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GAMMA IRRADIATION INFLUENCE ON WHEAT FLOUR GELATINISATION

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Abstract

Differences were detected by DSC between gelatinisation and amylose–lipid complex transition occurring in suspensions of control and irradiated with 30 kGy wheat flour characterised by a dry matter to water ratio equal to ca. 1:1 and the dependence of the results on the heating rate. Two steps viscosity was discovered using of Brabender viscograph for the wheat flour irradiated with 1–30 kGy dose (apart to an essential decrease in maximum viscosity) while a one step process occurs in the case of the control one. It was compared to one step viscosity jump observed in the case of rye flour, both control and irradiated. The results are discussed in terms of radiation induced changes in starch granules. Storage of the suspensions at –20°C led to an additional exothermic effect, preceding well-recognised gelatinisation effect.

Keywords: amylose–lipid complex transition, differential scanning calorimetry, gamma irradiation, gelatinisation, rye flour, viscosity, wheat flour

Introduction

Starch depolymerization and the creation of small molecular products taking place under influence of gamma irradiation [1–6] affect gelatinisation. This is because that gelling properties depend on the structure of starch macromolecule. Indeed, changes were discovered in the initial temperature of potato starch gelatinisation after irradiation [7] as well as in the viscosity of irradiated potato starch gels [8] and gels prepared from irradiated food containing starch [9, 10].

Our basic studies dealing with gamma irradiation influence on macro-structural properties of biopolymers are connected with the development of biopolymers modification and foodstuff sterilisation methods that apply ionising radiation [11–13]. The results we have obtained hitherto by X-ray diffraction showed on decrease in macromolecules ordering occurring in potato starch and different types of flour under influence of gamma irradiation [14–17]. We suppose therefore that the studies of gelatinisation carried out by DSC may be helpful for understanding the nature of structural transformations [18–33].

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On the other hand, the results obtained for radiation modified starch might be helpful for better understanding of gelatinisation processes, particularly as their nature is not fully recognised until now [26–33]. In the case of A type starches (for example wheat and rye starch) lipids are connected to starch macromolecules. Consequently, it appears possible that a transformation in starch macromolecules will result in changes in the structure and stability of amylose–lipid and amylopectin–lipid complexes [34–37].

Two endothermal effects that might be attributed to gelatinisation taking place in concentrated suspensions were discussed in a number of scientific works and led to several explanations of gelatinisation route [18–25, 38–42]. Starch melting endotherms have been reported to be connected to two processes like glass transition and melting. The other explanation have shown that gelatinisation of the more resistant material starts at higher temperature than gelatinisation of the less stable regions in granules [38–40]. The concept based on melting–recrystallisation phenomena was also expressed, followed by interpretation of gelatinisation in terms of liquid crystals transitions [41–42]. It is still evident, however, that gelatinisation of small round granules terminates at higher temperature than gelatinisation of the large oval ones. It results as well from DSC data collected for particular granules fractions, separated from the same starch sample and differing in size [23, 24, 38] as from observation of gelatinisation using of a hot stage microscope [43].

In our previous works [44, 45] the influence of the applied conditions during DSC measurements on the gelatinisation occurring in control and irradiated potato starch was tested. The differences between gelatinisation occurring in the control and the irradiated sample suspensions with high concentration (starch to water ratio ca. 1:1) were more evident than for suspensions with low concentration containing excess water (starch to water ratio ca. 1:4). These differences were, moreover, larger when the suspensions were slowly heated with a rate of 2.5°C min^{-1} than during faster heating with a rate of 5 or 10°C min^{-1}. Decrease in gelatinisation enthalpy accompanied by some modification of thermal effect profile might be also deduced on the basis of the preliminary results obtained for wheat flour [44] as well as decrease in temperature of the amylose–lipid complex transition. These preliminary data were obtained for concentrated suspensions during heating with a rate of 2.5°C min^{-1}.

In our current work, detailed differential scanning calorimetry (DSC) studies are presented concerning gamma irradiation influence on further gelatinisation and transition of amylose–lipid complexes. DSC results are related to those obtained for gelatinisation using the Brabender viscograph. Wheat flour was selected as an object of experiments in purpose to test whether gamma irradiation effect on starch might be noticed by DSC for the systems containing other components (i.e. proteins, lipids) apart from water. DSC studies were carried out for processes taking place in dense water suspensions (characterised by a dry matter to water ratio equal to ca. 1:1). The influence of the heating rate (2.5 and 10°C min^{-1}) on DSC results was tested for the control flour and the one irradiated with a 30 kGy dose and described in terms of kinetic restriction (activation energy). This relatively high dose was used in purpose of extending the irradiation effect and facilitating it's observation. The effect of the radiation dose (in the range of 1–30 kGy) on the viscosity changes taking place during

gelatinisation was tested for wheat flour and compared to those obtained for rye flour. The results are discussed in terms of the influence of gamma irradiation on macrostructural ordering in starch granules in flour.

