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DSC studies of retrogradation and amylose–lipid complex transition taking place in gamma irradiated wheat starch

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Abstract

The effect of gamma irradiation (^{60}Co) with doses of 5–30 kGy on the amylose–lipid complex transition and retrogradation occurring in gels containing ca. 50% and ca. 20% wheat starch was studied by differential scanning calorimetry (DSC) during heating–cooling–heating cycles (up to three cycles). Transition of the amylose–lipid complex occurs in all the irradiated samples at a lower temperature as compared to the non-irradiated starch. That effect was larger when the radiation dose was higher. A further thermal treatment causes a decrease of the transition temperature in the irradiated samples, with no effect or increase of that temperature observed for the non-irradiated ones. Irradiation hinders retrogradation taking place in 50% gels but facilitates the process occurring in 20% gels. The differences between the irradiated and the non-irradiated samples are more evident in the every next heating or cooling cycle as well as after storage and in the case of ca. 50% suspensions as compared to ca. 20% suspensions. The results point out to the deterioration of the structure of the complexes formed in the irradiated starch as compared to the non-irradiated one.

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Keywords: Wheat starch; Gamma irradiation; Gelatinisation; Amylose–lipid complex transition; Retrogradation; Differential scanning calorimetry (DSC)

1. Introduction

During the last decade interest has increased in the methods of food sterilisation and modification applying medium (1–10 kGy) and high doses (10–70 kGy) of irradiation [1–6] as well as radiation processing of industrial products that contain starch. Foods sterilised at high doses may be consumed by immunologically depressed patients and can be stored at room temperature (for example bakery products, readily prepared meals). Radiation modification enables, moreover, removal of antinutritional factors and inhibition of food allergies [3–6]. Doses of several dozen kGy are used for sterilisation of pharmaceuticals and medical devices and for starch modification. Accordingly, it appears desirable to acquire knowledge about the functional and structural properties of foods and starch alone irradiated using medium and high doses and in the development of appropriate physico-chemical testing methods. A good recognition of radiation influence on the properties of wheat starch is of great importance, since it constitutes a component of a number of food products. Simultaneously, there is a lack of data concerning the effect of ionising radiation on starch–lipid and starch–surfactant interactions (apart to our previous work [7–10]), while such systems are examined intensively in relation to food, pharmaceutical and other industries. The relationship between the structural properties of starch–lipid (surfactant) complexes and the digestibility of food is still the subject of studies.

Differential scanning calorimetry (DSC) is a valuable method for obtaining information about starch properties. Gelatinisation and Amylose–lipid complex transition occurring on heating of starch and flour suspensions as well as retrogradation taking place during the further storage of

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the resulting gels depend on the molecular structure of polysaccharides chains and their ordering in starch granules. The interaction of starch with lipids influences gelatinisation and hinders unprofitable recrystallisation of gels [11,12]. Formation of starch–lipid complexes occurs during gelatinisation taking place on heating of starch suspensions at temperatures above ca. 45 °C. The inclusion helical complex formed between lipids and amylose chains undergoes a partially reversible transition (of the order/disorder type) at higher temperature. Endothermal effects of the complexes melting are observed during heating at temperature above 80 °C, while exothermal effects of crystallisation occur during cooling. There is no evidence, however, for thermal effects connected to the formation of lipid complexes with the branched amylopectin macromolecules.

Our previous studies (conducted using WAXS, SAXS and DSC methods) have shown that degradation brought about by gamma irradiation [13] induces a decrease in the order of starch granules [14,15] and consequently influences gelatinisation [7–10,16]. It was also found that modification of lipids surrounding and lipids themselves resulting from the irradiation affect the properties of starch–lipid complexes formed in wheat starch and wheat flour [6–9]. In particular, the smaller enthalpies of gelatinisation of Amylose–lipid complex transition were determined in the cases of the starches irradiated with a dose of 30 kGy as compared to the non-irradiated ones. An essential decrease in the transition temperature was also found after irradiation. These results were attributed to a deterioration of the complex structure resulting due to irradiation. Moreover, the additional deterioration of the complex symmetry could be concluded after the further thermal treatment of the irradiated gels, on the basis of deterioration of thermal effects and their shift to lower temperature at each subsequent heating or cooling cycle. Simultaneously, the increase in the symmetry of the complex formed in the non-irradiated starch was concluded after the same thermal treatment. Furthermore, our preliminary results have demonstrated that differences in the storage effects on the irradiated and non-irradiated wheat starch and flour gels might result in the expanded differences between the structures of Starch–lipid complexes formed in such gels. It was found that the degree of retrogradation in the 50% gels of wheat starch was smaller after irradiation with a 30 kGy dose, while the degree of retrogradation of ca. 20% wheat flour was higher as compared to the respective non-irradiated specimens stored at the same conditions.

