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Starch viscoelastic properties studied with an acoustic wave sensor

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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

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(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

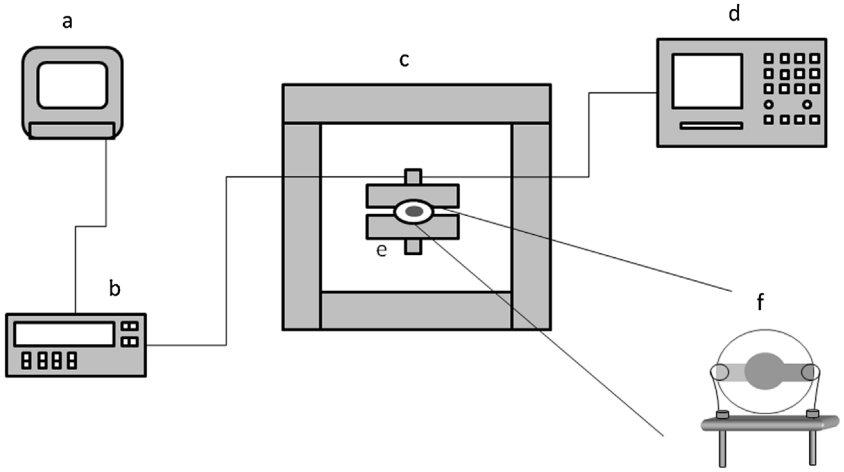

Fig. 1. Experimental layout used during the acoustic wave sensor measurements: (a) personal computer; (b) multimeter connected to a PT100; (c) thermostatic chamber; (d) impedance analyzer: (e) teflon cell with (f) quartz crystal.

by the impedance analyzer, after centring, with 300 Hz bandwidth. Series frequency of the quartz crystal and temperature of the suspension, measured by the Pt100 sensor immersed in the suspension, and previously calibrated, were recorded at 0.5 °C intervals.

At the end of each analysis, the quartz crystal was removed from the Teflon cell and was cleaned with hot water, followed by ethanol and acetone. After being dried, and before its insertion in the Teflon cell for a new experiment, the quartz crystal frequency was measured and compared with the initial value for the same cleaned crystal. Whenever its frequency was lower than before, or its resistance was not equal to 0, a new cleaning cycle was initiated.

After it was considered cleaned, the quartz crystal was screwed in the cell. Differences in the initial frequency value were allowed between experiments, as they resulted from the aperture and position of cables inside the oven.

Experiments were run with heating rates of 0.5, 1.0 and 2.0 °C/min. Experiments were replicated three times, and characteristic temperatures shown are the median of the founded values.

3. Results and discussion

3.1. Microscopy of the starch along heating

Fig. 2 shows the polarized light microscope images of the 2.5% (m/v) maize starch suspension heated at 2.0 °C/min, taken at four temperatures. The first image, obtained at 65.0 °C shows birefringence in the form of the typical maltese cross. This does not mean that the material is crystalline, but that there is a high degree of molecular order. Along heating, the number of maltese crosses is being reduced, which can be noticed comparing the images at 65.0 °C with the images at 69.0° and 70.0 °C. At 74.0 °C the material loses its birefringence.

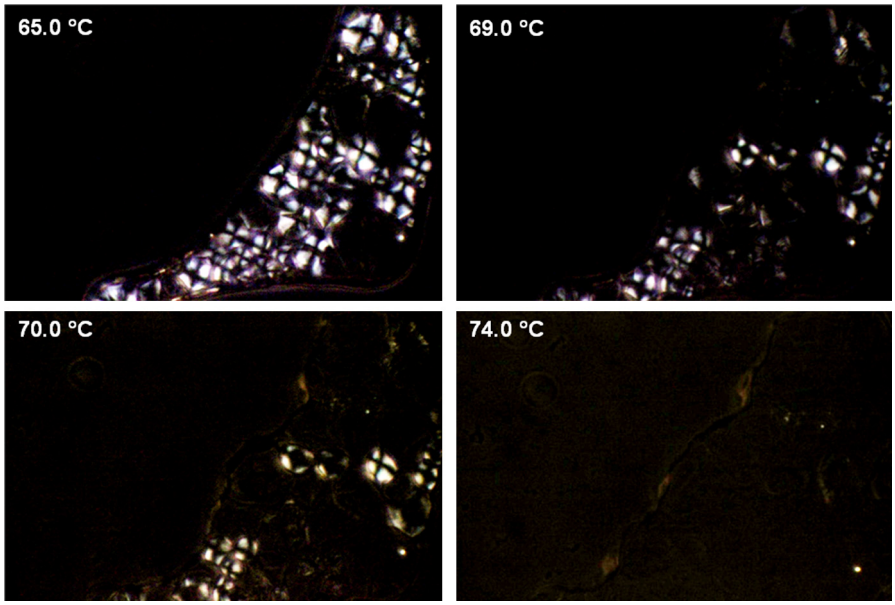

Fig. 2. Polarized light microscopy images of 2.5% (w/v) maize starch suspension taken along heating at 2.0 °C/min.

