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

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Abstract

The pasting behaviour of 20% high-amylose 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 pasting process was affected by the fatty acid chain length with myristic acid to promote, whereas palmitic and stearic acids to suppress it. The flow behaviour of amylomaize starch dispersions heated at 75, 85 or 98 °C was examined at these temperatures, in the presence of the above mentioned fatty acids. It was found that the rheological characteristics of the samples heated at 75 °C were those of shear thickening fluids whereas for the samples heated at 85 °C or 98 °C were those of either Newtonian or pseudoplastic fluids. This behaviour was found to be dependent on the fatty acid chain length. To explain the above mentioned effects of fatty acid addition to amylomaize aqueous dispersions during pasting as well as during heating, certain mechanisms were proposed which involve possible granule–granule interactions and complexed with lipids amylose molecules – granule interactions.

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

1. Introduction

The amylose content of most starches from tubers and seeds varies from 20% to 30%. There are, however, some other starches from amylose-extended mutants of barley, pea or maize very rich in amylose from 40% to 70% or even to 90% (Eliasson & Gudmundsson, 1996). These starches have unusual granular forms, weaker birefringence patterns and, when heated in water, swell to a much lesser extent than do their normal counterparts, indicating a very high degree of intermolecular association (Colonna, Buleon, Lemaguer, & Mercier, 1982). The gelatinization temperatures of high-amylose starches are higher than those of the normal and waxy maize starches. Waxy and regular maize starches gelatinize at 62–72 °C. On the contrary, high-amylose starches, although they begin to swell below 100 °C, temperatures greater than 130 °C are required to fully gelatinize and disperse these starches (Case et al., 1998). High-amylose starches have the ability to form strong gels and films. These particular properties opened the opportunity to develop new starch-based ingredients with unique functionalities. Examples of ingredients, which are commercially utilized, include fat replacers for dairy applications, new forms of resistant starch for increased dietary fiber in baked goods and nutritional products, and ingredients for crispy coatings on fried foods (Hullinger, van Patten, & Freck, 1973).

It is well known that the functionality of starches is significantly influenced by the presence of various compounds especially those which interact with the amylose fraction of the starch granule. Such compounds include fatty acids, fatty alcohols and monoglycerides which form inclusion complexes with the amylose molecules. In a preceded paper (Raphaelides & Georgiadis, 2006) the effect of fatty acids on the rheological behaviour of normal maize starch dispersions during pasting as well as during heating at various

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temperatures was studied and it was found that the fatty acid presence affects the pasting process by either promoting or retarding gelatinization depending on the fatty acid chain length. Besides, the addition of fatty acids in heated maize starch dispersions was found to affect the flow behaviour of the starch systems in various ways. That is, the viscosity of the systems was either significantly reduced or increased.

To the best of our knowledge, the influence of the addition of fatty acids on the rheological properties of concentrated amylomaize starch dispersions during heating has not been studied so far due to the difficulty in handling the starch systems during measurements at high temperatures and at the same time to avoid evaporation, or phase separation of the formed amylose–fatty acid complexes or even retrogradation. Thus, the aim of this paper was to study the effect of the fatty acid presence in amylomaize dispersions during heating, in a systematic way using a number of experimental techniques.

2. Materials and methods

Amylomaize starch type ZBB VII was a gift from NESTLE SA, Greece.

The starch characteristics were

Moisture content	11.9 ± 0.3%	(Gravimetrically determined by heating the samples at 130 °C for 1 h)
Apparent amylose	56.0 ± 0.5%	(Determined using the method of Morrison and Laignelet (1983))
Total amylose	68.1 ± 0.59%	(Sample was defatted with *n*-propanol by heating at 120 °C for three 2-h long consecutive times, each time new portion of *n*-propanol was used. The defatted sample was vacuum dried at 60 °C for six hours and the amylose content was determined the same way as the apparent amylose)
Protein content ($N \times 6.25$)	0.14%	(Determined using the Kjeldahl method)
Calcium content	46.5 (mg/kg)	(Determined by atomic absorption spectroscopy)
Lipid content	1178 mg	(Determined by glc)
Lipid composition (%)	FAME/100 g dry weight	
C16:0	43	
C18:0/18:1/18:2/18:3	57	
Gelatinization temperatures Onset	69.7 ± 0.7 °C	(Measured with a Perkin–Elmer DSC-6 differential scanning calorimeter)
Peak	74.2 ± 0.4 °C	
Granule size	11.4 ± 0.9 μm	(Mean diameter measured with a Malvern laser particle size analyzer)

Fatty acids, myristic (C14:0), palmitic (C16:0) and stearic (C18:0) (purity 99%), were obtained from Sigma Chemical Company and all other reagents were of analytical grade.

2.1. Instrumentation

The experiments were performed using a custom built instrument coded TR-1 RHEOMETER which has been described in detail, elsewhere (Raphaelides & Georgiadis, 2006; Xu & Raphaelides, 1998).

2.2. Starch pasting experiments

This series of experiments was carried out as follows: Aqueous starch dispersions (starch content 20% w/w, dry basis), were heated inside the sample vessel (capacity 1800 ml) of the rheometer up to 133 °C. The samples were heated under constant stirring at 50 rpm rotational speed. The sample contained only starch and water was designated as the control whereas the other three samples consisted of aqueous starch dispersion in which fatty acid potassium salt aqueous solution was added. Each sample contained a different fatty acid which was either myristic or palmitic or stearic. The fatty acid concentration employed exceeded by ~5% the concentration known to be necessary to quantitatively interact with the total amount of the available (apparent) amylose (56% of the total glucan) 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 4.5 ± 0.1 °C/min). During pasting, sample temperature and the torque developed by the stirrer were continuously recorded to the rheometer's control unit.

It has to be mentioned that the selected rotational speed value (50 rpm) was low enough not to cause any damage to the granules. This was microscopically confirmed to be the case in all series of experiments performed using the procedure described above.

In a separate series of experiments, each of the samples prepared in the manner described above was heated from