Journal of Food Engineering 94 (2009) 295–299

Contents lists available at ScienceDirect

Journal of Food Engineering

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

Assessment of starch gelatinization by ultrasonic and calorimetric techniques

C. Aparicio [a], P. Resa [b], L. Elvira [b], A.D. Molina-García [a], M. Martino [c], P.D. Sanz [a,*]

[a] Instituto del Frío, CSIC, MALTA CONSOLIDER TEAM, José Antonio Nováis 10, 28040 Madrid, Spain
[b] Instituto de Acústica, CSIC, Serrano 144, 28006 Madrid, Spain
[c] CIDCA-Facultad de Ciencias Exactas (UNLP), 47 y 116 (1900) La Plata, Buenos Aires, Argentina

ARTICLE INFO

Article history:
Received 8 January 2009
Received in revised form 11 March 2009
Accepted 27 March 2009
Available online 5 April 2009

Keywords:
Starch gelatinization
Ultrasound
Differential scanning calorimetry

ABSTRACT

The process of starch thermal gelatinization can be studied and monitored by employing both invasive and non-invasive techniques. In this paper, the ultrasound technique is compared with differential scanning calorimetry (DSC), a more traditional procedure. DSC is a convenient way to fulfill this objective although it is, by nature, an invasive, discontinuous and off-line technique. Among the main features of this ultrasound technique are its real-time performance and its intrinsic non-invasive character: a sample cell fitted with two piezoelectric ceramics as emitter and receptor, is used. A pulse generator and an oscilloscope are used to generate the emitted signal and to analyze the response, respectively. The procedure is tested using aqueous corn starch suspensions at two concentrations. The temperature is increased through the gelatinization interval, and the changes in ultrasound amplitude are recorded. Experimental data are in good agreement with those obtained by DSC. The progress of the gelatinization process can be followed by this method and the possibility of its use for on-line processes is considered.

1. Introduction

Starch and its derivatives are not only among the main natural food components but they also are extensively used to modify the physical properties of many food products as additives with different characteristics. Starch, the main energy reserve of plants, is a mixture of two glucose polymers, amylose and amylopectin. While amylose molecules are linear, resulting from α 1–4 glucose bonds, amylopectins include α 1–6 bonds, which give rise to branching (French, 1973). These molecules are packed in plant cells in highly ordered clusters, starch granules, insoluble in water and resistant to most chemical and enzymatic attacks. Consequently, starch in its native form is scarcely interacting with water or other food components and partially resistant to digestive enzymes (Fässler et al., 2006).

When starch is heated in the presence of water, an irreversible process called gelatinization takes place in which a number of internal starch hydrogen bonds are substituted by starch–water bonds. The crystalline order existing in the granules is eliminated; the chains of both component polymers extend and separate, and, associated with a large number of water molecules, interact with those from neighbouring granules, giving rise to a marked increase in viscosity and the creation of a three-dimensional gel structure (Parker and Ring, 2001). Once gelatinized, starch the chains are readily hydrolyzed by digestive enzymes.

Starch gelatinization is one of the most common processes taking place during food processing and also one of the most studied. The whole gelatinization process includes a number of overlapped steps: granule swelling, migration of amylose, gel formation... but it can be observed through many techniques as a single process. When it is induced by a uniform temperature increase, it occurs over a wide temperature interval (from 50 up to 70 °C), partly due to the lack of granule homogeneity. A number of interrelated properties of starch suspensions can be used to follow this process: such are its microscopic aspect (granule swelling, birefringence), volume, viscosity, turbidity, etc. (French, 1984; Miles et al., 1985). Differential scanning calorimetry (DSC), where the thermal energy required for maintaining a given rate of temperature change is recorded, is one of the main tools for the investigation of thermally induced starch gelatinization. Several parameters can be defined by DSC (though not exclusively by this technique): gelatinization temperature ($\mathbf{T_G}$, corresponding to that where half of the granules have lost their birefringence or to the midpoint of the DSC transition curve), initial or onset temperature ($\mathbf{T_{on}}$, where birefringence loss starts or the intercept of the baseline with the tangent to the gelatinization DSC peak first half), final or endset temperature ($\mathbf{T_{end}}$, where 90% of the granules have lost their birefringence or the intercept of the baseline with the tangent to the gelatinization DSC peak second half) (e.g., Spies and Hoseney, 1982). These temperatures, especially the gelatinization temperature, are characteristic of the biological origin of starch, and a reflection of its internal structure. Treatments altering this structure (such as chemical, enzymatic or high pressure ones) are also

