Carbohydrate Polymers 99 (2014) 68–73

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Starch viscoelastic properties studied with an acoustic wave sensor

M.D. Santos, M.T.S.R. Gomes*

CESAM/Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal

ARTICLE INFO

Article history:
Received 12 December 2012
Received in revised form 31 July 2013
Accepted 7 August 2013
Available online 20 August 2013

Keywords:
Starch
Maize
Rice
Gelatinization
Pasting
Piezoelectric quartz crystal
Acoustic wave sensor

ABSTRACT

Gelatinization and retrogradation of starch was followed in real time with an acoustic wave sensor. This study relies on the monitorization of the frequency of oscillation of a piezoelectric quartz crystal in contact with a 2.5% emulsion of a commercial maize starch, during heating and cooling. The technique showed to be very powerful and sensitive to most of the changes described in the literature, which have been elucidated by some other techniques. The value for the temperature of gelatinization found using the sensor was confirmed by the analysis of the same starch emulsion by polarized light microscopy. Temperatures of gelatinization were found to vary with the sample heating rate, as follows: 73.5 °C at 2.0 °C/min, 66.0 °C at 1.0 °C/min, and 65.0 °C at 0.5 °C/min. Hysteresis of the studied system was evidenced by the frequency shift before heating and after cooling till the initial temperature. Analysis performed on a 1.5% emulsion of a rice starch heated at 2.0 °C/min and cooled as before, evidenced no hysteresis and showed complete reversibility, in which concerns to the series frequency of the piezoelectric quartz crystal.

1. Introduction

Starch provides at least 35% of daily energy intake, although in some regions of the world this value can rise to 80% (Burrell, 2003). Besides starch nutrition value, its effect on the physical properties of many of our foods is of major importance. It contributes to the thickness of gravies, the gelling of puddings and the consistence and setting of cakes, pies and pizzas. Industry is trying to improve baked products in several ways, and, for instance, it was already realized that the incorporation of mono-glycerides in the dough retards bread firming (Biliaderis, 1998). Therefore, it became important to study starch functional properties, and their changes during food processing and storage (Copeland, Blazek, Salman & Tang, 2009).

Starch is a semicrystalline material, mainly made up of two D-glucose polymers: amylose, which is essentially unbranched, and amylopectin, which has a highly branched structure (Copeland et al., 2009). Minor constituents commonly found in starch include lipids, proteins, phosphorus and other minerals (Jacobs & Delcour, 1998).

Starch granules are made of concentric shells, where dense (semicrystalline) and less dense (largely amorphous) layers alternate. In the semicrystalline layer there is an overlap of crystalline and amorphous lamellae. The crystalline lamellae are made of amylopectin double helices, which have the branch points in the amorphous zones. Amylose location is still not completely known, although a possible location is in the amorphous layers, interspersed between amylopectin (Jacobs & Delcour, 1998).

Heating starch with water leads to gelatinization. There is no consensus on the gelatinization meaning, and the word is used in distinct ways by different chemists (Hoseney, 1998a). For some authors, (Hoseney, 1998b) gelatinization is characterized by the loss of birefringence, and those changes occurring after it are termed pasting. For others, three main steps are included under the same term: water diffusion to the inside of the granule, melting, characterized by a helix-coil transition, and crystals disintegration (Morales-Sanchez, Figueroa & Gaytan-Martínez, 2009). Pasting has also different meanings for different authors, and for Zeng, Morris, Batey and Wrigley (1997), it refers to the changes in viscosity, just before, during and after the "sensu strict event of gelatinization", which includes the changes in viscosity during gelation. Therefore, for these authors, pasting includes all changes observed during heating or cooling of starch.

Most of these changes are irreversible, although some order is regained in starch retrogradation (recrystallization). Retrograded amylose is resistant to acid and enzymic hydrolysis. The so-called resistant starch formed during thermal processing possess very interesting nutritional properties, and several beneficial effects in health, as it can reduce plasma glucose and insulin levels, and increase faecal bulking (Biliaderis, 1998).

Several techniques have been used to study the changes that starch undergoes during heating and cooling (Karim, Norziah & Seow, 2000). No single technique is capable of giving data that allow a complete understanding of the processes. Microscopy

* Corresponding author. Tel.: +351 234370722; fax: +351 234370084.
E-mail address: mtgomes@ua.pt (M.T.S.R. Gomes).

0144-8617/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.carbpol.2013.08.011

(Brouillet-Fourmann, Carrot & Mignard, 2003; Creek, Ziegler & Runt, 2006; Liu, Charlet, Yelle & Arul, 2002; Varatharajan, Hoover, Liu & Seetharaman, 2010), allows to inspect the morphology of the granules, but also the loss of birefringence. Thermal analysis (mainly DSC-differential scanning calorimetry) (Aparicio, Resa, Elvira, Molina-García, Martino & Sanz, 2009; Creek et al., 2006; Karim et al., 2000; Li & Yeh, 2001; Liu, Yu, Tong & Chen, 2010; Varatharajan et al., 2010; Xie, Yu, Chen & Li, 2008; Xu, Ponte & Chung, 1992), allowed to measure the gelatinization transition temperatures, and enthalpy. X-ray diffraction and NMR-nuclear magnetic resonance, allowed concluding that the detected enthalpic transition was due to double helical loss rather than to the loss of crystallinity (Hoover, 2001). Infrared spectroscopy is another technique that allows structural information (Karim et al., 2000; Liu et al., 2002; Varatharajan et al., 2010). Ultrasonic techniques (Aparicio et al., 2009; García-Álvarez, Salazar & Rosell, 2011; Lehmann, Kudryashov & Buckin, 2004; Lionetto, Maffezzoli, Ottenhof, Farhat & Mitchell, 2006), and mainly rheology (Brouillet-Fourmann et al., 2003; Karim et al., 2000; Liang & King, 2003; Varatharajan et al., 2010; Xu et al., 1992; Zeng et al., 1997) have also been used on starch studies.

