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APPLICATION OF MECHANICAL SPECTROSCOPY IN INVESTIGATIONS OF BREAD STALING AND STARCH RETROGRADATION

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In a study of the mechanical relaxation spectra of bread crumb and gelatinized starch, relaxation times of practical interest, i.e. from 1 s to 20 s, were found in the region of the plateau of the spectra. The relaxation intensity in this region is conditioned by the concentration of polymer-chain sections in a space network which makes it possible to calculate the average molecular mass (M_s) of the polymer network sections. A decrease of the M_s value of both bread crumb and starch gels may be attributed to a building of the sections monomers in orderly regions as well by a formation of new points of intersection associations.

In normal conditions the bread crumb may be considered to be an oversaturated starch and protein solution. From the point of view of thermodynamics the aggregation of macromolecular bread components in such a case seems to be an inevitable process.

On the basis of investigations carried out with the use of different methods Cornford et al. (1964), Mc Iver et al. (1968), Wilhoft (1973) and Wright (1971) suggest that the increase of the crystallinity level of the tested system is an evidence of the aggregation process.

It is generally agreed that the increase of crumb firming is the most important symptom of bread staling. This increase depends directly on the structure changes of the amorphous regions of the investigated material.

The distribution function of the molecular mass of the polymer network sections is the fundamental parameter of the structure of these regions. The study of the molecular phenomena taking place in bread staling and starch retrogradation processes requires the use of suitable

analytical methods measuring the structure changes of amorphous regions of bread and starch gels. One of the most efficient methods is mechanical spectroscopy.

EXPERIMENTAL

The mechanical spectroscopy (Eisenberg 1973, Perepechko 1975, Muzayama 1978) is based on the measurement of mechanical relaxation in the polymer system. With the change of temperature and frequency of the stress field, a maximum, minimum and plateau of the spectra of mechanical relaxation time of the polymer system were observed. This is a reflection of the composition and structure of the tested material. It is well known from the molecular theory of mechanical relaxation (Ferry 1969) that the distribution function $\varphi\,(M_s)$ of molecular mass of the polymer network sections is connected with the mechanical relaxation in the plateau of the spectra. The relaxation intensity can be expressed as follows:

$$H(\tau) = \frac{cRT}{\langle M_s \rangle} \int_0^\infty \sum_{p=1}^n \tau_p \delta(\tau - \tau_p) \cdot \varphi(M_s) dM_s \qquad (1)$$

where: c — concentration of polymer, R — gas constant, M_s — molecular mass of network sections, T — absolute temperature, τ — relaxation time, $\delta(\tau-\tau_p)$ — step function.

The spectrum of relaxation time $H(\tau)$ may be determined by measuring the real (J') and imaginary (J'') part of the complex compliance $(J = J'-J'')$ of the system.

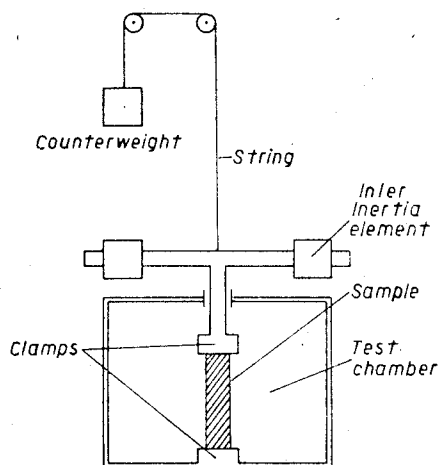The above mentioned mechanical compliance was recorded in this

Fig. 1

study by a very precise dynamic method of inverted torsion pendulum (Fig. 1).

The measuring device was built according to the authors own idea on the basis of the well-known general principle of mechanical spectroscopy (Eisenberg 1973, Perepechko 1975, Muzayama 1978). Visual readouts were made. The introduction of sensors (pick up) caused distortion in the distribution of unrestrained pulsation.

Samples were slender pieces of experimental material of a square cross-section (10×10 mm), mounted stiff in the measuring device.