* Corresponding author. Tel.: +34 915445607; fax: +34 915493627.
E-mail address: psanz@if.csic.es (P.D. Sanz).

0260-8774/$ - see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jfoodeng.2009.03.021

known to change the gelatinization temperature (French, 1984; Fernández et al., 2008).

Ultrasonic techniques have been employed (McClements, 1997; Ammann et al., 2005; Ammann and Galaz, 2003) to characterise foodstuffs, gelatine gels and gel-based emulsions, respectively, or to determine their physical properties, for example, in wheat dough (Letang et al., 2001; Álava et al., 2007). Gel formation has also been followed by ultrasound for different food types and components (Lee et al., 1992; Corredig et al., 2004). Ultrasonic spectroscopy was previously applied to the analysis of starch gelatinization by Lehmann et al. (2004). Starch retrogradation has also been recently studied with the help of ultrasound (Lionetto et al., 2006).

Comparatively DSC has been used for characterising many foodstuffs, including starch, for a long time. Nevertheless, the use of ultrasound techniques for this purpose could be advantageous in many industrial applications, fore example, on-line process monitoring. These advantages may derive from the different invasiveness of the methods: DSC is intrinsically invasive, while ultrasound techniques are essentially non-invasive. For that reason in this work, ultrasound technique has been employed to monitor the gelatinization process of corn starch suspensions in water submitted to a temperature gradient. Results have been compared with those of the well-known DSC technique in similar experimental conditions.

2. Materials and methods

2.1. Samples

Suspensions of 15% and 20% corn starch (Roquette Laisa España SA, Benifaio, Spain) in deionised water (Milli-Q, Millipore Research and Development, Bedford, MA, USA) were analyzed.

2.2. Ultrasound technique

The experimental ultrasound set-up is similar to the one previously used to determine the ice content in partially frozen foods (Aparicio et al., 2008) and it is shown in Fig. 1. The sample cell was a glass prismatic cubette with 64 ml volume and parallel walls separated by 46.64 mm. The cubette content was stirred by a magnetic stirrer to avoid starch granule sedimentation and to achieve a quicker thermal homogenization during heating. A 0.5 °C/min heating rate was used, as the optimal to rate to ensure equilibrium in the cell. Two piezoelectric elements (1 MHz) were placed, facing each other, against the external surface of the two opposite (and parallel) walls of the cubette. An acoustic wave was produced by a pulse generator (Panametrics 5072PR, Waltham, USA) in the first piezoelectric and recorded, after traversing the sample and arriving to the second one, with an oscilloscope (Tektronix TDS5032B Oregon, USA).

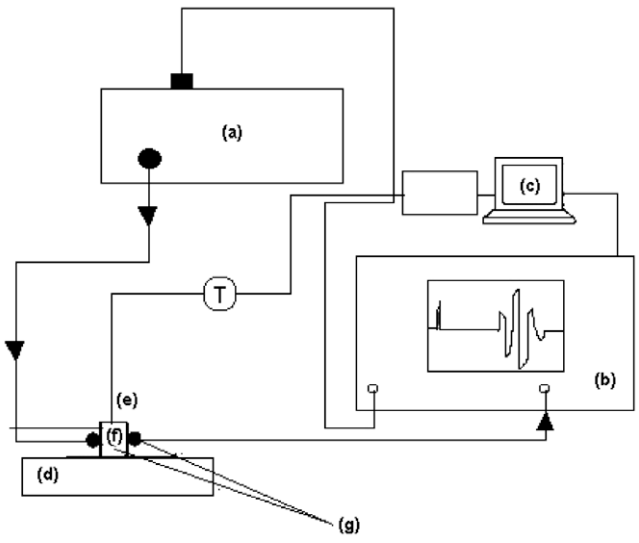

Fig. 1. Experimental set-up: (a) pulse generator, (b) oscilloscope, (c) computer, (d) magnetic stirrer, (e) thermocouple, (f) sample cell and (g) piezoelectric elements.