Experimental

Sample preparation and irradiation

Commercial wheat flour (2 batches of Polish 'Poznańska' type, I and II) was used. Rye flour (2 batches, I and II) was prepared by milling of commercial crop. Solid flour samples were irradiated in air at ambient temperature with doses of 1, 2.5, 5, 10, 15 and 30 kGy using ^{60}Co gamma sources. Irradiations were carried out in a Mineyola gamma cell, applying a dose rate of 0. 47 Gy s^{-1} and in an Issledovatiel gamma cell applying a dose rate of 1.53 Gy s^{-1}. Both devices are installed in the Department of Radiation Chemistry at the Institute of Nuclear Chemistry and Technology.

Methods

Pasting properties

Viscosity measurements were performed during heating of wheat and rye flour suspensions with a rate of 1.5°C min^{-1} using a Brabender type amylograph (Brabender Duisburg A/RH type A.S.1, Germany). Flour mass portions, equivalent to 70 g of flour with standard humidity of 15%, were suspended in 400 mL of distilled water (resulting suspensions contained ca. 13% of dry matter). Water content in flour samples was determined on the basis of mass loss after heating at 150°C for 1.5 h. Zero point on the viscosity scale was fixed for the cell containing distilled water. The parameter $\Delta\eta_{max}$ was calculated as the difference between the maximum viscosity value and the viscosity of suspension just before initiation of gelatinisation. For the irradiated wheat flour samples the $\Delta\eta_I$ value was also determined as the increase of viscosity connected to the first step of gelatinisation. The ratio was also calculated of the maximum viscosity found for the irradiated sample to that found for the control sample (η_{max}/η_{max}(contr)). Besides, T_0 and T_{max} were determined as the initial temperature of gelatinisation and the temperature where maximum viscosity is achieved. This temperature is generally treated as the final gelatinisation temperature. Viscosity of suspensions at 25°C (η_{25}) and before the initiation of gelatinisation process (η_0) was also determined.

Differential scanning calorimetry (DSC)

DSC measurements were carried out in an inert gas stream (nitrogen) applying the Perkin Elmer DSC-2C calorimeter installed in the University of Lund. Dense flour suspensions (concentration in the range 43.44–52.40%) were examined during heating at temperatures within 30–130°C. The instrument was calibrated with gallium (*m.p.*=29.8°C) and indium (*m.p.*=156.6°C). Covered aluminium pans from TA Instruments (USA) were used in the experiments and an empty pan with a double lid

was used as the reference pan. 10–15 μL of flour suspensions produced using twice distilled water were located in the pre-weighted DSC pans, which were then hermetically closed and re-weighted. The dry matter content of each individual sample was determined by drying, after scanning, punctured DSC pans in a heating cabinet at 105°C for 16 h.

DSC curves were obtained and the calculations were done by elaboration of raw experimental data applying software developed at Lund University. The baseline function was calculated after fixing of the six points on the DSC curve in the region nearest to thermal effect (in majority of cases, two before and four after complexion of thermal events). This calculated baseline was then subtracted from the raw experimental data and the resulting DSC curve was plotted. Total enthalpy of both processes (ΔH_t) and partial enthalpies of gelatinisation (ΔH_g) and of amylose–lipid complex transition (ΔH_a), as well as peak (T_{pg}, T_{pa}) and onset (T_{ong}, T_{ona}) temperatures of thermal effects corresponding to each process respectively were calculated basing on several duplicate measurements. Partial enthalpies were calculated simultaneously with total enthalpy as partial areas of thermal effect, after the appropriate selection of the point separating both areas. For onset temperature determination the tangential line was adjusted in the half altitude of the particular partial thermal effect. Onset was then calculated as the point of this tangential cross-section with a baseline. 5–6 measurements were done in the cases of endothermal effects of gelatinisation characterised by blurred boundaries recorded for the freshly prepared suspensions during heating with a rate of 2.5°C min^{-1}. Four measurements were done on heating with a rate of 10°C min^{-1}, when thermal effects characterised by the well defined boundaries were observed. Only the parameters obtained for the suspensions of control and irradiated samples with very close concentrations were compared.

