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Effect of fatty acids on the rheological behaviour of maize starch dispersions during heating

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Abstract

The pasting of 15% maize starch dispersions in the presence of myristic, palmitic or stearic acid anions, was monitored by on-line measuring parameters, such as torque development, pasting temperature, viscosity exhibited and granule swelling. The results indicated that the fatty acid chain length played a significant role in altering the rate of the gelatinization process. The flow behaviour of heated, at 75, 85 and 98 °C, 10% maize starch dispersions was examined at these temperatures, in the presence of the above mentioned fatty acids. It was shown, that the viscosity exhibited by the starch dispersions was greatly influenced by the fatty acid chain length, the temperature of heating, the addition of acid prior or after heating to the starch system and the state of fluid motion of the sample on testing. Certain mechanisms were proposed to occur in order to explain the behaviour of starch systems during pasting as well as during heating especially in the presence of compounds, which interact with starch components.

Keywords: Starch–fatty acid interactions; Starch rheology; Starch gelatinization; Maize starch

1. Introduction

Starch gelatinization is a complicated order–disorder transition whose mechanism is still not very clearly understood despite the numerous investigations which have been reported on this phenomenon over the last 50 years (Jenkins & Donald, 1998).

Starch undergoes gelatinization on heating of its granules in the presence of water. The granules start to swell, absorbing water and eventually their crystallinity is irreversibly lost. At the same time amylose leaches out of the granules and forms a continuous matrix in which the gelatinized granules, mainly consisting of amylopectin, are embedded. Starch gelatinization plays an important role during the processing of starch based food systems and considerably affects their physicochemical and functional properties. One of the properties which is of paramount importance for the starch based food and chemical industry is the considerable increase in viscosity of gelatinized starch dispersions. A number of researchers (Christianson & Bagley, 1983; Evans & Haisman, 1979; Okechukwu & Rao, 1995; Steeneken, 1989; Wong & Lelievre, 1982) attributed this increase to be greatly influenced by granule swelling and to a lesser degree by the amount of amylose leached out and postulated that there is a direct relationship between the viscosity exhibited by the starch pastes and the volume occupied by the swollen granules. However, microscopic studies (Hoover & Hadjiyev, 1981; Miller, Derby, & Trimbo, 1973) and starch granule swelling studies (Ziegler, Thompson, & Casasnovas, 1993) showed that the amylose matrix does play an important role in the viscosity increase of starch pastes. Moreover, rheological studies (Xu & Raphaelides, 1998) showed, that the viscosity exhibited by concentrated (10 and 15% w/w) maize starch pastes was affected by the amylose phase as well as by the swollen granules.

The degree of granule swelling and the amount of amylose or even amylopectin leached out is governed by a number of factors such as the amount of available water, the temperature and the time of heating, the presence of other substances which may or may not interact with either the starch components or the water, e.g. lipids, surfactants, sugars, salts and so on. For instance, it has been reported (Gray & Schoch, 1962; Hoover & Hadjiyev, 1981; Larson, 1980; Osman & Dix, 1960) that the presence of lipids retards the swelling of the granules and inhibits the leaching of amylose which may be due to the formation of inclusion complexes between amylose and lipid molecules. The antistaling effect of lipids in bakery products is

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attributed by some researchers (Krog & Nybo Jensen, 1970; Riisom, Krog, & Eriksen, 1984) to the formation of these clathrates.

To study the rheological properties of starch pastes in the presence of lipids, poses many problems since the formed inclusion complexes tend to precipitate and the starch molecules are prone to retrograde quite easily at ambient temperatures for concentrations normally encountered in industry. Most of the studies were conducted using either the Brabender visco-amylograph an empirical with low sensitivity instrument of little value for reliable scientific work or commercial rheometers whose use is limited to measurements performed at temperatures lower than those occurred on starch pasting, due to water evaporation from the samples on testing. Thus, the limited published work on the effect of lipids on the rheological properties of starch systems is full of conflicting data which rather add to the confusion than help to elucidate the effect especially under conditions similar to those encountered in industry.

The present study was initiated to investigate the rheological behaviour of maize starch dispersions during pasting or heating in the presence of fatty acids using experimental techniques which are suitable to simulate the conditions normally practiced in many starch based industrial processes.

2. Materials and methods

Commercial maize starch was purchased from GROUP AMYLUM SA, Greece. The starch characteristics were: moisture content 11.45%*, apparent amylose 21.5±0.6%**, total amylose 26.0±0.3%**, onset gelatinization 67.5±0.6 °C, peak gelatinization 72.0±0.5 °C***, granule size 16.0±0.6 μm****.

*Gravimetrically determined by heating the samples at 130 °C for 1 h.

**Determined using the method of Morrison and Laignelet (1983).

***Onset and Peak gelatinization temperatures measured with a Perkin–Elmer DSC-6 differential scanning calorimeter.

****Mean diameter measured with a Malvern laser particle size analyzer.

Fatty acids, myristic, palmitic and stearic (purity 99%) were obtained from Sigma Chemical Company and all other reagents were of analytical grade.

2.1. Instrumentation

The experiments were performed by a custom built instrument coded TR-1 RHEOMETER which has been described elsewhere (Xu et al., 1998). This is a multipurpose controlled stress pneumatic tube rheometer capable of measuring a wide range of liquids, suspensions and pastes at temperatures from −30 up to 140 °C.

The instrument has been modified and developed at our laboratory to be suitable to measure starch pastes with starch concentrations at least up to 30% (w/w). The control unit of the instrument was possible to be connected with one at a time of three types of sample jacketed stainless steel vessels, which differ only in their sample maximum capacity (which was 30, 70 and 1800 ml, respectively). All were thermostatically controlled either through a circulating heating medium of an external temperature controlled bath circulator or by means of electrical heating elements incorporated into the heating mantle of the vessels. Each vessel was equipped with two sets of mixing pins. One set was static, fixed at the bottom of the vessel and the other was mobile fixed on a rotating disk, which was attached to the lid of the vessel. In the two smaller vessels the static pins had twofold symmetry whereas the mobile ones had twofold symmetry and a centre pin. In the larger vessel, the static pins had threefold symmetry and the mobile ones fourfold symmetry and a centre pin. The pins in the larger vessel were hollow and three in a row of the static ones had incorporated thermocouples connected through a data acquisition card to the instrument's computer. Thus, this series of thermocouples provided accurate temperature measurements along the radius of the vessel. This configuration showed in the test trials of the vessels, to provide a very satisfactory mixing pattern to the starch systems under investigation. At the bottom of the vessel a measuring metal tubing was fixed serving as an outlet to the sample the vessel contained. In the present work the dimensions of the measuring metal tubings employed ranged: the length, from 30 up to 52 mm and the internal diameter (i.d.) from 0.975 up to 2.16 mm.

On the lid was also fixed a tubing serving as an inlet allowing the blowing of pressurized air inside the vessel, when it was required. The vessel was hermetically closed and the rotating disk was driven by a stirrer's electrical motor. In the case of the larger vessel the stirrer's motor was a modular mixing system (GLAS-COL, COLE—PALMER, USA) consisted of a mixer head (0–250 rpm, max torque 72.3 g-cm) and a controller in which both the selected speed of rotation and the torque developed were displayed and through a custom made data acquisition system were transferred to the instrument's computer.

