

Application of Amylographic Method for Determination of the Staling of Bakery Products

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Abstract

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Staling is the general term that describes the time-dependent loss in quality of flavour and texture of bakery products after their baking and during storage. A modified amylographic method (viscometric measurement using the pro-mylograph) for rapid evaluation of the staling rate of fine sweet wheat bakery products were verified. In comparison with the standard method using an amylograph the modified amylographic method consisted in the measurement performed at a constant temperature curve. The staling of bakery products was followed for several days by viscometric measurement of crumb slurry, penetrometry measurement of crumb firmness, and evaluation of sensory properties of bakery products. A significant correlation between viscometric results and penetrometry was found.

Keywords: bread; aging; viscosity of slurry; viscometric measurement of crumb; penetrometry; sensory evaluation

Staling is a complex process that starts immediately after baking when products are cooled. It can be described as a common result of physical, chemical, and sensory changes affecting the consumer's acceptability of baked product. Retrogradation or recrystallisation of starch polymers is supposed to be the main reason for staling (BECHTEL *et al.* 1953 and others).

The three-dimensional structure keeping a shape of baked wheat product is based on the spatial network of protein macromolecules, and during baking the main part of water from dough is absorbed by starch polymers. At the temperatures higher than 60°C gluten gel is denatured and water is transferred to starch polymers and serves in its gelatinisation. Starch polymers are changed from the partly crystalline microstructure to the disordered one, mainly due to the migration of water molecules inside the structure. During cooling after baking, water starts to migrate back to its original partly crystal lattice (RONDA *et al.* 2011).

Sensory changes of baked products are caused by the loss of moisture in the crumb, and by the retrogradation of starch polymers. During cooling

water migrates to the crust and in part is lost by evaporation (GRAY & BEMILLER 2003). The crumb consequently hardens.

Different direct or indirect methods are used to study the staling of baked products (KARIM *et al.* 2000). Direct objective instrumental methods usually employed a deformation measurement by the compression of the crumb or penetration of a spherical or half-spherical body into the crumb (penetrometer, texturometer, Instron, etc.) (BAIK & CHINACHOTI 2000).

Three main types of indirect measurements are used: a study of changes of microstructure by means of electron microscope (ROJAS *et al.* 2000; BÁRCENAS *et al.* 2006) or transmission microscope (HUG-ITEN *et al.* 2001), measurement of crystal growth by means of roentgen diffraction (DRAGSDORF & VARRIANO-MARSTON 1980; SMITS *et al.* 1998; RIBOTTA *et al.* 2004), and measurement of changes of enthalpy during crystal growth (VODOVOTZ *et al.* 1996; BAIK & CHINACHOTI 2000).

Another method of indirect measurement of rheological changes of bread crumb during staling was

proposed many years ago. The basic idea is that the solubility of starch in the crumb depends on the part of starch gel which has not yet returned to a crystalline structure. Consequently, the viscosity of crumb suspension in water can be changed during staling (YASUNAGA *et al.* 1968). The amylograph is designed to measure the viscosity of starch or flour suspension and its changes during heating. It is in principle a rotational viscometer with the rather complicated geometry of measuring space (ICC Standard 126/1). The method described in International Standard is based on the recording of viscosity changes during the heating of a suspension up to a maximum consistency (“peak viscosity” by the authors YASUNAGA *et al.* 1968) of fully gelatinised starch. In the works mentioned, a standard amylographic curve was plotted with the peak viscosity under the heating of slurry. The peak viscosity of crumb decreased continuously during the post-baking storage of bread and was also decreased by additions of malt to the bread formula. Some other authors obtained seemingly contradicting results when either decreases (YASUNAGA *et al.* 1968) or increases (XU 1985) were found out in viscosity with storage times.

Bakery improvers such as enzymes (amylases, lipases, proteases, pentosanases), emulsifiers, hydrocolloids, and their blends serve as additives to improve technological (rheological) and texture properties of dough and slow down the staling of bread and bakery products (HUG-ITEN *et al.* 2003; BÁRCENAS & ROSELL 2005; JIANG *et al.* 2005; MOAYEDALLAIE *et al.* 2010; ROSELL & SANTOS 2010; PATEL *et al.* 2012, etc.). The addition of improvers (mostly in ppm amount) affects the standard quality of dough and bread and also the staling process of bread.

The aim of this study was to verify a modified amylographic method (viscometric measurement using a promylograph) for evaluation of the staling process of fine sweet wheat bakery products. These results were compared with those of conventional methods such as penetrometry and sensory evaluation. Three different dough improvers were used with the purpose to prepare baked samples with different crumb quality and different staling rate. Staling rate means the changes of the crumb structure (crumb firming) over time.