The majority of measurements were done for suspensions, prepared directly in DSC pans and stored after preparation for few hours at ambient temperature. One set of the suspensions was, however, prepared earlier. These suspensions were stored for 6 h at ambient temperature and afterwards for 18 h at –20°C before they were placed into DSC pans. The measurements were done during few hours after the suspensions were removed from the frozener. This procedure was carried on because it permits, accordingly to our preliminary observation, to perceive additional exothermal effects in the low temperature region. These suspensions were examined during heating with a rate of 10°C min^{-1}.

Rough calculation of the apparent activation energy was performed using the Kissinger method [46]. The general formula:

$$\frac{\mathrm{d}\ln\frac{\Phi_{1/2}}{T_p^2}}{\mathrm{d}\frac{1}{T_p}} = -\frac{E_a}{R}$$

was adapted for gelatinisation and thus the following formula was used in calculation:

$$\frac{\ln\frac{\Phi_1}{T_{p1}^2}-\ln\frac{\Phi_2}{T_{p2}^2}}{\frac{1}{T_{p1}}-\frac{1}{T_{p2}}}=-\frac{E_a}{R}$$

where Φ and T_p mean a heating rate and a peak temperature of thermal effect, R is a gas constant and E_a is activation energy. Φ_1 , Φ_2 mean two heating rates applied at present experiments (equal to 10 and 2.5°C min^{-1}) and T_{p1} and T_{p2} are peak temperatures (average values) detected for two endothermal effects on heating with rates of 10 and 2.5°C min^{-1}, respectively.

Results and discussion

Pasting properties

The results ($\Delta\eta_{max}$, $\Delta\eta_I$ (η_{max}/η_{max}(contr), T_0 and T_{max} together with initial viscosity values η_{25} and η_0, water content in the flour sample and the irradiation conditions) are presented in Tables 1 and 2. The comparison of the selected amylograms obtained for the samples irradiated applying various conditions are presented in Figs 1 and 2.

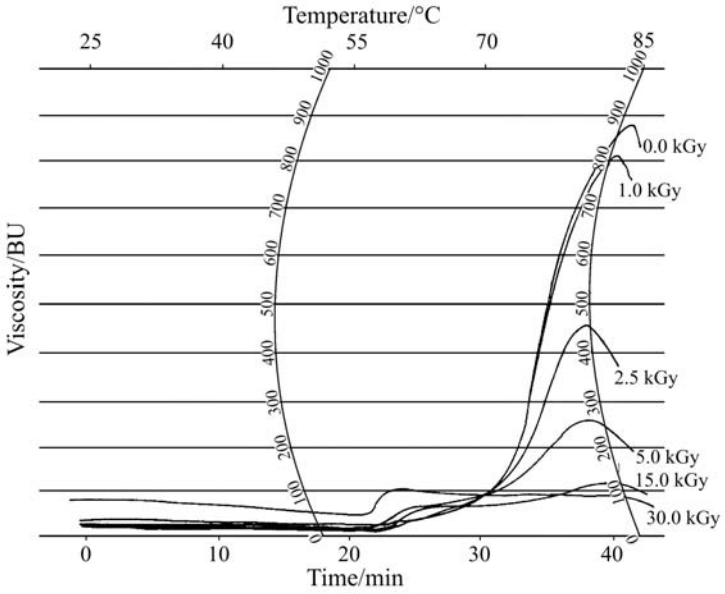

Fig. 1 Comparison of amylograms obtained for batch I of wheat flour, control and irradiated with 1, 2.5, 5, 15 and 30 kGy applying a dose rate 0.47 Gy s^{-1}. The measurements were done for the suspensions containing 12.97% of dry matter during heating with a rate of 1.5°C min^{-1}

Table 1 Irradiation conditions, water content and results obtained using of Brabender viscograph for the initial and irradiated samples of wheat flour batches WFI and WFII. The suspensions containing 13% of dry matter were heated with 1.5°C min^{-1}. η_{25} means viscosity at 25°C while η_0 – the viscosity directly before gelatinisation. (η_{max}/η_{max}(contr)) is the ratio between the maximum viscosity found for the irradiated sample to that found for the control sample. $\Delta\eta_{max}$ is the difference between maximum viscosity value and η_0 value, while $\Delta\eta_I$ is the difference in viscosity achieved in the first stage of the process. T_0 means the initial temperature of gelatinisation and T_{max} is the temperature, where maximum viscosity is observed