2.2. Starch pasting experiments

Two main series of experiments were carried out as follows: in the first series, aqueous starch dispersions (starch content 15% w/w), were heated inside the sample vessel (capacity 1800 ml) of the rheometer up to 95°C. The samples were heated under constant stirring at selected rotational speeds (40–50–60 rpm). This series of experiments were designated as the control ones. The experiments of the second series differed from those of the first series in that; fatty acid potassium salt aqueous solution was added to the starch dispersion at ambient temperature before the start of heating. The fatty acid concentration used exceeded by ∼5% the concentration known to be necessary to interact with the total amount of available (apparent) amylose present in the sample to form fully saturated, with fatty acid anions, amylose helices (Karkalas & Raphaelides, 1986).

For all experiments the following procedure was employed: A brief stirring, to achieve a satisfactory mixing of the starch slurry, was applied before the commencement of heating (heating rate 2.1 ± 0.1 °C/min). During pasting, sample temperature and the torque developed by the stirrer were continuously recorded to the rheometer's control unit. At specific time intervals, apparent shear viscosity was determined at a single specified shear stress value (830.8 Pa) set by the rheometer's control unit. The viscosity was calculated via a custom built software program.

Weighed amounts (~ 2 g) of the sample discharged from the measuring tubing of the vessel, at the specified time intervals of viscosity measurements, were collected in conical flasks each containing 200 ml warm water (55 °C) and the starch suspension was quickly dispersed in the water under mild magnetic stirring followed by cooling, into an ice-bath, to room temperature. To this dispersion (designated as LAD), loss of birefringence was microscopically checked, granule size measurement was performed and percentage of leached amylose was determined.

2.3. Flow behaviour experiments of heated starch systems

Three main series of experiments were carried out as follows: In the first series, aqueous starch dispersions (10% w/w starch) were heated inside the sample vessel (capacity 30 ml) of the rheometer at 75, 85 or 98 °C. To raise the temperature inside the vessel, from ambient to 75 °C, it took about 4 min, from ambient to 85 °C about 5 min and from ambient to 98 °C about 6 min. The samples were heated under constant stirring (50 rpm) at the predetermined temperatures for 30 min and then the measurements were conducted either under constant stirring or the samples were left to rest for 15 min before the commencement of the measurements. This series of experiments were designated as the control ones.

The experiments of the second series differed from those of the first series in that; fatty acid potassium salt aqueous solution was added to the starch dispersion at ambient temperature before the start of heating. The fatty acid concentration used exceeded by $\sim 5\%$ the concentration known to be necessary to produce fully saturated, with fatty acid anions, amylose helices as mentioned above.

The experiments of the third series were identical to those of the second series with the only exception that the fatty acid solution was added after the starch samples were heated at the predetermined temperature for 30 min. After the addition of the fatty acid solution the samples were stirred for additional 15 min to allow sufficient time for temperature equilibration and for the interaction between amylose and fatty acid to take place. Then the measurements were performed in the manner described above, i.e. either under constant stirring or having the sample at rest for 15 min prior to testing. Besides, granule size measurements were performed for each sample in all series of experiments, in the manner described above. Each set of measurements was replicated three times.

2.4. Granule size measurement

Granule size measurements were performed using a laser particle size analyzer (MALVERN Instruments, model Mastersize 2000, UK). An adequate volume (5–15 ml) of starch dispersion to obtain an obscuration 2–4% was added into 600 ml deionised water in a beaker, and granule size as the volume mean diameter D (4.3) was measured by employing a measurement standard operation procedure (SOP), consisted of: a brief sonication for 30 s, with the stirring pump of the instrument set at 1500 rpm and taking the mean value of five measurements with 5 s delay between them.

2.5. Leached amylose determination

A volume (30–35 ml) of supernatant after centrifugation (1500 g, 10 min) of the LAD was accurately weighed (0.001 g) into a Petri dish. The dry matter was estimated by drying overnight at 100 °C in an oven and the result was expressed as percentage of the leached apparent amylose.

2.6. Light microscopy

The birefringence of the heated granules was detected under polarized light using a ZEISS (model Axiostar, Germany) microscope.

3. Results

3.1. Effect of the fatty acid type and the fluid motion on the starch gelatinization rate.

Fig. 1(a–c), shows the changes in the torque value developed during the heating of starch dispersions (15%w/w starch) in the presence of fatty acids as affected by the speed of stirring. The selected rotational speed values were low enough not to cause any damage to the granules. This was microscopically confirmed to be the case in all series of experiments presented here.

Moreover, Zobel (1984) reported that a 10% maize starch dispersion stirred at 120 rpm for 30 min at 90 °C showed microscopically none granule breakage.

It can be seen that the addition of myristic acid anions not only accelerated to a certain degree the onset of gelatinization as it is clearly shown in (a) (40 rpm) and (b) (50 rpm) graphs but it also seems to promote changes in the starch system which resulted to a considerable increase of the torque applied. Indeed, the maximum torque value attained by the starch–myristate system was far higher than those of both the starch dispersion without fatty acid added (control) and the starch–palmitate and starch–stearate systems. As for the effect of the addition of palmitate and stearate anions to starch dispersions it can be seen that both fatty acids retarded the onset of gelatinization relative to that of the control and this retardation was dependent on the carbon chain length of the fatty acid molecule, i.e, the longer the chain is the longer the delay in the commencement of the gelatinization process appears to be.

