Xanthan effect on swelling, solubility and viscosity of wheat starch dispersions

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Abstract

Xanthan effect on swelling power (SP), solubility index (SOL) and granules status of wheat starch dispersions (2% w/w) was investigated. Control samples and samples with xanthan (0.09% w/w at the final solution) were prepared and heated at temperatures from 60 to 90 °C for 5 or 30 min. Additionally, the viscosity of starch–xanthan mixtures was calculated at different shear rates. Regarding these mixtures two preparation techniques were used: separate preparation of starch and xanthan solutions and subsequent mixing (a), or mixture of the powders prior to addition of water (b). Samples were heated at two different temperatures 75, 90 °C and times 5, 30 min. According to SP values and granules dimensions at 75 °C, xanthan addition enhanced swelling. It also enhanced starch polymers leakage at temperatures ≥80 °C. At higher temperatures lower SOL values were found than those of control samples. Furthermore, in the presence of xanthan the proportion of large granules was greater than this found in aqueous solution. However, xanthan induced granules folding, which was noticed even at relatively low temperatures (75 °C). With respect to viscosity, all samples showed pseudoplastic behaviour. Experimental values were fitted well by the Ostwald–de Waele model ( \( \sigma = k \cdot \gamma^n \) ). Consistency values (k) and flow index (n) were mainly influenced by the preparation technique and the heating temperature. Mixtures prepared with technique (a) had increased viscosity, consistency and pseudoplasticity. Mixtures prepared with technique (b) had irregular granules’ shape and size due to xanthan addition and bad adhesion between continuous and dispersed phase, which influence viscosity negatively.

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1. Introduction

Gelatinized starch consists of the continuous phase (amylose/amylopectin matrix) and the dispersed phase (starch granules). The rheological properties of such a composite depends on factors influencing both phases. Some of these factors influencing the dispersed phase are the granules’ size and its distribution, the granules’ shape and volume occupied, their rigidity and the interactions among them. Respectively, regarding the continuous phase, the matrix of amylose/amylopectin, the interactions between starch polymers and the interactions with the granules are very important factors (Clegg, 1995; Eliasson & Gudmundsson, 1996; Hermansson & Svegmark, 1996).

When starch dispersions are heated, granules’ swelling and starch polymers solubilization occur, which influence the properties of both continuous and dispersed phases. By increasing the temperature during heating, granules’ swelling increases as well (Li & Yeh, 2001). This is evident till a specific temperature. For rice starch granules peak swelling values were reached at 75 °C. Above this temperature granules’ disruption was observed (Yeh & Li, 1996). At 75 °C starch swelling can be also related to food quality. Kim and Seib (1993) reported that wheat starches with high swelling power (SP) at 75 °C yielded better eating quality of instant fried noodles. Swelling can also be positively related to the amount of soluble solids leached outside the granules during heating. However, for some starch types (potato, tapioca and waxy corn starch) SP decreases when more solids leached out during cooking at higher temperatures (Li & Yeh, 2001). The initial granule size influences also the swelling and it determines the onset of gelatinization (large
waxy corn starch granules increased gelatinization temperature, whereas small barley granules decreased it) (Mylarinen, Autio, Schulman, & Poutanen, 1998; Tsai, Li, & Lii, 1999). According to Li and Yeh (2001) the granule size of several starches had a positive effect on SP, till the temperature of 75 °C, since small barley granules displayed the greatest SP (Tang, Watanabe, & Mitsunaga, 2002). However, according to Sasaki and Matsuki (1998) and Tester and Karkalas (1996) the granule size does not influence the SP values.

Rheological behaviour of starch systems is also influenced by granules swelling and consequently by their volume fraction and their rigidity. When starch granules are swollen enough and can be deformed under applying shear force, pseudoplastic behaviour will be observed. On the contrary, when granules are rigid and they are not so readily deformed, dilatancy will be observed (Bagley & Christianson, 1982; Christianson, Baker, Loffredo, & Bagley, 1982). Rheological behaviour can be related to temperature as well, when observing dilatant behaviour in early stages of gelatinisation (low swelling) of corn starch (Okechukwu & Rao, 1995; Rao, Okechukwu, Silva, & Oliveira, 1997), but pseudoplastic at higher heating temperatures (85–90°C) (Rao et al., 1997). Pseudoplastic behaviour of gelatinized maize, waxy maize and wheat starch pastes was also reported by Nguyen, Jensen, and Kristensen (1998) and Noel, Ring, and Whittam (1993).

