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Swelling kinetics of waxy maize and maize starches at high temperatures and heating rates

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Abstract

For product and process development of starch-thickened products, it is essential to obtain data representative of the process conditions. Kinetics of granule swelling was followed when applying thermomechanical treatments in a lab simulator coupled to a rheometer. This lab simulator enables to follow the apparent viscosity development of starch dispersions for temperature profiles, heating and cooling rates as well as shear rates in the range of those encountered in industrial processes (pasteurisation/sterilisation in heat exchangers). Owing to sampling of the starch dispersions at different stages of the thermomechanical treatment (heating up to 120 °C and at a heating rate of 1 °C s^{-1}), the evolution of the granule size distribution of modified waxy maize, native waxy maize and native maize starch was obtained and compared to the apparent viscosity development. As expected, native starches were much more affected by the process than modified waxy maize starch, which maintained its granular structure. Kinetics of granule swelling is generally described as following a first-order kinetics except for the early stages of gelatinisation for which multi-order kinetics apply. However, most studies were done under isothermal conditions or at heating rates much lower that the one used in this work. In our case, for a hydrothermal treatment at high heating rates, it was found that granule swelling was best described by second-order kinetics.

Keywords: Starch; Gelatinization; Kinetics; Granule swelling; High heating rate

1. Introduction

Starch is the most widely used thickener in the food industry. The thickening of a starch dispersion during a thermomechanical treatment in excess water is the result of irreversible changes occurring at a temperature generally comprised between 60 and 70 °C. This behaviour is known as gelatinization/pasting (Atwell, Hood, Lineback, Varriano-Marston, & Zobel, 1988; Biliaderis, 1992) and corresponds to melting of crystallites and loss of birefringence, granules swelling, leaching of amylose in the continuous phase and eventually rupture of the granular structure. The pasting behaviour is influenced by the type of starch, concentration, shear rate, temperature–time profile as well as pH and presence of other ingredients (Thomas & Atwell, 1999).

Most industrial processes for starch-thickened products involve thermomechanical treatments at high temperature (pasteurisation, sterilisation), high heating rates (~1 °C s^{-1}) and medium to high shear rates (10–1000 s^{-1} in mixing processes or heat exchangers) (Loh, 1992). Native starches are in most cases not suitable for such conditions since high temperature and shear induce a loss of the granular structure. This drawback is one of the main reasons for the development of chemical modifications of starches, especially cross-linking. Depending on the level of cross-linking the granular structure can be maintained even under severe thermomechanical treatments (Thomas & Atwell, 1999).

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In order to be more efficient in product development, it is of interest to obtain data on gelatinisation behaviour of starch dispersions in real process conditions. Indeed the lack of such data, especially rheological, limits the estimation of coupled velocity/temperature profile and pressure drops in heat exchangers.

We (Lagarrigue & Alvarez, 2001) reviewed the methods to characterise the rheological behaviour during gelatinisation and showed that most studies were done at temperatures below 95 °C (Dolan & Steffe, 1990; Okechukwu and Rao, 1996b, 1996c; Walker, Ross, Wrigley, & McMaster, 1988). In some cases higher temperatures were applied (Breton, Korolczuk, Doublier, & Maingonnat, 1995; Nayouf, Loisel, & Doublier, 2003), however heating rates were either lower than process conditions (Nayouf et al., 2003) or, when higher, they could not be controlled (Breton et al., 1995; Dolan & Steffe, 1990).

In order to develop a model for the rheological behaviour of starch dispersions during gelatinisation, a kinetic approach was mainly used and is based on the correlation between rheological properties and extent of granule swelling (Bagley & Christianson, 1982; Dolan & Steffe, 1990; Doublier, Llamas, & Le Meur, 1987; Kokini, Lai, & Chedid, 1992; Okechukwu & Rao, 1995, 1996a). It is generally accepted that granule swelling follows a first-order kinetics (Kubota, Hosokawa, Suzuki, & Hosaka, 1979; Lund, 1984; Okechukwu & Rao, 1995), except at the early stages of gelatinisation for which multi-order kinetics apply (Lund, 1984). However, most studies were done during a series of isothermal conditions or for heating rates that are not representative of process conditions.

The objective of this paper is to investigate kinetics of granule swelling of modified waxy maize starch dispersions in a lab simulator that enables to reproduce temperature profiles, heating and cooling rates as well as shear rates in the range of those encountered in industrial processes. An attempt to extent the result to native waxy maize and native maize starch is presented.

2. Materials and methods

2.1. Raw materials

Native waxy maize starch (moisture content 12.1%), abbreviated WM, and native maize starch (moisture content 12.0%), abbreviated M, were supplied by Cerestar. Chemically modified waxy maize starch (acetylated distarch adipate, moisture content 12.3%), abbreviated MWM, was supplied by National Starch. Starch moisture content was determined according to the method ISO 1666 (130 °C, 1h30).