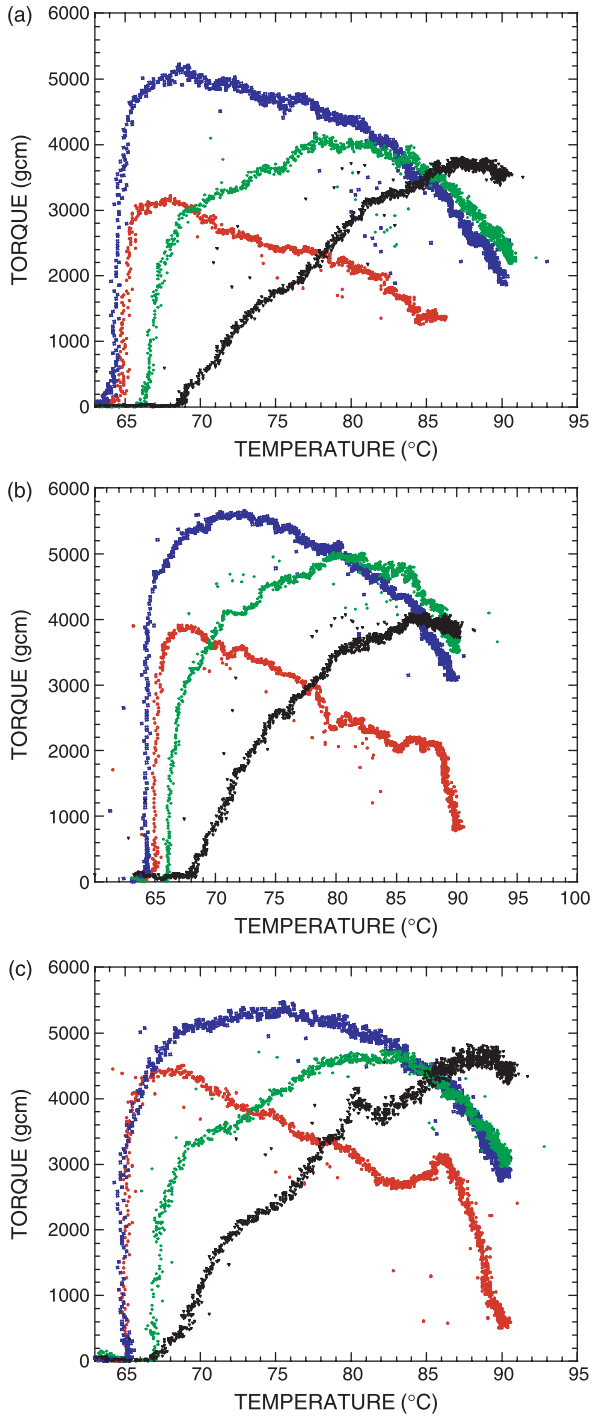

Fig. 1. Torque development during pasting of 15% maize starch dispersions in the presence of fatty acids, as a function of temperature of pasting. Line colours denote: Red, control sample (no fatty acid added); blue, sample with added myristic acid; green, sample with added palmitic acid; black, sample with added stearic acid. (a–c) denote mixing rotational speed of 40, 50 and 60 rpm, respectively.(For interpretation of the reference to colour in this legend, the reader is referred to the web version of this article).

Besides, the latter attained a much higher torque at the peak of gelatinization than the control.

The torque development during heating of the control seems to be dependent on the agitation rate, thus the lower the stirring speed employed the lower the maximum torque value attained. The same applies in the case of the starch–fatty acid systems but to a lesser degree.

Moreover, the presence of the fatty acid anions in the starch dispersion retarded the gelatinization rate and the results showed that the time needed to elapse for the completion of the process was proportional to the fatty acid chain length, i.e. the longer the chain was, the longer the time needed for gelatinization to complete.

As for the heat transport concerning the overall pasting process the results in Fig. 2(a and b) indicate that the pasting temperature profile exhibited in all cases, was independent of the presence of a fatty acid in the starch system. Besides, the mixing speeds employed did not affect the temperature increase with the time, because they were quite low and especially they did not alter the integrity of the granules. This is something which normally occurs in much higher stirring speeds where a considerable amount of starch granules disintegrates thus significantly affecting the fluidity of

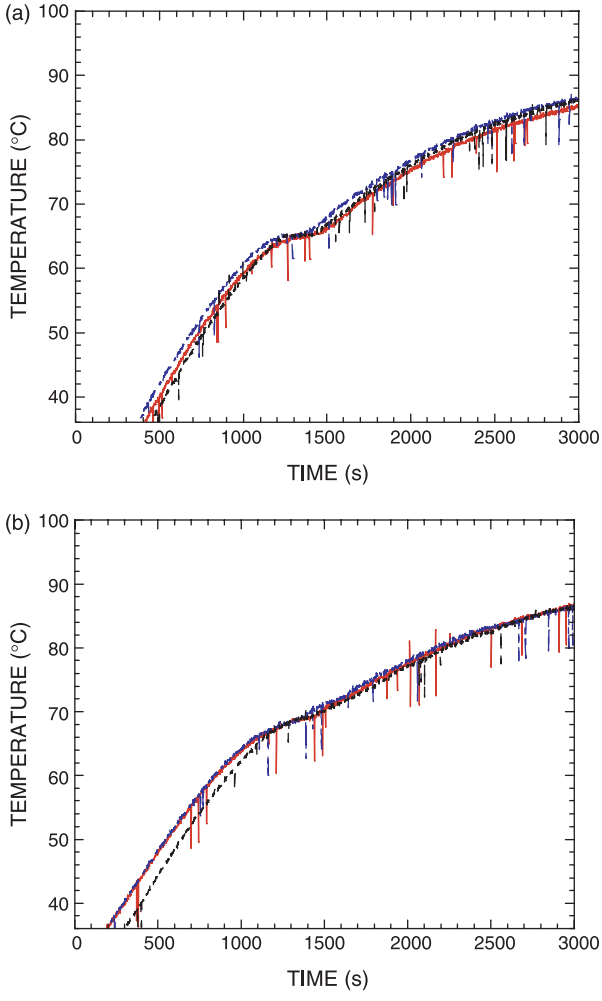

Fig. 2. Temperature curves of pasting as a function of time of heating, of 15% maize starch dispersions in the presence of fatty acids. (a) Curves referred to either the control sample (no fatty acid added), or the sample with added myristic acid or the sample with added palmitic acid. (b) Sample with added stearic acid. Red line, blue line and black line denote mixing rotational speed of 40, 50 and 60 rpm, respectively.(For interpretation of the reference to colour in this legend, the reader is referred to the web version of this article).

the system (Karapantsios, Sakonidou, & Raphaelides, 2000; Zobel, 1984). All temperature curves exhibit a thermal plateau at about 68°C, apart from those of the starch–stearate systems where instead of the plateau at this temperature appears a change in the slope of the temperature curve. This plateau could be attributed to the resistance in heat penetration shown by the starch granules since around this temperature the gelatinization process was well under way in all samples examined.

While, in the case of the control the torque increase could be mostly attributed to the granule swelling, this applies to a lesser degree in the case of the starch–fatty acid systems. Fig. 3(a–c) shows that within the heating temperature range from 63°C to 92°C, the change in the granule size was pronounced in the control samples. In fact, it is shown to be agitation rate dependent as in the case of torque development (Fig. 1). That is the higher the speed of stirring the larger the size of the granules became. This was to be expected since it was shown (Sakonidou, Karapantsios, & Raphaelides, 2003) that a mass transfer controlling step exists in the gelatinization process, i.e. the water diffusion from the bulk aqueous phase to the starch granule is agitation rate dependent. Moreover, it shows that the granules continued to swell as the gelatinization proceeded. As for the starch–fatty acid systems this does not apply since their granule swelling appeared to be independent from the agitation rate applied. Despite the practical difficulty to continuously obtain samples from the rheometer's sample vessel, as quickly as possible, as soon as the temperature of the onset of gelatinization was reached and throughout the pasting process; it can be seen that all starch–fatty acid systems showed a regular pattern of gradual limited increase in granule swelling, followed by a gradual decrease towards the temperature of the gelatinization completion. This decrease does not mean that the granules shrank back to their original size but it might be attributed to the increase of their deformability, possibly due to the leaching of amylose out of the granule. Thus, the granules became very compressible and when they were subjected to high centrifugal forces as it happened to be during the particle size measurements (1500 rpm pump speed), they were flattened and appeared to have smaller size.

An effort was made to estimate the amount of amylose leached out of the granules. This proved to be rather impossible and the results obtained were unreliable. As a characteristic example of this situation, Fig. 4 shows the amount of leached amylose as a function of the temperature of pasting of the starch dispersion (control) and of the starch–stearate system. It can be seen that up to 83 °C the amount of leached amylose rose proportionally to temperature rise, but beyond this value it sharply dropped. This does not mean that amylose was leached with lower rate but it should be due to the amylose entrainment by the swollen starch granules during centrifugation. Hence, it became impossible to siphon off the supernatant from a system where the swollen granules occupy all the space of the available volume. The same difficulty was experienced by other researchers (Okechukwu & Rao, 1995) as well. In the case of the starch–stearate system apart from the fact that amylose leaching was greatly suppressed possibly due to complexation of the acid anions with the amylose on the surface of the granules, most of the released available amylose interacted with the stearate anions to form complexes which are water insoluble at the temperature in which centrifugal separation of leached amylose from the dispersion took place. Hence this complexed amylose remained in the precipitate along with the gelatinized starch granules.