Viscosity can also be related to particle volume fraction ϕ. At intermediate volume fractions (0.1 < ϕ < 0.5)—found in starch systems of low concentrations like in our case—suspensions of rigid, spherical particles are usually shear-thinning (Dickinson, 1992).

By hydrocolloid addition, both structural and rheological characteristics can be altered. Starch’s gelatinization temperature (onset, peak and conclusion temperature) is not modified by hydrocolloids (Biliaderis, Arvanitoyannis, Izydorczyk, & Prokopowich, 1997; Liu & Eskin, 1998; Rojas, Rosell, & Benedico de Barber, 1999; Shi & BeMiller, 2002). However, swelling of granules can be affected by hydrocolloids addition, suggesting that swelling is enhanced in their presence (Rojas et al., 1999; Tecante & Doublier, 1999). According to Christianson (1982) and Christianson, Hodge, Osborne, and Detroy (1981) the addition of hydrocolloids can increase the shear forces applied on the granules as regards with the forces applied in starch—water suspensions. This fact affects significantly the breakdown of granules and the amount of material exuded into the continuous phase.

An addition of a given hydrocolloid, depending on its thickening capacity, usually results in a noticeable increase in starch viscosity (Tecante & Doublier, 1999). According to Alloncle, Lefebvre, Llamas, and Doublier (1989), Bahnassey and Breene (1994), Christianson (1982), Christianson et al. (1981), Liu and Eskin (1998), and Shi and BeMiller (2002) the viscosity of starch increases due to synergistic interactions of starch and gums. Christianson (1982) and Christianson et al. (1981) believe that gums form stable associations with starch solubles, which increase the viscosity of starch–gum mixtures. Alloncle et al. (1989) assume that the synergistic effect between starch and gums was observed because of different polymers phase separation, rather than due to intermolecular associations. Shi and BeMiller (2002) suggest that interactions between maize starch amylose and carboxymethylcellulose (CMC) are at least partially responsible for starch viscosity increase. However, wheat, tapioca and potato amylose did not seem to interact as strongly with CMC as maize amylose did. Although the existing information about starch swelling, the factors that influence it (temperature, soluble solids, initial granule size), its relation to rheological properties and the effects of added hydrocolloids on starch systems, there are still unknown aspects because of the complexity of such systems. Furthermore, according to the above information, there are many contradictory aspects, while the correlation of these properties to real food is still limited.

The aim of this study was to investigate the effects of temperature, heating time, xanthan addition on wheat starch granules swelling, solubilization and size during heating. The effects of preparation technique and heating conditions (temperature and time) on starch–xanthan mixture viscosity were also investigated.

2. Materials and methods

2.1. Materials

Wheat starch from Merck and xanthan gum from Sigma were used for the experiments. The intrinsic viscosity of xanthan aqueous solution, according to the Huggins’ equation (1942) as it was referred by Launay, Cuvelier, and Martinez-Reyes (1984), was [η] = 18.7 dl/g. Intrinsic viscosity was measured with a falling ball viscometer (HAAKE Mess-Technik GmbH u. Co, Germany boron silica glass density (ρ) = 2.20 g/cm³, diameter (d) = 15.643 mm). The moisture content of xanthan powder was 11.2 ± 0.1% (105 °C, 24 h, three replications).

For unheated starch granules, size distribution according to their average diameter was calculated. More than 300 granules were used for this reason. Light microscopy (LM) pictures obtained, were further treated using an image process analysis system (Image Pro Plus 1.3, Media Cybernetics, USA) and six different diameter categories were chosen. The size distribution of granules is shown in Table 1. The first three categories correspond to small to medium size and the other three to large size granules. The amylose content of starch determined by the method of Gilbert and Spragg (1964) was 20 ± 0.2%. The moisture content of samples was 11.5 ± 0.4% (105 °C, 24 h, three replications), the density of starch powder was 627.33 ± 7.02 kg/m³ and the ash content 0.13 ± 0.05% (450 °C, 3 h).
Table 1
Size distribution (diameter values) of unheated wheat starch granules