2.2. Methods

2.2.1. Thermomechanical treatment in a pressure cell

Thermomechanical treatment is performed in the pressure cell of a rheometer UDS 200® (Physica).

The cell is equipped with a cup (diameter: 27.1 mm) and a bob (diameter: 25.0 mm, length: 37.5 mm) and is designed to measure the flow behaviour of semi-liquid products up to a temperature of 140 °C without boiling (maximum pressure applied: 6 bars).

The cup was further adapted by our laboratory (Alvarez Leguizamo, 2006) in order to apply temperature profiles representative of thermal conditions encountered in processing of semi-liquid foods. The cup is equipped with a double jacket in which a cooling fluid (mineral oil) is circulating. It contains also heating resistances inserted at regular intervals in its wall. To control and impose the temperature profile, a predictive control algorithm based on least square method was developed. Heating and cooling rates applied at the surface of the cup are up to 3.5 °C s^{-1}. However even if the gap between the cup and the bob is small (1.1 mm), the temperature within the sample is not homogenous during such thermal treatment. At 1 °C s^{-1}, the temperature difference between the inner surface of the cup and the outer surface of the bob is around 20 °C for a starch suspension at 4%. As a remark, in heat exchangers, the temperature variation can be as well of the same order of magnitude. For instance Liao, Rao, and Datta (2000) developed a model to estimate temperature profiles in a tubular heat exchanger during gelatinisation of a starch suspension. For our experiments, a model was established (Lagarrigue, Alvarez, & Flick, 2007) in order to estimate the temperature profile the most representative of the sample treatment (temperature estimation at the middle of the gap). The estimated temperature will be named “mean sample temperature”. In most results presented below both temperatures (cup temperature, mean sample temperature) will be indicated.

During a thermal treatment apparent viscosity is measured at constant shear rate in the range 150–800 s^{-1}.

Starch dispersions (concentration C in g of dry starch per g of suspension) are prepared by rehydration of starch powders in deionised water during 30 min and are introduced in the pressure cell at room temperature. Pressure is set (up to 6 bars depending on the maximum temperature) and thermomechanical treatment and measurement are immediately started. In order to prevent sedimentation a shear rate of 800 s^{-1} is applied until the mean temperature is 55 °C. In this stage the flow is not laminar. In a second phase (starch gelatinisation) the shear rate is set according to the experimental conditions to be studied.

The cup is equipped with a sampling device, which consists of a 1 mm diameter hole in the upper part of the gap, which is filled with a metallic wire and closed by a screw in order not to disturb the measurement. After thermal treatment including cooling, the pressure is released and the metallic wire is replaced by a syringe. Since high temperature gradients are observed during those thermal treatments, it is important to ensure that the sample taken corresponds to the part of the sample present in the gap and not to the parts above and under the bob, which have undergone slightly different thermomechanical treatments.

The maximum volume taken is 0.6 ml and the bob is maintained under rotation during sampling in order to have a homogenous sample.

In order to determine kinetics of starch swelling, heating is stopped at regular intervals (5 or 10 °C) and the cup is cooled at 3.5 °C s^{-1} without applying any shear until the mean temperature reaches 40 °C. A sample is then taken according to the procedure described above. Examples of temperature profiles applied during this procedure are shown in Fig. 1. Some samples are also "well cooked" by heating up to 120 °C during 60 s. Okechukwu and Rao (1995, 1996a, 1996b, 1996c) also applied this methodology of rapidly cooling a starch paste at different stages of gelatinisation, however the cooling rate was not controlled.

Experimental conditions are shown in Table 1. Each experiment was done in duplicate. Influence of concentration, shear rate and heating rate were studied for the modified waxy maize starch.

2.2.2. Starch granule size distribution

Particle size distribution was measured with a laser granulometer Mastersizer S (Malvern Instruments) equipped with a 300 mm Fourier cell (range 0.05–879 μm). After the thermomechanical treatment, a few drops of the starch dispersion in water are introduced in the cell (100 ml) until the obscuration is around 20%, which corresponds to a dilution of about 1/100. All measurements were done at room temperature. Each replicate is analysed twice, therefore the values associated to a given thermomechanical treatment are an average over four measurements.

Results are analysed according to the Mie scattering theory. The refractive index of water and starch were taken as 1.33 and 1.53, respectively (Loisel, Tecante, Cantoni, & Doublier, 1998). Starch granule absorption was taken as zero.

The mean diameter in volume $D[4,3]$ (=mean diameter weighted by the volume of the particles) and the standard deviation of the distribution are considered.