The course of gelatinization process just soon after the onset (~68 °C) and up to ~92 °C was also monitored by measuring

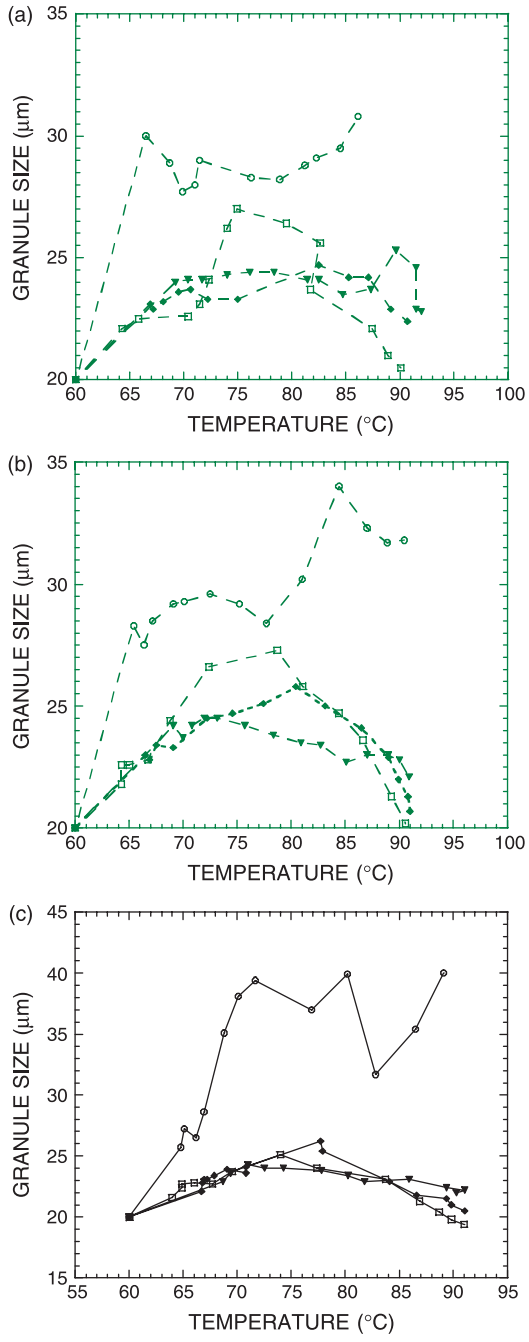

Fig. 3. Granule size as a function of pasting temperature of 15% maize starch dispersions in the presence of fatty acids: ○, control sample (no fatty acid added); □, sample with added myristic acid; ◆, sample with added palmitic acid; ▼, sample with added stearic acid. (a–c) Denote mixing rotational speed of 40, 50 and 60 rpm, respectively.

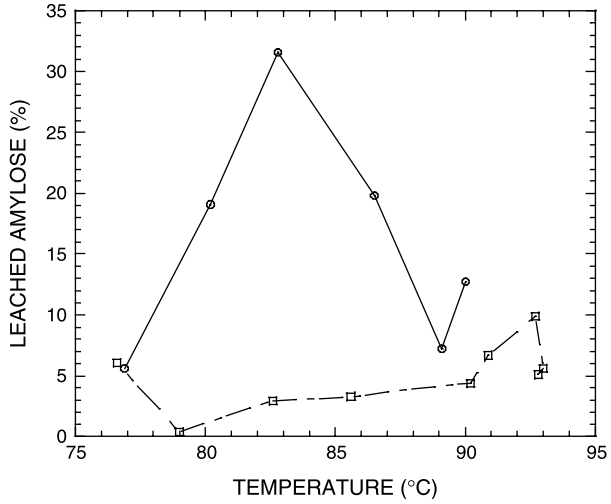

Fig. 4. Amylose leached out from maize starch granules on pasting as a function of pasting temperature. ○, 15% maize starch dispersion (control); □, 15% maize starch dispersion with added stearic acid. Rotational speed of mixing, 60 rpm.

the apparent viscosity at a fixed shear stress value (830.8 Pa) applied to all samples, at time intervals as short as possible. Fig. 5(a–c) shows the changes in viscosity as a function of temperature. It can be seen that all curves, i.e. those of the control and of the starch–fatty acid systems correlate well with the corresponding torque–temperature curves (Fig. 1). Thus, the viscosity of the control continuously decreased as the pasting proceeded, whereas in the case of the starch–fatty acid systems at the initial stage of pasting it increased and after reaching a peak value at temperature which differs from one system to the other it started to decrease following a pattern similar to that of the control. At the same temperatures the starch–fatty acid systems attained their maximum torque value and actually these temperatures were dependent on the carbon chain length of the fatty acids employed. That is the longer the chain length the higher is the temperature of the peak viscosity.

3.2. Flow behaviour of heated starch systems as affected by the temperature of heating.

The heating temperature selection, in this work, was based on certain assumptions. That is, in excess of water, which is actually the case here, at around 75 °C maize starch gelatinizes, i.e. it undergoes the so called first swelling, albeit not fully, whereas at 85 °C it should be almost totally gelatinized, i.e. the second swelling takes place (Doublier, 1989), even its crystallinity should have been lost (Jenkins & Donald, 1998). The 98 °C temperature was chosen since at this temperature the formed complexes may be dissociated, as DSC studies have shown to occur in model systems (Raphaelides & Karkalas, 1988), thus, any effect on the rheological behaviour of the samples attributed to the presence of these complexes was expected to be minimized or even eliminated. It was assumed, in this case, the starch components to behave in the manner like when the fatty acid molecules were not present.

Concerning the selection of the three fatty acids, this was based on their ability to readily interact quantitatively with the available amylose to form complexes under the conditions employed here, as it has been reported elsewhere (Karkalas & Raphaelides, 1986). Moreover, it was shown (Raphaelides, 1992, 1993) that model starch systems at pH 12, containing these three fatty acids exhibited a range of rheological behaviours, either in solution or in gel state, depending on their carbon chain length. The reason for using the fatty acids

