

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.

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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 $21.5 \pm 0.6\%^{**}$, total amylose $26.0 \pm 0.3\%^{**}$, onset gelatinization $67.5 \pm 0.6^\circ\text{C}$, peak gelatinization $72.0 \pm 0.5^\circ\text{C}^{***}$, granule size $16.0 \pm 0.6 \mu\text{m}^{****}$.

*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 $\sim 5\%$ 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).

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