No.	Dose/ kGy	Flour humidity/ mass%	η_{25}/ BU	η_0/ BU	$\frac{\eta_{max}}{\eta_{max}(contr)}$	$\Delta\eta_{max}$/ BU	$\Delta\eta_I$/ BU	$100\frac{\Delta\eta_I}{\Delta\eta_{max}}$	T_0/°C	T_{max}/°C
I	II	III	IV	V	VI	VII	VIII	IX	X	XI
Batch I irradiated applying a dose rate of 0.47 Gy s^{-1}										
1	0	12.4	30	20	1.00	850	0	0	58.0	89.5
2	1	13.8	15	10	0.93	800	≤15	≤1.9	58.0	88.6
3	2.5	13.3	20	10	0.52	440	25	5.7	58.0	87.5
4	5	12.5	20	20	0.30	240	40	16.7	57.5	87.1
5	15	11.9	25	15	0.11	85	45	52.9	57.5	86.5
6	30	12.4	80	45	0.11	55	55	100	57.0	63.0–64.0
Batch II irradiated applying a dose rate of 1.53 kGy s^{-1}										
7	0	14.1	25	10	1.00	940	0	0	59.5	88.8
8	1	13.9	25	10	0.78	730	≤25	≤3.4	58.0	90.1
9	2.5	13.8	25	10	0.57	535	30	5.6	58.0	89.5
10	5	13.8	20	10	0.36	335	45	10.4	57.4	88.0
11	10	14.2	35	25	0.18	145	40	27.6	57.1	85.0–86.5

Table 2 Irradiation conditions, water content and results obtained using of Brabender viscograph for the initial and irradiated samples of rye flour batches RFI and RFII. The suspensions containing 13% of dry matter were heated with 1.5°C min^{-1}. η_{25} means viscosity of the suspension at 25°C while η_0 means the viscosity value directly before gelatinisation. The zero point of the viscosity scale was fixed for distilled water. (η_{max}/η_{max}(contr) is the ratio between the maximum viscosity found for the irradiated sample to that found for the control sample. $\Delta\eta_{max}$ is the difference between maximum viscosity value and η_0 value. T_0 means the initial temperature of gelatinisation and T_{max} is the temperature, where maximum viscosity is observed

No.	Dose/ kGy	Flour humidity/ mass %	η_{25}/ BU	η_0/ BU	$\frac{\eta_{max}}{\eta_{max}(contr)}$	$\Delta\eta_{max}$/ BU	T_0/ °C	T_{max}/ °C
I	II	III	IV	V	VI	VII	VIII	IX
Batch I irradiated applying a dose rate of 0.47 Gy s^{-1}								
1	0	12.9	40	25	1.00	360	50.5	69.3
2	2.5	12.9	30	20	0.60	210	51.1	70.0
3	15	11.8	20	20	0.31	100	52.6	67.0–70.0
4	30	12.9	40	35	0.19	40	53.2	59.3–62.5
Batch II irradiated applying a dose rate of 1.53 kGy s^{-1}								
5	0	15.4	50	40	1.00	440	49.0	76.9
6	1	15.5	40	35	0.94	380	49.0	76.0
7	2.5	14.6	30	30	0.69	300	49.0	73.9
8	5	14.6	30	35	0.48	195	50.0	73.6
9	10	15.8	20	20	0.21	80	50.5	62.8–73.0

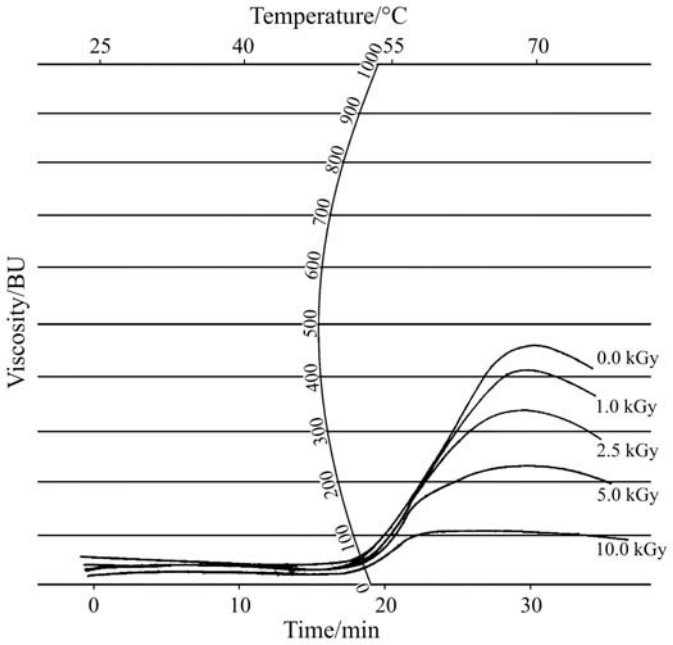

Fig. 2 Comparison of amylograms obtained for batch II of rye flour, control and irradiated with 1, 2.5, 5 and 10 kGy applying a dose rate 1.53 Gy s^{-1}. The measurements were done for the suspensions containing 12.97% of dry matter during heating with a rate of 1.5°C min^{-1}