MATERIAL AND METHODS

Fine sweet wheat loaves were made using the formula: white wheat flour T530 (100 kg) (MILLBA-

CZECH Ltd., Mlýn Louny, Louny, Czech Republic), fat (Favorit A, commercial margarine with 82% of fat) (18 kg) (KaKa CZ, Jeneč, Czech Republic), sugar (saccharose) (16 kg) (Tereos TTD, Ltd., Cukrovar Dobruška, Czech Republic), solid compressed yeast (standard commercial fresh bakery yeast *Saccharomyces cerevisiae*) (5.5 kg) (Lesaffre Česko, Olomouc, Czech Republic), powder dough improver (1.5 kg) (Mlýn Louny, Czech Republic), salt (1.2 kg) (K+S Czech Republic, Olomouc, Czech Republic), water (45 l).

Characteristics of the wheat flour used: moisture content (12.1% w/w), ash content (0.57% w/w, in dry matter – DM), wet gluten content (35% w/w), falling number (278 s), farinographic absorption (58.5% v/w). Three types of dough improvers were used (labelled A, B, V) with different effectiveness on crumb quality and staling. The improver A consisted of wheat flour (Mlýn Louny), emulsifier (LAMETOP 500), ascorbic acid, and the enzymes xylanase and lipase (Nutrilife EM-U), amylase (Nutrilife AM 17; all BASF, Ludwigshafen, Germany) and protease. The improver B consisted of wheat flour (Mlýn Louny), emulsifiers (LAMETOP 500 and Nutrisoft 55), ascorbic acid, and the enzymes xylanase and lipase (Nutrilife EM-U) and amylase (Nutrilife AM 17). The improver V consisted of wheat flour (Mlýn Louny), emulsifier (DATEM; BASF, Ludwigshafen, Germany), ascorbic acid, and the enzymes xylanase (Nutrilife CCX 10), amylase (Nutrilife AM 17), and glucose oxidase. The components of each improver are shown in descending order, and the exact amount of each component in the used improver is a part of the know-how of the mill and bakery MILLBA-CZECH. All components of improvers were provided by the producer Donauchem (Nymburk, Czech Republic). Components were added to wheat flour in the mill (Mlýn Louny).

Sweet loaves were made at the standard bakery plant (based on the Internal Standard of MILLBA-CZECH bakery). All the ingredients were homogenised in a spiral kneader (DIOSNA, Osnabrück, Germany) for 11 minutes. Ripening time of dough was 5 min (31°C, 80% humidity). Final proofing time was 65 min after shaping on an industrial roller and topping. Dough pieces were baked at 220°C for 13 minutes. After cooling the baked loaves were wrapped in polyethylene bags, stored at room temperature and analysed. The staling of cooled fine sweet loaves was evaluated by viscometric method, sensory evaluation and penetrometry.

Modified method for the measurement of staled crumb viscosity. The staling of fine sweet loaves was

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examined in order to test the method. In our work we measured the gelatinisation of crumb slurry with T2-E promylograph (Max Egger, St. Blasen, Austria), which was based on the entirely same principle of measurement as amylograph (ICC Standard 126/1). The method for the measurement of staled crumb viscosity using a promylograph was developed by the authors on the basis of series of experiments on a laboratory scale and also in an industrial bakery plant. The modified amylographic method demonstrated the characteristics of starch polymers at a constant temperature rate (30°C) while YASUNAGA *et al.* (1968) showed the pasting characteristics of starch in baked bread at an increasing temperature.

60 g of fresh or staled crumb from the central part of fine sweet loaves was mixed with 145 ml of water (30°C) in the mixer bowl for 1 min to make a homogeneous suspension (slurry). The mixer slowest speed should be used to avoid slurry foaming. The slurry was placed into a rotating bowl with the pins fixed inside. Measuring head with the pins was immersed into slurry. Depending on slurry viscosity, the measuring head was turned and the angle of turning was proportional to viscosity. The viscosity of crumb slurry was recorded at the constant temperature of 30°C in empirical units of promylograph (PE) for 10 min of constant mixing and the highest value (maximum on the curve) was shown on display. The changes of crumb viscosity of fresh and stale loaves were drawn in diagrams depending on the time of storage in hours. Viscometric results were expressed as means of duplicate analysis and evaluated using the T2-E promylograph software (based on Instructions for Measurements with Max Egger Promylograph Apparatus, St. Blasen, Austria).