<table>
<thead>
<tr>
<th>Average diameter (μm)</th>
<th>Percentage of total granules (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5–10</td>
<td>38.30</td>
</tr>
<tr>
<td>10–17.5</td>
<td>28.07</td>
</tr>
<tr>
<td>17.5–25</td>
<td>23.10</td>
</tr>
<tr>
<td>25–32.5</td>
<td>9.06</td>
</tr>
<tr>
<td>32.5–40</td>
<td>1.17</td>
</tr>
<tr>
<td>&gt;40</td>
<td>0.30</td>
</tr>
</tbody>
</table>

2.2. Swelling powder, solubility index and amylose determination

SP and solubility index (SOL) were determined using a modification of the method of Leach, McCowen, and Schoch (1959). Starch dispersions of 2% were put in centrifugal tubes and heated in a water bath at temperatures of 60–90 °C for 5 and 30 min. The average heating rate as recorded by thermocouples placed in tubes was 18 °C/min. During heating, in order to prevent granules' sedimentation, middle stirring was applied periodically using glass stirrers. In order to prevent water loss, all tubes were covered with plastic covers. After heating, samples were centrifuged (3000 rpm, 15 min). Precipitated paste was separated from supernatant and had been weighed ($W_p$). Both phases were dried at 105 °C for 24 h and the dry solids in precipitated paste ($W_{ps}$) and supernatant ($W_s$) were calculated. SP is the ratio of the weight of swollen starch granules after centrifugation (g) to their dry mass (g).

$$SP = \frac{W_p}{W_{ps}}$$ (hydrated granule (g)/dry granule in precipitate paste (g))

The SOL is the percentage of dry mass of solubles in supernatant to the dry mass of whole starch sample ($W_s$).

$$SOL = \frac{W_s}{W_0} \times 100\% \text{ (soluble solids (g)/dry mass of whole starch sample (g))}$$

For determining SP and SOL of samples containing xanthan, powders of wheat starch and xanthan, were mixed. Deionized water was added in order to produce a solution with starch concentration 2% (w/w) and xanthan 0.09% (w/w). Samples were stirred with a magnetic stirrer gently, in order to keep the granules in suspension. Afterwards, with the help of an automatic pipette, 10 ml were put in each centrifugal tube. The procedure was continued as it was described for pure starch suspensions. It was assumed that the whole xanthan amount was remained in supernatant and was subtracted in order to calculate SOL values. For each measurement of SP and SOL 4–8 replicates were used. Amylose content in supernatant was determined iodometrically by the method of blue value (Gilbert & Spragg, 1964). Two replicates for each measurement were used.

2.3. Dimensions of granules and microscopic observations

After the heating process and cooling to room temperature, suspensions of starch or starch–xanthan samples were put onto object glasses and were stained with lugol solution (1%, mixture of 1:KI 1:2), covered with coverglasses, and were observed using LM microscope at 10 × and 40 × magnification. Photos were taken using a video camera (SONY, CCD-Iris) and stored in a computer. With an image analysis system (Image Proplus 1.3, Media Cybernetics, USA), photos were further treated for improving their quality. A filter was used to bring out fine details of the image (Sharpen 5 × 5) and brightness/contrast was adjusted accordingly. The average area, the minimum, maximal, average diameter and the aspect ratio (ratio of length of horizontal to vertical axes, $x/y$) were calculated after converting pixels to μm with means of known reference lengths. Objects with aspect $>1.8$ were rejected, because they related to artifacts or disrupted granules parts. For size measurements more than 250 granules were used from different photos and samples. For temperatures greater than 75 °C, the outline of granules was very faint and it was difficult to measure granules dimensions. Therefore their measurement was considered inappropriate.

2.4. Viscosity measurement

Starch–xanthan mixtures were prepared using two techniques: separate heating of starch dispersions and xanthan solutions, and subsequent mixing (technique (a)), or powders mixing, adding water and heating samples thereafter (technique (b)). Heating process was the same as described above for SP and SOL calculation. Two heating temperatures were chosen 75 and 90 °C and two heating times of 5 and 30 min accordingly. Viscosity was measured with a controlled shear stress SR5 rheometer (Universal Stress Rheometer/Rheometrics Scientific CP, USA) with a plate–plate geometry at a distance of 0.5 mm. The diameter of the upper plate was 20 mm. The temperature was constant ($25 \pm 0.2$ °C) by circulating water from a constant temperature circulator. All samples remained for temperature equilibration for 10 min between the plates before starting the experiments. Shear rate applied was in the range of 0.6–1800 (s$^{-1}$). For each measurement 2–4 different samples were used.