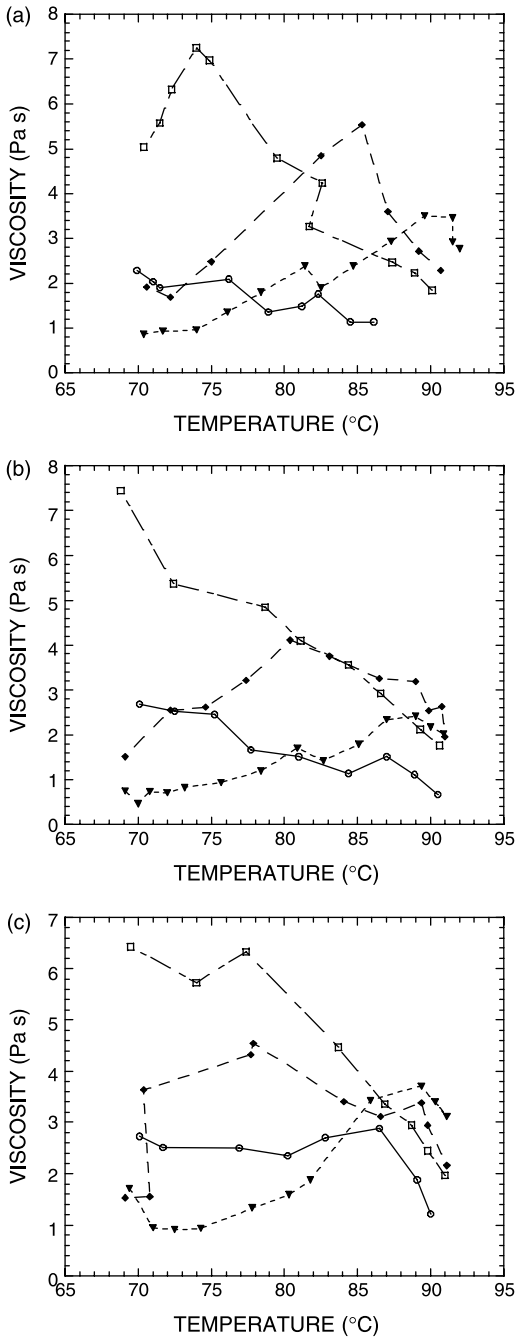

Fig. 5. Viscosity at 830.8 Pa shear stress, as a function of pasting temperature of 15% maize starch dispersions in the presence of fatty acids: ○, control sample (no fatty acid added); □, sample with added myristic acid; ◆, sample with added palmitic acid; ▼, sample with added stearic acid. (a–c) denote mixing rotational speed of 40, 50 and 60 rpm, respectively.

as potassium salts is that they are water soluble and in their most active form, i.e. as monomers. Hence, they become totally available to participate in complex formation in contrast to other methods employed by other workers in which this does not apply (Fanta, Shogren, & Salch, 1999; Raphaelides & Karkalas, 1988).

Fig. 6 shows the effect of myristate anions' presence in the flow behaviour of maize starch dispersions heated at 75, 85 or 98 °C, added to starch prior to heating (a) and after heating (b). It can be seen, that myristic acid, at 75 °C, in both cases augmented the viscous character of the starch dispersion and this is in agreement with the results of Figs. 1 and 5. At 85 °C, it seems no effect to occur in both case, and the curves of the control and the starch–myristate system almost coincided within experimental error. At 98 °C, it can be seen that there was a reduction in viscosity due the presence of the myristate ions regardless of whether they were added before or after heating.

Fig. 7 (a and b) shows that the flow pattern of the sample at 75 °C, in which palmitic was added to the starch system prior to

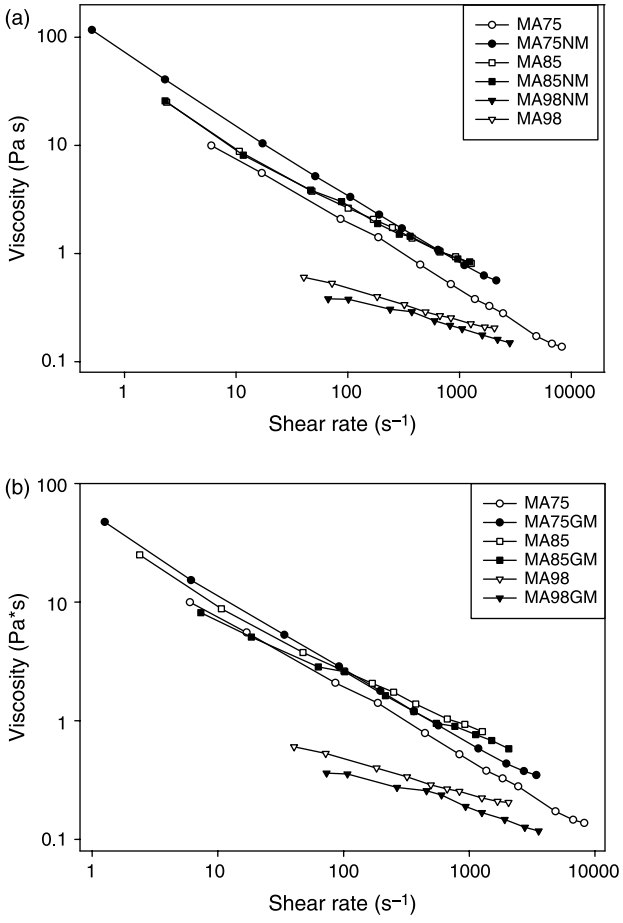

Fig. 6. Flow curves of 10% maize starch dispersions in the presence of myristic acid K salt. Codes denote: MA75, MA85, MA98 control samples (no acid added) heated and measured under constant stirring at 75, 85, 98 °C, respectively. (a) Codes denote: MA75NM, MA85NM, MA98NM, myristic acid, added to the starch system prior to heating. Heated and measured under constant stirring at 75, 85, 98 °C, respectively. (b) Codes denote: MA75GM, MA85GM, MA98GM, myristic acid added to the starch system after heating. Heated and measured under constant stirring at 75, 85, 98 °C, respectively.

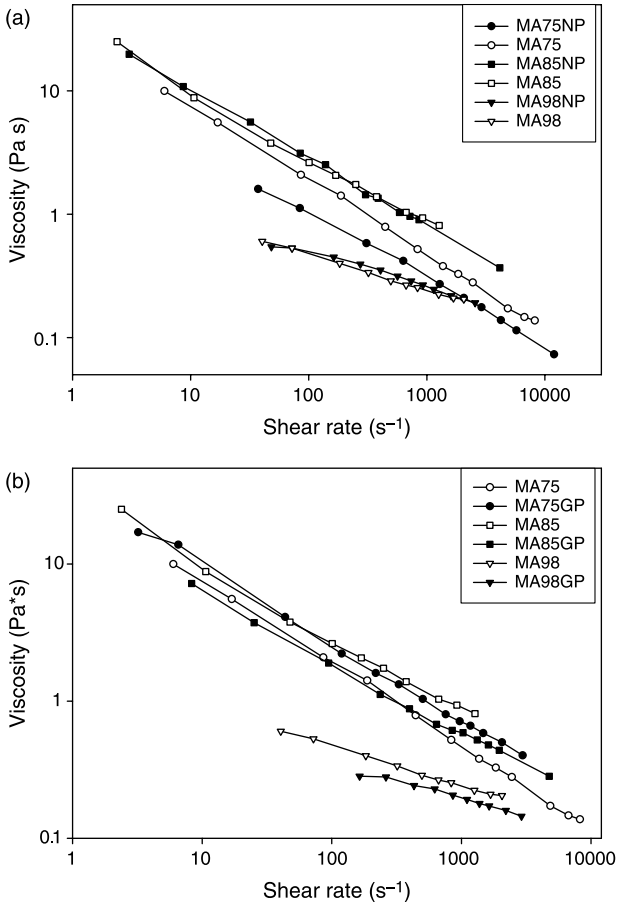

Fig. 7. Flow curves of 10% maize starch dispersions in the presence of palmitic acid K salt. Codes are the same as in Fig. 6. P denotes palmitic acid.

heating, was opposite to its homologous with myristic acid. In this case, its viscosity was 2.5 times lower than that of the control, whereas the viscosity of the starch–myristate system was almost twice as that of the control. At 85 °C the addition of palmitic acid to the gelatinized starch system caused a reduction in the viscosity in comparison to that of the control. The other curves of starch–palmitate system exhibited the same patterns as those of starch–myristate ones with the exception of that at 98 °C in which the palmitate was added prior to heating. In this case there was no effect on the flow behaviour of the starch system and the flow curves of the control and the starch–palmitate system are identical.

