served was identical with that used for detection of irradiation in bone and eggshell by the EPR method. This signal is specific for hydroxyapatite that appears in some extent in exoskeletons of shrimps and crabs. However, the results of model studies on these products were not reliable enough. For that reason, crustacea are not quoted until now in European Standard EN 1786 among food products that can be examined by EPR method to prove their irradiation [3]. The most reliable results have been obtained with lobsters [4]. The results of the examination of various crustacea species indicated that the EPR signal is more or less influenced by the variety, origin and age of crabs.

Nowadays, the Laboratory for Detection of Irradiated Food has more and more orders for detection of irradiation in shrimps. Part of them are delivered in cuticles. A method adapted to accomplish the detection of irradiation in shrimps is a thermoluminescence measure. However, the analytical procedure is much time-consuming and needs several days to receive the final result.

The aim of present study was to prove, whether the EPR examination of cuticles taken from shrimps could be used as a screening method for the detection of irradiation in this product. The earlier results obtained with irradiated cuticles of shrimps only seem promising [5].

In a model study commercial shrimps were irradiated in a $^{60}Co$ source with doses of 1, 3 and 7 kGy. The technological dose recommended for microbial decontamination of shrimps is between 3 and 7 kGy.

Cuticles taken from the shrimp body were cleaned, dried and subsequently crushed to small pieces to be measured by the EPR method. The resultant spectra recorded with cuticles irradiated with 3 and 7 kGy are shown in Fig.1. The positions of coefficient g (spectroscopic splitting factor), specific for irradiated hydroxyapatite, are marked with arrows. The signal is a singlet of axial symmetry with $g_x$=2.0035, $g_y$=1.9973 and $g_z$=2.0017, respectively.

The positions of all three g's in the magnetic field are easily distinguished in the spectrum of cuticle irradiated with 7 kGy (Fig.1b). However, in the spectrum of cuticle irradiated with 3 kGy the positions of $g_z$ and $g_x$ are not very well defined although the experienced EPR operator can establish them with a precision which could be perhaps satisfactory enough for identification of radiation treatment (Fig.1a).

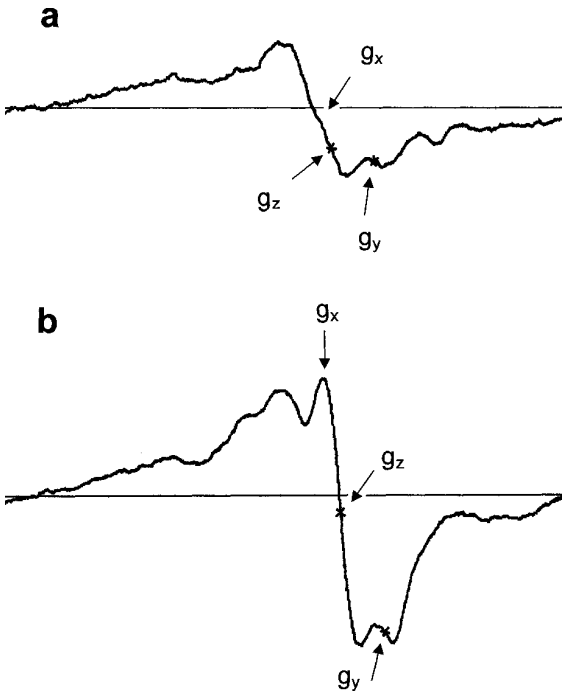


Fig.1. The EPR spectra (first derivatives) recorded with cuticles taken from shrimps irradiated with 3 kGy (a) and 7 kGy (b). The positions of g values specific for irradiated hydroxyapatite are marked with arrows: $g_x$=2.0035, $g_y$=1.9973, $g_z$=2.0017.

In conclusion, it can be postulated that the EPR measurement of cuticles of shrimps can be adapted in the Laboratory as preliminary, screening test proving the irradiation of shrimp. It has to be stressed, however, that the lack of a specific, hydroxyapatite born EPR signal in the spectrum cannot suggest that sample was not irradiated.

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# DSC STUDIES OF RETROGRADATION AND AMYLOSE-LIPID TRANSITION TAKING PLACE IN GAMMA-IRRADIATED WHEAT STARCH

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The course of gelatinisation and retrogradation occurring during heating of starch and flour suspensions depend on the structure of starch granules. In the case of wheat flour, retrogradation depends additionally on the presence of lipids. In fact, binding of lipids to the polysaccharide chains was found to resist recrystallisation of starch gels.