A negligible decrease in viscosity connected with the increase in mobility of suspension particles was noticed during the first stage of flour water suspensions heating (observed at 25–58 and at 25–49°C in the case of wheat and rye flours respectively) (compare Tables 1, 2 columns IV and V). The one step increase in viscosity connected to gel formation was observed for both initial wheat flour samples in the temperature range 58.0–89.5 and at 49.0–77°C for the initial rye flour samples.

The maximum viscosity arising from gelatinisation was smaller in the case of suspensions of all the irradiated samples when compared to those of the control ones (Tables 1 and 2, columns VI, VII). The differences were noticed already after irradiation with doses of 1 kGy. Only a negligible rise in viscosity was caused by gelatinisation, occurring in suspensions of both wheat and rye flour irradiated with doses of 30 kGy due to the presence of degraded material resulting from irradiation [2, 3].

The character of viscosity changes indicates a two-step gelatinisation occurring in wheat flour samples irradiated with doses in the range from 2.5 to 15 kGy while only a one step process was observed for the control samples (Fig. 1). In the first gelatinisation step taking place at the temperature range up to ca. 64°C, small but a prompt increase in viscosity was noticed. It results in $\Delta\eta_I$ values in the range from 25 to 45 BU for the samples irradiated with doses from 2.5 to 15 kGy (Table 1, column VIII) corresponding to 5.6–52.9 % of the total viscosity increase $\Delta\eta_{max}$ (Table 1, column IX). Slow increase of

viscosity was observed afterwards in the temperature range up to ca. 79°C followed by a rapid viscosity progress connected with the predominant gelatinisation process. Only a negligible viscosity rise was noticed in the temperature region to ca. 64°C for the samples irradiated with a dose of 1 kGy (Table 1, points 2 and 8).

It might be concluded that the first stage of viscosity rise results probably from gelatinisation of the modified material, while at a higher temperature the non-modified material gelatinises. The initial ascent in viscosity increases and the progress in viscosity corresponding to the second gelatinisation step decrease when the radiation dose rises. As a result, after the irradiation with a 30 kGy dose, the one step rapid viscosity increase occurred only in the very first stage at the low temperature range 57.0 to 62.5°C and no viscosity ascent was noticed at higher temperature. Maximum viscosity was noticed at a broad range of low temperatures from 63.0 to 64.0°C in comparison to 89.5°C found for the control sample. It was followed by a slight decrease and a further plateau on the viscosity curve in the broad temperature range up to 88.6°C.

One step gelatinisation may be concluded on the basis of examination of viscographs recorded for all the irradiated samples of rye flour, just as in the case of the control ones (Fig. 2). Within the rye flour sample irradiated with 30 kGy (0.47 Gy s^{-1}) (Table 2, point 9), however, viscosity increase was completed at a temperature essentially (ca. 10°C) lower than the one recorded for the control flour sample, similarly to the wheat flour irradiated under the same conditions. Small but constant value was noticed in the range 59.5–62.5°C in comparison to 69.3°C found for the appropriate control sample. Slow decrease in viscosity occurred at higher temperatures. The viscosity of the suspension obtained from the sample irradiated with a dose of 10 kGy (batch II, 1.53 Gy s^{-1}) became also constant in the broad range 63.0–73.0°C of higher temperature and decreased very slowly on further heating (Fig. 2).

Decrease in T_{max} was perceived after irradiation in the cases of both wheat and rye flour (Table 1, column XI; Table 2 column IX). The lower values of the initial gelatinisation temperature were found in the case of the irradiated wheat flour samples, as compared to these determined for the control ones (Table 1, column IX). A decrease in the temperature of gelatinisation may be concluded, therefore for both examined batches of wheat flour. On the contrary, in the case of rye flour, when no additional preliminary step in viscosity progress occurs, an increase in the initial temperature of gelatinisation was found after irradiation (Table 2, column VII).