Penetrometry. The crumb firmness was measured on a penetrometer (PNR-12; Petrotest Instruments, Dahlewitz, Germany) during staling. The higher the penetration depth of the crumb, the slower the staling process. Penetrometry instructions were based on the producer's Petrotest Instruments (http://www.imeth.ch/downloads/petrotest-98-1301_pnr.pdf). Results of penetrometry crumb firmness were expressed as means of quadruple analyses.

Sensory evaluation. A panel of 7 skilled persons (3 women, 4 men) evaluated sensory changes during the storage of fine sweet loaves. Skills of the panellists were verified by an accredited laboratory at University of Chemistry and Technology (UCT) in Prague. Sensory evaluation was carried out based on internal methodology of UCT in Prague and MILLBA-CZECH

(KADLEC *et al.* 1986). Complex properties of loaves as well as crumb consistency parameters (toughness, chewiness, etc.), taste and flavour were tested using a hedonic scale that can reach maximum 100 points in total. The results were presented as mean value for each parameter obtained from 7 panellists.

Statistical analysis. In order to compare the predictive ability (relationships) of tested methods of staling evaluation and to emphasise the importance of modified amylographic method, correlation coefficients between obtained data of promylograph and penetrometry, promylograph, and sensory evaluation, and also sensory evaluation and penetrometry were calculated. Correlation analysis was performed by means of Microsoft Excel 2010 (Microsoft Windows, Tulsa, USA) on a significance level of 0.01% and 0.05%. Moreover, error bars with standard deviations for all data points of promylograph, penetrometry and sensory evaluation were calculated by Microsoft Excel 2010.

RESULTS AND DISCUSSION

The measurements of crumb viscosity, crumb firmness and sensory parameters of bakery products were carried out every 4 h during 80 hours. The results are shown in Figure 1 for bakery products with improvers A, B, V, respectively.

In general, penetrometry and modified viscometric measurements using a promylograph describe the physical nature of staling process, these methods describe changes in starch gels and changes in mechanical properties of the crumb over time. Specifically penetrometric changes reflect mainly the hardness and toughness of the crumb structure and they can significantly depend on the proportion of gelatinized and recrystallised starch. Also changes of viscometric measurements of the crumb slurry without heating depend on the proportion of starch gels and crystals during staling.

As seen in Figure 1, both curves from penetrometer and promylograph showed considerably more significant changes during the staling of bakery product. In most cases the staling rate was higher up to approx. 30 h (a little more with improver V). It was due to the specific composition of improver V (different emulsifier as compared to improver A and/or B). The emulsifier DATEM (as a component of the improver V) is a hydrophilic, anionic, highly effective emulsifier. DATEM has excellent stabilising properties

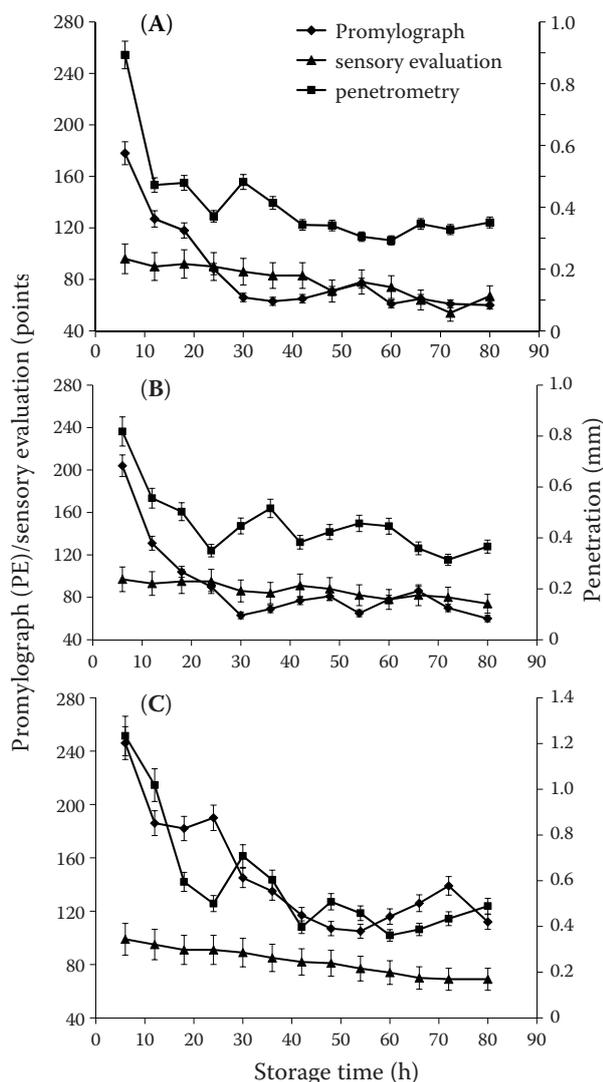


Figure 1. Changes of viscometric values (promylograph, units PE), firmness values (penetrometry, in mm), and sensory evaluation (scores) of the crumb during storage: (A) Improver A, (B) Improver B, and (C) Improver V