Fig. 8(a, b) shows that the addition of stearic acid to starch system prior to heating caused a series of significant changes in the flow behaviour of starch dispersions depending on the temperature of heating. The most pronounced effect is shown at 75 °C (Fig. 8a) where the sample exhibited a Newtonian behaviour and a viscosity which was 25 times lower than that of the control (no fatty acid added) which on the contrary showed pseudoplastic behaviour as did all the other samples examined in this work. At 85 °C, the viscosity of the starch–stearate system was more than four times lower than that of the control, whereas at 98 °C the viscosity of the starch–stearate system is almost double of that of the control. As for the samples in which the stearate ions added to the starch system

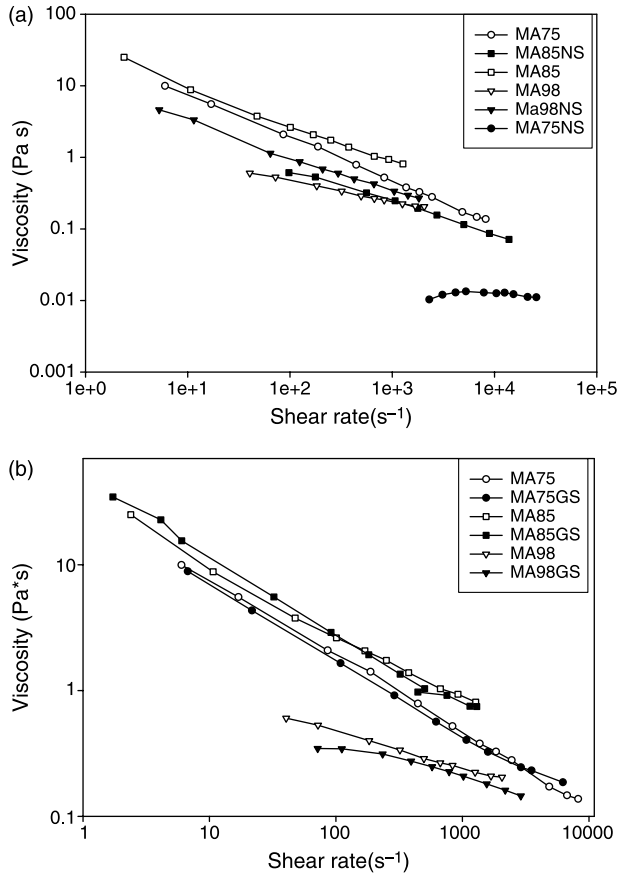

Fig. 8. Flow curves of 10% maize starch dispersions in the presence of stearic acid K salt. Codes are the same as in Fig. 6. S denotes stearic acid.

after gelatinization the results did not show any appreciable changes to occur.

4. Discussion

The pasting experiments revealed that the presence of fatty acids in the starch dispersion significantly altered the mechanism of the gelatinization process. It is generally accepted (Morrison, 1995; Parker & Ring, 2001), that with the commencement of the gelatinization process, water enters to the granule and gradually solubilises the amylose which leaches out of the granule. At the same time as more water is absorbed by the granule it swells and its size, is greatly increased. When fatty acid anions are present in the starch system, it appears that they effectively control the leaching of amylose and consequently control the swelling of the granules. It seems that the leaching of solubilised amylose is a prerequisite for the continuous entrance of water into the granule causing its continuous swelling during pasting. That is, no amylose leaching, then no water entry to the granule hence no granule swelling. How effective the fatty acids are to inhibit the granule swelling it depends on their carbon chain length and the longer the chain the more effective the acid is. SEM microscopic studies of potato starch heated at 80 °C in the presence of monoglycerides with chain length from 14 to 18 carbon atoms revealed that the granules remained virtually intact even after heating for 30 min in excess of water (2.5% starch) (Hoover & Hadjiyev, 1981).

The fact that the starch–fatty acid systems exhibited a more viscous behaviour on pasting than the control and even the myristic acid appeared to accelerate the gelatinization process, could be attributed to the following mechanism: At the onset of gelatinization the surface of the granules is covered by a 'hairy' layer of low molecular weight, partly leached out amylose which is still bound to the granule. Due to the presence of fatty acid ions in the milieu of these mobile leached amylosic chains, amylose–fatty acid interaction takes place and helices are formed on the surface of the granules. It is known (Banks & Greenwood, 1971; Godet, Tran, Delage, & Buleon, 1993) the conformation of the amylose helix is such that it is hydrophobic within the central cavity where the guest molecules are located and exposes active hydroxyls to the adjacent milieu which could enhance hydrogen bonding. Moreover, since the carboxyl group of the fatty acid molecule is located outside the helix cavity due to its bulkiness (Carlson et al., 1979; Godet et al., 1993; Snape, Morrison, Maroto-Valer, Karkalas, & Pethrick, 1998) this is also active to react with adjacent molecules. Thus, the hydrodynamic volume of starch granules increases due to the formation of temporary links between adjacent granules based on hydrogen bonding at the active sites of the protruding amylose helices. Consequently, the viscosity of the starch–fatty acid system was significantly increased.

The rates of the viscosity increase of the starch–fatty acid systems examined in this work, followed the order: starch–myristate, was faster than the starch–palmitate which was faster than the starch–stearate. A plausible explanation of this classification could be: the shorter length of the myristate molecule allows it to interact with short amylosic chains, whereas the palmitate needs longer amylosic chains and the stearate even longer. Since, it is known (Banks & Greenwood, 1975; Christianson, Baker, Loffredo, & Bagley, 1982) that during gelatinization the shorter amylosic chains are the first to leach out this seems to be quite possible to occur.

Why the viscosity in both the control and the starch–fatty acid systems after reaching a peak, gradually started to decrease this should be attributed to the increasing deformability of the starch granules due to continuous amylose leaching in relation to increasing temperature of heating.

As far as the flow behaviour of heated starch systems in the presence of fatty acids is concerned, it can be seen from the graphs (Figs. 6– 8) that all systems are pseudoplastic fluids with the exception of the starch–stearate system heated at 75 °C which showed Newtonian behaviour. Actually, all data fit very well ($R^2 > 0.94$) the power law flow equation:

$$\sigma = K^n$$

where σ is the shear stress (Pa), $\gamma\cdot$ is the shear rate (s^{-1}), K is the consistency coefficient (Pa s^n), and n is the flow behaviour index (dimensionless)

Table 1 shows calculated values of K and n of all flow curves shown in Figs. 6–8. The shear thinning behaviour of heated maize starch dispersions was also reported by other

Table 1
Power law parameters K and n of 10% maize starch and maize starch–fatty acid systems heated at various temperatures