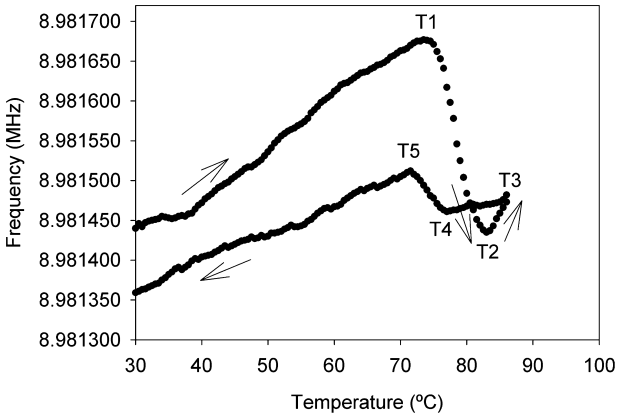

Fig. 3. Frequency of the quartz crystal in contact with a 2.5% (w/v) maize starch suspension while heated at 2.0 °C/min, and cooled at a rate of approximately −0.3 °C/min till 48 °C and −1 °C/min bellow it.

3.2. Frequency changes of an acoustic wave sensor along heating and cooling of a maize starch suspension

When starch was immersed in water, water begins to enter into the granule, which slightly swells.

Fig. 3 shows the series frequency of the quartz crystal in contact with 2.5% (w/v) maize starch/water suspension, during heating (2.0 °C/min) from room temperature to 86.0 °C, and cooling. It can be seen that, from room temperature to *T*1, frequency increased slowly and no discontinuities are found. During this period it is possible that amylose and water start diffusing out of the granules, but no net increase in viscosity, which would be accompanied by a frequency decrease, could be noticed. Therefore, it can be concluded that there are no appreciable dissolution of amylose and that viscosity slightly decreases with increasing temperature, as for most materials (Xie et al., 2008). It is also possible to explain some irregularities on the frequency increasing by a mix of both mentioned phenomena, each of them affecting the frequency in a contradictory manner. Although the AT cut of the piezoelectric quartz crystal assures some frequency stability with temperature changes, within room temperature range, it cannot be ignored that, for such higher temperatures as the ones employed in these experiments, an increase in the frequency of a clean blank crystal was observed. Total increase was however much smaller than the observed changes and cannot by itself explain them.

*T*1 (73.5 °C) corresponds to an inflection point, and it matches the temperature at which birefringence was lost. *T*1 marks the temperature of amylopectine fusion: gelatinization temperature for some authors (Biliaderis, 1998), pasting temperature for others (Bao, 2008). These terms are sometimes used according to the technique: gelatinization temperature when determined by DSC, and pasting temperature, if determined by RVA (Rapid Visco-analyser) (Bao, 2008). Beyond *T*1, granules are irreversible swelled, amylose leached from the granules (Biliaderis, 1998; Hoseney, 1998b) and viscosity increased, giving rise to a marked quartz crystal frequency decrease, which attains its lowest value at *T*2. Amylopectin melting allows freeing the amylose which was trapped between the amylopectin layers, and to a smaller extent, confined within the crystalline amylopectin (Brouillet-Fourmann et al., 2003).

It has been reported that the temperature at which amylopectin melts depends on the water content and decreases with it (Brouillet-Fourmann et al., 2003). Therefore, for samples with high water content, as the one here studied, melting temperature precedes gelification, which is not always the case.

After amylopectin beginning to melt and amylose released, the interlayer amylopectin chains, which act as links, become movable, and a partial burst of the granules may take place, converting them into smaller softer entities (Brouillet-Fourmann et al., 2003). At *T*3 there are eventually no more granular entities. As amylopectin, due to its branched nature, has relatively low intrinsic viscosities (Biliaderis, 1998), we assist to an increase in frequency. At such high temperatures (between *T*2 and *T*3) it is also possible to have a second contribution to the observed frequency increase (viscosity decrease), which is the dissociation of the amylose–lipid complexes, with the transformation of the helical amylose structures to the more fluid random coil state (Xu et al., 1992). The extension of this last contribution is limited by the amount of lipids in the starch, and the lipid chain length, as complex stability increases with chain length (Tufvesson, Wahlgren & Eliasson, 2003). Work will be undertaken in a near future in order to prove or discard this hypothetical contribution to take place under the present experimental conditions of temperature and heating rate, and with this particular maize starch sample.