Our previous studies have shown that degradation resulting from gamma irradiation induces a decrease in order of starch granules [1,2] and

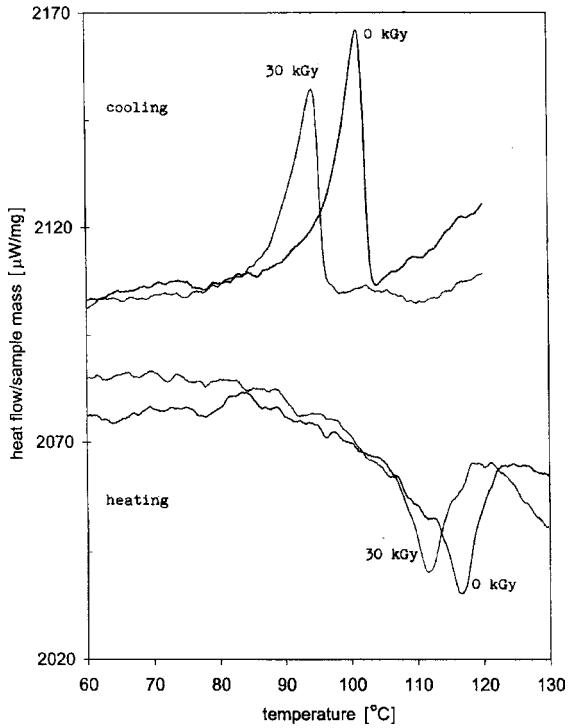


Fig. Comparison of the amylose-lipid transition endothermal effects recorded during the third heating and exothermal effects, observed during the third cooling in the case of the dense (50%) suspensions. Heating and cooling were performed with a rate of 10°C/min.

influences gelatinisation taking place during heating of starch and flour suspensions [3-7]. It was also found that modification in lipids surrounding brought about by gamma irradiation affect amylose-lipid complex transition taking place in wheat starch and wheat flour [3-6]. In particular, an essential decrease in transition temperature was found after irradiation performed with a dose of 30 kGy. Furthermore, our preliminary results have demonstrated that differences in storage effects on the irradiated and non-irradiated wheat starch and flour gels and might result in the expanded differences in the amylose-lipid structure formed in such gels.

At present, DSC (differential scanning calorimetry) studies were continued for wheat starch, non-irradiated and irradiated using doses in the range from 5 to 30 kGy. The influence of the conditions applied during DSC measurements on the possibility to observe differences between the amylose-lipid complex transition and retrogradation taking place in the non-irradiated and particularly irradiated starch samples was checked. Special interest was given to the influence of thermal treatment and further storage on the processes occurring in dense (*ca.* 50%) and watery (20-25%) starch gels.

Table 1. The values of peak temperature determined for themal effect of the amylose-lipid complex transition taking place in the non-irradiated samples and those irradiated with various doses obtained during heating at a rate of 10°C/min.

| Dose [kGy] | Heating cycles | | | Cooling cycles | | |
|---|---|---|---|---|---|---|
| | I | II | III | I | II | III |
| 20% suspensions | | | | | | |
| 0 | 99.1 | 102.0 | 102.5 | 83.6 | 83.5 | 83.4 |
| 5 | 99.0 | 102.0 | 102.3 | 83.5 | 83.5 | 83.5 |
| 10 | 98.9 | 101.3 | 100.7 | 83.0 | 82.6 | 82.0 |
| 20 | 97.5 | 100.7 | 100.2 | 82.3 | 81.7 | 81.4 |
| 30 | 99.0 | 100.3 | 99.6 | 81.6 | 80.6 | 80.1 |
| 50% suspensions | | | | | | |
| 0 | 112.1 | 116.0 | 116.2 | 99.4 | 99.9 | 100.2 |
| 5 | 112.5 | 115.7 | 115.6 | 99.5 | 99.5 | 99.7 |
| 10 | 112.6 | 114.9 | 114.6 | 98.8 | 98.3 | 97.8 |
| 20 | 112.3 | 113.9 | 113.7 | 97.4 | 96.5 | 96.1 |
| 30 | 112.2 | 113.4 | 112.6 | 96.3 | 95.3 | 94.9 |

Wheat starch was a Sigma product. Irradiations were carried out with $^{60}Co$ radiation in a gamma cell "Issledovatel" in the Department of Radiation Chemistry, Institute of Nuclear Chemistry and Technology. DSC studies were carried out during heating-cooling-heating cycles (up to 3 heating processes) in the temperature range 10-150°C. The measurements were performed at heating and cooling rates of 10, 5 and 2.5°C/min. A Seiko DSC 6200 calorimeter installed at the University of Lund was used. Transition enthalpy ($\Delta H$) as well as peak and onset temperature ($T_p$, $T_{on}$) were determined.

