J Therm Anal Calorim (2012) 108:185–189
DOI 10.1007/s10973-011-2029-0

A DSC study of the effect of bread making methods on bound water content and redistribution in chitosan enriched bread

Garry Kerch · Alexander Glonin · Janis Zicans · Remo Merijs Meri

Received: 8 August 2011 / Accepted: 26 October 2011 / Published online: 16 November 2011

Abstract The effect of bread making methods on bound water migration from crumb to crust and moisture redistribution during bread storage at room temperature was studied. Comparative analysis of water behavior in bread crusts and crumbs was performed using differential scanning calorimetry method. Water vaporization enthalpies and temperatures of water vaporization peaks were determined and compared for bread produced by a single stage, straight dough method and bread produced by a two stage, sponge-and-dough method. The effect of chitosan on the crust and the crumb properties was analyzed for the breads produced by both methods.

Keywords Bread · Chitosan · Bound water · Staling · Sponge-and-dough method

Introduction

Bread is a highly complex heterogeneous thermodynamically unstable and dynamic composite system with high porosity and high water content [1, 2]. Hydrated gluten is the continuous phase of wheat flour dough. Starch granules form discontinuous phase of wheat flour doughs. Bread can be considered as interpenetrated network of gluten and starch biomolecules [2].

Bread staling is a complex process involving multiple mechanisms (amylopectin retrogradation, water migration and redistribution between crumb and crust and between starch and gluten) where molecular interactions occur at multiple temporal and spatial scales [2–4]. Mechanisms of bread staling are not yet completely understood and not described clearly enough for the time being. It was suggested that water migration has a stronger influence on bread firmness than the retrogradation of amylopectin [5] and that staling of bread during storage can be subdivided at least into two stages with different mechanisms [6–9].

Water added to flour to make dough hydrates the gluten, penetrates the starch and allows gluten strands and starch particles to slide on each other during enlargement of the gas cells [10]. All the water in bread is bound water [7].

Methods of bread making can be subdivided into straight dough method and sponge-and-dough method. All ingredients are mixed together in one stage using straight dough method. According to sponge-and-dough method ingredients are combined in two stages, a portion of the flour (from 40 to 60% of the total amount), water and yeast are first mixed forming the sponge. The sponge is allowed to ferment and in the second stage the sponge is added to the rest of the ingredients and the mixture ferments again.

Differential scanning calorimetry (DSC) is an appropriate method to study water contents and water binding energy in bread [3, 7, 8, 11–16] and other food products [17].

It was observed [18] that bread produced using sponge-and-dough method has higher volume of loaves.

The effect of chitosan on water migration and bread staling through the adsorption of positively charged chitosan molecules on negatively charged starch surface was demonstrated recently [7–9].

G. Kerch (✉)
Faculty of Food Technology, Latvian University of Agriculture, Jelgava, Latvia
e-mail: garrykerch@lycos.com

A. Glonin
Latgales Maiznica, Riga, Latvia

J. Zicans · R. Merijs Meri
Institute of Polymer Materials, Riga Technical University, Riga, Latvia

The aim of this research was to demonstrate how differences in bread making process affect the state and distribution of water in fresh bread and migration and redistribution of water during staling, as well as effect of chitosan at different dough mixing processes, using differential scanning calorimetry method.

Materials and methods

Sample preparation

Doughs were prepared with two different methods: with straight dough method and by sponge-and-dough method.

Dough with straight dough method was prepared based on the following formulation: 500 g wheat flour, 35 g sugar, 17 g dry yeast, 8 g salt, 10 g butter, chitosan 10 g, and 260 g water.

The sponge-and-dough mixing method consists of two distinct stages. Sponge was first set by using the following formulation: 280 g wheat flour, 150 g water, and 17 g dry yeast. The sponge was set to rise at 27 °C. After 16 h the sponge is ripe and 220 g of wheat flour, 110 g water, 35 g sugar, 8 g salt, and 10 g chitosan were added and fermented 3 h.