From *T*3 to *T*4, a gel is formed. A gel is a liquid system with the properties of a solid. Polymers interact to form a continuous network, and water is held in the gels. The structure of amylose gels is a continuous network of rigid double helical crosslinks, junction zones, interconnected by more mobile amorphous single chain segments (Biliaderis, 1998). Frequency decreases as rigidity increases. Creek et al. (2006) reported the formation of gel like morphologies at quench temperatures between 70 and 110 °C, while spherulites needed much higher heating temperatures (>170 °C) to be formed. Amylopectin gelation occurs at higher concentrations, usually >10% (Biliaderis, 1998). Higher final viscosities were reported in the presence of lipids, which has been explained by the formation of gels with a more widely spaced junction zones due to the reduction availability of amylose (Copeland et al., 2009). Amylopectin does not effectively complex with lipids (Biliaderis, 1998).

Starch gels are metastable, nonequilibrium states and undergo some structural transformations, as chain aggregates or crystallization (Biliaderis, 1998). From *T*4 to *T*5 some order is re-established, but the system does not return to the frequency observed at *T*1. Interaction between starch chains would increase with storage time and, eventually, formation of crystals of amylopectin takes place. This process is called retrogradation, meaning going back to the crystalline state, and one must remember that in the native granule only amylopectine was crystalline, not amylose. Amylose tends to retrograde as a precipitate in dilute solutions or to form gels in concentrated solutions (Biliaderis, 1998). Hysteresis can be seen, as final frequency at room temperature is much lower than the initial value. Liu et al. (2010) mentioned the memory effect that leads a disordered chain to go back and retrograde to an ordered structure, but say that after gelatinization, the free amylose sterically hinder the restoration of double helices of amylopectin and prevent them from, according to their memory, returning to their original state. Therefore, the number of restored double helices decreases. According to the authors, while the reformation of coil-helix develops rapidly, the reassociation and interaction between helices requires longer times.

3.3. Frequency changes of an acoustic wave sensor in contact with a maize starch suspension, at different heating rates

Fig. 4 shows the frequency of a quartz crystal in contact with a 2.5% (w/v) maize starch suspension while heating at a slower heating rate than before (1 °C/min), and Fig. 5 shows a similar experiment performed at a heating rate of 0.5 °C/min.

Those figures present marked changes when compared to Fig. 3. What is immediately noticed is the much larger difference between the frequency at the beginning and ending of the heating/cooling cycle, when comparing Fig. 3 to Fig. 4. It is also easy to notice that, by the ending of the cooling cycle, there are no frequency values

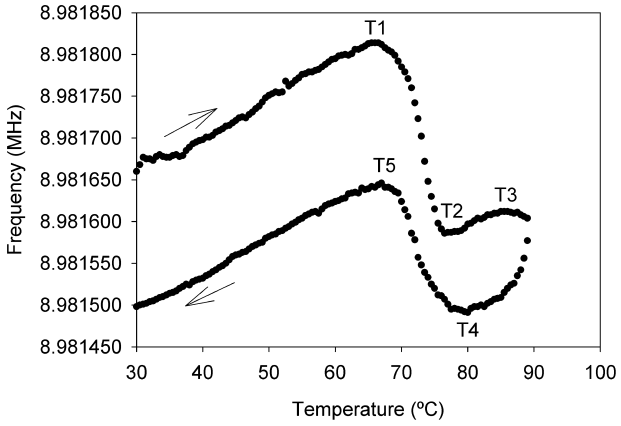

Fig. 4. Frequency of the quartz crystal in contact with a 2.5% (w/v) maize starch suspension while heated at 1.0 °C/min, and cooled at a rate of approximately −0.3 °C/min till 48 °C and −1 °C/min bellow it.

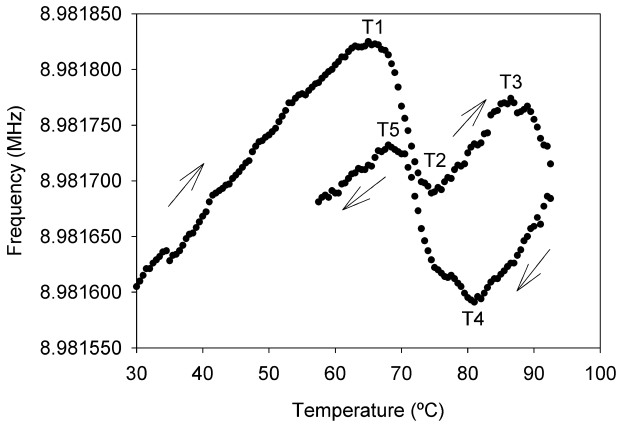

Fig. 5. Frequency of the quartz crystal in contact with a 2.5% (w/v) maize starch suspension while heated at 0.50 °C/min, and cooled at a rate of approximately −0.3 °C/min till 48 °C and −1 °C/min bellow it.

on Fig. 5, which is due to the fact that series frequency ceased to exist, as there is no zero phase (Yang & Thompson, 1993). From these observations, it can be concluded that hysteresis, meaning irreversibility, increases as heating rate decreases.