The wave amplitude (ΔV) was determined as the maximum voltage recorded by the oscilloscope (Fig. 2). The amplitude data were normalized considering a transition between two states model. Sound speed was determined as the ratio between twice the distance travelled by the sound waves and the time of flight (Δt) of the ultrasound wave between the two echoes. Experiments were performed at least in triplicate.

2.3. Differential scanning calorimetry (DSC)

Thermal gelatinization of the starch suspensions was followed with a DSC calorimeter DSCQ1000 (TA Instruments Inc., New Castle, DE, USA). Hermetically sealed aluminium pans were used to avoid water evaporation. They were filled with the starch aqueous suspensions (10 μl) and they were allowed to rest for an hour before experimentation. Starch dry weight was determined by weighing the perforated, oven-dried pans after the experiments. A serial of scan rates from 10 to 0.5 °C/min were carried out to compare both with the ultrasound experiments performed at 0.5 °C/min and the more common published DSC thermograms (at 10 °C/min). Experiments were performed at least in triplicate.

A specific analysis program TA Universal Analysis 2000 (TA Instruments Inc., New Castle, DE, USA) was used to calculate the thermal parameters. Integration of heat-per-mass-unit over temperature was performed on DSC thermograms to ease comparison with ultrasound data.

3. Results and discussion

Among the phenomena constituting the gelatinization process, granule swelling, associated to the loss of birefringence is reported as the initial step and it is followed by reduction in crystallinity. This seems to be a cooperative process, triggering the completion of the process. Slower diffusion-controlled steps include amylose chains migration and gel formation. The different techniques employed to study starch gelatinization observe phenomena taking place at different stages, and do not always agree in the temporal or temperature scales. Corn starch loss of birefringence has been reported to have an onset, mid-point and endset of, respectively, 62, 67 and 72 °C (Snyder, 1984). Meanwhile, the temperature at which the first major rise in viscosity occurs, for a 7.5% corn starch suspension, is 70.5 °C (Morton et al., 1984). Nuclear magnetic resonance allows differentiating three stages of gelatinization, the first corresponding to reversible hydration and swelling, a second defined by loss of birefringence (62–74 °C) where some granule structure still remains, and the third (74–92 °C) where the last vestiges of granule structure are broken, with further alterations in mobility (Zobel, 1984). Additionally, starch being a natural and far from homogeneous product, a wide degree of variation is found in the same species, among different cultivars (Ji et al., 2003).

Fig. 3 shows the typical plot of normalized ultrasound amplitude versus temperature, for starch suspensions of the two studied concentrations. Normalization was used to account for differences in the absolute values of ultrasonic transmitted waves found among different individual experiments. Data were normalized by using the initial and final raw data baselines (for each individ-