Chitosan with viscosity 29 cP and degree of deacetylation 97% was kindly supplied by Primex (Siglufjordur, Iceland). Dough mixer "MONO" (Swansea, UK) was used to make dough. The rolls were baked in confectionery oven "MONO" (Swansea, UK) at 200 °C for 12 min. The rolls were then cooled at room temperature for 30 min and packed in polypropylene bags.

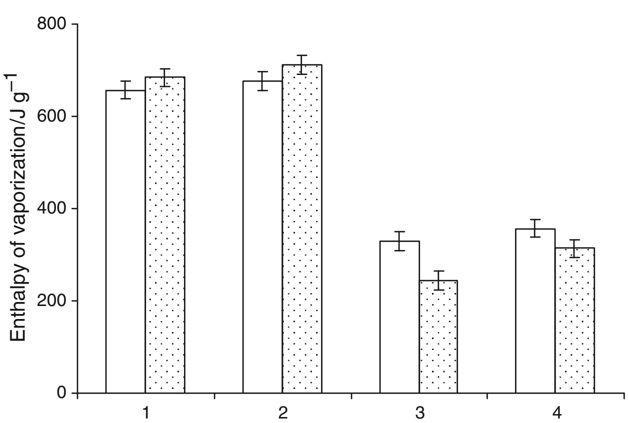

Fig. 1 Enthalpies of water vaporization in the fresh bread crumb (*1* and *2*) and crust (*3* and *4*) produced with a single stage, straight dough method (*1* and *3*) and produced with a two stage, sponge-and-dough method (*2* and *4*) containing chitosan (*filled bars*) and without chitosan (*open bars*)

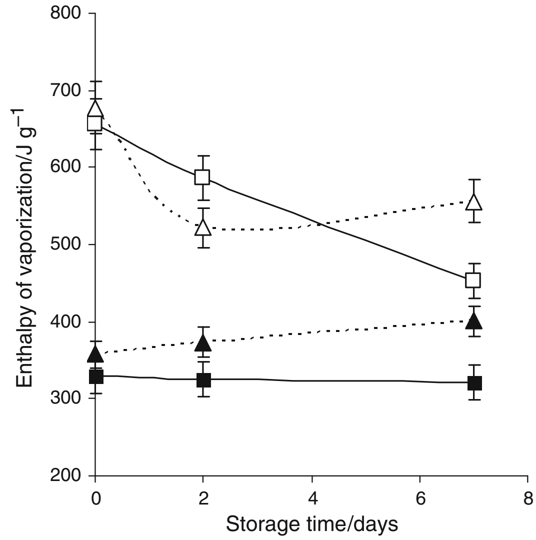

Fig. 2 Changes of enthalpies of water vaporization during storage in the crumb (*solid lines*, *empty squares*) and in the crust (*solid lines*, *filled squares*) of bread produced by a single stage, straight dough method and enthalpies of water vaporization in the crumb (*dashed lines*, *open triangles*) and crust (*dashed lines*, *filled triangles*) of bread produced by a two stage, sponge-and-dough method

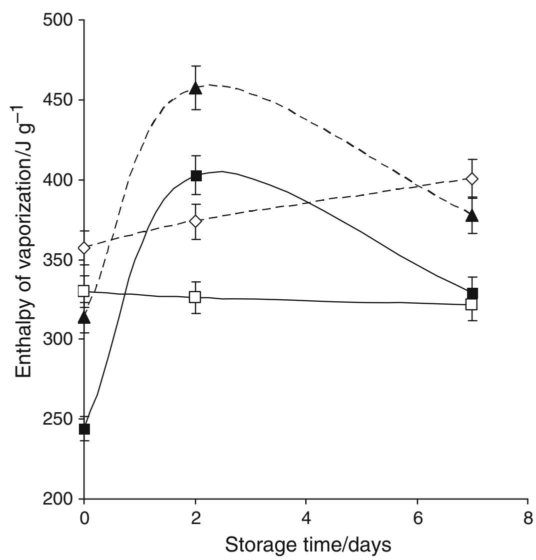

Fig. 3 Changes of enthalpies of water vaporization during storage in the crust of bread produced by a single stage, straight dow method (*solid lines*) and produced by a two stage, sponge-and-dough method (*dashed lines*) without addition of chitosan (*open squares* and *open diamonds*) and containing chitosan (*filled squares* and *filled triangles*)

