Journal of Food Engineering 96 (2010) 505–509

Contents lists available at ScienceDirect

Journal of Food Engineering

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

Starch gelatinization as measured by rheological properties of the dough

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ARTICLE INFO

Article history:
Received 2 April 2009
Received in revised form 16 August 2009
Accepted 31 August 2009
Available online 4 September 2009

Keywords:
Gelatinization
Dough
Starch
Rheological properties
Viscoelasticity

ABSTRACT

Rheological properties of gluten-free dough (GFD) as well as conventional gluten containing dough (CGD) during processing were measured. Both CGD and GFD were examined in terms of mechanical spectrum, in the frequency range 0.1–10 Hz, at constant deformation $\gamma = 0.01$, at different temperatures. As a result changes in viscoelasticity of dough during selected stages of bread production (mixing–proofing–baking) were obtained. Changes in complex moduli of GFD and CGD, at a frequency of 1 Hz were measured. Curves obtained showed the changes in tan(delta) (phase shift) with time and allowed calculations of first derivatives which indicated the temperatures of gelatinization of the starches present in the studied systems (wheat, corn and potato). The results of rheological measurements were compared to DSC results of appropriate dough samples. It was concluded that rheological measurements followed by derivative calculations are useful for determining the gelatinization temperature of starches included in the dough.

1. Introduction

During the preparation of dough, gluten protein molecules become hydrated and interact to form three-dimensional structure (Schofield, 1986) in which are uniformly dispersed starch granules and which determine the rheological properties of dough (Li et al., 2003; Tsiami et al., 1997).

During bread baking starch granules are prone to swelling and gelatinization. The conditions in which these phenomena occur, determine the quality of the final food products. In the scientific literature different additives and ingredients have been used to modify the gelatinization–gelation processes, namely the pasting properties of starch. Sugars added to starch mixtures increased the gelatinization temperature and the paste viscosity by decreasing the availability of water (Evans and Haisman, 1982; Spies and Hoseney, 1982). Salt addition resulted in an improvement of the integrity of the starch granules and an increase in the paste consistency (Ganz, 1965). Salts also retarded the retrogradation of the starch (Chang and Liu, 1991).

In recent years the demand for gluten-free products has been on the rise and so the interest on gluten-free bread production is constantly growing. Gluten matrix is a major determinant of the important rheological characteristics of dough, such as elasticity, extensibility, resistance to stretch, mixing tolerance, and gas holding ability (Lazaridou et al., 2007). Several rheological techniques, including dynamic oscillation, creep and stress relaxation, extensional measurements and flow viscosimetry have been used in many studies for probing fundamental mechanical properties of gluten (Janssen et al., 1996; Lee and Mulvaney, 2003; Schober et al., 2005) and wheat dough (Baltsavias et al., 1997; Edwards et al., 1999, 2001, 2003; Janssen et al., 1996; Phan-Thien and Safari-Ardi, 1998; Safari-Ardi and Phan-Thien, 1998; Weipert, 1990) as well as for establishing relation between those properties and quantity attributes of the end-products (Carson and Sun, 2001; Dobraszczyk and Morgenstern, 2003; Wang and Sun, 2002). However, the use of rheometry in studies of gluten-free dough rheological behaviour has been rather limited (Haque and Morris, 1994; Sivaramakrishnan et al., 2004; Lazaridou et al., 2007).

The replacement of gluten protein involves incorporation of starch, non-starchy hydrocolloids and dairy proteins into a naturally gluten-free flour base (rice or corn flour) to mimic viscoelastic properties of gluten and to improve structure, sensory attributes and shelf-life of gluten-free products (Sanchez et al., 2002; Sivaramakrishnan et al., 2004; Ahlborn et al., 2005; McCarthy et al., 2005; Schober et al., 2005; Lazaridou et al., 2007; Moore et al., 2006).

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doi:10.1016/j.jfoodeng.2009.08.033

The presence of hydrocolloids influenced melting, gelatinization, fragmentation and retrogradation of starch process (Fanta and Christianson, 1996; Kokini et al., 1992; Lai and Kokini, 1991; Rojas et al., 1999). These effects were shown to affect pasting properties, dough rheological behaviour (Armero et al., 1995; Rojas et al., 1999) and bread staling (Armero and Collar, 1998; Davidou et al., 1996). Gelatinization of cereal starch dispersions in the presence of different non-starchy hydrocolloids strongly influenced the viscosity of the hot starch paste (Bahnassey and Breene, 1994; Fanta and Christianson, 1996).