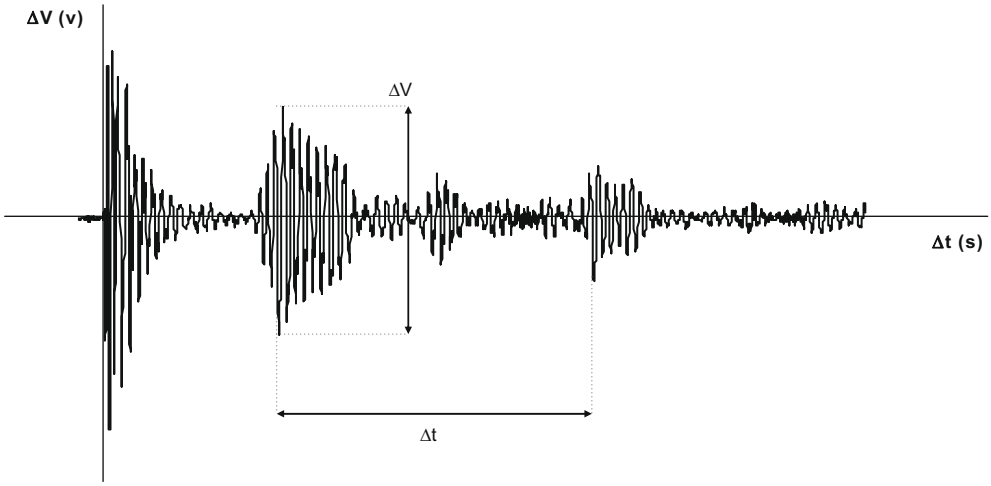

Fig. 2. Schematic procedure for ultrasound measurement: the amplitude of the signal, ΔV, is represented against the time of flight, Δt.

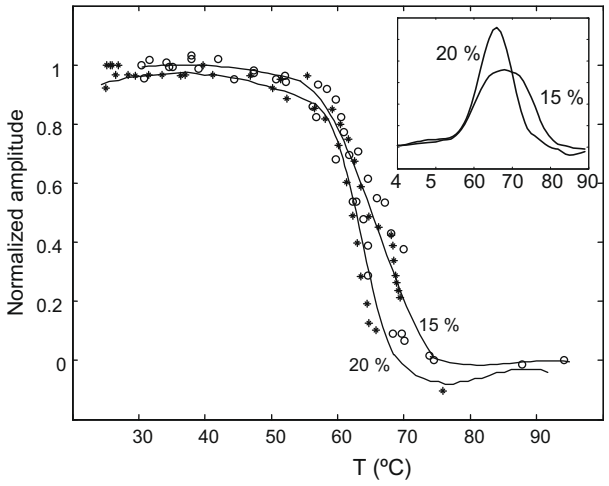

Fig. 3. Plot of normalized ultrasound amplitude vs. temperature for corn starch: 15% (○) and 20% (∗) w/v suspensions. Lines shown are polynomial fittings without analytical value. Insert: derivative of ultrasonic amplitude vs. temperature (experimental data after smoothing and spline interpolation).

ual) experiment. The average of the initial or final data points recognized as belonging to the baselines was employed. Inserted in Fig. 3 appears the derivative of ultrasonic amplitude vs. temperature (experimental data after smoothing and spline interpolation). Derivation was made analytically after the amplitude curves (taking discrete increments on amplitude and temperature and working out the derivative for each one). Later standard smoothing and spline interpolation procedures were applied to reduce noise on the curves.

The pulse generated in the emitter piezoelectric element is converted in a mechanical wave that crosses the sample and is received by the opposite piezoelectric element which converts it back into an electrical signal. Then it is recorded and also represented, in real time, in the oscilloscope (Fig. 2). Amplitude is related to the energy dissipated in traversing the sample; while, sound speed is related to the compressibility coefficient of the sample. Both parameters depend ultimately and in a complex way on the structural changes undergone by starch during the process of gelatinization.

The thermal parameters of starch gelatinization obtained by means of ultrasound amplitude analysis show a good agreement with those obtained, for the same samples, by DSC. Lehmann et al. (2004) reported three regions in the temperature profile of the ultrasound speed for 25% w/v corn starch in water, when submitted to an ascending temperature ramp of 2 °C/min from 37 to 97 °C. Table 1 shows that gelatinization temperatures for 25% w/v corn starch thermograms reported by Lehmann et al. (2004) were higher than those reported by us for lower but close starch/water ratios. However, data variability was reported by these authors for individual experiments with the same starch/water ratio. The evolution of the normalized ultrasound amplitude with temperature for the two concentrations studied to a two-state model allows following gelatinization process, induced by the temperature ramp. Fig. 3 shows plateau at lower and higher temperature values, connected by a sigmoidal transition region corresponding to the gelatinization process. Onset ($\mathbf{T_{on}}$) and endset ($\mathbf{T_{end}}$) temperatures were determined as the intercepts between the sigmoidal and the plateau tangents; and the mid-point ($\mathbf{T_G}$) temperature was calculated as 50% of the transition (Fig. 4). In Fig. 4 data were normalized by using the initial and final raw data baselines (for each individual) experiment. The average of the initial or final data points recognized as belonging to the baselines was employed. Obtained values are shown in Table 1.