Table 1 shows the values of the characteristic temperatures obtained for the three experiments with different heating rates. *T*1 and *T*2 are lower as the heating rate decreases. This is not surprising as, with the decreasing of the heating rate, the system takes more time achieving the same temperature, kinetically allowing changes and rearrangements of the system.

However, *T*3 is the same temperature irrespectively of the heating rate (86.0 °C). This is the temperature which was related with gelification. A period of frequency decrease always follows *T*3 and it does not matter if temperature continues to raise after *T*3, or it begins to cool down. The process that begins at *T*3 (86.0 °C) is completed sooner at higher heating rates, while temperatures *T*4 are lower. Although starting at higher *T*4, the system tends to recover

Table 1
Gelatinization and pasting characteristic temperatures obtained at several heating rates.

Temperatures (°C)/ heating rate (°C/min)	*T*1	*T*2	*T*3	*T*4	*T*5
2.0	73.5	83.0	86.0	77.0	71.5
1.0	66.0	76.5	86.0	80.0	68.0
0.5	65.0	74.5	86.5	81.0	66.5

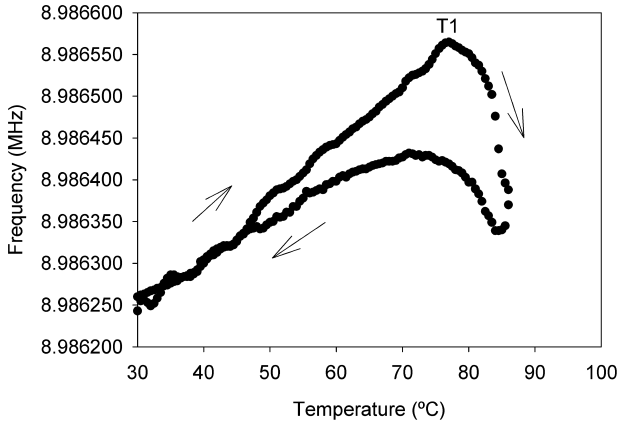

Fig. 6. Frequency of the quartz crystal in contact with a 1.5% (w/v) rice starch suspension while heated at 2.0 °C/min, and cooled at a rate of approximately −0.3 °C/min till 48 °C and −1 °C/min bellow it.

the original order till temperatures close to *T*1, with differences between *T*5 and *T*1 from 1 to 2 °C.

3.4. Frequency changes of an acoustic wave sensor along heating and cooling of a rice starch suspension

For comparison, a sample of a rise starch was also analyzed. Fig. 6 shows the series frequency of the quartz crystal in contact with 1.5% (w/v) rice starch/water suspension, during heating (2.0 °C/min), and cooling. Comparing Fig. 3 with Fig. 6, it is possible to see that the frequency plot *vs.* temperature for the two different starches, maize and rice, respectively, are very different. Such differences cannot be attributed solely to the difference in starch, as water content has also changed. Anyway, these figures show that the technique is sensitive to changes in the system composition. Frequency plot on Fig. 6 shows a continuous decrease between 77 °C (*T*1) and 84.5 °C. The frequency increase between *T*2 and *T*3, seen for maize starch and discussed previously, is not present. *T*1 is higher for the rice suspension, which is consistent with a more heat resistant starch. Besides, with rice starch, after cooling, the system returns to the initial frequency, showing the establishment of a new organization.

4. Conclusion

From this work it can be concluded that most of the changes occurring within the gelatinization phenomena markedly affect the frequency of oscillation of a piezoelectric quartz crystal in contact with the starch/water system. Among the most important phenomena detected is the amylopectin fusion, at *T*1, the state of highest viscosity, at *T*2, the disappearance of all granular entities (*T*3), the formation of a gel (*T*4) and from, *T*4 to *T*5, the re-establishment of some of the lost order.

However, as series frequency ceases to exist for low moisture content suspensions, some other electric parameters must be measured instead, with sensitivities that must be evaluated in future work. The use of an acoustic wave sensor to study gelatinization limits system disturbance, and it was shown that temperature of gelatinization matched the one obtained by polarized light microscopy.

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