Sample*	Isothermal heating time (min)	Consistency coefficient (K) (Pa s^n)	Flow behaviour index (n)
MA75	30	30.65	0.4
MA85	30	33.75	0.47
MA98	30	1.77	0.71
MA75NM	30	69.0	0.36
MA75NP	30	12.06	0.47
MA75NS	30	0.01	1.00
MA85NM	30	31.85	0.46
MA85NP	30	36.60	0.45
MA85NS	30	5.19	0.56
MA98NM	30	1.26	0.74
MA98NP	30	1.73	0.73
MA98NS	30	9.98	0.51
MA75GM	45	49.35	0.38
MA75GP	45	34.75	0.44
MA75GS	45	25.30	0.42
MA85GM	45	20.49	0.53
MA85GP	45	19.17	0.50
MA85GS	45	47.20	0.40
MA98GM	45	20.49	0.53
MA98GP	45	1.06	0.76
MA98GS	45	1.11	0.76

*The numbers denote the temperature of heating. Code MA denotes starch system (control). Codes NM, NP, NS, denote the starch system with added, prior to heating, myristic, palmitic, stearic acid, respectively. Codes GM, GP, GS, denote the starch system with added, after heating for 30 min at the predetermined temperatures, myristic, palmitic, stearic acid, respectively, and then heated for a further 15 min. (Total time of isothermal heating 45 min).

researchers (Christianson & Bagley, 1983; Doublier, Llamas, & Le Meur, 1987; Evans & Haisman, 1979), with the exception of Okechukwu and Rao (1995) who reported that maize starch (2.6%) dispersions heated up to 80 °C showed shear thickening behaviour. This discrepancy might be due to the fact that Okechukwu and Rao (1995), performed viscosity measurements at 20 °C. At this temperature the development of some kind of order in the starch system should be expected thus the rheological behaviour observed could not reflect that existing at the temperature of heating the starch system.

The flow curves data confirmed the results obtained from the pasting experiments and support the proposed mechanism of the pasting process described previously. Thus, the presence of myristic acid caused an increase in viscosity of the system at the first stage of the gelatinization process (heating temperature 75 °C), whereas the palmitic and the stearic acids reduced the viscosity since at this temperature the gelatinization process was effectively prohibited. Granule size measurements of all starch systems examined in this series of experiments revealed (Fig. 9a–c) that at 75 and 85 °C all three acids when they were added to the starch system prior to heating, they managed to keep fairly low the degree of granule swelling whereas when they were added after heating the degree of granule swelling was not appreciably altered and was a little lower than that of the control. Although it can be seen that at 75 °C the degree of granule swelling caused by the presence of the fatty acids was proportional to the carbon chain length of the fatty acids (Fig. 9a) the very low viscosity exhibited by the starch–stearic

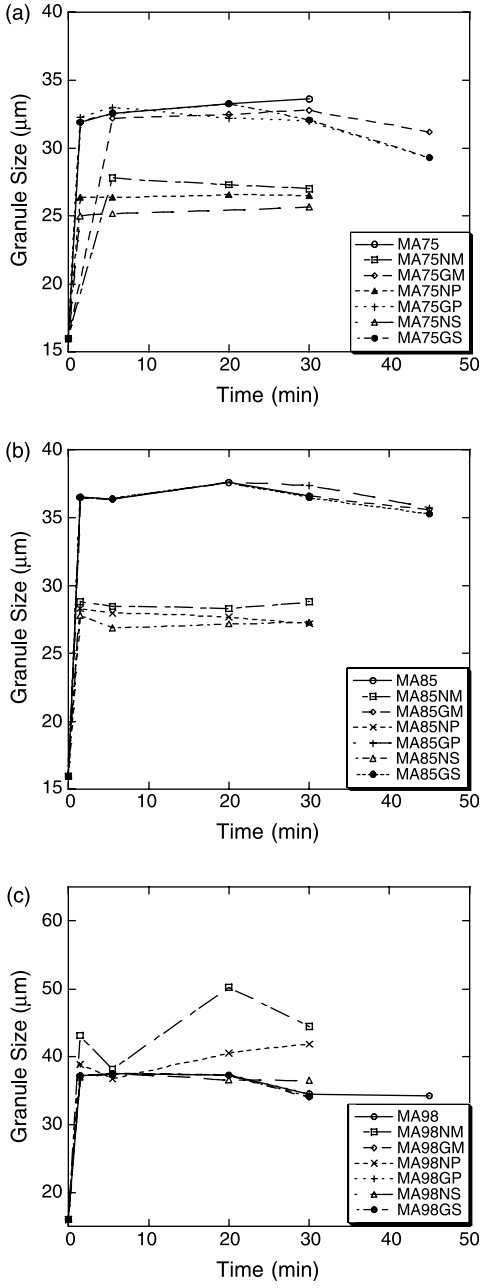

Fig. 9. Granule size of 10% starch dispersions in the presence of fatty acids as a function of time of heating at : (a), 75 °C; (b), 85 °C; (c), 98 °C. Codes are the same as in Figs. 6–8.

system (Fig. 8a) proves that the flow properties of the starch system governed not only by the swollen granules but also by the amount of leached amylose. When, the amount of leached amylose was the same in the starch–pamitate and starch–stearate systems with that of the control then the effect of these two acids to the viscosity of the system was negligible (Figs. 7b and 8b). It must be remembered that at 75 °C about 20% of the available amylose is being leached out of the granule and this is with the lowest molecular weight (Christianson et al., 1982). Godet, Bizot, and Buleon (1995) reported that the critical size of amylose molecule to complex with lauric acid (C:12) is 20–30 glucosyl residues whereas for the palmitic acid (C:16)

is 30–40 glucosyl residues, i.e. about the chain length to accommodate two fatty acid molecules per chain. At 98 °C where the starch granules acquired their final degree of swelling regardless of whether the fatty acids were present in the system or not, it can be seen that the presence of the fatty acids caused a reduction to the viscosity exhibited by the starch system and this could be attributed to the interaction of the available leached amylose with the fatty acid molecules. The interaction caused the change of the molecular conformation of the amylose molecules from random coil to extended helix thus reducing the hydrodynamic volume of the amylose molecules with the consequent fall in the viscosity of the starch system. It is known (Karkalas & Raphaelides, 1986; Raphaelides, 1992), that amylose complexation with fatty acids in alkaline solution (pH 12) caused reduction to the amylose solution viscosity due to this coil to helix transition.

As it was previously postulated, at 98 °C it was expected the already formed helices to have been dissociated. However, it has been demonstrated (Le Bail et al., 1999) that within the time scale of the experiments of this work, crystalline amylose–fatty acid complexes can be formed when aqueous starch dispersions are heated over 88 °C and up to 115 °C. This means that the form of these existing helices should be that of the II form which is considered to be more stable and compact (Biliaderis & Galloway, 1989; Biliaderis, Page, & Maurice, 1986; Karkalas, Ma, Morrison, & Pethrick, 1995; Raphaelides & Karkalas, 1988) than that formed in temperatures below 90 °C which is designated as I form (Biliaderis & Galloway, 1989). This suggestion was proved to be correct when some of theses samples were thermally analyzed by DSC. The thermograms obtained for these starch–fatty acid systems revealed a single endotherm with a peak around 115 °C which can be attributed to the II form of the amylose–fatty acid complexes.

The notable exception is the starch–stearic acid system in which the acid added to the starch system prior to heating exhibited higher viscosity than that of the control. This was also observed to occur in the pasting experiments (Fig. 1), where it can be seen that the starch–stearate system developed its peak of viscosity after the heating temperature passed over the 90 °C, at which temperature the viscosity of the control was greatly reduced. In this case it is suggested that the starch–stearic system exhibited a behaviour similar to that shown by the starch–myristic system at 75 °C.