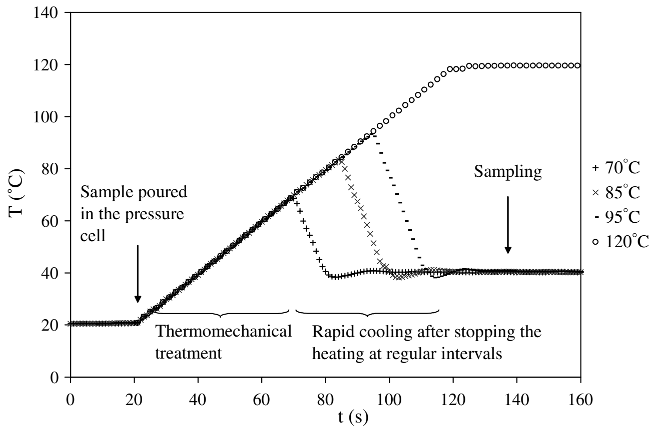

Fig. 1. Examples of some cup temperature profiles (heating rate: 1 °C s^{-1}, cooling rate: 3.5 °C s^{-1}).

2.2.3. Swelling capacity and solubility index

Swelling capacity of the starches and leached amylose in the continuous phase were determined according to swelling-solubility measurements (Doublier et al., 1987; Leach, McCowen, & Schoch, 1959). Starch dispersions (0.5% w/w) were centrifuged during 15 min at 1000*g*. The weight of the sediment as well as the starch concentration in the supernatant was determined. The swelling capacity, Q, is defined as the weight of the swollen granules divided by the weight of dry starch (Bagley & Christianson, 1982). The solubility index (S in percentage), as defined by Doublier et al. (1987), is expressed as the weight of solubilised starch in the supernatant divided by the total weight of dry starch. Doublier et al. (1987) defined the volume fraction, ϕ, occupied by a starch dispersion at the concentration C (g of dry starch/g of starch suspension) by the following equation: $\phi = (1 - S/100) \times CQ$. For the chemically modified starch, the solubility index is neglected for all thermomechanical treatments.

3. Results and discussion

3.1. Modified waxy maize starch swelling at high heating rate

The evolution of the granule size distribution of the MWM starch during heating up to 120 °C at a heating rate of 1 °C s^{-1} and under a shear rate of 400 s^{-1} is shown in Fig. 2. The uncooked starch consists of granules having a diameter from 4 to 30 μm, with a mean diameter in volume equal to 15.5 μm and a standard deviation equal to 5.1 μm. During heating swelling of the granules is observed, the main changes occurring for a cup temperature comprised between 65 and 85 °C or a mean sample temperature comprised between 54 and 72 °C. At the highest temperature ($T = 120$ °C, cooking time = 60 s), observations under the microscope indicate that the granular structure is maintained. The granule size distribution is almost the same as for the treatment limited to 95 °C. The size distribution is comprised between 8 and 76 μm, with a mean diameter in volume equal to 39.6 μm and a standard deviation of 11.9 μm. Those values are in agreement with those obtained for a similar starch by other authors (Nayouf et al., 2003; Tecante & Doublier, 1999; Ziegler, Thompson, & Casasnovas, 1993). It has to be noted that the granule size dispersion during heating at high heating rate is not only the result of an heterogeneity of starch granules size and ability of swelling, but also of the temperature inhomogeneity in the gap of the measuring cell. Indeed due to the high heating rate the temperature difference across the gap is of 20–22 °C as calculated according to the thermal model presented by Lagarrigue et al. (2007). The size distribution might then be larger, especially at the beginning of the gelatinisation, than what would be expected for a treatment without thermal gradient.

The increase in granule size induces an increase in apparent viscosity, which is shown in Fig. 3. The evolution

Table 1
Experimental conditions

Starch type	C (% w/w)	Shear rate (s^{-1})	Heating rate (°C s^{-1})	$T_{max\ cup}$ (°C)[a]
MWM	2.6–3.1–4.0	400	1	From 65 to 95 °C, every 5 °C–120°C[b]
MWM	3.1	400	0.25–0.5–1	From 65 to 95 °C, every 5 °C–120 °C[b]
MWM	3.1	400–800	1	From 65 to 95 °C, every 5 °C–120 °C[b]
WM	3.1	400	1	From 65 to 95 °C, every 5 °C–110 °C
M	4.0	400	1	From 65 to 95 °C, every 5 °C–110 °C

[a] $T_{max\ cup}$ indicates the cup temperature at the end of the heating phase of the thermomechanical treatment.
[b] After the heating phase to 120 °C, this temperature was maintained during 60 s.

