

Modelling corn starch swelling in batch systems: effect of sucrose and hydrocolloids

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Abstract

Hydrocolloids are used in starch-based products to improve stability and to obtain specific textural characteristics. In stirred batch systems with constant jacket temperature, xanthan gum, guar gum and sodium alginate (1% w/w) were added to corn starch (10% w/w) and sucrose (15% w/w) in aqueous systems to test their effects on granule swelling, starch gelatinization temperatures and viscoelastic behavior of the hot paste. As heating is not instantaneous, time–temperature relationships cannot be avoided. In this regard, heat penetration was faster in viscoelastic systems with lower complex dynamic modulus (G^*) values, while pastes containing gums showed lower heat transfer rates during gelatinization. Microscopy and image analysis were applied to describe the granule swelling process in starch gelatinization. Starch granule swelling was considerably reduced by the presence of gums due to the lower heating rates and the decreased mobility of water molecules. The presence of sucrose increased starch gelatinization temperatures, measured by differential scanning calorimetry; gum addition did not show a significant influence on these temperatures. The effect of time and temperature on the starch swelling process was modelled considering, as driving force, the difference between the instantaneous mean curvature of the granule (reciprocal of the diameter) and the asymptotic curvature. Gelatinization rate constants were calculated for the different pastes and the lowest values were observed for starch pastes added with gums. Activation energies ranged from 80 (± 14) to 119 (± 3) kJ mol⁻¹, being comparable to values reported in the literature for starch gelatinization measured by different methods.

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1. Introduction

The formulation of starch-based sweet products often involves addition of sucrose and hydrocolloids, the latter being usually incorporated into starch-based food formulations to improve stability (avoiding syneresis) or to obtain specific textural characteristics (Glicksman, 1982). Frequently used hydrocolloids are xanthan gum, sodium alginate or guar gum, which reduce the adverse effects of starch retrogradation during freezing and frozen storage (Ferrero, Martino, & Zaritzky, 1994, 1996; Ferrero & Zaritzky, 2000). Several authors (Biliaderis & Prokopowich, 1994; I'Anson et al., 1990; Ikeda,

Yabuzoe, Takaya, & Nishinari, 2001; Kohyama & Nishinari, 1991; Slade & Levine, 1988) have analyzed the effect of different sugars on starch gelatinization and retrogradation. In spite of the beneficial effects of certain sugars and hydrocolloids in retarding or inhibiting starch retrogradation, the highly hydrophilic characteristics of these components may decrease water availability causing difficulties for starch dispersion and gelatinization.

Starch gelatinization is a complex process, involving granule swelling and disruption. Amylose is leached out and amylopectin remains inside the swollen, partially disrupted granule. The degree of granular collapse is related to heating time, temperature and the type of mechanical treatment applied to the sample (Zobel, 1984). Hydrocolloids interact with the amylose outside the starch granule to produce a more complex matrix of amylose and hydrocolloid surrounding the gelatinized

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Nomenclature

A	heat transfer area (m^2)	Re	Reynolds number
C_p	specific heat ($\text{J kg}^{-1} \text{K}^{-1}$)	t	time (min)
D	mean diameter of the starch granules distribution (μm)	T	instantaneous uniform temperature in the batch ($^{\circ}\text{C}$)
D_i	granule diameter (μm)	T_c	temperature of the thermostatic bath ($^{\circ}\text{C}$)
D_L	asymptotic value of D at long heating times (μm)	T_i	initial sample temperature ($^{\circ}\text{C}$)
$D_{4,3}$	average diameter defined in Eq. (1) (μm)	T_0	initial gelatinization temperature ($^{\circ}\text{C}$)
E_a	activation energy (kJ mol^{-1})	T_p	peak gelatinization temperature ($^{\circ}\text{C}$)
G^*	dynamic complex modulus (Pa)	U	overall heat transfer coefficient ($\text{J m}^{-2} \text{min}^{-1} \text{K}^{-1}$)
G'	dynamic elastic or storage modulus (Pa)	Nu	Nusselt number
G''	dynamic viscous or loss modulus (Pa)	V	paste volume in the beaker (m^3)
J	heating rate coefficient (min^{-1})	ω	oscillation frequency (Hz)
k	rate constant for the swelling process ($\mu\text{m}^2 \text{min}^{-1}$)	ρ	paste density (kg m^{-3})
n_i	number of granules of diameter D_i	γ	deformation used in the frequency sweep experiments, in the linear viscoelastic range (%)
Pr	Prandtl number	γ_{\max}	maximum deformation in the linear viscoelastic range (%)
R	universal gas constant		

granules. As a consequence, rheological properties and the heat transfer coefficient could be modified.