According to the literature the ranges of gelatinization temperatures of wheat, corn and potato starch were: 51–79, 62–84, and 57–80 °C, respectively (Chaiwanichsiri et al., 2001; Singh et al., 2003).

It is widely known that different additives influence to varying extent the gelatinization of starch (Kowalski et al., 2008; Sikora et al., 2008; Sikora and Krystyjan, 2009). However no mention has been found, concerning possibilities of measurement of starch gelatinization temperature in the dough during baking by the use of rheological measurements.

The aim of the present work was to study the starch gelatinization by measurement of the mechanical spectrum of the dough during its processing. Such approach can be useful in measurement of viscoelasticity of the dough on selected steps of dough/bread production, as well as in measurement of gelatinization temperature of the starches in the studied systems.

2. Materials and methods

2.1. Materials

2.1.1. Materials for gluten-free dough (GFD)

- Corn starch – Roquette Freres, Lestrem, France,
- potato starch – superior, PPZ Bronislaw, Sp. z o. o., Poland,
- corn flour 250–50 – Boly ZRT, Boly, Hungary,
- guar gum – Lotus Gums & Chemicals, Jodhpur, India,
- locust bean gum – C.E. Roeper GmbH, Hamburg, Germany,
- highly methylated pectin (apple), WEJ-4 – ZPOW Pektowin Sp. z o. o., Jaslo, Poland,
- hydroxypropylmethylcellulose (HPMC) – DOW Europe GmbH, Stade, Germany,
- gluconic acid lactone – A.H.A. International Co. Ltd., Hefei, China,
- fresh running water,
- dried baking yeasts, SAF-Instant red – Lesaffre Group, Strasbourg, France,
- salt – Janikosoda S.A., Janikowo, Poland,
- sucrose – Sugar Plant Krasnystaw, Siennica Nadolna, Poland,
- rapeseed oil – ZT Kruszwica S.A., Poland,
- powdered milk, full – 26% fat, S.M. Mlekovita, Wysokie Mazowieckie, Poland.

Two kinds of gluten-free dough (GFD) were prepared. GFD 2 – contained all above mentioned ingredients, and GFD 1 – all, but locust bean gum.

2.1.2. Materials for conventional, gluten containing dough (CGD)

- Wheat meal, type 55 – Moulins Soufflet, Pornic, France,
- salt – Janikosoda S.A., Janikowo, Poland,
- dried baking yeasts, SAF-Instant red – Lesaffre Group, Strasbourg, France,
- improver – Freshbake, Puratos, Belgium,
- fresh running water.

2.2. Methods

2.2.1. Gluten-free dough (GFD) preparation

1. Mixing 12 min: 3 min at slow turns, and 9 min at fast turns.
2. Proofing I – in kneading trough – 30 min.
3. Dividing and forming into pieces of 70 g.
4. Proofing II – in pieces – 20 min, proofing chamber (40 °C, humidity 80%).
5. Baking – 20 min, temperature 230 °C.

2.2.2. Conventional, gluten containing dough (CGD) preparation

1. Mixing components (flour, water, yeasts, salt, improver) – 9 min, 26 °C.
2. Resting – 10 min.
3. Scaling 70 g pieces.
4. Proofing – 35 °C, 60 min, and humidity – 95%.
5. Baking 20 min, 230 °C.

2.2.3. Sampling

The dough samples were collected during the dough production three times:

(a) directly after kneading, at 30 °C,
(b) during the first step of proofing, at 40 °C, before moulding,
(c) after final proofing, at 40 °C.

2.2.4. Rheological measurements

Rheometer RheoStress RS 1 (Gebrueder Haake, GmbH, Karlsruhe, Germany) equipped with a system of two parallel plates, with diameters of 60 mm (PP 60) was used. After the final gap of 1 mm was reached, the edges were covered by paraffin oil in order to avoid evaporation of the sample.

Samples were examined in terms of mechanical spectrum, in the frequency range of 0.1–10 Hz, at constant deformation $\gamma = 0.01$, at the temperature of 30 °C (step a), 40 °C (step b and c). Then the sample from (step c) was heated up to 95 °C, for 900 s (15 min), kept at 95 °C for 300 s (5 min), and then cooled to 40 °C, during 2700 s (45 min). During the heating and cooling (40 – 95 – 40 °C) the mechanical spectrum was measured at the constant frequency of 1 Hz, and finally, after the temperature of 40 °C was reached, the mechanical spectrum was measured again (0.1–10 Hz, $\gamma = 0.01$).