To determine J' i J'' for the sample being investigated on that pendulum, it is necessary to measure the frequency (v_1) and logarithmic decrement (Δ_1) of the oscillating system with the sample and the same parameters of the system without the sample (v_2, Δ_2): Then

$$J' = 4\pi^2 I^{-1} C^{-1} \left\{ v_1^2 \left(1 - \frac{\Delta_1^2}{4\pi^2} \right) - v_2^2 \right\}^{-1} \qquad (2)$$

and

$$J'' \cong 4\pi I^{-1} C^{-1} \left\{ v_1^2 \left(1 - \frac{\Delta_1^2}{4\pi^2} \right) - v_2^2 \right\}^{-2} \times (v_1^2 \Delta_1 - v_2^2 \Delta_2) \qquad (3)$$

where: I — moment of inertia of the oscillating system, c — shape factor.

For rectangular samples (Timoshenko, Goodier 1951) when the ratio width (b) and thickness (a): $\frac{b}{a} \leqslant 1,2$; c may be calculated from the approximative relation:

$$c = \frac{1}{0,13 \left(1 + 0,0815 \frac{b}{a} \right) a^2 b^2} \qquad (4)$$

l — length of sample

RESULTS AND DISCUSSION

In the case of wheat — rye bread crumb and concentrated wheat starch gels investigated in this study, relaxation times of practical interest, i.e., from 1 s to 20 s were found in the region of the plateau of the spectra and remained in this region irrespective of the aging progress. Figure 2 shows that the relaxation intensity ratio at $\tau = 1$ s and at $\tau = 20$ s equals 1 and does not change during the aging of bread.

Experimental results obtained in this study show that the temperature — time superposition principle (Ferry 1969) can not be applied for the examined polymer systems. It offers no possibilities for a precise determination of changes in the distribution function of the polymer
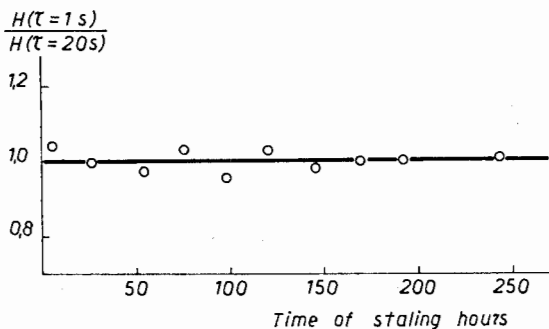
Fig. 2

network sections. It was stated, however, that the determination of change of average molecular mass $\langle M_s \rangle$ of these sections was possible.

The following simple relation, which originates from equation [1], makes it possible to calculate the M_s value for concentrate porous gels:

$$\langle M_s \rangle = \frac{1000\rho}{1+w_o} \cdot J'(\tau_{pl})RT \qquad (5)$$

where: ρ — density of sample, w_o — moisture content d.b., $J'(\tau_{pl})$ — real part of complex compliance of sample subjected to the action of periodical shear stress changes with the frequency corresponding to the plateau region of the relaxation spectrum.

Fig. 3 shows exemplary changes of the average molecular mass of the polymer network sections in the wheat starch gels and wheat — rye bread crumb aging at 20°C and examined about 0,2 Hz.

The changes $\langle M_s(t) \rangle$ can be satisfactory described in both cases by the same empirical equation:

$$\langle M_s \rangle = \left\{ \frac{1}{M_o} + \left(\frac{1}{M_\infty} - \frac{1}{M_o} \right) \left(1 - \frac{t}{e\nu} \right) \right\}^{-1} \qquad (6)$$

where: ϑ — time constant, M_o and M_∞ — limit values of $\langle M_s \rangle$ when $t \to 0$ and $t \to \infty$.

Similar dependences $\langle M_s(t) \rangle$ found for bread crumb and starch gel of approximately 50% moisture content tend to confirm the role of starch retrogradation as the major factor in bread staling (Jankowski 1973).