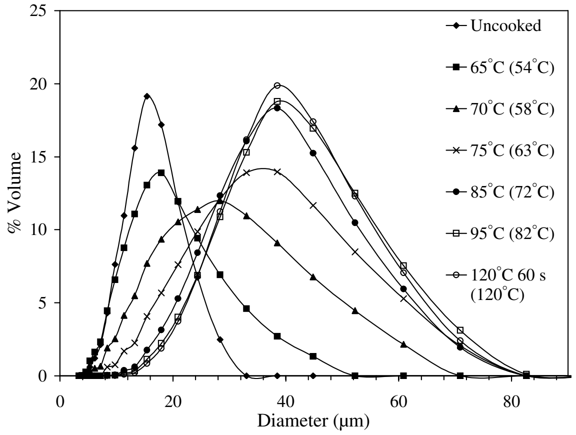

Fig. 2. Granule size distribution evolution of MWM starch during a thermomechanical treatment (concentration: 3.1% w/w, shear rate: 400 s^{-1} and heating rate: 1 °C s^{-1}). The temperatures indicated correspond to the maximum value of the cup temperature and of the mean sample temperature (between brackets).

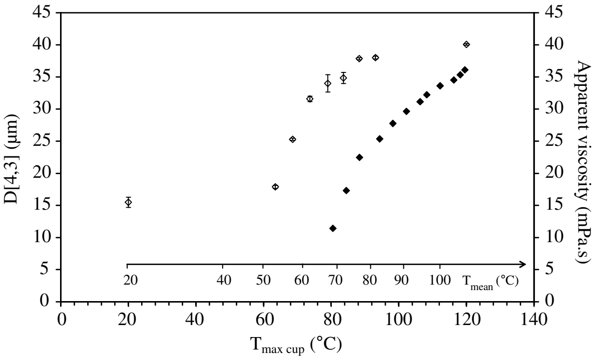

Fig. 3. Evolution of the mean granule diameter (◇) in comparison with the increase in apparent viscosity (◆) for MWM starch during the thermomechanical treatment (concentration: 4.0% w/w, shear rate: 400 s^{-1} and heating rate: 1 °C s^{-1}). The temperatures indicated correspond to the cup temperature and the mean sample temperature.

of the mean diameter indicates a two stage process during gelatinisation as suggested by Kokini et al. (1992): a steep increase corresponding to a fast absorption of water by the granules, followed by a slower increase which might be due to a diffusional phenomenon. Although the beginning of the viscosity increase cannot be determined precisely due to the sensitivity of the instrument, it seems that the contribution of the swollen granules to the viscosity of the system start to become significant above a certain volume fraction. The increase in apparent viscosity occurs for a mean sample temperature comprised between 65 and 70 °C, whereas the increase of the diameter occurs already for a temperature of about 55 °C. According to the starch supplier, the increase of viscosity for this starch occurs around 65 °C and the maximum viscosity is achieved at 80–85 °C (5% w/w starch dispersion measured with a Brabender viscograph), which confirm also that the temperature calculated at the middle of gap is more representative of the mean thermal treatment than the temperature of the cup. Ziegler et al. (1993) also observed a temperature difference of the same order of magnitude between the increase of viscosity of waxy maize starches (Brabender viscograph) and the increase in mean diameter measured directly in a laser granulometer cell which was heated up at 4.8 °C min^{-1}.

The evolution of the granule mean diameter in volume $D[4,3]$ and the swelling ratio, expressed as $(D/D_0)^3$ with D_0 equal to the mean diameter of the uncooked starch, are summarised in Table 2. The swelling ratio is compared with the swelling capacity, Q, obtained according to swelling-solubility measurements. For the highest temperatures, the swelling capacity was significantly higher than the swelling ratio obtained through the particle size measurements. As noticed by Nayouf et al. (2003), the centrifugation method might overestimate the swelling capacity since it does not take into account interstitial water in between the swollen starch granules contained in the sediment. The same authors reported slightly higher swelling capacity values for a starch having a similar type of chemical modification but a lower extent of cross-linking. In order to estimate the volume fraction occupied by the starch granules, the swelling capacity instead of the swelling ratio was used. According to Doublier et al. (1987) and Steeneken (1989), the rheological behaviour of a starch suspension depends on the volume fraction range. Especially for ϕ above 0.7 (concentrated regime), the deformability of the starch granules play an increasing role. Steeneken (1989) also mentions that the ability of the starch granules to swell up to their maximum size depends on the value of the volume fraction (diluted or concentrated regime). The volume fraction occupied by the starch granules during heating is shown in Table 2 for the different concentrations studied. The concentrated regime might be reached only for the 4% w/w suspension heated at 120 °C (ϕ

Table 2
Mean diameter in volume D [4,3], swelling ratio $(D/D_0)^3$, swelling capacity Q and volume fraction ϕ ($\phi = CQ$) of starch suspensions according to maximum temperature applied during the thermomechanical treatment (shear rate: 400 s^{-1} and heating rate: 1 °C s^{-1})