Experimental data were fitted to Ostwald–de Waale model ($\sigma = k \cdot \gamma^n$) using Excel 2000 software. The parameters $k$ and $n$, which are related to consistency and flow index, respectively, were used for comparisons among samples. Furthermore, the apparent viscosities of different samples at shear rate 100 s$^{-1}$ were calculated from the above power law equation.
2.5. Statistical analysis

Analysis of variance for multiple comparisons (ANOVA) using Statgraphic 2.1 Statistical Graphics System Software (Statistical Graphics Corp, Rockville, MD, USA) was performed in order to find differences among samples tested. Least significant differences (LSD) were calculated by the Fisher’s test. Differences were considered significant when \( p \leq 0.05 \). With respect to SP and SOL, comparisons were performed calculating the average values of the variables over the temperature range previously used (60–90 °C), considering as main effects the heating time and the addition of xanthan. Analysis of variance was repeated so as to find the effects of heating temperature and time on SP and SOL values for each sample type (starch dispersions or starch/xanthan mixture). For \( k \) and \( n \) values, analysis of variance was performed taking into account three different factors (heating temperature, heating time and preparation technique) and their interactions.

3. Results and discussion

3.1. Swelling power and solubility index

Wheat starch granules swelling is confirmed to be a two stage process (Blanshard, 1979; Kokkini, Lai, & Chedid, 1992). An initial low swelling was noticed till 75 °C and a great one thereafter (Fig. 1). Experimental values were fitted well using polynomial equations. SP values were calculated for 30 min heating and were similar to those referred by Eliasson (1986) and Eliasson and Gudmundsson (1996) for the same heating time. According to statistical analysis (Table 2) they were not any statistical differences for average SP values between samples heated for 5 and 30 min. However, when statistical analysis was performed comparing SP values at each temperature from 60 to 90 °C for two heating times (5 and 30 min) differences were found for samples heated for 5 and 30 min at 85 and 90 °C. It seems that the heating time was significant at high heating temperatures due to extensive granules swelling.

According to Tester and Morrison (1990) the swelling process is rapid during the first 5–10 min at a certain temperature and continues with further heating. Takahashi and Seib (1988) reported that amylose creates crystals with wheat starch lipids and particularly with lysolecithin, which are being formed at 50–60 °C, a process that inhibits excessive granules’ swelling. At temperatures greater than 85 °C the crystallites melt therefore swelling is enhanced, a fact that justifies fast swelling increase above 80 °C.

By adding xanthan swelling of granules was amplified (Fig. 1). Rojas et al. (1999) noticed also increase in wheat

![Fig. 1. Swelling power (g/g) at different heating temperatures for two heating times, 5 min (○) and 30 min (●). Close symbols: starch dispersion with added xanthan, open symbols: starch dispersion in aqueous solution (control samples).](image)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Time of heating (min)</th>
<th>SP values (g/g)</th>
<th>SOL values (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Without xanthan</td>
<td>5</td>
<td>10.33</td>
<td>5.01</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>11.37</td>
<td>6.57</td>
</tr>
<tr>
<td>With xanthan</td>
<td>5</td>
<td>12.88</td>
<td>5.44</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>14.18</td>
<td>7.51</td>
</tr>
</tbody>
</table>

Data in the same column with different letter differ significantly (\( p < 0.05 \)).

* LS means.
granules’ swelling by xanthan addition. Swelling was not a two-stage process, as it was for control samples, but a gradual swelling increase was noticed. Statistical differences between the average SP at 5 and 30 min heating were not noticed, as it was also found in control samples. Differences between the SP values at 5 and 30 min were found only in samples heated at 75, 85 and 90 °C. Although samples with xanthan showed greater values of SP, the rate of swelling increase was lower from 85 to 90 °C during 30 min heating, compared to control samples. It is suggested that at high heating temperature and time the presence of xanthan can decrease granules’ swelling capacity.

The effect of xanthan addition in starch dispersions was greater by comparing the soluble solids leaked out from granules, regarding samples with and without xanthan (Fig. 2). The values of soluble solids found in control samples were similar to those reported by Eliasson (1986) and Eliasson and Gudmundsson (1996) during 30 min heating. By increasing the temperature, the amount of soluble solids in the continuous phase increased gradually, compared to SP increase, which was a two stage process.