The observed decrease of the $\langle M_s \rangle$ value can be caused by a building of section monomers in orderly regions as well by a formation of new points of intersection associations of the starch macromolecules. The first of these processes corresponds to the growth of crystallites from instantaneous nuclei and the relation formulated in equation 3 can be
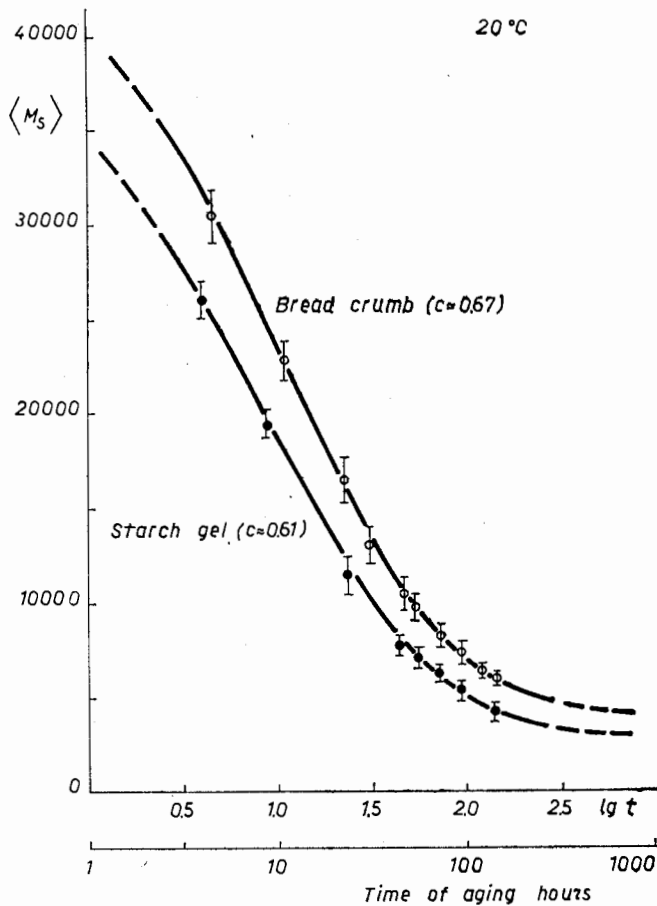
Fig. 3

obtained assuming that the crystallisation kinetics can be described by the theory of Avrami (1941). Equation 3 can be also obtained by means of theoretical considerations assuming that the factor causing a decrease of $<M_s>$ is the formation of new joints that do not constitute crystallization centres. The consideration of these joints between the polymer network sections is proportional to the reciprocal of the molecular mass of the sections: $n \sim M_s^{-1}$.

An explanation as to which of the afore-mentioned processes plays a greater role in bread staling requires further research. Such research is now being carried out with the use of the mechanical spectroscopy method.

As can be seen from the results of introductory investigations, the application of this method may contribute to an explanation of the nature of the molecular processes of bread staling.

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ZASTOSOWANIE SPEKTROSKOPII MECHANICZNEJ W BADANIACH CZERSTWIENIA CHLEBA I RETROGRADACJI SKROBI

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Streszczenie

W pracy badano zjawisko relaksacji mechanicznej miękiszu chleba i stężonych żeli skrobiowych. Ważne z praktycznego punktu widzenia czasy relaksacji, tzn. od 1 s do 20 s zlokalizowano w płaskiej strefie widma relaksacji mechanicznej. Intensywność relaksacji w tym obszarze jest kontrolowana przez stężenie segmentów makrocząsteczek tworzących sieć przestrzenną. Powyższy fakt umożliwia obliczenie średniej masy cząsteczkowej (M_s) tych segmentów. Analiza zmian widm relaksacji mechanicznej starzejącego się miękiszu chleba i żelu skrobiowego wykazuje systematyczny spadek wartości (M_s). Obserwowane zmiany mogą być wywołane zarówno wbudowaniem monomerów segmentów w obszary uporządkowane, stanowiące węzły sieci przestrzennej, jak i tworzeniem się nowych punktów połączeń międzysegmentalnych.