$T_{\text{max cup}}$ (°C)	D[4,3] (μm)	$(D/D_0)^3$	Q (g/g)	ϕ
20 (Uncooked)	15.5 (±0.3)	1.0	1.0	0.03 ($C = 2.6\%$) 0.03 ($C = 3.1\%$) 0.04 ($C = 4.0\%$)
70	25.7 (±0.6)	4.6	5.1 (±0.8)	0.13 ($C = 2.6\%$) 0.16 ($C = 3.1\%$) 0.21 ($C = 4.0\%$)
75	32.8 (±0.3)	9.5	6.8 (±0.7)	0.18 ($C = 2.6\%$) 0.21 ($C = 3.1\%$) 0.27 ($C = 4.0\%$)
80	36.1 (±0.5)	12.6	12.0 (±0.9)	0.31 ($C = 2.6\%$) 0.37 ($C = 3.1\%$) 0.48 ($C = 4.0\%$)
85	36.3 (±0.2)	12.9	13.2 (±0.8)	0.34 ($C = 2.6\%$) 0.41 ($C = 3.1\%$) 0.53 ($C = 4.0\%$)
95	37.4 (±0.5)	14.1	17.0 (±0.6)	0.44 ($C = 2.6\%$) 0.53 ($C = 3.1\%$) 0.68 ($C = 4.0\%$)
120	39.6 (±0.5)	16.7	23.0 (±0.9)	0.60 ($C = 2.6\%$) 0.71 ($C = 3.1\%$) 0.92 ($C = 4.0\%$)

= 0.92), however, as mentioned earlier, this value might be overestimated due to the measurement method.

The influence of the heating rate on the mean diameter evolution of the MWM starch as a function of the cup temperature is shown in Fig. 4. Although the increase in granule mean diameter follows the same trend for a heating at 1 °C s^{-1} or 0.25 °C s^{-1}, the steep increase occurs at lower cup temperatures for the lowest heating rate. We explain this by considering the inhomogeneity of temperature in the gap which decreases with a lower heating rate. Indeed, the temperature difference in the gap during heating at 1 °C s^{-1} is around 20–22 °C, whereas it is only about 5–6 °C for a heating rate of 0.25 °C s^{-1}. The granule mean diameter represents a mean between diameters of granules that have been submitted to different heating kinetics according to their location in the gap. For a given cup temperature, the temperature near the bob is lower for a high heating rate so that more granules remains unswollen. When the mean granule diameter is considered as the function of the mean sample temperature, the difference in granule swelling is much less dependent on the heating rate. When the majority of the granules in the whole gap reach almost the maximum swelling ($T_{\text{cup}} = 80$ °C), no differences are observed for the two heating rates. For the highest heating rate (1 °C s^{-1}), the dispersion of the distribution during the steep increase of the granule size is higher than for the lowest heating rate (0.25 °C s^{-1}). The dispersion of the distribution increases from 5.2 (uncooked starch) to 11.9 μm (end of cooking), however the high dispersion values observed during the first stage of gelatinisation (16–18 μm) probably also come from the heterogeneity of thermal treatment in the gap. Indeed Okechukwu and Rao (1995, 1996b, 1996c) presented standard deviations that are the highest as the end of the thermomechanical treatment (done at constant temperature).

The shear rate has little influence on the swelling kinetics of MWM in the range investigated (400–800 s^{-1}) as can be seen in Fig. 5a. This can be explained by the fact that this type of starch has a low sensitivity to shear and that the range of shear rates investigated is quite narrow. On the other side an heterogeneity of temperature in the gap might induce also a strong heterogeneity of shear rates in the gap especially at the beginning of gelatinisation. In the early

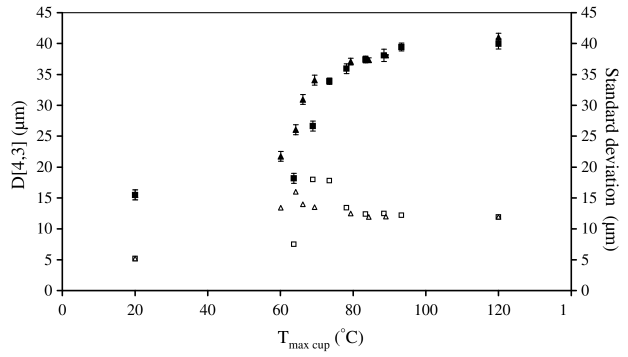

Fig. 4. Evolution of the mean granule diameter and standard deviation of a 3.1% w/w MWM starch dispersion during heating at 1 °C s^{-1} (■: diameter, □: standard deviation) or 0.25 °C s^{-1} (▲: diameter, △: standard deviation) and at a shear rate of 400 s^{-1}.