Thermal analysis

Differential scanning calorimetry (DSC) thermograms were obtained using a differential scanning calorimeter DSC "Mettler 300" (Mettler-Toledo AG, Schwerzenbach, Switzerland) equipped with a software for determination of onset, peak, endset temperatures, and peak's area. The

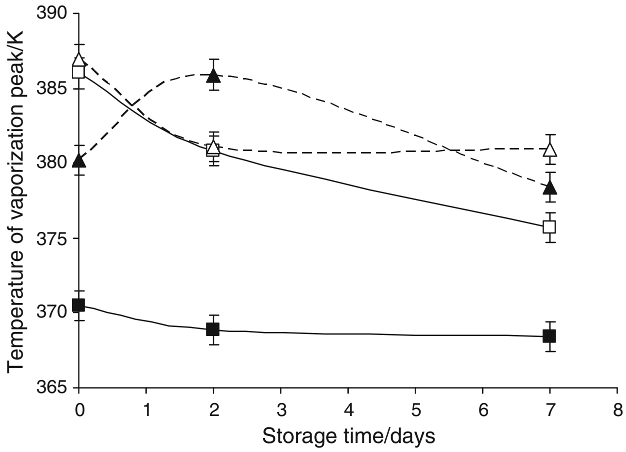

Fig. 4 Changes of the temperatures of water vaporization peaks during storage in the crumb (*open squares* and *open triangles*) and in the crust (*filled squares* and *filled triangles*) of breads produced with a single stage, straight dough method (*solid lines*) and produced with a two stage, sponge-and-dough method (*dashed lines*)

DSC temperature scale and heat flow were calibrated by using a standard indium sample.

Approximately 10 mg samples from bread crumb and crust were placed into aluminum pans, and then a lid was secured by crimping in such a way as to prevent pressure buildup and to allow vaporized moisture to escape easily from the pan during the heating cycle. The samples were placed in the sample compartment at $T = 25$ °C and then scanned from $T = 25$ °C to $T = 150$ °C with a heating rate of 10 °C/min to volatilize the water. Each measurement was performed in triplicate.

Results and discussion

Enthalpy of water vaporization is propotional to water content in polymer networks [19]. Enthalpies of water vaporization in the fresh bread crumb and crust produced by a single stage, straight dough method and produced with a two stage, sponge-and-dough method containing chitosan and without chitosan are shown in Fig. 1. No significant difference in water vaporization enthalpies, and consequently, in water content in the crumb was observed for fresh breads produced by both methods, but water content in the fresh bread crust is essentially lower for breads containing chitosan. It is known that crust loses its crispness when water migrates during bread storage from crumb to crust and water content rises above a critical value [20]. So because of the lower water content more crispy crust can form in fresh breads containing chitosan.

Water vaporization enthalpy (content of tightly bound water) in the crust did not change during storage for the bread produced with a single stage, straight dough method and increases for the bread produced with a two stage, sponge-and-dough method (Fig. 2). Water vaporization enthalpy in the crusts for the breads produced by both methods and containing chitosan is lower for the fresh bread (Fig. 1), higher after 2 days of storage (first stage of staling) and don't differ essentially after 7 days of storage (second stage of staling) (Fig. 3) if compared with a bread without chitosan.

The energy of water binding (temperature of vaporization peak) in the crust during first stage of staling increases for the bread produced by a two stage, sponge-and-dough method and slightly decreases for bread produced with a single stage, straight dough method (Fig. 4).

The energy of water binding in the crust during second stage of staling decreases for bread produced by a two stage, sponge-and-dough method and don't change for bread produced by a single stage, straight dough method (Fig. 4).

