Journal of Thermal Analysis and Calorimetry, Vol. 79 (2005) 19–27

DSC STUDIES OF γ-IRRADIATION INFLUENCE ON AMYLOSE–LIPID COMPLEX TRANSITION IN WHEAT FLOUR

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DSC studies were carried out in the heating–cooling cycles for non-irradiated and irradiated with γ-rays (^{60}Co) using 30 kGy dose wheat flour. The differences between gelatinisation and reversible transition of amylose–lipid complexes occurring in suspensions of non-irradiated and the irradiated flour (characterized by a dry matter to water ratio of 1:1 and 1:3) depend on the conditions applied in DSC measurements (concentration, heating/cooling rate) and on the preceding treatment of samples. An essential decrease in the temperature of amylose–lipid complex transition was discovered after irradiation. Retrogradation is inhibited in the dense gels of the irradiated samples as compared to the initial ones. The results are discussed in terms of radiation-induced destruction of the polysaccharide chains and lipid modification.

Keywords: *amylose–lipid complex transition, DSC, γ-irradiation, gelatinisation, retrogradation, wheat flour*

Introduction

γ-irradiation induces physico-chemical changes in starch macromolecules [1–9]. Degradation followed by formation of polysaccharides with shorter chains as the superior products has appeared to be a predominant process, occurring due to free radical mechanism [1–4]. Only little amount of small molecular products, alike alcohols, aldehydes or hydrogen peroxide were discovered in irradiated starches [1] in regard to reactions occurring on the end of the polysaccharide chains. Although recombination of free radicals may lead to creation branched products, it's probability is not very high. Degree of cleavage of starch macromolecules depend on the applied irradiation dose [4, 5], while no differences were discovered between the nature of processes taking place in starches irradiated with high and low doses.

The above chemical changes induces decrease of ordering in starch grains [6–9] and influences gelling properties [10–13]. These problems were discussed in details in our previous papers [13, 14]. Apart, a creation of the amylose–lipid and amylopectin-lipid complexes occurs in A-type starches. The probability of formation of such complexes, as well as their structure depends on the starch macromolecule structure alone (the chain length and number of branches) as well as on the lipid molecule type. Therefore, the change in structure of starch macromolecules resulting from irradiation and modifying the lipid surrounding, as well as possible changes in the lipid molecules are expected to affect the possibility of forming complexes, their structure and stability.

Differential scanning calorimetry (DSC) was proved to be an appropriate method for examining the structure of amylose–lipid complexes [15–18], apart the other properties connected to gelatinisation or retrogradation [19–34]. It is so because thermal effects of the reversible transition (of order–disorder type) of the complex are observed in the range of temperature above gelatinisation. DSC capability for studying of retrogradation taking place during storage of starch gels regards gelatinisation of the recrystallised phase occurring during the further heating.

Our basic studies are connected with development of biopolymer modification and foodstuffs sterilisation methods that apply ionising radiation. In our former work [13], DSC studies concerned gelatinisation and amylose–lipid complex transition taking place in the non-irradiated and the irradiated using a 30 kGy dose wheat flour. The results were related to the pasting properties [13]. Water suspensions (characterised by a dry matter to water ratio equal to ca. 1:1) were examined during the primary heating with a rate of 2.5 and 10°C min^{-1}. The essential differences were then observed between the amylose–lipid complex transition occurring in both samples. It appeared, therefore, interesting to compare this reversible transition occurring also during cooling of the gelatinised non-irradiated and irradiated samples.

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1388–6150/$20.00

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Our present paper describes more detailed DSC studies dealing with γ-radiation influence on the amylose–lipid complex structure. Simultaneously, the studies concerning gelatinisation were continued. A dose of 30 kGy was used, just as in our previous work, in purpose of extending the irradiation effect and facilitating its observation. DSC analyses were performed in the heating–cooling cycles for the dense and the watery suspensions characterised by a dry matter to water ratio equal to ca. 1:1 and 1:3, respectively (a dry matter content was in the range of 47.8–54.1% and 24.7–27.4%). Up to two heating and two cooling processes were applied.