Rheology allowed making very interesting observations. However, these observations are made in the presence of a shear rate. In non-Newtonian systems, viscosity changes with the shear rate. Shear rate may alter the starch system itself, and viscosity can be affected by the time involved in making the measurement. It is known that shear thinning is observed as molecules of soluble starch become oriented in the direction the system is being stirred. This has some practical implications as a thick soup cannot be obtained under excessive stir (Hoseney, 1998b). Shear thinning varies with the starch, and generally, the more soluble starches the more they go thinner on shearing.

Although the use of such a wide range of techniques renders difficult to compare the properties of these starches, Hoover emphasized the advantages of using those techniques collectively to obtain a deep inside into the physicochemical properties of starches (Hoover, 2001). This paper shows the contribution that acoustic wave sensors can make to these studies. Although the idea of using this kind of sensors in the food industry is not new (Dewar, Ash, German & Joyce, 2006), and the use of these sensors to follow gelation of hydroxypropyl methylcellulose was already shown (Verissimo, Pais & Gomes, 2010), we are not aware of published data of such a sensor following starch gelatinization and retrogradation. In the current application, the acoustic wave sensor was not used in its gravimetric most known facet, but as a device able to sense viscoelastic changes. After the work of Bruckenstein and Shay (1985), the dependence of the frequency upon the viscosity and density of the liquid medium in contact with the piezoelectric crystal was mathematically described.

$$\Delta f = -2.26 \times 10^{-6} n f^{3/2} \sqrt{\eta_l d_l} \quad (1)$$

This equation shows that, in a liquid, the crystal experiences a frequency shift (Δf/Hz) proportional to the square root of the product of density (d_l/g cm^{-3}) and viscosity (η_l/g cm^{-1} s^{-1}). In the equation f/Hz is the fundamental resonance frequency and n is the number of faces of the crystal in contact with the liquid (n = 1 or 2), the constant 2.26×10^{-6} Hz^{-1} g^{-1} cm^2 was calculated for an AT-cut quartz crystal.

The monitorization of the series frequency during heating and cooling of a maize starch suspension showed the power of the technique to detect the changes on this system. The large number of inflection points, observed on the frequency *vs.* temperature plot, is synonymous of the large amount of information the technique is able to offer, with minimum disturbance of the system.

The present study was applied to 2.5% (w/v) starch emulsions in water. Series frequency ceases to exist for starch much higher concentrations, and although other parameters could still be followed, as an impedance analyser was used in this work, this is the only parameter that could be followed with most oscillators, and used in low budget laboratories. Low starch concentrations are not common, and not used when producing baked goods. However, according to Hoseney (1998b) even if our findings do not apply to concentrated starch in water systems, it is still important to understand them. Higher starch concentrations deserve to be studied in the future.

The frequencies of oscillation of a bare quartz crystal in contact with the starch suspension along heating and cooling is here presented, and explained, at the light of previous knowledge of the phenomena obtained by other techniques, and described on the literature by several authors.

2. Experimental

2.1. Reagents and materials

A commercially available maize starch (Maizena), and rice starch from Sigma Aldrich (S7260) were used. Starch was dispersed in Milli-Q water by stirring at room temperature for 30 min, to produce starch suspensions of known concentrations.

Nine MHz AT cut, HC-6/U piezoelectric quartz crystals were purchased at ICM – International Crystal Manufacturing Co, Inc. Crystals were polished with gold electrodes.

2.2. Apparatus

Fig. 1 shows the experimental layout. The quartz crystal was placed inside an home-made Teflon cell, between two o-rings. An opening on the top of the cell allows to introduce 1.00 mL of the starch suspension. The Teflon cell was placed inside a thermostatic chamber Friocell 55 Medcenter Einrichtungen GmbH, to allow heating at a programmable rate and to cool it. Cooling rate of the chamber was not programmable and it was approximately −0.3 °C/min till 48 °C, and −1 °C/min bellow it. A Pt 100 temperature sensor immersed in the suspension allows measuring its exact temperature. In order to prevent evaporation, the Teflon cell was closed with a septum.

The piezoelectric quartz crystal was connected to an HP 4395A Network/Spectrum/Impedance Analyser (Hewlett-Packard) coupled with an HP 43961A impedance test kit and HP 16092A spring clip fixture.

Polarized light microscopy of maize suspensions was performed on an Olympus BH2-UMA with a hot stage Mettler FP82HT and a central processor Mettler FP90. Images were recorded with a camera Canon EOS 550D.

2.3. Experimental procedure

2.3.1. Microscopic analysis

Polarizing light microscope images of the 2.5% (w/v) maize suspension were obtained while heating from 30.0 °C to 85.0 °C, at 2.0 °C/min.

2.3.2. Analysis with the acoustic wave sensor

The starch suspension (1.00 mL) was placed in the Teflon cell in contact with one face of the piezoelectric quartz crystal. The temperature of the oven was programmed to start at 30 °C and to rise till 90 °C at defined heating rates, after which it was cooled down. Series resonance frequency was obtained