According to preliminary experiments the amount of soluble solids was affected by heating rate in greater extent than SP was. Thebaudin, Lefebvre, and Doublier (1998), who used for the preparation of starch dispersions great heating rate and a strong agitation (750 rpm), found greater values of wheat soluble solids (6.7 and 34.9% at 75 and 85 °C, respectively, whereas for the same temperatures the values obtained at this study were 2.5 and 9.3%). Takahashi and Seib (1988) found also greater values (3.5 and 11.9% at 75 and 85 °C correspondingly) than the values mentioned in this study. It should be mentioned that the whole heating process had a duration of 40 min, whereas in our research the values mentioned were obtained after heating starch dispersions for 30 min. However, relatively to the heating time (5 and 30 min), the average values of soluble solids did not differ significantly (Table 2), as it was also found for SP values.

By adding xanthan the amount of soluble solids in the continuous phase were initially increased, compared to the respective amount found in samples without xanthan. After a certain temperature (>80 °C), control samples showed greater values of soluble solids. In the presence of xanthan the amount of polymers leaked out from the granules increased slightly from 75 to 90 °C compared to the continuous increase of polymers released in aqueous solution. At 90 °C and 30 min heating the soluble solids by xanthan addition were the 60% of the respective amount in aqueous solution.

According to statistical analysis the average values of soluble solids in two heating times (5 and 30 min) did not differ significantly (Table 2). However, when statistical analysis was performed for soluble solids in every temperature varying from 60 to 90 °C, differences were found between the two heating times (5 and 30 min) for samples heated at 75, 80 and 85 °C, suggesting that there is a temperature range, where the leakage of starch polymers is enhanced.

Generally the amount of exudates was small; consequently it is suggested that the main component leaked out from the granules was amylose. In order to prove this suggestion, amylose amount was calculated (Table 3) and similar values to the total amount of solids leaked outside the granules, were obtained. Some variations compared with the soluble solids values were noticed because the assumption that the whole amount of xanthan is remained in the continuous phase is not completely true; a small amount of xanthan can sediment with the granules. This overestimation of xanthan amount in the continuous phase

![Fig. 2. Soluble solids (%) at different heating temperatures for two heating times, 5 min (△) and 30 min (□). Close symbols: starch dispersion with added xanthan, open symbols: starch dispersion in aqueous solution (control samples).](image-url)
can cause an underestimation of starch solids leaked out the granules.

About the role of xanthan on starch systems the following assumptions can be mentioned. According to Abdelmola, Hember, Richardson, and Morris (1996), starch molecules can interact and a network can be created at concentrations well below ‘close-packing’. Xanthan promotes adhesive interactions among the gelatinized granules. It is assumed that it can entrap them keeping them closely. This can enhance the forces applied to them, facilitating water entering (increasing swelling), amylose solubilization and its exudation. By increasing further temperature the leaked amylose and the xanthan in the continuous phase create a film around the granules and inhibit further swelling and polymers leaking out. The inner pressure increases, which, at higher temperatures can facilitate the disintegration of granules compared to granules’ status in aqueous solution. The creation of amylose film around the granules is also referred by Langton and Hermansson (1989), who claim that this film can influence the behaviour of granules on rehydration and reheating and was also observed by Mandala, Palogou, and Kostaropoulos (2002) in potato starch–xanthan mixtures.

3.2. Dimensions of granules and microscopic observations

The area distribution of starch granules heated at 75 °C for 5 and 30 min is illustrated in Fig. 3 for both control samples and samples with xanthan.

It is known that there are two wheat granules’ categories, the small, spherical B-granules, and the large, lenticular A-granules. Although A-granules represent the 90% of the total weight of granules, as a number are, 20% (Hermansson & Svegmark, 1996; Hoseney, 1998). Since the swelling of lenticular wheat starch granules involves an initial radial expansion at lower temperatures, followed by tangential expansion at higher temperatures (Bowler, Williams, & Angold, 1980), then the use of area change was considered more representative instead of mean diameter.

According to area classification the first category is corresponded to small B-granules with area lower or equal to 75 μm². These granules are not gelatinized and keep their original dimensions. Concerning control samples heated at 75 °C for 5 min, it can be noticed that ~50% of the total number of granules keep their original dimensions. Assuming that the small B-granules represent more than 80% of total granules number, at least 60% of their population remain intact. This proportion was reduced to 45% by

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Heating time (min)</th>
<th>Amylose percentage a (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>5</td>
<td>2.09</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>2.98</td>
</tr>
<tr>
<td>65</td>
<td>5</td>
<td>2.44</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>3.55</td>
</tr>
<tr>
<td>70</td>
<td>5</td>
<td>4.17</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>6.94</td>
</tr>
<tr>
<td>75</td>
<td>5</td>
<td>6.50</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>8.55</td>
</tr>
<tr>
<td>80</td>
<td>5</td>
<td>5.50</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>8.53</td>
</tr>
<tr>
<td>90</td>
<td>5</td>
<td>6.13</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>10.09</td>
</tr>
</tbody>
</table>

a Coefficient of variation: 2–15%.