of emulsion; it is able to stabilise the starch-protein complex. It is one of the best antistaling components (STAMPFLI & NERSTEN 1995; PŘÍHODA *et al.* 2003; MOAYEDALLAIE *et al.* 2010). Consequently, the crumb of bakery products with DATEM addition remained smooth and soft for a longer time.

Besides DATEM, the enzymes like amylases and xylanases had a significant effect on the staling of bakery products from a practical point of view. Amylases may release high amounts of low molecular weight dextrans, which influence the staling process (LIN & LINEBACK 1990; MARTIN & HOSENEY 1991). Dextrans interfere with the ability of amylopectin retrogradation and interfere with protein-starch

interactions (HAROS *et al.* 2002). Xylanases strongly affect the arabinoxylan fraction of flours, and arabinoxylans are known by their high influence on staling. Xylanases transform water-insoluble arabinoxylans into a soluble form which binds water in dough and also in the crumb of final bread and bakery products (BUTT *et al.* 2008). The other non-starch components of improvers had a negligible influence on staling.

The curves obtained using both penetrometric and modified amylographic (promylograph) assessments represented the changes of physical properties of the crumb during staling. The curve obtained by promylograph demonstrated these changes more appositely compared with penetrometry. The curves also suggested a good and comparable possibility to differentiate between the effects of improvers on the staling rate and final degree of recrystallized starch polymers. The improver V showed the best results as already mentioned.

The results obtained from promylograph and penetrometry were in accordance with those from scan electron microscopy and roentgen diffraction (SLUKOVA *et al.* 2014). It supported results presented in this work and the main purpose of this work that the application of promylograph could be a commonly available simple way of rapid determination of the staling of bakery products.

Promylograph, as an alternative of amylograph, is a common rheological device used in mill and bakery laboratories especially in Czech Republic, Austria, Slovak Republic, and Hungary. The obtained results from promylograph and amylograph are comparable (PŘÍHODA *et al.* 2003). So the proposed modified viscometric measurements of the crumb using a promylograph could be acceptable for operational purposes of rapid and practicable evaluation of bakery product staling.

Sensory evaluation reflects the wider aspects of bakery product quality in comparison with penetrometry and viscometric measurement. Specifically, sensory evaluation covers both textural parameters and characteristics (such as toughness, hardness, and chewiness), and also the taste and flavour of bakery products. Moreover, the significant and conclusive results of sensory evaluation highly depend on stable evaluation conditions, certified panellists etc.

The decrease of sensory quality was almost linear during the storage period of analysed bakery products (Figure 1). In regard to the complex quality assessment of bakery products, neither crumb properties nor sensory evaluation were proved as predictive methods for determination of staling.

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Table 1. Correlation coefficients between the results of different methods (viscometric measurements using promylograph, penetrometry, sensory evaluation) describing the crumb staling for three used improvers ($n = 13$, critical value 0.684 for $\alpha = 0.01$; critical value 0.553 for $\alpha = 0.05$)

Relation	Improver		
	A	B	V
Promylograph vs penetrometry	0.879	0.857	0.812
Promylograph vs sensory evaluation	0.685	0.677	0.802
Sensory evaluation vs penetrometry	0.620	0.528	0.785

Error bars obtained from promylograph, penetrometry and sensory evaluation data are shown for each of the improvers in Figure 1. The correlation coefficients between the results of promylograph and penetrometry, promylograph and sensory evaluation, and also sensory evaluation and penetrometry are shown for each of the improvers in Table 1. The correlation coefficient between the results of modified amylographic method (promylograph) and penetrometry was high, in all cases with the coefficients considerably higher than the critical value for the significance level of 0.01%.

CONCLUSION

The method of viscometric measurements of crumb slurry in water using a promylograph was confirmed as a sufficiently rapid method for the evaluation of bakery product staling. Different recrystallization rate of starch polymers could be estimated based on the results of the measurement. Results of viscometric measurements were in strong correlation with results of penetrometry; the dependence of these results was proved. It follows that the modified amylographic method could be used as a simple alternative method to penetrometry for the evaluation of bakery product staling.

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