2.2.5. DSC measurements

Shimadzu DSC-60 Differential Scanning Calorimeter was used for measurements (Shimadzu Corporation Kyoto Japan). Samples (about 20 mg) were positioned in the capsule, closed and weighted. Capsules were left in the chamber of DSC apparatus for 10 min, at 30 °C and thereafter heated to 100 °C at a constant speed of 10 °C/min. As a reference the empty capsule was used. The temperature axis was calibrated by the use of indium.

2.3. Statistical analysis

Statistica 7.0 software was used (StatSoft, Tulsa, OK, USA). One-way analysis of variance was carried out with the Duncan test at $\alpha = 0.05$ confidence level.

3. Results

Fig. 1 shows the changes in viscoelasticity of the two gluten-free (GFD 1, GFD 2) and a gluten containing dough (CGD) during selected stages of bread production. Both gluten-free doughs (GFD 1 and GFD 2 contained starches (corn and potato starch) and non-starchy hydrocolloids such, as hydroxyprophylmethylcellulose (HPMS), pectin, guar gum and/or locust bean gum; these were used instead of wheat flour in the CGD formulation. In general, the replacement of gluten protein involves incorporation of starch, non-starchy hydrocolloids and/or dairy proteins into a naturally gluten-free flour base (rice or corn flour) in order to mimic visco-elastic properties of gluten (Sanchez et al., 2002; Sivaramakrishnan et al., 2004; Ahlborn et al., 2005; McCarthy et al., 2005; Schober et al., 2005; Moore et al., 2006).

The curves showing changes of tangent delta with frequency (0.1–10 Hz) continuously decrease after kneading and proofing. However, in CGD after kneading, a small increase of this parameter was observed (Fig. 1c).

The curve showing changes in tangent delta values with frequency in GFD 1 after final fermentation has significantly higher values, in comparison with those after kneading (Fig. 1a). The same was observed in CGD (Fig. 1c). Heating followed by cooling caused radical fall in the tangent delta of each dough investigated (Fig. 1a–c).

As stated before, in GFD 1 significant decrease in tangent delta after final proofing was observed (Fig. 1a). This phenomenon could be explained by higher compression of dough, caused by the applied procedure. The same phenomenon was not observed in the case of GFD 2, where an additional hydrocolloid (locust bean gum) was introduced into the recipe of the dough. An application of this hydrocolloid caused higher resistance of dough to mechanical stress. An improvement in the viscoelastic properties of dough by incorporation of hydrocolloids is related to the molecular structure and chain conformation of polysaccharides (Lazaridou et al., 2007). Non-starchy hydrocolloids are often used as gluten substitutes in gluten-free formulations (Rojas et al., 1999). According to the above mentioned application of locust bean gum, the third non-starchy hydrocolloid, into gluten-free dough formulation increased viscoelastic properties of the dough. The action of locust bean gum could be explained in terms of its structure. The latter has twice fewer side chains than guar gum, which can help to form a better structure in the gluten-free dough as a whole (Glicksmann, 1982; Sikora and Krystyjan, 2009).