To characterize thermal transitions in starch systems (gelatinization, retrogradation, and glass transition), differential scanning calorimetry (DSC) was used by different authors (Biliaderis, Page, Maurice, & Juliano, 1986; Chang & Liu, 1991; I'Anson et al., 1990; Kohyama & Nishinari, 1991; Miles, Morris, Orford, & Ring, 1985; Slade & Levine, 1991).

From a rheological stand point, starch suspensions are viscoelastic systems (Ellis, Ring, & Whittham, 1989) and their overall behavior depends on both, the matrix of dissolved macromolecules and the presence of swollen granules. Maximum viscosity is attained in systems where the granules are not completely broken and still keep their identity (Luallen, 1985). Therefore, granule size influences the rheological behavior of the gelatinized starch paste (Evans & Haisman, 1979; Evans & Lips, 1992; Okechukwu & Rao, 1995). Usually, the increase in starch volume or degree of swelling has been measured upon the exclusion of blue dextran from the granules (Tester & Morrison, 1990). In this method, equal volumes of starch suspension and aqueous blue dextran solution are thoroughly mixed and then centrifuged to separate the swollen granules from the interstitial and supernatant water. The absorbance at 620 nm of the diluted blue dextran in the supernatant is measured and the amount of blue dextran excluded from gelatinized starch granules is related to the volume occupied by the granules; this volume can be calculated from the extent of dilution in the blue dextran solution. However, this method cannot be applied in starch pastes including

hydrocolloids because most of them increase the viscosity of the dispersing phase. This effect keeps particles in suspension and the separation by centrifugation is not possible.

In most published works on gelatinization kinetics, experiments have been conducted at constant temperatures. In industrial production, however, gelatinization of the starch pastes is conducted in stirred vessels, in contact with a heating medium at a constant temperature. But, under these conditions, the heating period required to attain the final temperature is not negligible and depends on system size and geometry, and on thermophysical and rheological properties that affect the heat transfer coefficient. In fact, as transient conditions cannot be avoided even at laboratory scale, gelatinization cannot be analyzed considering ideal isothermal conditions. Yoshimura, Takaya, and Nishinari (1999) have analyzed the effect of xyloglucan addition on corn starch gelatinization and retrogradation in batch systems. In previous works we have also analyzed the effect of other hydrocolloids (xanthan, guar, alginate) and sucrose on starch gelatinization, glass transition temperatures and rheological behavior (Ferrero & Zaritzky, 2000) but, the contributions on starch gelatinization modelling in stirred batch systems under non-isothermal conditions are scarce in the literature.

The objectives of the present study were: (i) to analyze the effect of hydrocolloids on the rheological behavior of starch gelatinized pastes and on their heating rates; (ii) to experimentally characterize the swelling process of corn starch granules in the presence of sucrose and hydrocolloids by light microscopy and image

analysis during batch gelatinization under transient thermal conditions; (iii) to relate the effect of gums and sucrose on corn starch gelatinization temperatures (measured by DSC) with the granule swelling; (iv) to model the swelling process considering the effects of time and temperature in the batch system.

2. Materials and methods

2.1. Preparation of samples

Samples were prepared with corn starch (25% amylose), hydrocolloids (xanthan gum, guar gum or sodium alginate) and sucrose in aqueous solutions. Commercial corn starch was provided by Molinos Río de La Plata, Argentina; Saporiti Hnos SACIF (Argentina) provided the commercial hydrocolloids and Anedra (Argentina), the sucrose.

The range of ingredient concentrations selected in the present work was based on food product formulations such as puddings, custards and other desserts so as to get practical technological applications. Component concentrations were: starch, 10% w/w; sucrose, 15% w/w and hydrocolloid (xanthan or guar gum or sodium alginate), 1% w/w. They were dry-mixed and then slowly added to a predetermined amount of water under constant stirring. Control samples were aqueous systems containing: (i) starch (10% w/w) and (ii) starch (10% w/w) and sucrose (15% w/w).