A range of DSC scans were performed at different heating rates (Fig. 5), for 15% w/v starch suspensions (similar results were obtained for 20% suspensions – data not shown). Table 2 shows how the range of gelatinization (the difference between onset and endset temperatures) and $\mathbf{T_G}$ increased with heating rate. The gelatinization process has been described as comprising several associated phenomena with different kinetic characteristics (Biliaderis et al., 1986; Ratnayake and Jackson, 2009). While at 10 °C/min the thermogram obtained shows an overall similar aspect to that of a reversible process between two states, at slower rates the coupling of these processes would be different and the resulting thermogram would appear distorted. A possible explanation of the rate-dependence of starch DSC thermograms could be that, once dissolution of the starch granule has reached a certain degree, as induced by temperature, a non-reversible process would be triggered, in which starch polymeric chains would exit from the granules and interact with solvent and other granules. This migration process, actually chain diffusion, is dependent on time rather than on temperature and, so, the coupling with the previous processes would strongly depend on the scan rate employed.

Considering the suspension viscosity, thermal gelatinization process is characterised by drastic changes. The initial increase is due in a first stage, to the swelling of the starch granules both through an increase of their actual particle size and by the large

Table 1
Corn starch gelatinization temperatures: onset (T_{on}), gelatinization (T_G) and endset (T_{end}) results from sound amplitude measurements and DSC at heating rate of 0.5 °C/min. Also tabulated are the values from literature (Lehmann et al., 2004). In this case there are two independent data sets (ds1 and ds2) at heating rate of 2 °C/min.

Starch suspensions	Gelatinization parameters (°C)	From sound amplitude	From DSC		Literature	
			0.5 °C/min	2 °C/min	ds1	ds2
15% w/v	T_{on}	56.4	61.0	60.9	–	
	T_G	65.2	65.6	66.4	–	
	T_{end}	73.8	68.6	71.7	–	
20% w/v	T_{on}	57.6	57.3		–	
	T_G	62.8	65.7		–	
	T_{end}	68.6	69.1		–	
25% w/v	T_{on}	–	–		61.0	62.5
	T_G	–	–		67.9	71.8
	T_{end}	–	–		73.7	78.3

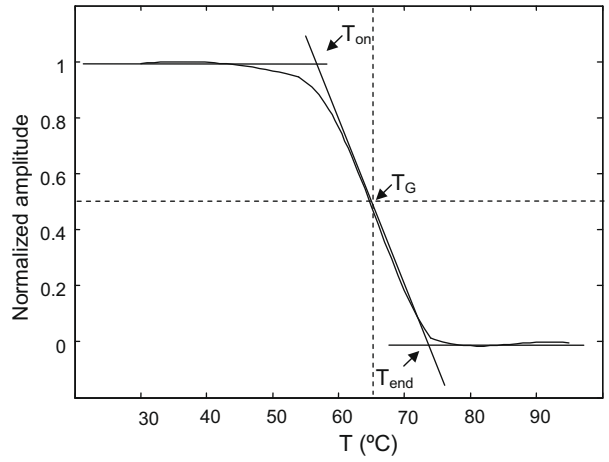

Fig. 4. Plot of normalized amplitude vs. temperature showing the procedure employed for obtaining starch gelatinization temperature (T_G), gelatinization onset temperature (T_{on}) and gelatinization endset temperature (T_{end}).