The studies carried out until now concerned the influence of irradiation with the dose of 30 kGy. Moreover, the studies of the storage effect on retrogradation and Amylose–lipid complex structure had only a preliminary character. The purpose of the present detailed study was to determine the effect of irradiation carried out using doses in the range from 5 to 30 kGy on the properties of Amylose–lipid complex formed in wheat starch as well as on retrogradation taking place in the gels. The influence of thermal treatment connected to the DSC measurements and effect of the further storage on the possibility to observe differences between transition of the Amylose–lipid complex occurring in the non-irradiated and the irradiated starch gels was tested. The radiation effects on the processes occurring in the gels characterised by the primary dry matter to water ratio of 1:1 and 1:4 were studied. Terms dense and watery suspensions/gels are used in the next paragraphs in relation to these systems, respectively.

2. Experimental

Solid native wheat starch of Sigma production (S-5127) containing ca. 11.7 wt% of water was irradiated with ^{60}Co gamma rays with doses of 5, 10, 20 and 30 kGy applying a dose rate of 1.00 ± 0.05 Gy s^{-1}. Irradiations were carried out in air at room temperature in a gamma cell Issledovatiel, installed in the Department of Radiation Chemistry in the Institute of Nuclear Chemistry and Technology, Warsaw, Poland.

DSC studies were carried out in an inert gas stream (nitrogen) during heating–cooling–heating cycles (up to three heating/cooling processes) within the temperature range of 5–150 °C. A Seiko DSC 6200 calorimeter was used, operating at heating and cooling rates of 10 °C min^{-1}. The instrument was calibrated with gallium (Mp = 29.8 °C) and indium (Mp = 156.6 °C). Covered aluminium pans from TA Instruments (20 μL large) were used in the experiments and a pan with aluminium oxide was used as the reference. Portions of starch (ca. 2.2 mg and ca. 4.2 mg in purpose to prepare ca. 20% and ca. 50% suspensions, respectively) were weighted directly in the pre-weighted DSC pans and the required amounts of twice distilled water were added. The pans were then hermetically closed and re-weighed. The residues obtained after the first DSC analyses were stored at 4 °C for 7 days (in the case of watery samples) or at ambient temperature for 13 days (dense suspensions) and then the analyses were repeated applying the single heating/cooling cycle. The sample pans

Table 1
The values of peak temperature (T_p, °C) determined for thermal effects of the transition of Amylose–lipid complex taking place during heating

Dose (kGy)	Heating cycle (°C)		
	I	II	III
Dense gels (48.31–50.01%)			
0	112.1 ± 0.3	116.1 ± 0.2	116.2 ± 0.2
5	112.5 ± 0.1	115.7 ± 0.1	115.6 ± 0.2
10	112.6 ± 0.2	114.9 ± 0.3	114.6 ± 0.2
20	112.7 ± 0.2	113.9 ± 0.2	113.4 ± 0.1
30	112.2 ± 0.2	113.3 ± 0.2	112.1 ± 0.3
Watery gels (21.98–23.78%)			
0	99.0 ± 0.1	101.9 ± 0.5	102.0 ± 0.5
5	98.9 ± 0.5	101.5 ± 0.7	101.4 ± 0.7
10	98.9 ± 0.4	101.3 ± 0.5	100.7 ± 0.5
20	97.5 ± 0.4	100.7 ± 0.5	100.2 ± 0.5
30	97.3 ± 0.5	100.3 ± 0.1	99.5 ± 0.3