2.2. Granule swelling and starch gelatinization in batch systems

Batches of 200 g were heated for 20 min in an open beaker 14 cm in height and 8.5 cm in diameter, immersed in a thermostatic bath set at 90 °C, and stirred continuously at approximately 700 rpm to achieve an efficient mixing in the vessel. On account of the beaker geometry and the maximum heating time used (20 min), water evaporation during heating was limited, reaching no more than 4% of the total batch weight. In order to have in all batches the same total solids content, water evaporation was compensated immediately after the heating period by adding hot water up to the initial batch weight. To model the swelling process, accurate temperature measurement as a function of time was required. Thermocouples were placed at the center and border of the batch. Measurements showed that temperatures increased with time however they were uniform in the stirred pastes; experimental time–temperature data were modeled by non-linear expressions.

Pastes were observed by light microscopy and their viscoelastic properties were immediately measured by dynamic rheological tests after the heating period.

2.3. Microscopy observations

Samples were observed in a Leitz Ortholux II microscope (Germany) under polarized light to control the gelatinization process by verifying loss of birefringence.

Aliquots were taken halfway between the center and the border of the batch beaker, at different heating times; then extended on a microscope slide and stained with iodine solution (0.08 M I₂, 0.12 M KI) to carry out microscopy observations. The necessary micrographs were analyzed in order to have a sample of at least 200 granules at each sampling time during heating. Micrographs were scanned, digitized and analyzed with the Image Pro Plus software (Media Cybernetics, USA) to obtain the average diameter of granules as a function of time and temperature. With this software the average diameter is calculated as the average length of diameters measured at 5° angles around the centroid of each granule. As counting and sizing are automatically done, a well-stained sample is needed to obtain good contrast.

Measurements were used to obtain frequency histograms (%) as a function of the granule diameter; the mean value of the *D* distribution was calculated.

The average particle size *D*_{4,3} related to the volume effectively occupied by the granule was also determined as follows:

$$\bar{D}_{4,3} = \frac{\sum_{i=1} n_i D_i^4}{\sum_{i=1} n_i D_i^3} \quad (1)$$

where *n_i* is the number of granules of diameter *D_i*.

Mean granule sizes were modelled as a function of heating time and temperature. Rate constants and activation energies were calculated using SYSTAT software (SYSTAT Inc. USA) for the different systems tested.

2.4. Rheological measurements

Aliquots of the thermally treated pastes (corn starch with and without sucrose and hydrocolloids) were taken from the batch after 20 min heating time and rheological measurements were done in a Haake RV20 oscillatory rheometer (Haake, Germany) at 84.5 °C ± 0.1 °C, using a plate–plate sensor system with 1 mm gap between plates. This temperature was equal to the final value reached by the pastes in the batch. The test allowed the comparison of the viscoelastic properties of pastes containing different hydrocolloids and their influence on the heating rate in the batch. Data were analyzed using the Oscillation 2.0, Haake software. Two types of rheological tests were conducted: (a) deformation sweeps at constant frequency to determine the maximum deformation (γ_{\max}) a sample can experience in the linear viscoelastic range and (b) frequency sweeps (from 0.01 to 10 Hz) at constant deformation within the linear viscoelastic range. By this procedure, the mechanical spectra were obtained recording the dynamic moduli *G'*, *G''* and

G^* as a function of frequency. G' is the dynamic elastic or storage modulus, related to the material response as a solid, while G'' is the viscous dynamic or loss modulus, related to the material response as a fluid. The complex modulus G^* is defined as $(G'^2 + G''^2)^{1/2}$ and represents the overall viscoelastic response of the system.

2.5. Differential scanning calorimetry measurements

Gelatinization of corn starch with and without hydrocolloids and sucrose was also studied by DSC using a Polymer Laboratories calorimeter (Rheometrics, UK) in order to determine gelatinization temperatures. Starch–water samples containing sucrose and gums were prepared following the method described above. Once a homogeneous system was obtained, the hermetic aluminum DSC pans were filled with 10–15 mg aliquots for the thermal analysis runs. The heating rate for gelatinization tests was $10\text{ }^\circ\text{C min}^{-1}$, starting at $20\text{ }^\circ\text{C}$ and ending at $120\text{ }^\circ\text{C}$; an empty double pan was used as reference. Onset, peak and final gelatinization temperatures were calculated using the equipment software.