The possible influence on gelatinisation temperature of the particular products resulting from starch radiodepolymerisation (acids, monosaccharides and the other small molecular products) was discussed in the previous paper [45]. An essential protein content in the sample may influence flour gelatinisation as well [47–48], particularly that both gelatinisation and denaturation take place at a similar temperature range. Consequently, denaturation of wheat proteins participates in the total change in viscosity taking place during heating. It is also known that a number of proteins transforms and that denaturation of some globular proteins occurs under influence of gamma irradiation [49]. Therefore, the presence of the modified protein probably lead to increase in the initial viscosity of the flour–water mixtures. No separate endothermal effect was observed by DSC for denaturation of proteins in flour.

Differential scanning calorimetry

The control wheat flour (batch I) and the sample irradiated with a highest dose of 30 kGy (0.47 Gy s^{-1}) were examined. The results are presented in Table 3. The examples of DSC curves are presented in Figs 3, 4.

Two endothermal processes occur during heating, such as starch gelatinisation and amylose–lipid complex transition [34–37, 47–48]. The occurrence of two gelatinisation processes can be concluded on the basis of the gelatinisation thermal effect profile. The presence of the additional maximum (a shoulder) on endothermal effect of gelatinisation above peak temperature is typical for starch suspensions having concentration larger than 40% in particular [20, 39, 40, 45].

The occurrence of two gelatinisation processes was less apparent for the irradiated sample, as compared to the control one. It can be deduced on the basis of the decrease in height of the first gelatinisation maximum and disappearance of the border between two steps, that the enthalpy of the first gelatinisation stage is smaller in the case of the irradiated flour than that of the control sample. A similar result was found earlier for potato starch [44, 45] and attributed to the structural changes resulting in starch granules after irradiation. Decrease after irradiation in the altitude of the first gelatinisation maximum was evident during heating with a rate of 2.5°C min^{-1} (Figs 3, 4).

Gelatinisation of the irradiated sample occurs at a lower temperature during heating at 10°C min^{-1} than that of the control sample. Both peak and onset temperature of the irradiated sample were smaller than those of the control one (Table 3, points 1, 2, column V and VI). On the contrary, negligible higher values of peak and onset temperature

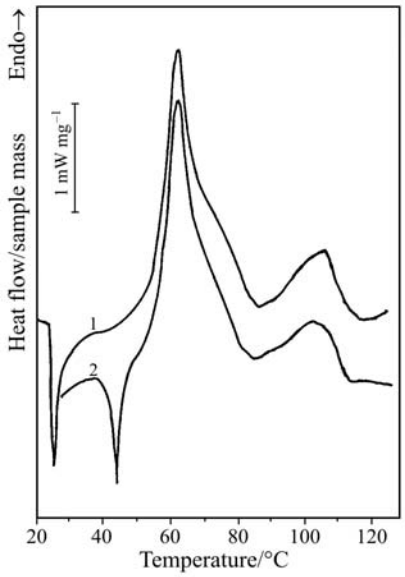

Fig. 3 Examples of DSC curves recorded during heating with a rate of 10°C min^{-1} for the suspensions of wheat flour WF1, control and irradiated with 30 kGy (0.47 Gy s^{-1}): curve 1 – control (47.30% of dry matter), curve 2 – irradiated (46.27% of dry matter)

Table 3 DSC results obtained for the reference non-irradiated sample of wheat flour (batch I) and the sample irradiated with a 30 kGy dose applying a dose rate 0.47 Gy s^{-1} ΔH_g, T_p^g, are the average values of enthalpy, peak and onset temperature determined for gelatinization, while ΔH_a, T_p^a, T_{on}^a, are the appropriate values determined for amylose–lipid complex transition and ΔH_t is the total value of enthaly determined for both processes

No.	Dose/ kGy	Concentration/ mass%	Heating rate/ °C min^{-1}	T_p^g/ °C	T_{on}^g/ °C	T_p^a/ °C	T_{on}^a/ °C	ΔH_t/ J g^{-1}	ΔH_g/ J g^{-1}	ΔH_a/ J g^{-1}
I	II	III	IV	V	VI	VII	VIII	IX	X	XI
1	0	47.30–51.08	10	62.4±0.3	54.7±0.3	107.6±0.8	92.0±1.5	11.4±1.0	9.1±1.0	2.3±0.2
2	30	45.06–46.79	10	61.4±0.2	53.2±0.5	102.7±0.8	86.9±2.0	10.0±1.0	8.1±1.0	1.9±0.3
3	0	46.67–52.40	2.5	59.1±0.5	50.2±0.5	105.4±0.5	88.3±2.5	13.7±0.8	11.0±1.0	2.7±0.4
4	30	43.44–48.22	2.5	59.9±0.5	51.2±0.5	101.8±0.8	84.6±3.0	11.2±0.8	8.2±1.0	3.0±0.8