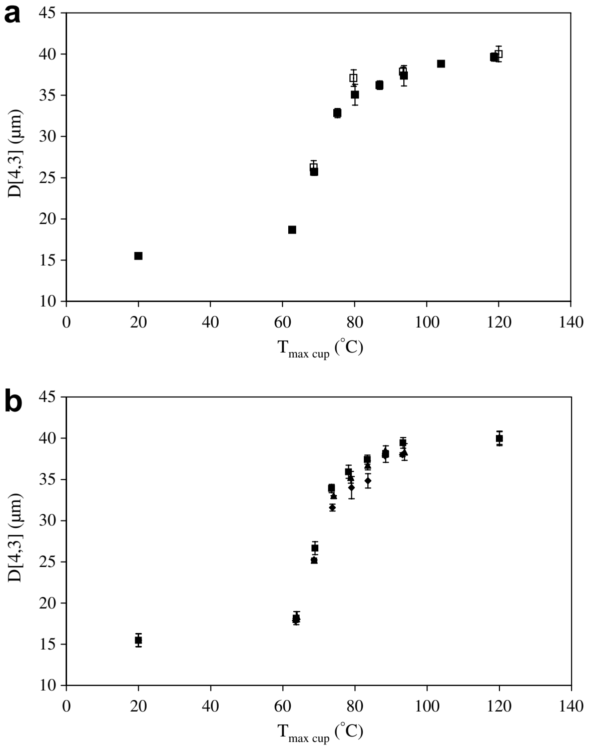

Fig. 5. (a) Influence of the shear rate (■: 400 s^{-1} and □: 800 s^{-1}) on the mean granule diameter of a 3.1% w/w MWM starch dispersion during heating at 1 °C s^{-1}. (b) Influence of the concentration (▲: 2.6% w/w, ■: 3.1% w/w and ◆: 4.0% w/w) on the mean granule diameter of MWM starch during heating at 1 °C s^{-1} and under a shear rate of 400 s^{-1}.

stages of gelatinisation, granules located close to the outer cup start to swell, increasing the viscosity of the corresponding fluid layer, whereas the granules close to the inner bob are still not gelatinising. The shear rate in the fluid layer close to the inner bob might then be higher than the set shear rate, whereas it might be the contrary for the fluid layer close to the outer cup.

The influence of the concentration of MWM (in the range 2.6–4.0%), on the swelling kinetics for a heating rate of 1 °C s^{-1} is presented in Fig. 5b. A comparable evolution of the mean granule diameter is obtained in this concentration range. This was also observed by Tecante and Doublier (1999) for a similar type of starch in the range 2–4%.

3.2. Modelling of modified waxy maize starch granule swelling kinetics

For iso-thermal conditions most authors presented the kinetics of granule swelling as a first-order reaction (Kubota et al., 1979; Lund, 1984; Okechukwu & Rao, 1995) although early stages of gelatinisation obey rather to a multiple order (Lund, 1984). Some authors also suggested also that gelatinisation could not be described by a single reaction but rather by a set of reactions (Kokini et al., 1992).

As Okechukwu and Rao (1996a, 1996b, 1996c) and Rao and Tattiyakul (1999), we define the degree of gelatinisation (X) by a diameter ratio: $X = (D_t - D_0)/(D_m - D_0)$, where D_t is the mean diameter at the time t of the heating process, D_0 the mean diameter of the uncooked starch and D_m the maximum mean diameter. Mean diameter in volume $D[4,3]$ will be considered. The maximum mean diameter was taken as the average of the maximum diameters obtained for the different thermomechanical treatments at 120 °C, 60 s ($D_m = 40.0 \pm 0.7$ μm).

Although a first-order kinetics could enable to describe the steep increase in the degree of gelatinisation, a better fit was obtained with a second-order kinetics and this enabled to obtain the best fit for the diameter evolution up to 85–90% of gelatinisation.

The reaction of granule swelling is thus expressed as a second-order kinetics for the degree of gelatinisation X:

$$\frac{dX}{dt} = V(T)(1 - X)^2 \tag{1}$$

The rate constant, V, is dependent on temperature and was assumed to follow an Arrhenius law:

$$V(T) = V_0 \exp\left(-\frac{E_a}{RT_{\text{mean}}(t)}\right) \tag{2}$$

where V_0 (s^{-1}) is the rate constant, E_a the activation energy (J mol^{-1}) and R the gas constant (8.31 J mol^{-1} K^{-1}). We consider in the model the mean sample temperature as it is representative of the mean treatment in the gap.

Therefore the following equation is obtained.

$$\frac{X}{1 - X} = \frac{D_t - D_0}{D_m - D_t} = V_0 \int \exp\left(-\frac{E_a}{RT_{\text{mean}}(t)}\right) dt \tag{3}$$

The activation energy, E_a, is then adjusted (in the range 0–90% gelatinisation degree) in order to obtain the best correlation coefficient for the linear relation between $(D_t - D_0)/(D_m - D_t)$ and the integral $\int \exp(-E_a/RT_{\text{mean}}(t))\,dt$. An example of the identification of the activation energy is shown in Fig. 6. Table 3 summarises the values for the different conditions shown in Table 1. The activation energy is comprised between 75.7 and 140.5 kJ mol^{-1}. No trend can be observed with regard to the influence of the heating rate, concentration or shear rate for this set of data. The variability of the activation energy was attributed to the precision of the data fitting method. Especially the result is influenced by the precision of the calculation of the degree of gelatinisation.