Fig. 3. Average area distribution of granules heated at 75 °C for 5 and 30 min in aqueous and xanthan solutions.
increasing heating time to 30 min. In the presence of xanthan for 30 min heating, the portion of small granules decreased further to ~38% of their initial number.

If we consider that the last two categories include the originally large A-granules, a slight increase can be noticed from 5 to 30 min heating for control samples. By xanthan addition, the percentage of large granules was considerably greater and reached 30 and 40% of the total population for heating time of 5 and 30 min, respectively. Compared to the respective control sample, this is the double amount.

It is clear that by xanthan addition there is a gradual granules’ population shift from all categories to greater dimensions. Considering that gelatinization temperature for wheat granules is in the range of 50–60 °C (Addo, Xiong, & Blanchard, 2001; Lorenz & Kulp, 1978; Noel et al., 1993) and that for all granules population this could be varied from 10 to 15 °C (Eliasson & Gudmundsson, 1996), there are some granules at 75 °C that have just begun or have not yet begun to gelatinize. Granules at 75 °C of control samples can be classified from small to medium size, whereas granules in xanthan solution from medium to large size (Table 4). However, there are not very large granules with diameter greater than 40 μm, which indicates that at this temperature even the large granules have not reached their maximum swelling. By adding xanthan or by increasing heating time the variability in values is also increased.

In Fig. 4 stained wheat granules are presented, heated at 75 and 85 °C for 30 min. As it can be seen, and it is already mentioned, at 75 °C there are many small granules, which have not been gelatinized. There are also swollen granules without losing their original shape and some of them have a lighter blue colour in the center because of the amylose solubilization. By increasing the heating temperature granules swell further, but they continue keeping their shape. By adding xanthan, more granules are folded even at 75 °C, confirming the above assumption that xanthan increases the forces exerted to granules, making them to be deformed. At 85 °C even more granules are folded, but they are not disrupted.

Solubilization of amylose seems to be more extensive by adding xanthan, according to the lighter blue colour in the center of granules compared with control samples. Solubilization is the first step for amylose leakage.

According to Gallant, Bouchet, and Baldwin (1997) starch granules are organized in a manner that they have radial ‘channels’ to be predominantly composed of semi-crystalline or amorphous material. Through these channels amylose can leak out from the granules during gelatinization. Fannon, Hauber, and BeMiller (1992a,b) and Fannon, Shull, and BeMiller (1993) have observed, that along the equatorial groove, there are surface pores. These pores are the external openings of the interior channels and permit amylose leakage. This is in agreement with the assumption of Langton and Hermansson (1989), who claimed that solubilized amylose is transported outside the granules through openings in the equatorial groove. In the presence of xanthan, at higher temperatures, amylose leakage is hindered. That suggests that except of the film created around the granules, the excessive granules folding could also deform granules surface openings and could hinder amylose leakage.

Table 4
Mean values and standard deviation of starch granules’ area and diameter heated at 75 °C for 5 and 30 min. Control samples and samples with xanthan

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature (°C)/time of heating (min)</th>
<th>Mean area (μm²)</th>
<th>Standard deviation (μm²)</th>
<th>Mean diameter (μm)</th>
<th>Standard deviation (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Without xanthan</td>
<td>75/5</td>
<td>242</td>
<td>409</td>
<td>13.12</td>
<td>10.40</td>
</tr>
<tr>
<td></td>
<td>75/30</td>
<td>331</td>
<td>540</td>
<td>15.85</td>
<td>12.09</td>
</tr>
<tr>
<td>With xanthan</td>
<td>75/5</td>
<td>445</td>
<td>706</td>
<td>18.29</td>
<td>13.92</td>
</tr>
<tr>
<td></td>
<td>75/30</td>
<td>594</td>
<td>743</td>
<td>21.50</td>
<td>15.05</td>
</tr>
</tbody>
</table>