3. Results and discussion

3.1. Starch gelatinization in batch conditions: influence of mixture composition on heating rate

Stirred batch systems heated in a thermostatic bath showed absence of thermal gradients and unsteady state conditions. Measured curves of temperature vs. time showed lower heating rates for samples added with gums (Fig. 1). The macroscopic thermal balance for the batch was expressed as:

$$\rho V C_p \frac{dT}{dt} = UA(T_c - T) \quad (2)$$

where: ρ = paste density; T = instantaneous uniform temperature in the batch; V = volume of the paste in the beaker; C_p = specific heat; U = overall heat transfer

coefficient; A = heat transfer area; T_c = temperature of the heating medium (thermostatic bath).

Integration of Eq. (2) considering T_i = initial temperature ($25\text{ }^\circ\text{C}$), leads to the following expression:

$$\frac{T - T_c}{T_i - T_c} = \exp\left(\frac{-UA}{\rho C_p V} t\right) \quad (3)$$

Eq. (3) was fitted to experimental data of Fig. 1 and values of $J = UA/\rho C_p V$ were calculated for each paste system (Table 1).

Eq. (3) was plotted together with experimental data in Fig. 1. As conditions were kept the same in all the experiments, coefficient J can be related to the heating rate in each sample since it is proportional to the overall heat transfer coefficient U . Table 1 shows that systems containing gums (xanthan, guar and alginate) exhibited lower J values, than those shown by starch-only and starch–sucrose pastes. For Newtonian fluids, the heat transfer coefficient in the stirred vessels can be expressed as a function of the Re and Pr numbers (Geankoplis,

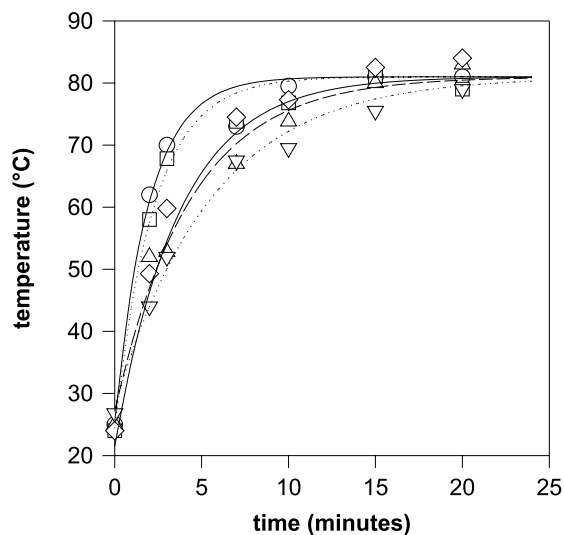


Fig. 1. Experimental points and mathematical models (lines) of temperature as a function of the heating time for suspensions in stirred vessels of: (○, —) starch 10%; (□, ...) starch 10% + sucrose 15%; (Δ, ---) starch 10% + sucrose 15% + xanthan gum 1%; (∇, ...) starch 10% + sucrose 15% + guar gum 1%; (◇, —) starch 10% + sucrose 15% + sodium alginate 1%.

Table 1
Heating rate coefficient (J), dynamic moduli (G^* , G' and G'') and limit granule diameter (D_L) for different starch–sucrose systems

System	J (min^{-1})	G^* (Pa)	G' (Pa)	G'' (Pa)	D_L (μm)
Starch	0.51 (0.06)	690 (6)	662 (10)	170 (8)	31.7 (1.0)
Starch + sucrose	0.44 (0.05)	986 (11)	945 (15)	279 (13)	25.7 (0.5)
Starch + sucrose + alginate	0.27 (0.02)	1905 (10)	1861 (9)	410 (10)	26.0 (0.7)
Starch + sucrose + xanthan	0.23 (0.03)	2242 (31)	2159 (41)	592 (35)	23.9 (1.0)
Starch + sucrose + guar	0.15 (0.01)	2837 (21)	2795 (29)	473 (47)	17.4 (0.6) ^a

Standard errors are shown between parentheses. G^* , G' and G'' at $84.5\text{ }^\circ\text{C}$ at $\omega = 1\text{ Hz}$. D_L = after 20 min.

