. P. (1988). Correlation of starch recovery with assorted quality factors of four corn hybrids. *Cereal Chemistry*, 65(5), 392–397.

Zhong, Z., & Sun, S. (2005). Thermal characterization and phase behavior of cornstarch studied by differential scanning calorimetry. *Journal of Food Engineering*, 69, 453–459.