

## ACTIVITY OF WATER IN STALING BREAD

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**Summary.** The effect of storage on wheat-rye bread was investigated using water activity and dynamic mechanical analysis. The time course of changes in the water activity in bread crumb in the process of staling reflects the occurrence of spatial cross-linking of the macromolecular components of bread crumb from the amorphous regions and the effect of restructuralisation of starch spherulites disintegrated in the process of baking. The above mechanisms have considerably different kinetics. The time constant of the initiation of connections in the amorphous phase is over 6h, whereas the time constant of the recrystallisation process reaches about 90 h. The postulated changes in the bread crumb structure are reflected in the time evolution of the dynamic mechanical properties of bread.

**Keywords:** bread, staling, water activity, DMA.

### INTRODUCTION

The bread crumb contains from 80 to 85% of water, which is necessary to ensure the optimum course of starch gelatinisation and denaturation of gluten on baking, and to ensure a desired elasticity of bread crumb. The mechanism of formation of the molecular structure of bread has been relatively well recognised [1] and is based on the disappearance of the crystalline structure of starch spherulites in temperatures above their melting point and at the presence of water in the amount sufficient for complete hydration of starch chains. Moreover, on baking gluten proteins undergo denaturation and linear molecules of amylose diffuse from the zone of spherulites into the amorphous region of the crumb. Large and branched macromolecules of amylopectins undergo a local phase transition to the disordered phase in which the microfibriles formed by the

branches are disintegrated and the bihelical structures characteristic of starch polymers are unfolded. Because of a very high viscosity in the region, the diffusion transportation of amylopectine molecules outside the original location of the spherulites is very limited in few–minutes duration of the baking process.

The water relations in the dough before and during the baking process are assumed as follows. The native starch in temperatures below the gelatinisation point can bind about 30% of water, the remaining amount is bound by gluten, although its concentration in flour does not exceed several per cent. On the process of baking, denaturation of gluten proteins and starch gelatinisation force water transportation towards polysaccharide components. It is reasonable to assume that in the process of bread staling, which involves mainly starch recrystallisation by way of gradual reappearance of spherulites, the water transportation will take place in the opposite direction. However, as the sorption capacity of the amorphous phase [built of denatured gluten and amylose extracted from the spherulites] has changed in the meantime, the effect of water evacuation from the region of recrystallising spherulites can be manifested as changes of the water activity in the system. Therefore, a study has been undertaken to determine the changes in water activity in the crumb of bread in the process of staling. The results were expected to bring more information about the molecular mechanisms of staling and the possibility of controlling bread quality and durability.

#### MATERIAL AND METHODS

The material studied was commercial wheat-rye bread (70:30). One hour after the end of baking, from the middle part of the bread crumb cylindrical samples were cut out for measurements of water activity ( $A_w$ ) and rectangular samples – for mechanical measurements. The cylindrical samples were cooled down to 23°C, and to prevent water evaporation were placed in polyethylene ziploc bags. The samples were kept in the bags for 2 hours to ensure the resorption of water vapour condensed on the bread crumb as a result of its cooling. The bread samples for farther mechanical studies were sterilised by ethanol aerosol and stored in hermetic polyethylene bags.

The water activity in staling bread crumb was measured by MMAW-4 apparatus with a thermostated measuring chamber and forced air circulation. The cooled and sterilised by ethanol aerosol cylindrical samples 1 cm in height and 4 cm in diameter were placed in a hermetically closed chamber of the apparatus for the whole time of the experiment. The process of staling was conducted in the

static atmosphere conditions. The forced air circulation was turned on only for the time of 15 minutes when the water activity was registered at a given stage of the staling process.

Measurements of the mechanical properties of the bread crumb were performed in the system of dynamical-mechanical analysis (DMA) using the method of free vibrations in the system of reversed torsional pendulum [2]. The upper and lower ends of rectangular samples size  $8\text{cm} \times 1\text{cm} \times 1\text{cm}$  were mounted in a movable and immovable clamp, respectively, in the termohygrostatic cell of the measuring system. The angle of the initial rotation of the sample did not exceed  $15^\circ$ . The damping decrement was measured and the period of vibrations was recorded electronically with an accuracy to  $10^{-4}$  s. On the basis of the relations between the parameters of the measuring system, parameters of the sample, periods of vibrations and dumping decrements of the system with and without the sample, we could calculate the dynamic shear modulus ( $G_f$ ) and tangent of loss ( $tgD$ ) for the samples at different stages of the process of staling.