^a Limiting granule diameter not attained.

1993) which are mostly dependent on viscosity. In the case of viscoelastic systems such as starch pastes, the overall heat transfer coefficient will depend on thermal properties and rheological behavior.

3.2. Rheological studies

Mechanical spectra at a constant deformation value $\gamma = 4\%$ ($\gamma < \gamma_{\max}$) were obtained for the different samples at the final heating temperature (84.5 °C). The dynamic moduli of the pastes at $\omega = 1$ Hz (G' , G'' and G^*) are shown in Table 1. In all cases, G' (related to the elastic response) was higher than G'' (related to the viscous response) in the frequency range studied, despite G'' was not negligible. Upon the classification of Ross-Murphy (1995), these characteristics would correspond to an entangled macromolecule system.

Table 1 shows that sucrose addition increases G^* values. Cheer and Lelievre (1983), for systems tested at 30 °C and containing 3–4% w/w starch and different sucrose concentrations, reported an increase in the dynamic elastic modulus (G') as a function of sugar concentration up to approximately 12% w/w. According to their results, the effect of sucrose may be related to changes in the granule size distribution, modification of the viscosity by decreasing the dielectric constant of the solvent, dehydration action and by hydrogen bond formation. The influence of different sugars on corn starch gelatinization and retrogradation was extensively studied by Ikeda et al. (2001) and Yoshimura et al. (1999) using force deformation curves, dynamic viscoelasticity and DSC. Biliaderis and Prokopowich (1994) attributed the effect of different sugars on starch retrogradation to their compatibility with water structure. Thus, solutes which cause little perturbations in the water network may have a greater access to the hydration layer of the starch chains; this situation creates a localized environment of increased viscosity producing a strong anti-plasticizing effect compared to water alone.

As shown in Table 1, starch pastes added with gums increased their G^* ; the highest values being produced by guar. A satisfactory decreasing linear correlation ($r^2 = 0.989$) between the complex modulus G^* and the heating rate coefficient J was observed for all samples tested (Fig. 2). Thus, lower heat penetration rates can be associated to systems exhibiting higher values of the complex viscoelastic modulus G^* .

3.3. Microscopy observations

Small samples were removed from the batch at different times for microscopy observations. For each sample, the diameter distribution of starch granules was plotted in frequency histograms. For all samples, it was found that granule identity was not lost after the entire gelatinization period.

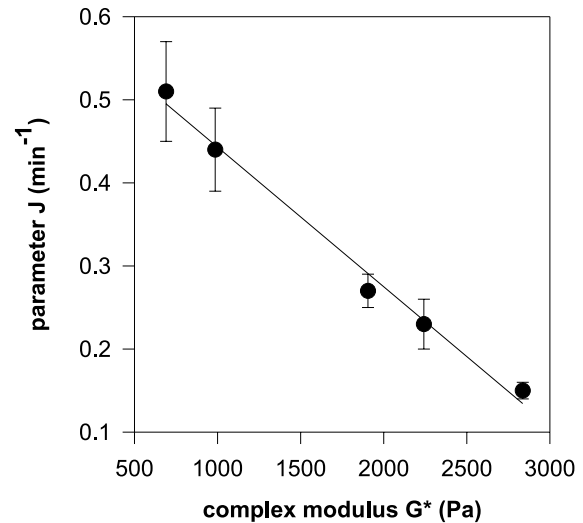


Fig. 2. Heating rate coefficient (J , min^{-1}) as a function of complex modulus (G^* , Pa). Full line: linear regression.