Activation energy of gelatinisation has been widely determined by DSC (Calzetta-Resio & Suarez, 2001; Karapantsios, Sakonidou, & Raphaelides, 2002; Pielichowski, Tomasik, & Sikora, 1998; Spigno & De Faveri, 2004), however, up to our knowledge, few data based on swelling and rheological data have been published. For example, Okechukwu and Rao (1996a, 1996b, 1996c) reported an activation energy of 62.4 kJ mol^{-1} for maize starch (2.6% w/w) using a first-order kinetics for the evolution of the degree of gelatinisation. Based on rheological data, Dolan and Steffe (1990) reported an activaton energy of gelatinisation of 740 kJ mol^{-1} also for maize starch (5.5–7.3% w/w).

3.3. Applicability to native waxy maize and maize starches

This methodology was applied to native waxy maize and maize starches. The evolution of the mean granule diameter for a thermomechanical treatment at a heating at 1 °C s^{-1} and under a shear rate of 400 s^{-1} is shown in Fig. 7a and b.

The uncooked native waxy maize starch has a mean granule diameter in volume equal to 16.1 μm. The onset of swelling of the granules is observed for a cup temper-

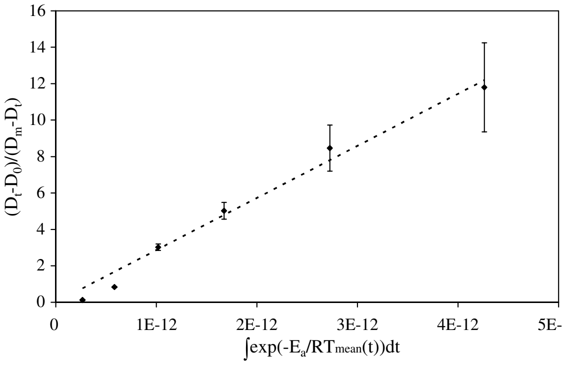

Fig. 6. Evolution of $X/(1 - X)$ as a function of the temperature – time history expressed as the integral of $\exp(-E_a/RT_{\text{mean}}(t))$ for a 3.1% w/w MWM starch dispersion (heating rate: 1 °C s^{-1}, shear rate: 400 s^{-1}). The best correlation ($r^2 = .983$) is obtained for $E_a = 84.8$ kJ mol^{-1}.

Table 3
Activation energy (E_a) and correlation coefficient (r^2) for the different thermomechanical treatments applied to suspensions of modified waxy maize starch

C (% w/w)	Shear rate (s^{-1})	Heating rate (°C s^{-1})	E_a (kJ mol^{-1})	r^2
2.6	400	1	140.5	.987
3.1	400	1	84.8	.983
3.1	400	0.5	107.2	.951
3.1	400	0.25	90.6	.977
3.1	800	1	75.7	.987
4.0	400	1	116.4	.998

ature of around 65 °C, which corresponds to a mean sample temperature of 54 °C. The mean granule diameter increases up to a cup temperature of 84 °C or a mean sample temperature of 74 °C. For heating temperatures above this limit, the results indicate a degradation of the starch granules. Since the granules are then quite sensitive to shear, the sampling procedure might affect the particle size distribution. This might also explain the scattering of the data for the highest temperatures (the values shown in Fig. 7a are then only indicative in that stage). Under the microscope, some ruptured granules are clearly observed when the cup temperature is about 110 °C. At 120 °C, the suspension contains mainly ruptured granules. The kinetic model for granule swelling is therefore only applied during the part of the heating when no ruptured granules are present ($T_{\text{max cup}}$ below 85 °C). The maximum mean granule diameter was taken as the average of the maximum values obtained for different thermomechanical treatments ($D_m = 43.1 \pm 1$ μm, unpublished data from the authors). For the standard thermomechanical treatment, the activation energy is then equal to 146 kJ mol^{-1} ($r^2 = .997$).