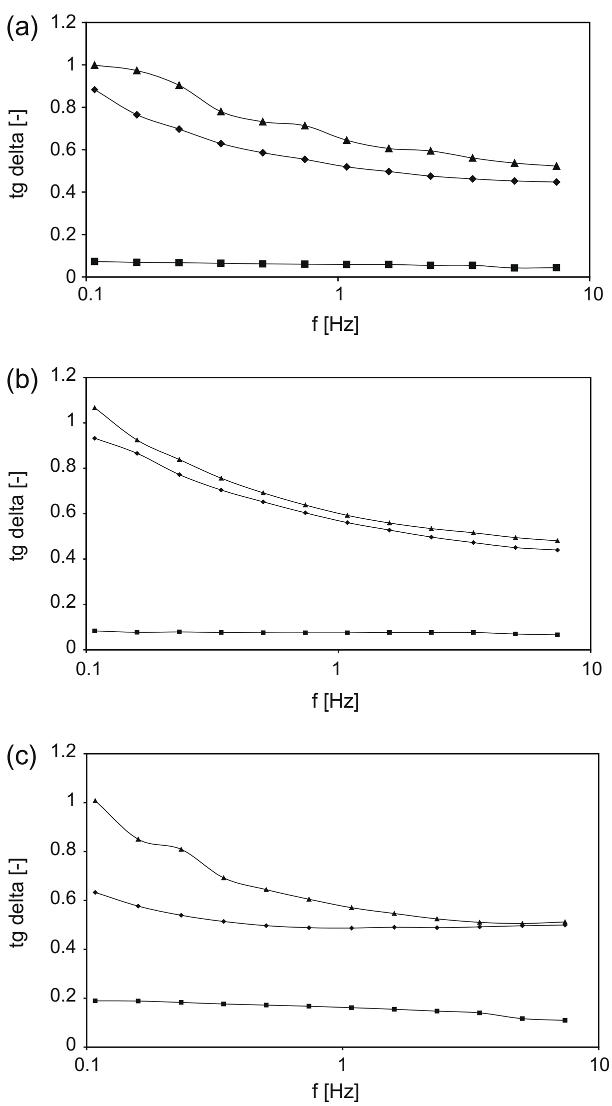

Fig. 1. Changes in (a) GFD 1, (b) GFD 2, (c) CGD viscoelasticity during selected stages of bread production, (♦ – after kneading, ▲ – after final fermentation, ■ – after heating and consecutive cooling).

In the Fig. 2 the changes in the complex moduli (G^*) of GFD 1, GFD 2 and CGD during rheological measurement are presented.

It is obvious, that the conditions applied in the rheometer did not simulate those prevailing in a real baking process. These experiments were carried out for two reasons. One was to establish the temperature of starch gelatinization in the dough, which is the main subject of this study, and which could be achieved in the measuring system of rheometer. Another reason was the temperature of core of the loaf during baking process. Cauvain (2001) claimed that temperature range of 92–96 °C could ensure the final quality of bread.

As evident from Fig. 2, the complex moduli increase with change in temperature. To an approximation, these changes can be regarded as characteristics of gelatinization, determined by Brabender viscograph or RVA (Bahnassey and Breene, 1994; Evans and Haisman, 1982; Rojas et al., 1999). An analysis of the changes in complex moduli (G^*) permits the identification of the start and the end of gelatinization. An observation of complex moduli changes during heating and cooling of dough led to interesting conclusions. CGD curve differed significantly from gluten-free ones. After the commencement of gelation process, the curves for gluten-free dough moduli increased continuously. On the other hand, the complex modulus curve of gluten containing dough showed firstly a maximum then a minimum, and then increased continuously. This shape observed in the case of CGD resembles that of a typical Brabender viscogram for wheat starch (Cornell and Hoveling, 1998). In the Brabender viscograms the maximum shows the increasing viscosity of starch suspension during gelatinization, followed by minimum and subsequent increase in viscosity on cooling (Fig. 2).

The next step in this study was the determination of the mechanical spectra of both CGD and GFD, at the frequency of 1 Hz. As a result the curves were obtained, which presented

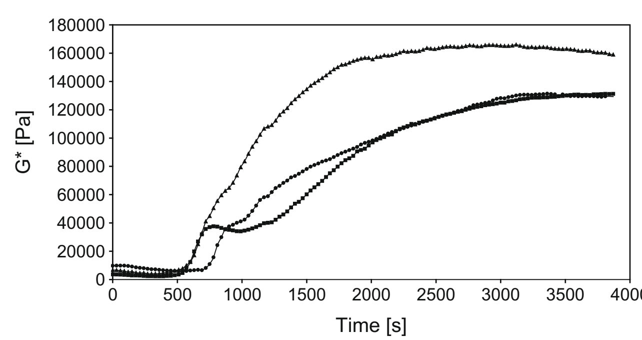

Fig. 2. Changes in complex moduli of GFD 1, GFD 2 and CGD during heating and cooling (40 – 95 – 40 °C), (♦ – GFD 2, ▲ – GFD 1, ■ – CGD).

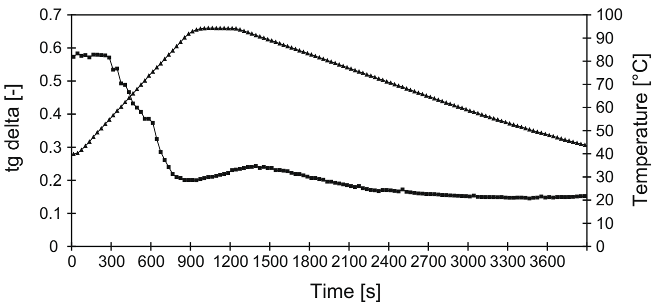

Fig. 3. Changes in tan(delta) of dough (CGD) during heating and cooling (40 – 95 – 40 °C), at 1 Hz, (♦ – CGD, ▲ – temperature profile).