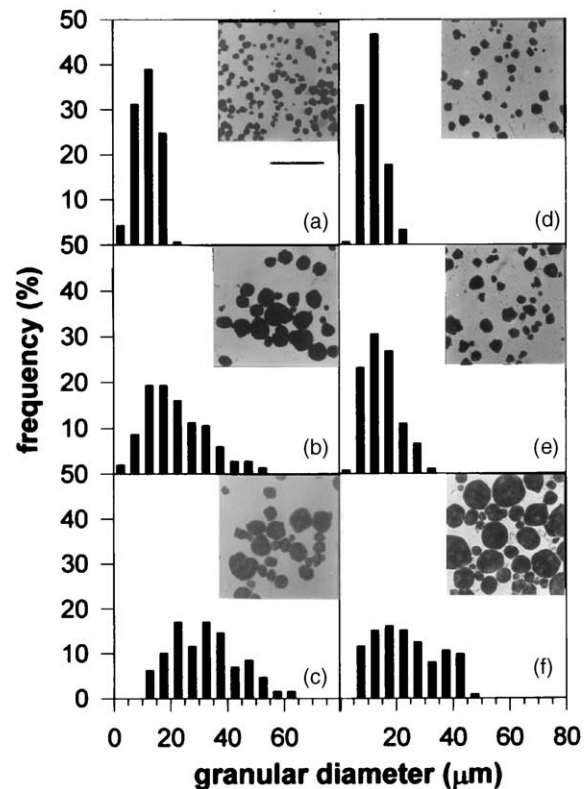


Fig. 3. Histograms of granular diameter of starch pastes 10% after (a) 2 min (62 °C), (b) 10 min (79 °C) and (c) 20 min (82 °C) of heating and of starch 10% + sucrose 15% + xanthan gum 1% after (d) 2 min (52 °C), (e) 10 min (72 °C) and (f) 20 min (83 °C) of heating. Inserted micrographs show typical granule populations corresponding to each heating time. Scale bar = 100 μm .

Fig. 3 shows histograms of granular diameters of the starch pastes without additives (Fig. 3a–c) as well as with sucrose and xanthan gum (Fig. 3d–f) for different

heating times. Temperatures associated to each heating time are plotted in Fig. 1. Histograms did not follow a Gaussian distribution because they are skewed towards low granule diameters. Along with each histogram, inset micrographs show typical granule populations corresponding to each heating time; dark granules appearance is due to dying with iodine solution.

Mean average diameter of the starch granules were plotted as a function of the corresponding thermal history for the several samples tested (Fig. 4). The initial average diameter of the starch granule was $11.2 \mu\text{m}$ (SE = 0.3). Mean average diameters increased with heating time and temperature but to a different extent depending on the time–temperature data.

As reported by other authors, corn starch gelatinizes and swells strongly between 62 and 72 °C, the swelling becoming rather slow at higher temperatures (Kokini, Lai, & Chedid, 1992). Under the batch conditions, an initial period is required for the granule to reach the minimum temperature to begin swelling. In this regard,

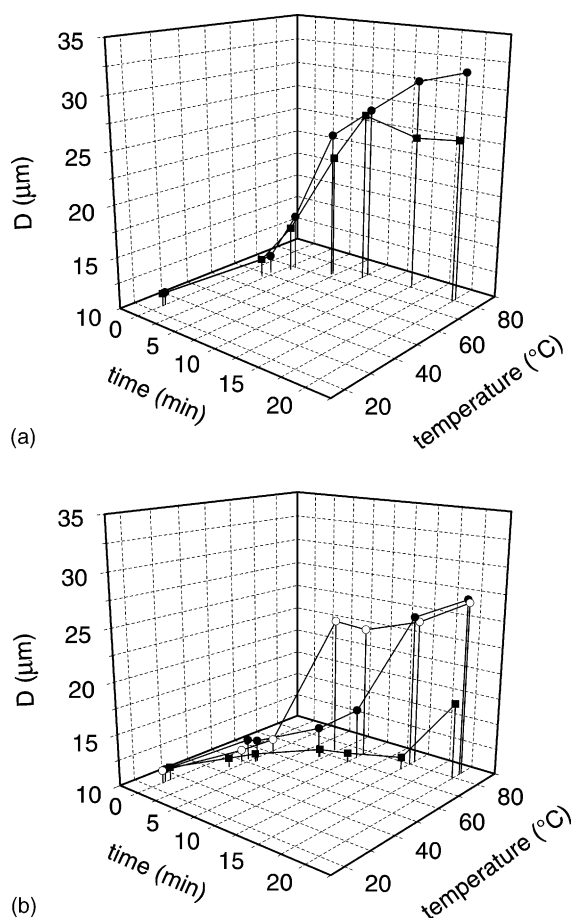


Fig. 4. Average starch granular diameter as a function of time and temperature for (a) (●) starch 10%; (■) starch 10% + sucrose 15% and (b) (●) starch 10% + sucrose 15% + xanthan gum 1%; (■) starch 10% + sucrose 15% + guar gum 1%; (○) starch 10% + sucrose 15% + sodium alginate 1%.