Fig. 4. LM photos of starch granules stained with lugol solution heating for 30 min at different temperatures: (a,b) control samples heated at 75 and 85 °C, respectively; (c,d) samples with xanthan heated at 75 and 85 °C, respectively. Original magnification of the photos 400 ×, magnification used for these photos 540 ×.
3.3. Viscosity measurements

In Fig. 5 the apparent viscosity versus the shear rate is presented for samples prepared at two different temperatures, with different preparation techniques (a) and (b) but using the same heating time. The two temperatures (75 and 90 °C) were chosen according to the results obtained after measuring SP and SOL at different temperatures. At 75 °C swelling is not great but granules remain intact and keep their shape; at 90 °C granules are folded and soluble amount showed great differences according to preparation technique.

All samples showed pseudoplastic behaviour with constant viscosity values at high shear rates. Greater \( \eta \) values were obtained by preparing samples separately (technique (a)). The flow behaviour of all samples was examined by using Ostwald–de Waele model \( (\sigma = k \cdot \dot{\gamma}^n) \). \( k \) values related to the samples’ consistency, and \( n \) values related to flow index, were calculated (Table 5). Samples were compared according to heating conditions (temperature and time) and preparation technique. In regard to the heating conditions, with temperature increase, generally \( k \) values increase as well although \( n \) values decrease accordingly. \( k \) values differ also in relation to the preparation technique. Greater values were obtained by using technique (a), whereas \( n \) values obtained, were lower indicating that samples became more pseudoplastic.

According to the \( F \)-values calculated for \( n \) values, the preparation technique, the heating temperature and their interactions influence significantly the rheology of samples, whereas the time was not significant. However, its interaction with heating temperature was significant. Heating time was not significant neither for average SP nor for SOL values.

Viscosity and consequently \( k \) values in a starch–gum system depend on the exudates present in the media and increase in their amount increases also the viscosity (Christianson, 1982). As it is known, others factors, such as granules’ size, their size distribution, their volume fraction and their compressibility determine also the rheology of a gelatinized starch suspension.

The consistency of a starch suspension, \( k \), increased exponentially with granule diameter, while the flow

![Viscosity-shear rate curves for starch–xanthan mixtures heated at 75 or 90 °C for 30 min prepared with two different techniques (a) and (b).](image)

### Table 5

\( k \) and \( n \) coefficients of Ostwald–de Waele equation for starch–xanthan mixtures prepared at different temperatures and time with two different techniques

<table>
<thead>
<tr>
<th>Heating conditions</th>
<th>Preparation technique</th>
<th>F values for ( n ) values</th>
<th>Main effects</th>
<th>Interactions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Technique (a)</td>
<td>Technique (b)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>Time (min)</td>
<td>( k ) (Pa s(^n))</td>
<td>( n )</td>
<td>( \eta_{100} ) (mPa s)</td>
</tr>
<tr>
<td>75</td>
<td>5</td>
<td>0.64 0.56 84</td>
<td>0.31 0.63 56</td>
<td>A</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>0.68 0.60 100</td>
<td>0.19 0.73 55</td>
<td>B</td>
</tr>
<tr>
<td>90</td>
<td>5</td>
<td>0.62 0.59 94</td>
<td>0.46 0.61 76</td>
<td>C</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>0.70 0.56 92</td>
<td>0.54 0.60 85</td>
<td></td>
</tr>
</tbody>
</table>

A, preparation technique; B, temperature; C, time of heating. \*differ significantly for \( p < 0.05 \). \( R^2 \) for Oswald–de Waele model were >0.99 for most samples. For samples prepared with technique (a) and (b) at 75 °C for 5 min \( R^2 \) was 0.988 and 0.975, respectively.
behaviour index \( n \), decreased linearly with increase in the extent of gelatinization, which was accompanied by an increase in standard deviation of the granule size. The variation of \( k \) with granule size and that of \( n \) with SD were found to be independent of temperature over 70–90 °C (Okechukwu & Rao, 1995; Rao et al., 1997).

According to Wong and Lelievre (1981) dynamic viscosity and storage modulus of wheat starch pastes increased with the volume fraction \( \varphi \) of the swollen granules as a power law, a fact that was also observed by Ellis, Ring, and Whittam (1989) at high \( \varphi \).