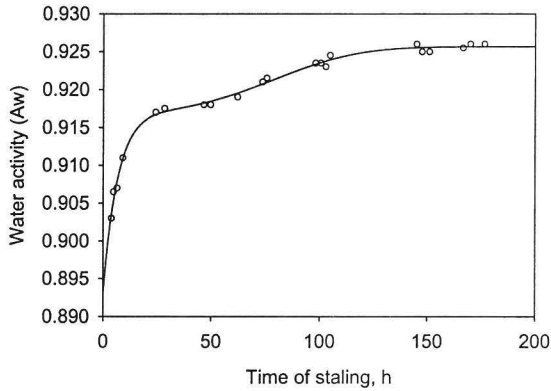
## RESULTS AND DISCUSSION

An exemplary course of changes in the water activity in wheat-rye bread crumb in the process of staling at  $23^\circ\text{C}$  observed on a period of 200 hours, is presented in Fig. 1. As follows from the figure, the water activity increases from  $A_w \sim 0.9$  to over 0.925. A preliminary analysis of the water activity changes has shown that it can be approximated by a superposition of the two kinetic functions type:

$$F_i = A_i + D_i \left\{ 1 - \exp \left[ - \left( \frac{t}{\tau_i} \right)^{m_i} \right] \right\} \quad (1)$$

with a different value of the exponent  $m$ . The two functions correspond to the theory of crystallisation kinetics proposed by Avrami [3,4,5]. The equation with the exponent  $m = 3$  describes a process of formation of three-dimensional crystalline structures, whereas that with  $m = 1$  can describe the stage of nucleation of the crystalline phase or the stage of growth of the ordered one-dimensional structures.

The component of the  $F(t)$  dependence described by the equation with  $m = 1$  could correspond to the processes of water release as a result of nucleation of bonds between the chains of macromolecules in the amorphous phase of the bread crumb or as a result of resprialisation of these molecules indicating the one-dimensional ordering of the structure. However, according to the NMR results [6],



**Fig. 1.** Course of changes in the water activity in wheat-bread crumb in the process of staling at 23°C.

relatively weak hydrogen bonds, with no significant water release. Thus, interpretation of the effect of the water activity increase in breadcrumb at the beginning stage of staling process demands a more advanced theoretical analysis.

It can be shown that according to the thermodynamical theory of polymer solutions proposed by Flory [7], in the systems in which interchain connections may develop into a spatial network, the solvent activity can be described by:

$$Aw_{am} = \exp \left\{ \ln(1 - v_2) + v_2 + \chi_1 v_2^2 + V_1 n_j \left( \frac{f v_2^{-2/3}}{2} - 1 \right) \right\} \quad (2)$$

where  $v_2$  – the volume contribution of the polymer in the system,  $\chi_1$  – a parameter describing interactions between the solvent and the polymer,  $V_1$  – molar volume of the solvent,  $n_j$  – the number of interchain connections in a unit volume of the system,  $f$  – functionality of these connections.

The fourth term of the above equation represents an excess of the chemical potential of the solvent following from the elastic response of the macromolecular spatial network. The above relationship implies that an increase in the concentration of the connections among the chains ( $n_j$ ) should lead to a proportional increase in the values of  $\ln(Aw)$ .

In the process analysed we can also expect the release of water previously bound in the disordered spherulites of starch, and later evacuated as a result of crystallisation of these spherulites. As it has been shown for simple systems the water activity can be described by an exponential function of the contribution of free water in the system [8].

in the first stage of the process of staling the relaxation rate  $R_1$  exponentially increases with a time constant of a few hours, while an increase in the water fraction should lead to a decrease in the relaxation rate. Therefore, the observed increase of  $R_1$  as a function of the time of staling can result directly from the changes in molecular dynamics involving the formation of a polymer spatial network stabilised by

Fig. 2 presents the changes in the water activity in the semi-logarithmic coordination system to obtain linear dependencies of the water activity on the degree of cross-linking of the amorphous regions and the degree of crystallisation of the regions undergoing recrystallisation.

The course of the water activity in the first phase of the staling process can be described by the Avrami equation with  $m = 1$ . The constant of the cross-linking in the amorphous phase takes a value of  $\tau_{am} = 6$  h, which is close to that obtained by the NMR method [6].

The reconstruction of the three-dimensional crystalline structures is manifested as the appearance of the component described by the equation with  $m = 3$ . The time constant of the process of starch recrystallisation takes a value of  $\tau_c = 90$  h and is comparable with the results reported by other authors [1,6].

The results of DMA measurements have proved to be well correlated with the course of changes in the water activity in the bread crumb studied. The curve illustrating changes in the dynamic shear modulus  $G_I$  (Fig. 3) in the time period corresponding to the time constant of the process of recrystallisation reveals an inflection point, evidencing the strengthening of the breadcrumb structure at this stage of the staling process.