granule diameter kept constant up to approximately 60 °C (Fig. 4) and as gelatinization starts, the diameter increases rapidly for samples without gums. At the end of heating time (20 min), sucrose added systems showed a lower average granule diameter ($25.7 \mu\text{m}$, SE = 0.5) compared with starch pastes without sucrose ($31.7 \mu\text{m}$, SE = 1.0). Granules in samples added with gums, also showed a lower swelling at the end of heating. Starch pastes containing alginate exhibited the greatest granule swelling among the systems with gums while those pastes with both sucrose and guar showed the lowest (average final diameter = $17.4 \mu\text{m}$, SE = 0.6). Considering that the guar-added pastes had the highest G^* , the lower swelling experienced by the starch granules could be attributed to the lower mobility of water molecules. It is known that the diffusion coefficient of water is proportional to the reciprocal of system viscosity in Newtonian fluids (Geankoplis, 1993; Reid, Prausnitz, & Sherwood, 1977).

Values for $D_{4,3}$ parameter in the starch granules were also calculated as a function of heating time and temperature. The final $D_{4,3}$ obtained in the different systems tested were: starch, $43.3 \mu\text{m}$; starch–sucrose, $36.0 \mu\text{m}$; starch–sucrose–xanthan gum, $35.6 \mu\text{m}$; starch–sucrose–guar gum, $26.2 \mu\text{m}$ and starch–sucrose–alginate, $34.0 \mu\text{m}$. The correlation coefficient found by linear regression between both the average measured diameter and the $D_{4,3}$ was 0.96, demonstrating that both descriptors (D and $D_{4,3}$) are useful to evaluate granule swelling in starch gelatinization. For simplicity, the average granule diameters are used in the subsequent analysis.

3.4. Differential scanning calorimetry measurements

Initial (T_0), peak (T_p) and final (T_f) gelatinization temperatures were determined by DSC for the different starch pastes (Table 2). A significant shift (up to 6 °C) to higher temperatures was observed due to sucrose addition; this can be attributed to different reasons: reduction in water activity, which could make starch gelatinization more difficult in the presence of sugars (Derby, Miller, Miller, & Trimbo, 1975), the effect of sugar–starch interactions (Lelievre, 1976; Spies & Hoseney, 1982) and the anti-plasticizing effects of sugars compared to water (Biliaderis & Prokopowich, 1994; Ikeda et al., 2001).

Table 2 shows that the addition of 1% of gums to starch–sucrose–water systems did not change significantly the gelatinization temperatures. Therefore, water availability was not modified by the addition of gums at this concentration level.

By comparing the initial gelatinization temperatures (T_0) measured by DSC (Table 2) to those required to start swelling in starch granules (Fig. 4), it was observed that initial swelling temperatures are lower than T_0 because the hydration of amorphous zones (plastici-

zation) precedes the melting process (Biliaderis et al., 1986).

3.5. Mathematical modelling of the starch swelling process under non-isothermal conditions

Average diameters of the starch granules (D) measured at different times during the heating period were used along the recorded thermal histories to model the starch swelling process in stirred batch systems.

Different kinetic equations were proposed to fit the experimental data of D as a function of time and temperature, and the following equation:

$$\frac{dD}{dt} = k \left(\frac{1}{D} - \frac{1}{D_L} \right) \quad (4)$$

was the best to represent changes in mean granule diameter during swelling and starch gelatinization at a given temperature T , in excess of water.

In Eq. (4), D is the mean diameter of the starch granules distribution at each time t , while D_L is the measured asymptotic value of D at long heating times (limiting diameter); k is the rate constant exhibiting an Arrhenius behavior $k = k_0 \exp(-E_a/RT)$.

This expression was used in previous works to represent size particles changes upon the curvature ($1/D$) (Ferrero, Martino, & Zartitzky, 1992). As granule size increases, during granule swelling, the driving force decreases and it can reach zero when reaching the final asymptotic diameter (D_L). As indicated in Eq. (4), the driving force is the difference between the instantaneous mean curvature and the asymptotic one.