After 2 days of storage (first stage of staling) the content of bound water in the crumb of the bread produced by a two stage, sponge-and-dough method is lower than in the crumb of bread produced by a single stage straight dough method but after 7 days of storage (second stage of staling) the content of bound water in the crumb of the bread produced by a two stage, sponge-and-dough method is higher than in the crumb of the bread produced by a single stage, straight dough method (Fig. 2). So higher rate of

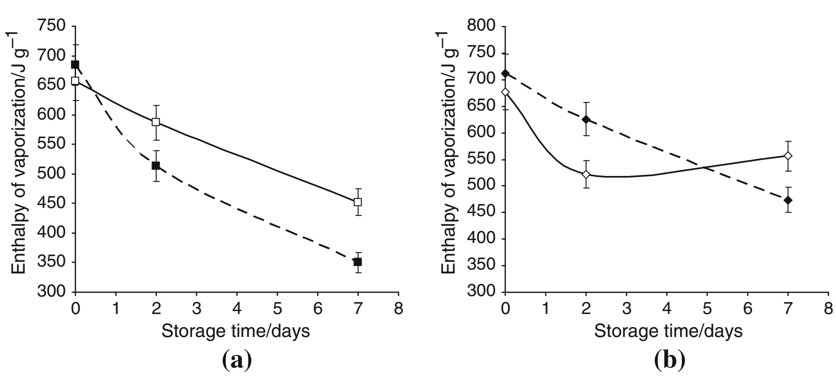

Fig. 5 Changes of enthalpies of water vaporization during storage in the crumb of bread produced with a single stage, straight dough method (**a**) and bread produced with a two stage, sponge-and-dough method (**b**) without chitosan (*open squares* and *open diamonds*) and containing chitosan (*filled squares* and *filled diamonds*)

water migration from crumb to crust at the first stage of staling and lower rate of water migration at the second stage of staling was observed for the bread produced by a two stage, sponge-and-dough method. It is known that increased moisture content of breads increases the rate of starch retrogradation [2, 21].

It was observed [22] that bread moisture content was higher for sponge-and-dough process and that sponge-and-dough process resulted in softer breads with low staling rate. Our data show that the difference appears only during bread storage (Fig. 2). In the fresh bread the essential difference in water content was observed for bread crust containing chitosan.

The slight increase of vaporization enthalpy during the second stage of staling (Fig. 2) can be related to the migration of a portion of water from gelatinized starch toward the more rigid amorphous and crystalline domains that so became unfreezable [1, 7, 23, 24].

Chitosan accelerates the decrease of bound water content during staling in the bread produced by a single stage, straight dough method and slow downs the decrease of bound water content during the first stage of staling in the bread produced by a two stage, sponge-and-dough method (Fig. 5). So chitosan can delay the staling during first 2–3 days of storage (first stage of staling) for bread produced with a two stage, sponge-and-dough method and accelerate the staling of bread produced with a single stage, straight dough method [7].

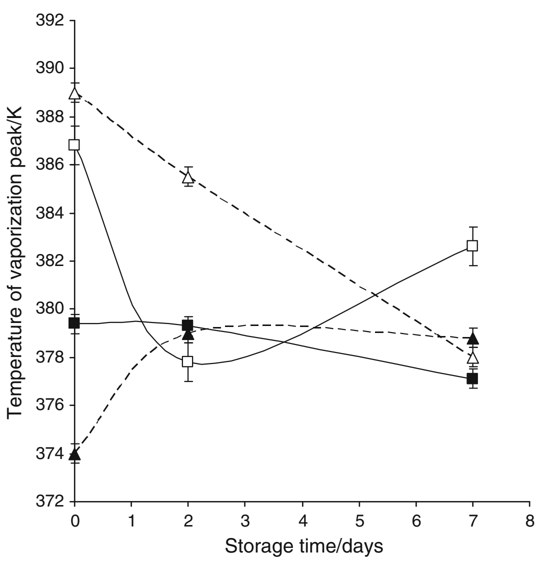

Fig. 6 Changes of the temperatures of water vaporization peaks during storage in the crumb (*open squares* and *open triangles*) and in the crust (*filled squares* and *filled triangles*) of breads containing chitosans and produced with a single stage, straight dough method (*solid lines*) and produced with a two stage, sponge-and-dough method (*dashed lines*)