4.1. Effect of stirring

In an effort to elucidate further the mechanisms, which affect the flow behaviour of starch–fatty acid systems another series of experiments was conducted. Thus, samples prepared in the manner described above were allowed to rest for 15 min, at the predetermined temperatures prior to the commencement of the measurements. This period of time was judged to be sufficient for any kind of cross linking, likely to occur among the components of the system, to be able to take place, at least to a measurable degree. Fig. 10, shows a series of flow curves of maize starch–palmitic acid dispersions heated at the three

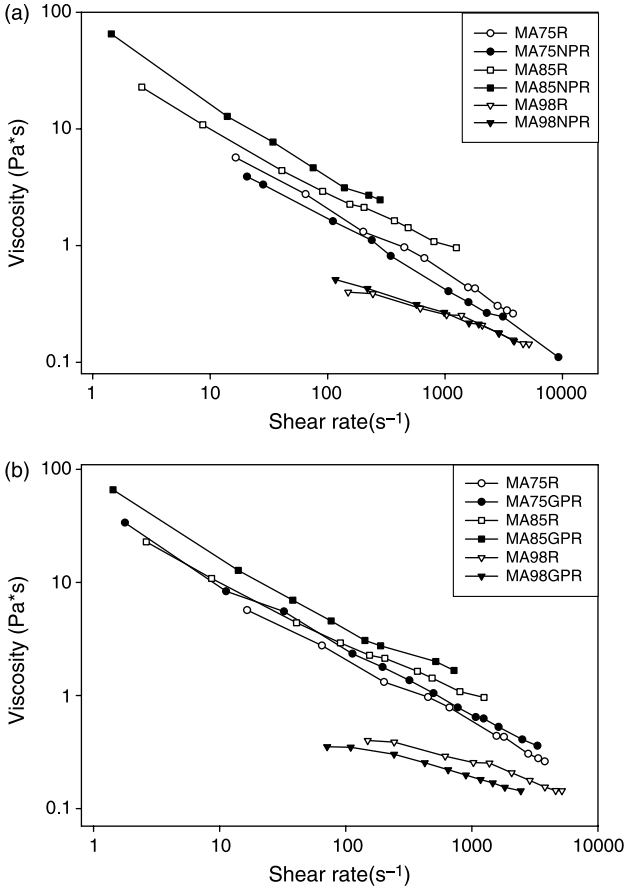

Fig. 10. Flow curves of 10% maize starch dispersions in the presence of palmitic acid K salts, heated and measured at rest at 75, 85 or 98 °C. Codes are the same as in Fig. 6. R denotes the sample rested 15 min prior to testing at the specified temperature.

predetermined temperatures for the previously specified time intervals (30 or 45 min) and measured after a 15 min rest interval. It can be seen for the samples heated at 75 °C and 98 °C, the flow patterns are identical to those of the samples heated at the same temperatures and measured under constant stirring (Fig. 7). In the case of the starch systems heated at 85 °C, it can be seen that the flow patterns are different from those exhibited by the samples measured under constant stirring. Both samples, i.e. fatty acid addition prior to heating or after heating showed the same flow behaviour at rest, which is that their viscosity was higher than that of the control. This might be due to the formation of amylose–palmitate helices bound to the surface of the granule, which interacted, with the adjacent granules thus increasing their hydrodynamic volume and consequently exhibited higher viscosity than the control.

A complementary series of experiments involving starch–palmitic samples prepared and heated at 85 °C as previously described, were also performed. After heating at 85 °C, they were cooled down to 75 °C under constant stirring. When the temperature reached at 75 °C, the samples were allowed to rest for 15 min prior to testing. Fig. 11(a,b) shows the flow curves obtained from these experiments as well as the flow curves of the homologous experiments heated and measured at 75 °C. It can be seen that the samples heated at 85 °C and measured at

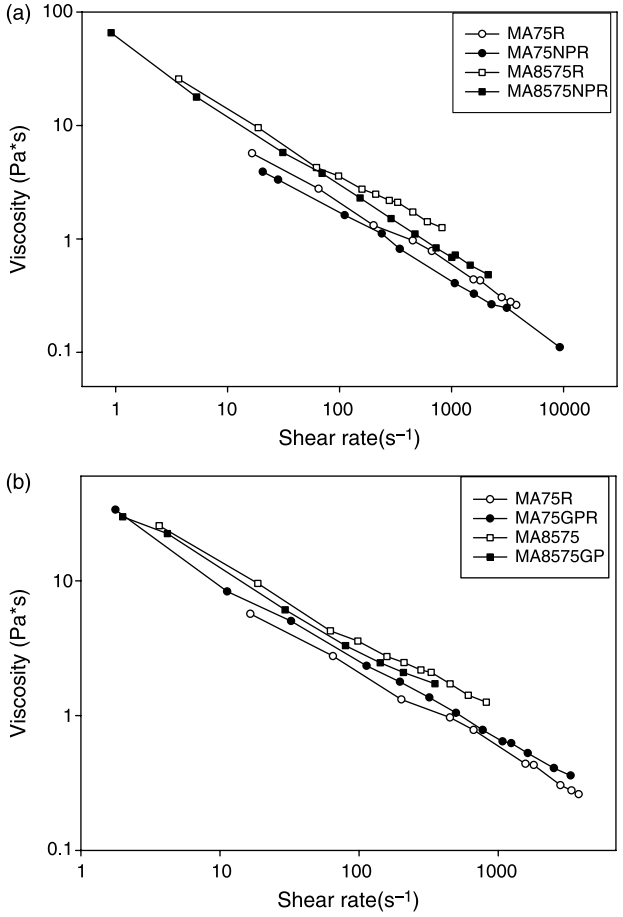

Fig. 11. Flow curves of 10% maize starch dispersions in the presence of palmitic acid.(a) Heated and measured at 75 °C, after 15 min rest. Codes denote: MA75R, control; MA75NPR, palmitic acid added to starch system prior to heating; MA75GPR, palmitic acid added to starch system after heating. (b) Heated at 85 °C then cooled to 75 °C and measured after 15 min rest at this temperature. Codes denote: MA8575R, control; MA8575NPR, palmitic acid added to starch system prior to heating; MA8575GPR, palmitic acid added to starch system after heating.

75 °C exhibited higher viscosity than the control heated and measured at 75 °C, which could be attributed to the higher degree of granule swelling attained the starch granules at 85 °C than at 75 °C. Thus despite the fact that all samples tested at 75 °C, nevertheless, these heated at 85 °C showed to be more viscous. This demonstrates the role of granule swelling, in affecting the flow behaviour of starch systems despite the presence of other molecules, which can interact with starch components thereby altering the rheological properties of starch pastes.

5. Conclusions

In this study it was demonstrated that the presence of fatty acids in starch dispersions considerably affects their rheological behaviour in various ways. That is, on pasting the addition of fatty acids effectively controls the leaching of amylose and retards the gelatinization process, by prohibiting granule swelling. On the other hand, the viscosity of a starch dispersion can be drastically reduced when is heated in the presence of a fatty acid or it can be increased when the fatty acid is added in the starch dispersion either before heating or after heating. The parameters which influence the kind and the size of these changes were the fatty acid chain length, the extent of gelatinization of the starch granules, the temperature of sample heating and testing and the state of the sample motion during testing.

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