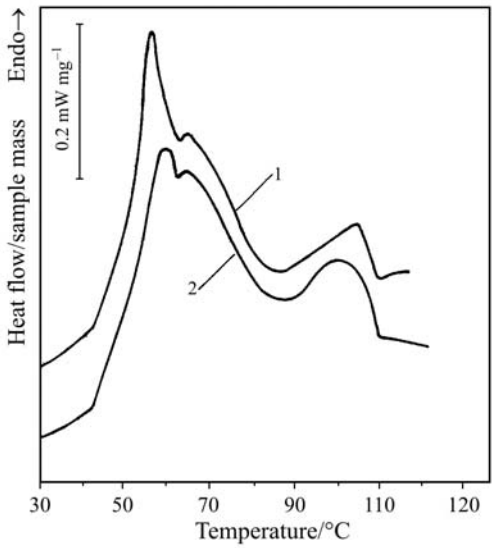

Fig. 4 The examples of DSC curves recorded on heating with a rate of 2.5°C min^{-1} for the suspensions of wheat flour WF1, control and irradiated with 30 kGy (0.47 Gy s^{-1}): curve 1 – control (46.67% of dry matter), curve 2 – irradiated (48.22% of dry matter)

were found in the case of the irradiated flour heated with a rate of 2.5°C min^{-1} than those recorded for the non-irradiated one (Table 3, points 3 and 4). It results from the fact that the change in the heating rate induces various shifts in the temperature range of the endothermal effect of gelatinisation observed for the irradiated and control samples. (A similar effect was noticed before for gelatinisation of potato starch [45].) It might be supposed that these differences can be attributed to the differences in kinetics of the two gelatinisation processes occurring in the concentrated suspensions of the control and the irradiated samples. Generally, the faster the heating, the higher is the expected onset and peak temperature. This temperature shift depends, however, on the magnitude of the activation energy. The smaller influence of the heating rate on DSC thermal effect observed for the irradiated sample, suggests a larger activation energy of the process occurring in the irradiated flour than of that taking place in the control one. It seemed interesting, therefore, to express differences between the control and the irradiated samples in terms of the differences in apparent activation energy. Due to a possible complexity of gelatinisation processes, the proposed description is of formal character.

It was not possible to perform an accurate calculation basing on the scarce data presented in Table 3. The attempt was made, however, to evaluate the coarse apparent activation energy of the process using the Kissinger's method, similarly as in the work of Lai *et al*. [25]. The values of an apparent activation energy equal to ca. $38.4 \cdot 10^4$ and to ca. $85.1 \cdot 10^4$ J mol^{-1} were obtained for the control and the irradiated samples respectively. The activation energy was, therefore, ca. 2 times larger (in terms of a mole) for the irradiated wheat flour than for the control one. It is worth to mention, moreover, that irradiation with a dose of 30 kGy causes an essential decrease in the molecular mass, due to a de-

crease in the macromolecule chains length [2, 3]. Accordingly, a higher ratio of both values of activation energy is expected when expressed in terms of mass.

Different irradiation influence on the initial temperature of gelatinisation may be concluded in the case of various types of flour and starch, depending on the method and the conditions applied in measurements. Therefore, a decrease after irradiation in the initial temperature of potato starch gelatinisation was concluded by Oreshko and Korotchenko [7] on the basis of viscosity changes, while an increase in gelatinisation temperature arises from our preliminary DSC results obtained for potato starch [44, 45]. Our present results suggest that differences in conclusions may partially be caused by kinetics.

Amylose–lipid complex transition was observed in the irradiated sample at a lower temperature than in the control one during heating with a rate of 10 and of 2.5°C min^{-1}. The average values of peak and onset temperature are presented in columns VII and VIII in Table 3. Moreover, the endothermal effect of this transition was rather sharp in DSC curves of control flour, but shouldered in DSC curves of the irradiated one. A lower temperature of the transition taking place in the irradiated flour as compared to that occurring in the control sample indicates smaller stability and therefore lower complex symmetry. Blurred profiles of thermal effects indicate the increased heterogeneity of complexes (characterised by various transition temperatures) present in the irradiated sample as compared to the control one.

It was difficult to separate the broad and relatively small endothermal effects of gelatinisation and of amylose–lipid complex transition and to calculate exact enthalpies of particular processes, especially when a small heating rate of 2.5°C min^{-1} was applied. Smaller average values were obtained, however, in both cases for total enthalpy as well as for enthalpies of the both partial processes taking place in suspensions of the irradiated sample than for those occurring in the control one. The average values of total enthalpy calculated in the broad temperature range from the beginning of gelatinisation to the end of amylose–lipid complex transition are given in Table 3, column IX. The respective average values of the enthalpies of gelatinisation and of amylose–lipid complex transition determined on the basis of integration of the appropriate partial area, are given in columns X and XI of Table 3.