The rate constant k was obtained at each temperature from Eq. (4) using a differential approach adapted to

non-isothermal conditions (Levenspiel, 1976). It requires the knowledge of $\Delta D/\Delta t$ and D at the mean temperature of each time interval and also D_L . For each sample tested, experimental data of D as a function of time and temperature (Fig. 4) were used to numerically calculate $\Delta D/\Delta t$ in each time interval (Δt) for a mean interval temperature T . These calculations were used to determine the k values. In samples for which D_L was measured, the activation energy of the process (E_a) was obtained from the linear regression of $\ln k$ vs. $1/T$. Correlation coefficients r^2 ranged between 0.87 and 0.99. The values obtained for k at different temperatures as well as those of the activation energy are shown in Table 3.

At the same temperature (Table 3), differences in k values among the samples with and without gums addition could be attributed to changes in water diffusivities, which are lower in more viscous samples. Values for k in guar gum added systems are not shown because the D_L was not reached after the heating time of 20 min.

The activation energies obtained in the present work (Table 3) are similar to those reported in the literature for gelatinization in rice and corn starches studied by different methods. In this regard, Suzuki, Kubota, Omichi, and Osaka (1976) have used a rheological method (parallel plate plastometer), Bakshi and Singh (1980) obtained data from amylose/iodine blue value, Lund and Wirakartakusumah (1984) have applied isothermal DSC technique, Cabrera, Pineda, Duran de Bazua, Segurajauregui, and Vernon (1984) employed the differential alkali solubility method. Activation energies reported by these authors ranged from 75 to 104.5 kJ mol⁻¹.

Table 2

Effect of the addition of sucrose and hydrocolloids on the initial (T_0), peak (T_p) and final (T_f), gelatinization temperatures of aqueous starch pastes

System	T_0 (°C)	T_p (°C)	T_f (°C)
Starch + water	66.9 (0.2) ^a	72.0 (0.1)	78.4 (0.3)
Starch + sucrose + water	72.9 (0.2)	77.6 (0.2)	83.6 (0.3)
Starch + sucrose + water + alginate	73.3 (0.1)	78.5 (0.1)	84.2 (0.1)
Starch + sucrose + water + xanthan gum	73.3 (0.3)	78.2 (0.2)	84.2 (0.4)
Starch + sucrose + water + guar gum	72.3 (0.1)	77.0 (0.1)	82.4 (0.1)

Assays were performed in sextuplicate.

^aStandard error of the means.

Table 3

Rate constants (k) and activation energy (E_a) for the swelling process during corn starch gelatinization

	k ($\mu\text{m}^2 \text{min}^{-1}$) at average temperature (°C)				(E_a) (kJ mol ⁻¹)	$\ln k_0$	r^2
	65	70	75	80			
Starch	54	87	140	122	94 (11)	37 (4)	0.95
Starch + sucrose	67	107	167	253	89 (6)	36 (2)	0.98
Starch + sucrose + alginate	15	23	33	48	80 (14)	30 (7)	0.87
Starch + sucrose + xanthan gum	11	20	37	67	119 (3)	45 (1)	0.99

Standard errors are shown between parentheses. r^2 : correlation coefficient of the linear regression.

4. Conclusions

In stirred batch systems, heating is not instantaneous and a transient time–temperature relationship cannot be avoided.

Heat penetration was faster in viscoelastic systems with lower G^* moduli. Gums added starch pastes showed lower heating rates during gelatinization.

Microscopy observations and image analysis is a useful method to describe the granule swelling process in starch gelatinization, especially in those samples where other techniques are difficult to apply. Starch granule swelling was considerably reduced by the presence of gums because of the lower heating rates and the reduced mobility of water molecules.

DSC measured starch gelatinization temperatures were increased by the presence of sucrose. In contrast, the effect of gums addition on these temperatures was not significant.

The effect of time and temperature on the starch swelling process was modelled considering the driving force as the difference between the instantaneous mean curvature of the granule ($1/D$) and the limiting one. Rate constants were calculated for the different pastes, the lowest values being observed for starch pastes added with gums. Activation energies ranged between 80 (± 14) and 119 (± 3) kJ mol⁻¹ being comparable to values reported in the literature for gelatinization of different starches measured by diverse methods.

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