Eliasson (1986) observed that more highly swollen (and presumably softer) granules lead to a reduction in a starch paste rigidity. Carnali and Zhou (1996), who used an artificial starch gel (granules of corn starch freed of amylose combined with purified amylose solution), found that the rigidity of granules influence the rheology of pastes/gel proportionally to the temperature at which they have been pasted. At 70 °C granules are not fully swollen, they are relative rigid but the reinforcement of paste by them is not strongly dependent on their rigidity. At 85 °C, however, granules are more swollen, have high volume fraction \( \varphi \) and they are less rigid than these swollen at 70 °C. At this higher \( \varphi \), the reinforcement attributes are very much controlled by granules’ individual rigidity.

However, in systems investigated, soluble solids and swelling cannot be directly correlated to \( k \) or \( n \) values, because xanthan influence their values, since it seems to affect the granules’ rigidity and shape but also the adhesion between the continuous phase and granules.

According to the above assumptions, in our research, samples heated with xanthan (technique (b)) at 90 °C, have an increased \( \varphi \)—not granules’ rupture observed—and consequently their viscosity should be lower comparing to samples prepared at 75 °C. However, this does not happen and it seems that xanthan makes granules more rigid. This increased rigidity is caused due to a film creation around the granules by xanthan and solubilized amylose and due to adhesive interactions among the granules as it was mentioned before. Consequently granules cannot act as fillers, that reinforce the continuous phase.

Furthermore, continuous phase is affected by xanthan addition notably. This late assumption issues by the fact that samples prepared without xanthan (technique (a)) at 90 °C have similar viscosity values to those prepared with xanthan, although the last ones contain more rigid granules, have a greater standard deviation of the granule size and normally they should have an increased viscosity. Besides, at 75 °C the amount of amylose present in the continuous phase is greater in samples prepared by technique (b) but their viscosity is significant lower. For the role of xanthan in continuous phase several assumptions exist. According to Shi and BeMiller (2002) amylose–gum interactions are the main responsible for viscosity increase. They refer two possible models:

Model A as the assumption proposed by Abdulmola et al. (1996): gum molecules interact with amylose molecules leached from granules and adhere partially swollen granules.

Model B proposed by them: gum molecules interact with leached amylose molecules, produce a viscosity increase via synergism, and/or prevent retrogradation.

However, opposite assumption has been reported supposing that incompatibility phenomena unlike polymers, i.e. amylose and xanthan could cause phase separation (Alioncle & Doulbier, 1991). Additionally, the presence of swollen starch granules favours the mutual exclusion of amylose and amylopectin (Conde-Petit & Escher, 1995), since in binary mixtures like starch–xanthan, an exclusion effect may occur, where interactions between chain segments of the same type are favoured energetically in comparison with interactions between different polymer species. Like molecules are concentrated in local domains in a type of phase separation (Eidam, Kulicke, Kuhn & Stute, 1995).

Xanthan does not seem to act synergistically with starch and does not enhance the viscosity of the mixture when samples are prepared by technique (b). It is more probable that due to excluded volume effect of starch granules, local concentration of xanthan in continuous phase increase and phase separation of xanthan–amylose polymers is promoted. Phase separation phenomena were also observed by Mandala and Palogou (2003) in potato starch of higher concentration and xanthan systems during starch gelation and in wheat starch–xanthan systems stored for a long period at ambient conditions (Mandala, Michon, & Launay, 2003).

4. Conclusions

The addition of xanthan in starch dispersions increases the swelling of granules during heating and many large granules are observed even at relatively low temperature (75 °C). Amylose leakage increases also during heating, but at high temperature (>80 °C) it is restricted. Due to xanthan effects on granules swelling and SOL, one would expect that the viscosity and consistency of starch/xanthan mixtures heated together at 75 °C would be relatively high (technique (b)). However, viscosity values were greater for samples prepared with technique (a). It seems that many other factors influence the structure of the resulted mixture. Xanthan is concentrated around the swollen granules, increasing the shear forces applied to them and forming with the already leached amylose, a film around their surface. The main disadvantage is that the deformed granules cannot enhance the consistency of the continuous phase. They seem to be rather rigid and xanthan interposition seems to influence negatively both their cohesion and their connection to the overall polymers.
matrix. Additionally, amylose does not seem to interact with xanthan in the continuous phase, and different polymers exclude each others.

Further investigation should be done in order to understand better xanthan role in such systems. Many factors are changed during heating that should be taken into consideration and increase the complexity of such systems. It is believed, that it is better to focus on some specific factors e.g. xanthan concentration and preparation technique at certain heating temperature and time in order to simplify interpretations.

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References