The above postulated effect of fast cross-linking of amorphous regions in the initial phase of staling was not manifested in the measured values of  $G_I(t)$ . This fact may

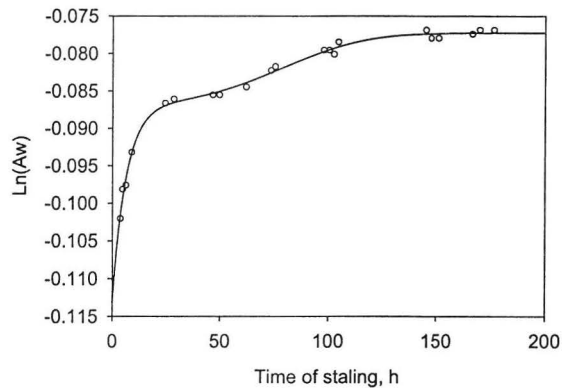


Fig. 2. The changes in the water activity in staling bread in the semi-logarithmic coordination system.

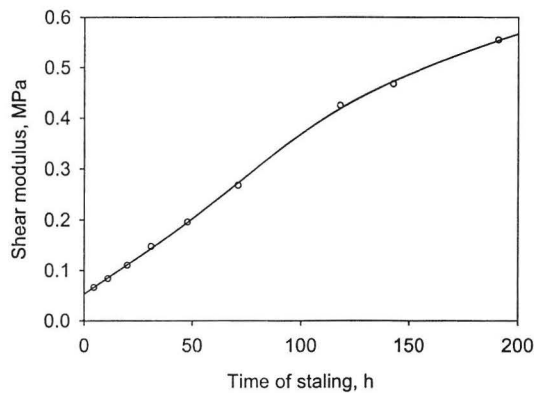
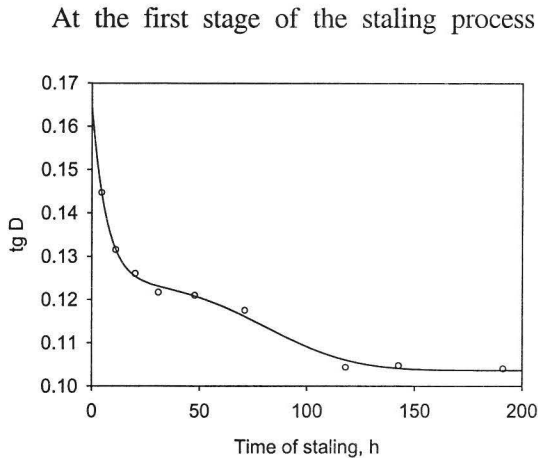


Fig. 3. The time changes in the dynamic shear modulus of staling bread.

indicate a low energy of the initial connections with the involvement of a small number of hydrogen bonds, undergoing dissociation as a result of the applied stress. A gradual increase of the elasticity modulus at the subsequent stages of the staling process suggests that these connections can be strengthened for instance by formation of bihelical associations. No notable correlation between this effect of strengthening of the connections and the changes in the water activity, implies that the number of connections ( $n_j$  in eq. 2) formed at the first stage of the staling process, does not change at the subsequent stages. The above interpretation has been confirmed by the results of the internal friction measurements (Fig. 4).



**Fig. 4.** The time changes in the internal friction of staling bread.

At the first stage of the staling process the values of  $tgD$  fast decrease in correlation with the course of the cross-linking process in the amorphous regions observed in  $Aw(t)$  measurements. The effect of strengthening of the connections formed manifested on the curves  $G_I(t)$  is not reflected in the measurements of internal friction and only recrystallisation of spherulites and the appearance of the regions of a diminished ability to dissipate mechanical energy, are responsible for a significant decrease of  $tgD$ .

## CONCLUSIONS

The time course of changes in the water activity in bread crumb in the process of staling reflects the occurrence of spatial cross-linking of the macromolecular components of bread crumb from the amorphous regions and the effect of restructuring of starch spherulites disintegrated in the process of baking. The above mechanisms have considerably different kinetics. The time constant of the initiation of connections in the amorphous phase is over 6 h, whereas the time constant of the recrystallisation process reaches about 90 h. The postulated changes in the bread crumb structure are reflected in the time evolution of the dynamic mechanical properties of bread as a function of the time of staling.

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## AKTYWNOŚĆ WODY W CZERSTWIEJĄCYM PIECZYWIE

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**Streszczenie.** Zjawisko czerstwienia pszenno-żytniego pieczywa zbadano metodami analizy aktywności wody oraz analizy dynamiczno-mechanicznej. Czasowy przebieg zmian aktywności wody w miękiszu czerstwiejącego pieczywa odzwierciedla zjawisko przestrzennego sieciowania wielkocząsteczkowych składników miękiszu, zlokalizowanych w obszarach amorficznych oraz efekt odbudowy sferolitów skrobi dezintegrowanych w procesie wypieku. Wymienione mechanizmy odznaczają się zasadniczo różnymi kinetykami. Stała czasu inicjacji połączeń w fazie amorficznej przekracza 6 godz., natomiast stała czasu rekrytalizacji sferolitów osiąga 90 godz. Postulowane zmiany w strukturze miękiszu pieczywa znajdują odzwierciedlenie w zmianach czasowych właściwości dynamiczno-mechanicznych pieczywa.

**Słowa kluczowe:** chleb, czerstwienie, aktywność wody, DMA.