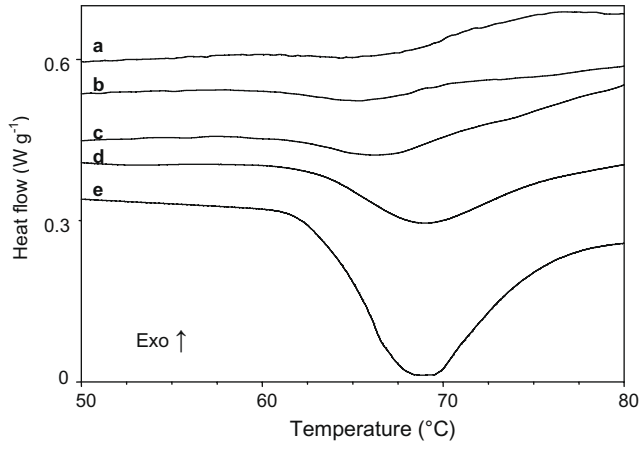

Fig. 5. DSC thermograms for 15% (w/v) corn starch suspensions at different scan rates: (a) 0.5 °C/min, (b) 1 °C/min, (c) 2 °C/min, (d) 5 °C/min and (e) 10 °C/min.

Table 2
DSC results at different heating rates for 15% w/v corn starch gelatinization temperatures: onset (T_{on}), gelatinization (T_G) and endset (T_{end}).

Heating rate (°C/min)	T_{on}	T_G	T_{end}
0.5	61.0	65.6	68.6
1	62.35	65.5	69.1
2	60.9	66.4	71.7
5	62.7	67.7	72.4
10	64.0	68.0	76.2

number of water molecules associated to them. Later, polysaccharide polymeric molecules are released to the solution, mainly amylose but also some amount of amylopectin. Finally, the discrete granules become interconnected by the interactions formed among their extended polymeric chains. When the granules get broken, the suspension viscosity decreases.

Fig. 6 shows the result of integrating over temperature starch thermograms at different heating rates. It fits well to a two-state transition for a high scan rate (e.g., 10 °C/min). Especially for the region up to a few degrees over the gelatinization temperature, the two-state model can still be applied to rates as low as 0.5 °C/min, the rate employed in ultrasound experiments, although the shape of the thermogram suggest a different temporal relation among processes (hydration, swelling, hydrogen bond re-ordering).

The parallelism between the ultrasound amplitude and calorimetric data for starch gelatinization can be extended further. The insert in Fig. 3 shows a plot of the derivative of the amplitude versus temperature, similar to DSC thermograms. The enthalpy increment of the gelatinization process is proportional to the increment between the pre- and post-gelatinization levels of amplitude (or to the equivalent area under the transition derivative curve). Raw experimental data presented in Fig. 3 showed a reduced reproducibility in the baseline, which is ascribed to the influence of the stirring employed to keep starch granules in suspension (data not shown), and different data sets were, so, normalized to enable comparison of the changes taking place upon gelatinization. It is

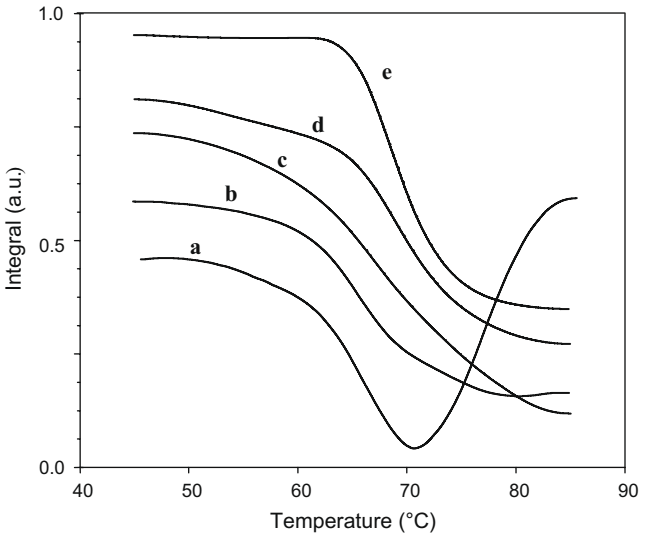

Fig. 6. Integrals over temperature of the thermograms shown in Fig 5: scan rates: (a) 0.5 °C/min, (b) 1 °C/min, (c) 2 °C/min, (d) 5 °C/min and (e) 10 °C/min.