On the basis of the low value of maximum viscosity found by amylography and corresponding to the reduced ability for gel creation, one can expect that only a negligible gelatinisation effect will be observed by DSC for a wheat flour sample irradiated with a 30 kGy dose. A rather small decrease in gelatinisation enthalpy was noticed, however, after irradiation of the sample as compared to that determined for the control flour, similarly to the results of Barabassy *et. al*. [9, 10]. Our results confirms that the effect observed by DSC corresponds to the order destruction (crystalline or macromolecular) of starch, while viscosity changes are connected with gelatinisation of ordered and not ordered starch regions. In fact, it was discovered recently in situ by Waight *et al*. [41] that both endothermic processes destruction of crystalline and the macromolecular ordering take place during gelatinisation. Our present results show, moreover, that the enthalpy recorded within endothermal effect corresponds mainly to destruction of the crystalline ordering. The small decrease in this enthalpy corresponds well to the small decrease in the

sample crystallinity, found previously for the irradiated starch using WAXS [14, 17] but not to the essential destruction of macromolecular order recorded by SAXS [15–17] and connected to macromolecules degradation, confirmed at present by viscosity data.

An exothermal process occurring before gelatinisation at the temperature range 20–45°C was noticed during heating of both control and irradiated wheat flour suspensions stored previously at –20°C for 18 h. The peak of the narrow exothermal effect connected with the process was found for both the control and the irradiated flour at temperature range of 23.8–42.3°C. Small enthalpy values in the range from 0.2 to 0.7 J g^{-1} were determined for both samples. The effect was not noticed in the case of any sample examined directly after preparation or stored for a few hours at ambient temperature. The origin of this exothermal effect is not recognised. It seems however, that this effect might be related to the processes of the suspensions ageing, in particular to interaction of granules with water in frozen state [21, 29, 51, 52].

The exothermal effect and the endothermal effect of gelatinisation were relatively well separated in DSC curves of the control sample, while the borders between both effects were blurred in those of the irradiated one. This is connected with the indistinct beginning of the endothermal effect recorded on the DSC curve of irradiated wheat starch gelatinisation. A well defined beginning of the process was detected on the DSC curve for the control sample.

Conclusions

The differences were observed between endothermal effects of gelatinisation and amylose–lipid complex transition occurring in suspensions of control and irradiated with 30 kGy wheat flour. It is certified, therefore, that such differences might be noticed for the more complex systems containing the other components (proteins) apart to starch and water. The results show a decrease in the crystallinity of the irradiated sample, as well as an increase in the heterogeneity of the amylose–lipid complexes and their lower symmetry and stability. In particular, a decrease in gelatinisation enthalpy and a meaningful decrease in temperature of the amylose–lipid complex transition was detected after irradiation.

An essential decrease in gel formation capability was confirmed for both wheat and rye flour after irradiation applying doses in the range from 1 to 30 kGy in regard to starch degradation. The character in viscosity rise differs for the irradiated wheat and rye flours. A two-stage process was observed in irradiated wheat flour using the Brabender viscograph, while one step was detected for the control wheat flour and all the rye flour samples.

On the basis of comparison of the results obtained using DSC and the Brabender viscograph, it can be concluded that irradiation slightly influences the crystalline ordering and that the crystalline regions are probably more resistant to radiodepolymerization than the amorphous ones. It confirms our conclusion obtained for the irradiated potato starch using wide-angle X-ray scattering [14, 17].

The differences between the temperature of endothermal effects of gelatinisation recorded for the control and the irradiated samples depend on the applied heating

rate. It is in regard to the fact that dependence of gelatinisation temperature on the heating rate differs for the control and the irradiated sample because of the kinetic parameters. An increase in activation energy of gelatinisation of the crystalline starch fraction can be concluded after irradiation.

The exothermal process can be observed in the temperature range 20–45°C in the case of flour suspensions stored in temperature –20°C before measurements.

Accordingly to our knowledge these are the first results comparing the influence of heating rate on gelatinisation and transformation of amylose–lipid complexes in the control and the irradiated flour accompanied by the first attempt to describe the phenomenon in terms of kinetic parameters. Two-step viscosity increase during gelatinisation taking place in irradiated wheat flour as well as the exothermal effect attributed to an ageing of flour suspensions were described the first time.

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