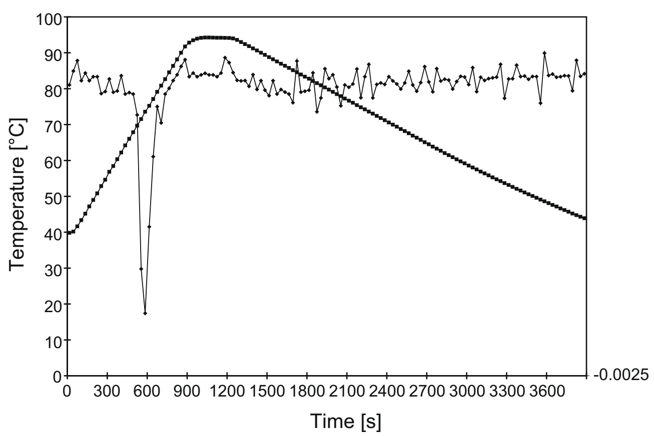

Fig. 4. First derivative of tan(delta) changes with time – a method for determining the gelatinization temperature of starch in any dough, (♦ – CGD, ■ – temperature profile).

Table 1
Gelatinization temperatures of the dough determined by the two methods.

	Measurement method	GFD 1	GFD 2	CGD
Temperature of gelatinization (°C)*	DSC	76.73 ± 1.79a	77.00 ± 0.56a	79.76 ± 0.49a
	Rheological	80.45 ± 2.83a	77.31 ± 0.13a	77.21 ± 2.50a

Duncan test, one-way analysis of variance, α = 0.05.
* Median values of duplicates.

tangents delta changes in time, at increasing and decreasing temperatures, and constant frequency. As an example appropriate curves of tangents delta changes of gluten containing dough (CGD) are shown in the Fig. 3.

By calculating the first derivative of the curve (dtgdelta/dt), the inflection points were identified, which precisely correspond to the temperatures of gelatinization of the starch incorporated in the dough. An example of inflection point obtained for CGD is presented in Fig. 4.

During bread baking starch granules swell and gelatinize. The conditions in which these phenomena occur, determine the quality of the bread. Gelatinization temperatures, determined by the inflection point varied from each other, depending on the type of dough (Table 1). They were higher for gluten-free dough – 80.45 and 77.31 °C, respectively for GFD 1 and GFD 2, and lower for gluten containing dough – 77.21 °C. Higher values of gelatinization temperature of gluten-free dough as compared to gluten containing dough can be explained by the sucrose content of the gluten-free dough recipes. This is consistent with the papers of Evans and Haisman (1982), and Spies and Hoseney (1982), who claimed that sugars added to starch mixtures increased the gelatinization temperature and the paste viscosity by decreasing water availability.

The measurement of gelatinization temperatures by DSC allowed comparing the rheological results with those obtained by DSC. Thus, the following temperatures of gelatinization were obtained 76.73, 77.00 and 79.76 °C for GFD 1, GFD 2 and CGD, respectively. Values obtained by both DSC and rheological methods do not differ significantly (Duncan test).

According to literature, the ranges of gelatinization temperatures of wheat, corn and potato starch were: 51–79, 62–84, and 57–80 °C, respectively (Chaiwanichsiri et al., 2001; Singh et al., 2003). Values obtained in this experiment fall within these ranges.

According to many researchers (Fanta and Christianson, 1996; Kokini et al., 1992; Lai and Kokini, 1991; Rojas et al., 1999) the presence of hydrocolloids influenced melting, gelatinization, fragmentation and retrogradation of starch during thermal treatment. These effects were shown to affect pasting properties, and rheological behaviour of dough (Armero et al., 1995; Rojas et al., 1999).

The mechanical spectra (complex moduli, tangents delta) changes with time, and the inflexion points on the tangent delta curves – enabled determination of gelatinization temperature of starch incorporated into the systems. Certainly, the gelatinization temperatures of starch could be measured by e.g. DSC, RVA and/or Brabender viscograph, however precise measurements are possible in model systems, containing only starch. In the blended systems, such as dough, the measurement is limited by several factors. The work presented appears to be a good and cost effective solution in this area.

4. Conclusions

Determination of mechanical spectrum of dough enables:

- measurement of viscoelasticity of the dough during selected steps of dough/bread production,
- measurement of gelatinization temperature of the starch(es) in the studied systems.

Acknowledgements

This study has been carried out with financial support from the Commission of the European Communities, FP 6, Thematic Area "Food quality and safety", FOOD-2006-36302 EU-FRESH BAKE. It does not necessarily reflect its views and in no way anticipates the Commission's future policy in this area. This study has also been supported by the Polish Ministry of Science and Higher Education, grant No. 162/6 PR UE/2007/7.

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