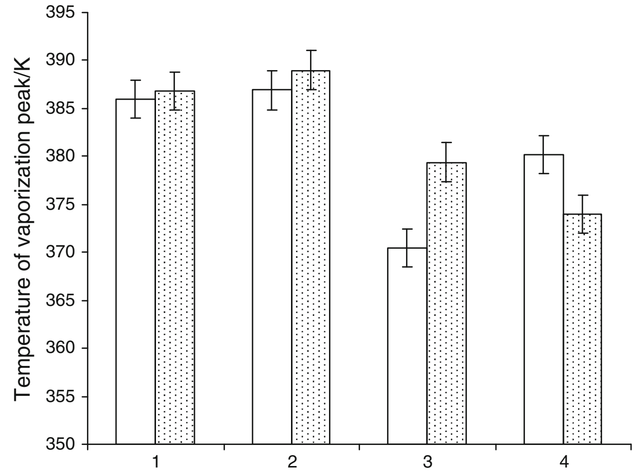

Fig. 7 Temperatures of water vaporization peaks in the fresh bread crumb (*1* and *2*) and crust (*3* and *4*) produced with a single stage, straight dough method (*1* and *3*) and produced with a two stage, sponge-and-dough method containing chitosan (*filled bars*) and without chitosan (*empty bars*)

The energy of water binding in the crumb during second stage of staling decreases more rapidly for the bread produced by a single stage, straight dough method than for the bread produced by a two stage, sponge-and-dough method (Fig. 4).

The energy of water binding in the crumb containing chitosan decreases during first stage of staling and increases during second stage of staling for the bread produced by a single stage, straight dough method and essentially decreases during both stages of staling for bread produced by a two stage, sponge-and-dough method (Fig. 6).

In the fresh bread crumb addition of chitosan do not affect essentially the energy of water binding, but in the crust addition of chitosan decreases the energy of water binding (the temperature of water vaporization peak), if the bread was produced by a two stage, sponge-and-dough method, and increases the temperature of water vaporization peak (the energy of water binding to bread components) if the bread was produced by a single stage, straight dough method (Fig. 7).

Conclusions

Water vaporization enthalpy and bound water content in crusts of the fresh breads containing chitosan is essentially lower than in crusts of breads without chitosan. Due to the water content is much lower than critical value more crispy crust can be expected to form in fresh breads enriched with chitosan. During the first stage of staling (first 2 and 3 days of storage at room temperature) bound water content in crusts increases with higher rate for breads containing chitosan. Non-monotonic changes of the temperature of vaporization peak (energy of water binding to food components) were observed in the crust of bread produced by a two stage, sponge-and-dough method and enriched with chitosan. The temperature of vaporization peak increases during first stage of staling and decreases during second stage of staling. The breads produced by a two stage, sponge-and-dough method have higher rate of water migration from crumb to crust at the first stage of staling and lower rate of water migration at the second stage of staling than the breads produced by a single stage, straight dough method. Chitosan accelerates the decrease of bound water content in crumb during storage at room temperature in the bread produced by a single stage, straight dough method and slow downs the decrease of bound water content during the first stage of staling in the bread produced by a two stage, sponge-and-dough method.

Acknowledgements This study was carried out within 6th Framework Programme CRAFT project “New chitosan formulations for the prevention and treatment of diseases and dysfunctions of the digestive tract (hypercholesterolemia, overweight, ulcerative colitis, and celiac diseases)” and within the ESF Project “Formation of the research group in food science”. Contract No. 2009/0232/1DP/1.1.1.2.0/09/APIA/VIAA/122.