not possible to obtain information of the absolute amplitude increments form a normalized plot (the difference between initial and finals amplitude is always one). But DSC enthalpy increment for starch gelatinization is also proportional to the maximum slope (approximately at mid-transition) of the amplitude curve (corresponding to the maximum of the derivative curve). This parameter can be also obtained from the normalized curve and the relation of it for the two starch concentrations studied corresponds, within experimental error, to the concentration ratio (data not shown).

Even for the same technique, the thermal parameters for starch gelatinization show variations depending on heating rate or other experimental variables, as seen in Table 2 for DSC assays. So, data of DSC corresponding to the same scan rates for the present work ultrasound experiments and those of Lehmann et al. (2004) have been included in Table 1. Heating rate seems to be a very important parameter to consider since similar results were obtained with different techniques but the same heating rates.

The effect of concentration, in the narrow range considered here (15–20% w/v), appears to be non-significant. The gelatinization behaviour of starch is believed to be strongly affected by water content but only when its fraction is reduced under 0.7 (French, 1984).

While the DSC technique is based on the measurement of heat capacity and the detection of process-associated enthalpy, ultrasound techniques are mainly based on measurements of mechanical character. For this reason, the information obtained from each technique would not be absolutely corresponding. In this relation, sound speed, although showing a decrease in the gelatinization region appears less precise and useful to determine gelatinization parameters. Temperature dependence prior to the onset of gelatinization can be observed and the main change in sound speed occurs at higher temperatures than those found by other techniques, which can be attributed to further events in the starch thermal gelatinization. These include further chain intermixing and increase in viscosity affecting the whole suspension volume, with a strong influence on the mechanical properties of the system, but not corresponding to the known gelatinization parameters. The amplitude of the sound wave has been chosen in order to obtain information more closely related to the gelatinization process, since it is more representative of the energetic state of the system and it renders more accurate results.

4. Conclusions

DSC is generally considered to be a very accurate technique while rheological methods yield information on mechanic behaviour. However, non-invasive ultrasound monitoring can be advantageously used for several proposes, such as following gelatinization processes in a variety of laboratory and industrial environments and situations, including reactors, continuous production processes, transport pipes, etc. The ultrasound-derived parameters, being directly related to viscosity, can be employed to obtain information on the mechanical properties of starch at a given stage of the process and also shed light on the different processes occurring during the overall gelatinization. Also, the possibility of obtaining consistent data by ultrasound motorization and DSC, enables comparison of the energetic and hydrodynamical aspects of the process, which can throw light on the finer details of starch gelatinization process.

Acknowledgements

This work has been supported by the "National Plan of Spanish I + D + I MEC" through the projects AGL2007-63314/ALI, and CSD2007-00045 MALTA CONSOLIDER-INGENIO 2010 L. and the CSIC, MEC: 200550F0191.

References

Álava, J.M., Sahi, S.S., García-Álvarez, J., Turó, A., Chávez, J.A., García, M.J., Salazar, J., 2007. Use of ultrasound for the determination of flour quality. Ultrasonics 46, 270–276.

Ammann, J.J., Galaz, B., 2003. Sound velocity determination in gel-based emulsions. Ultrasonics 41 (7), 569–579.

Ammann, J.J., Apablaza, V., Galaz, B., Flores, C., 2005. Ultrasonic sound velocity measurement in samples of soft materials through under-resonance excitation. Ultrasound in Medicine and Biology 31, 485–491.

Aparicio, C., Otero, L., Guignon, B., Molina-García, A.D., Sanz, P.D., 2008. Ice content and temperature determination from ultrasonic measurements in partially frozen foods. Journal of Food Engineering 88, 272–279.