Modification of the amylose-lipid structure in wheat starch, in particular a decrease of the complex symmetry, can be concluded already after irradiation with a dose as high as 5 kGy. It is shown by a decreased temperature of the complex transition (Fig., Table 1), in particular observed during the successive heating and cooling cycles. The difference between the irradiated and the non-irradiated samples became more easily seen in each

Table 2. DSC results obtained for the non-irradiated and irradiated wheat starch gels (residues after the first DSC analysis, containing after the procedure *ca.* 60% of dry matter), carried out in the heating-cooling cycle after 13 days of storage.

| Dose [kGy] | Retrogradation | | Amylose-lipid complex transition | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | heating | | | cooling | | |
| | $\Delta H$ [$Jg^{-1}$] | R [%] | $T_p$ [°C] | $T_{on}$ [°C] | $\Delta H$ [$Jg^{-1}$] | $T_p$ [°C] | $T_{on}$ [°C] | $\Delta H$ [$Jg^{-1}$] |
| 0 | 9.51 | 80 | 110.5 | 112.4 | 1.92 | 127.1 | 122.3 | -1.29 |
| 5 | 8.30 | 72 | 109.1 | 111.3 | 1.50 | 125.3 | 119.4 | -0.85 |
| 10 | 7.60 | 67 | 107.0 | 109.7 | 1.33 | 124.2 | 116.7 | -0.73 |
| 20 | 6.37 | 62 | 105.2 | 108.0 | 1.09 | 121.8 | 117.0 | -0.66 |
| 30 | 6.14 | 56 | 104.4 | 107.3 | 0.71 | 110.8 | 109.2 | -0.36 |

Table 3. DSC results obtained for the non-irradiated and irradiated wheat starch gels (residues after the first DSC analysis, containing *ca*. 25% of dry matter) carried out in the heating-cooling cycles after 7 days of storage. Nd – not detected.

| Dose [kGy] | Retrogradation | | Amylose-lipid complex transition | | | | |
|---|---|---|---|---|---|---|---|
| | | | heating | | cooling | | |
| | $\Delta H$ [$Jg^{-1}$] | R [%] | $T_p$ [°C] | $\Delta H$ [$Jg^{-1}$] | $T_p$ [°C] | $T_{on}$ [°C] | $\Delta H$ [$Jg^{-1}$] |
| 0 | Nd | 0.0 | 102.7 | 1.46 | 84.3 | 86.5 | -1.71 |
| 5 | 0.50 | 4 | 102.3 | 1.16 | 83.0 | 85.2 | -1.15 |
| 10 | 1.11 | 9 | 101.1 | 1.27 | 82.3 | 84.1 | -1.06 |
| 20 | 2.00 | 16 | 100.3 | 1.67 | 82.2 | 84.0 | -1.79 |
| 30 | 3.26 | 28 | 99.5 | 1.21 | 79.9 | 82.2 | -1.51 |

next cycle. It is because thermal treatment causes a decrease of transition temperature in all the irradiated samples (showing further deterioration of the complex structure under the influence of thermal treatment), with no effect or increase of transition temperature observed in the non-irradiated starch. The effect was observed for 50% (dense) suspensions/gels as well as for 20% (watery) suspensions/gels.

Retrogradation of wheat starch during storage occur more easily in dense suspensions than in watery ones. It was stated that irradiation hinders retrogradation taking place in dense suspension (Table 2, columns 2 and 3), but facilitates retrogradation taking place in watery ones (Table 3, columns 2 nad 3). In purpose of direct comparison of irradiation effect on retrogradation, the yield of retrogradation R was calculated as a percentage of the initial enthalpy of gelatinisation determined during the first heating. This parameter included the decrease in gelatinisation enthalpy brought about by irradiation.

Storage of the gels induces a decrease in the temperature of the amylose-lipid complex transition as compared to the last cycle of the first analysis (Tables 1-3), accordingly to the occurring recrystallisation of gels. This result differs from the increase in the transition temperature observed after irradiation for wheat flour [6]. That decrease was, however, more significant in the case of all the irradiated samples than in the case of the initial sample. As a result, the differences between the irradiated and non-irradiated samples are more easily detected after storage.

The better differentiation between the amylose-lipid complex transition taking place in particular samples accompanied by the better reproducity were obtained in the case of dense suspensions as compared to the watery suspensions as well as during the first analysis performed for the recrystallised gels.

The work was sponsored in the frame of the Polish Ministry of Scientific Research and Information Technology research grant No. 2P06T 026 27.

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# PHYSICOCHEMICAL CHANGES TAKING PLACE IN BOVINE GLOBULINS UNDER THE INFLUENCE OF GAMMA IRRADIATION STUDIED BY THERMAL ANALYSIS

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Recently, gamma irradiation became more and more often applied for modification of biopolymers. Radiation modification of protein based polymers as well as the present development of gamma irradiation techniques as a method of food sterilisation and preservation induces necessity of better recognition of the physicochemical changes occurring in proteins after gamma irradiation. Estimation of the applicability of particular physicochemical methods for detection of the structural modifications taking place under influence of gamma irradiation corresponds to that problem.

Chemical transformations of amino acids, breakdown of peptide bonds, and hydrogen and disulphide bridges, as well as crosslinking of the chains might occur under the influence of ionising radiation and affect the tertiary structure of proteins and their physicochemical properties. Nature of damage that result from radiation processes taking place in the solid state might differ from those carried out in the water environment.

During the last years, differential scanning calorimetry (DSC) became a useful method for life sciences and was applied widely in structural studies