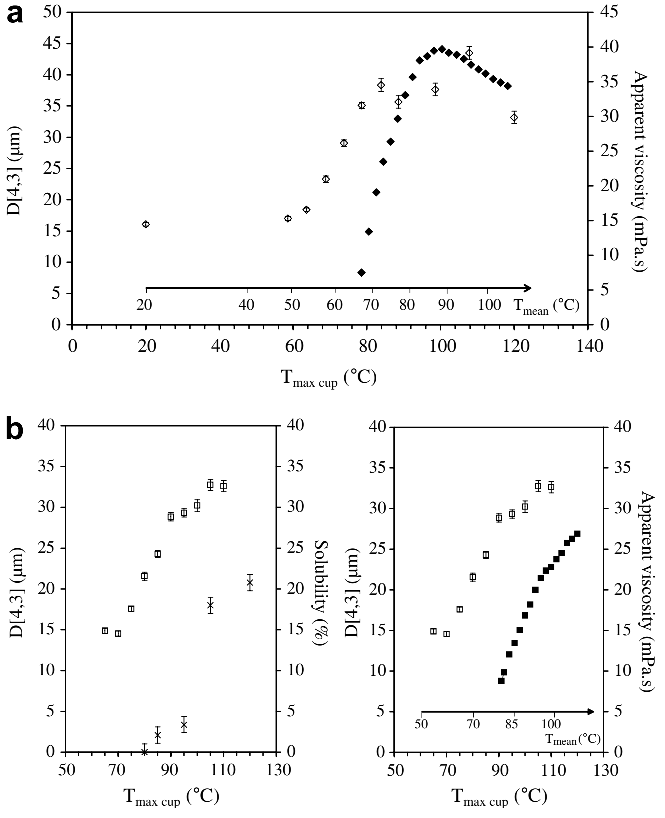

Fig. 7. Evolution of the mean granule diameter in comparison with the increase in apparent viscosity for (a) a 3.1% w/w native waxy maize starch dispersion (◇: mean diameter,◆: apparent viscosity) and (b) a 4.0% w/w native maize starch dispersion (□: mean diameter, ■: apparent viscosity) during the thermomechanical treatment (shear rate: 400 s^{-1} and heating rate: 1 °C s^{-1}). In the case of maize starch, the evolution of the solubility index (×) is shown.

The uncooked native maize starch (Fig. 7b). has a mean granule diameter in volume equal to 12.6 μm. The onset of swelling of the granules is observed for a cup temperature of around 75 °C, which corresponds to a mean sample temperature of 64 °C. The difference in gelatinisation temperature between waxy maize and maize starch is in accordance with the literature (Thomas & Atwell, 1999). For native maize starch, two stages of granule swelling can be observed. Up to a cup temperature of 90 °C (mean sample temperature of 78 °C), a steep increase in mean granule diameter is observed. In this stage, the percentage of starch in the continuous phase is quite low (solubility index below 5%), as well as the content of ruptured granules observed by microscopy. Above a mean sample temperature of 80 °C, the increase in granule mean diameter is much slower, while the solubility index is increasing sharply up to about 21% (mean sample temperature of 110 °C). This increase in two stages for the mean granule diameter has been previously described by Doublier et al. (1987). The kinetic model for granule swelling is therefore only applied in the first stage; the value of the maximum granule diameter was nevertheless taken as the maximum value obtained for this thermomechanical treatment ($D_m = 33 \pm 0.8$ μm). The activation energy is then equal to 212 kJ mol^{-1} ($r^2 = .994$). The swelling-solubility measurements also indicate that the swelling capacity increases up to a value of about 10 in the first phase of swelling. Therefore, the volume fraction occupied by the starch granules ($\phi = (1 - S/100) \times CQ$) is increasing up to 0.39 in this stage of swelling.

The evolution of the apparent viscosity of the native waxy maize and maize starch dispersions during the same treatment is shown in Fig. 7a and b. As previously observed for the MWM starch, apparent viscosity increase of waxy maize starch occurs at a temperature which is 10–15 °C higher than for the increase in granule size. However, in the case of maize starch this difference is noticeably higher (15–20 °C). This is in accordance with the observations of Ziegler et al. (1993) for those two starches. For waxy maize starch and contrary to the MWM starch, a decrease in apparent viscosity is observed for a cup temperature of 100 °C (mean sample temperature of 88 °C) as a result of the rupture of the granules. This decrease in apparent viscosity is not observed for maize starch under the conditions studied. This might have been the case if the thermal treatment had been maintained for a few minutes.

4. Conclusion

This methodology enables to characterise, in-situ and in a small scale equipment, both the swelling and rheological behaviour of starch dispersions that are submitted to thermomechanical treatments representative of process conditions: high heating rate (from 0.25 to 1 °C s^{-1}), high temperatures (above 100 °C) and relatively high shear rates ($\sim$100–1000 s^{-1}). Data on granule swelling and resulting apparent viscosity development were obtained under controlled temperature and shear conditions and a kinetic model was used to describe this evolution. A second-order kinetics was successfully applied to account for the swelling of a modified waxy maize starch until temperatures above 100 °C. This type of model can also be applied for native waxy maize starch until the granules start to rupture or for native maize starch when the solubility index is still low. Such data for thermomechanical conditions representative of some food processing conditions might be useful for process modelling provided they are linked to the evolution of the rheological properties of starch suspensions in such conditions.

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