Biliaderis, C.G., Page, C.M., Maurice, T.J., Juliano, B.O., 1986. Thermal characterization of rice starches: a polymeric approach to phase transitions of granular starch. Journal of Agricultural and Food Chemistry 34, 6–14.

Corredig, M., Verespej, E., Dalgleish, D.G., 2004. Heat-induced changes in the ultrasonic properties of whey proteins. Journal of Agricultural and Food Chemistry 52, 4465–4471.

Fässler, C., Arrigoni, E., Venema, K., Hafner, V., Brouns, F., Amadò, R., 2006. Digestibility of resistant starch containing preparations using two *in vitro* models. European Journal of Nutrition 45, 445–453.

Fernández, P.P., Sanz, P.D., Martino, M.N., Molina-García, A.D., 2008. Partially-gelatinised starches by high hydrostatic pressure as oligoelement carriers. Spanish Journal of Agricultural Research 6 (Special issue), 129–137.

French, D., 1973. Chemical and physical properties of starch. Journal of Animal Science 37, 1048–1061.

French, D., 1984. Organization of starch granules. In: Whistles, R.L., Bemiller, J.N., Paschall, E.F. (Eds.), Starch: Chemistry and Technology, second ed. Academic Press Inc., pp. 184–248.

Ji, Y., Wong, K., Hasjim, J., Pollak, L.M., Duvick, S., Jane, J., White, P.J., 2003. Structure and function of starch from advanced generations of new corn lines. Carbohydrate Polymers 51, 439–450.

Lee, H.O., Luan, H., Daut, D.G., 1992. Use of an ultrasonic technique to evaluate the rheological properties of cheese and dough. Journal of Food Engineering 16, 127–150.

Lehmann, L., Kudryashov, E., Buckin, V., 2004. Ultrasonic monitoring of the gelatinisation of starch. Progress in Colloid and Polymer Science 123, 136–140.

Letang, C., Piau, M., Verdier, C., Lefebvre, L., 2001. Characterization of wheat–flour–water doughs: a new method using ultrasound. Ultrasonics 39, 133–141.

Lionetto, F., Maffezzoli, A., Ottenhof, M.A., Farhat, I.A., Mitchell, J.R., 2006. Ultrasonic investigation of wheat starch retrogradation. Journal of Food Engineering 75, 258–266.

McClements, D.J., 1997. Ultrasonic characterization of foods and drinks: principles, methods and applications. Critical Reviews in Food Science and Nutrition 37, 1–46.

Miles, M.J., Morris, V.J., Orford, P.D., Ring, S.G., 1985. The roles of amylose and amylopectin in the gelation and retrogradation. Carbohydrate Research 135 (2), 271–282.

Morton, M.W., Rutenberg, M.W., Solarek, D., 1984. Starch derivatives: production and uses. In: Whistles, R.L., Bemiller, J.N., Paschall, E.F. (Eds.), Starch: Chemistry and Technology, second ed. Academic Press Inc., pp. 312–388.

Parker, R., Ring, S.G., 2001. Aspects of the physical chemistry of starch. Journal of Cereal Science 34 (1), 1–17.

Ratnayake, W.S., Jackson, D.S., 2009. Starch gelatinization. Advances in Food Nutrition Research 55, 221–268.

Snyder, E.M., 1984. Industrial microscopy of starches. In: Whistles, R.L., Bemiller, J.N., Paschall, E.F. (Eds.), Starch: Chemistry and Technology, second ed. Academic Press Inc., pp. 661–673.

Spies, R.D., Hoseney, R.C., 1982. Effect of sugars on starch gelatinization. Cereal Chemistry 59, 128–131.

Zobel, H.F., 1984. Gelatinization of starch and mechanical properties of starch pastes. In: Whistles, R.L., Bemiller, J.N., Paschall, E.F. (Eds.), Starch: Chemistry and Technology, second ed. Academic Press Inc., pp. 285–309.