References

1. Ribotta PD, Le Bail A. Thermo-physical assessment of bread during staling. LWT—Food Sci Technol. 2007;40(5):879–84.
2. Gray JA, BeMiller JN. Bread stalling: molecular basis and control. Compr Rev Food Sci Food Saf. 2003;2:1–21.
3. Curti E, Bubici S, Carini E, Baroni S, Vittadini E. Water molecular dynamics during bread staling by nuclear magnetic resonance. Lebensm-Wiss Technol. 2011;44(4):854–9.
4. Schiraldi A, Fessas D. Mechanism of staling: an overview. In: Chinachoti P, Vodovotz Y, editors. Bread staling. Boco Raton: CRC Press; 2001. p. 1–17.
5. Purhagen JK, Sjöö ME, Eliasson AC. Staling effects when adding low amounts of normal and heat-treated barley flour to a wheat bread. Cereal Chem. 2008;85(2):109–14.
6. Coultate T Food. The chemistry of its components. Cambridge: RSC Publishing; 2009.
7. Kerch G, Rustichelli F, Ausili P, Zicans J, Merijs Meri R, Glonin A. Effect of chitosan on physical and chemical processes during bread baking and staling. Eur Food Res Technol. 2008;226: 1459–64.
8. Kerch G, Glonin A, Zicans J, Merijs Meri R. A DSC study of the effect of ascorbic acid on bound water content and distribution in chitosan-enriched bread rolls during storage. J Therm Anal Calorim. 2011. doi:10.1007/s10973-011-1485-x.
9. Kerch G, Zicans J, Merijs Meri R. The effect of chitosan oligosaccharides on bread staling. J Cereal Sci. 2010;52:491–5.
10. Swanson CO. The physical properties of dough. Minneapolis: Burgess Publishing Co; 1943.
11. Vodovotz Y, Hallberg L, Chinachoti P. Effect of aging and drying on thermomechanical properties of white bread as characterized by dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC). Cereal Chem. 1996;73:264–70.
12. Eliasson AC. Differential scanning calorimetry studies on wheat starch—gluten mixtures: I. Effect of gluten on the gelatinization of wheat starch. J Cereal Sci. 1983;1(3):199–205.
13. Czuchajowska Z, Pomeranz Y. Differential scanning calorimetry, water activity, and moisture contents in crumb center and near-crust zones of bread during storage. Cereal Chem. 1989;66(4): 305–9.
14. Schiraldi A, Piazza L, Riva M. Bread staling: a calorimetric approach. Cereal Chem. 1996;73(1):32–9.
15. Jagannath JH, Jayaraman KS, Arya SS, Somashekar R. Differential scanning calorimetry and wide-angle X-ray scattering studies of bread staling. J Appl Polym Sci. 1998;67(9):1597–603.
16. Serventi L, Sachleben J, Vodovotz Y. Soy addition improves the texture of microwavable par-baked pocket-type flat doughs. J Therm Anal Calorim. 2011. doi:10.1007/s10973-011-1415-y.
17. Gliguem H, Ghorbel D, Grabielle-Madelmont C, Goldschmidt B, Lesieur S, Attia H, Ollivon M, Lesieur P. Water behaviour in processed cheese spreads DSC and ESEM study. J Therm Anal Calorim. 2009;98(1):73–82.
18. Puhr DP, D’Appolonia BL. Effect of baking absorption on bread yield, crumb moisture and crumb water activity. Cereal Chem. 1992;69(5):582–6.
19. Lu X, Cheng X, Sun Y. Study on the swelling behaviour of copolymer hydrogel. Chin J Polym Sci. 1986;2:134–41.
20. Le Meste M, Roudaut G, Davidou S. Thermomechanical properties of glassy cereal foods. J Therm Anal Calorim. 1996;47(5): 1361–75. doi:10.1007/BF01992833.
21. Rogers DE, Zeleznak KJ, Lai CS, Hoseney RC. Effect of native lipids, shortening, and bread moisture on bread firming. Cereal Chem. 1988;65(5):398–401.
22. Khorasanchi N, Peighambardoust SH. Effect of “sponge-and-dough” and “straight” dough preparation methods on dough properties and the quality of pan bread. J Food Res (Univ. Tabriz) Fall 2010-Winter. 2011;20/3(2):99–111.
23. Baik MY, Chinachoti P. Effects of glycerol and moisture redistribution on mechanical properties of white bread. Cereal Chem. 2002;79(3):376–82.
24. Hallberg LM, Chinachoti P. A fresh perspective on staling: the significance of starch recrystallization on the firming of bread. J Food Sci. 2002;67(3):1092–6.