The processes occurring during heating and cooling were also examined after three days of storage at ambient temperature of the dense gelatinised samples containing non-irradiated and irradiated matter in purpose to study retrogradation and influence of the temperature treatment followed by retrogradation on the amylose–lipid complex. Apart the suspensions stored before the first analyses at depressed temperature (4 and –20°C) were examined and the possibility to detect differences between the initial and the irradiated flour was determined after storage. The results were compared with those obtained during the first heating in our previous studies [13] and with those obtained at present for fresh suspensions and retrograded gels.

Experimental

Sample preparation and irradiation

Commercial wheat flour (Polish-produced, type 'Poznańska') was used. Irradiation with ^{60}Co γ-rays was performed in air at ambient temperature with a dose of 30 kGy applying a dose rate of 0.47 Gy s^{-1} in the γ-cell Mineyola. The device is installed in Department of Radiation Chemistry, Institute of Nuclear Chemistry and Technology.

DSC

DSC measurements were carried out in an inert gas stream (nitrogen) in the heating–cooling cycles in the temperature range of 10–150°C. The Seiko DSC 6200 calorimeter installed at the University of Lund was used. The instrument was calibrated with gallium (*mp*=29.8°C) and indium (*mp*=156.6°C). Covered aluminium pans (hermetic type, 20 μL large) from TA Instruments (USA) were used in the experiments. The pan containing Al_2O_3 standard was used as the reference pan. Flour suspensions in twice distilled water were located in the pre-weighed DSC pans, which were then hermetically closed and re-weighed. The pans kept air-tightness during all the experimental cycle. Flour portions of 2.5–3 mg were used for preparation of the watery suspensions (characterised by dry matter content of 24.7–27.4 mass%) while 5–6 mg were used in the dense suspensions (47.8–54.1 mass%). 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. The enthalpies as well as peak (Tp_g, Tp_a) and onset (Ton_g, Ton_a) temperatures of thermal effects corresponding to gelatinisation and to amylose–lipid complex transition, respectively, were calculated basing on several duplicate measurements. The initial temperature T_{0a} (determined at the starting point of bending of the DSC curve) instead of the onset temperature was determined for the amylose–lipid complex transition occurring during heating, because of an irregular profile of thermal effects. Total enthalpy of both processes (ΔH_t) as well as partial enthalpies of particular process (ΔH_g) and (ΔH_a) (expressed in terms of anhydrous matter) were calculated on the basis of endothermal effects recorded during heating. The linear baseline was used in all the cases, in purpose of comparison the enthalpy values obtained for the non-irradiated and irradiated flour. Several calculation modes were tried for each experimental set with slightly modified integration limits and the final results were then determined as the average values. The average variances of the results were determined on the basis of the variances obtained for several measurements and calculations performed using of the modified limits.

Accordingly to the purpose of our studies, the analysis of amylose–lipid complex transition occurring during cooling and secondary heating appeared to be of major importance. The number of measurements carried out in the particular experiments depended, therefore, on the possibility to analyse the exothermal effects recorded during cooling. More measurements were done in the cases of these effects characterised by blurred boundaries than in the cases of those characterised by the well-defined boundaries. Consequently, 4–5 measurements were carried out for dense suspensions during heating with a rate of 5°C min^{-1} and cooling with 2.5°C min^{-1}, whereas 3–4 measurements were performed for both dense and watery suspensions during heating and cooling with a rate of 10°C min^{-1}. Only the parameters obtained for the suspensions of non-irradiated and irradiated samples with very close concentrations were compared. Due to fluctuation of baselines, the graphs with selected experimental curves were plotted after performing a suitable smoothing.

Results

Primary DSC analyses of fresh suspensions

DSC measurements were carried out during a single heating–cooling cycle. The results obtained during heating and the experimental conditions are presented to-

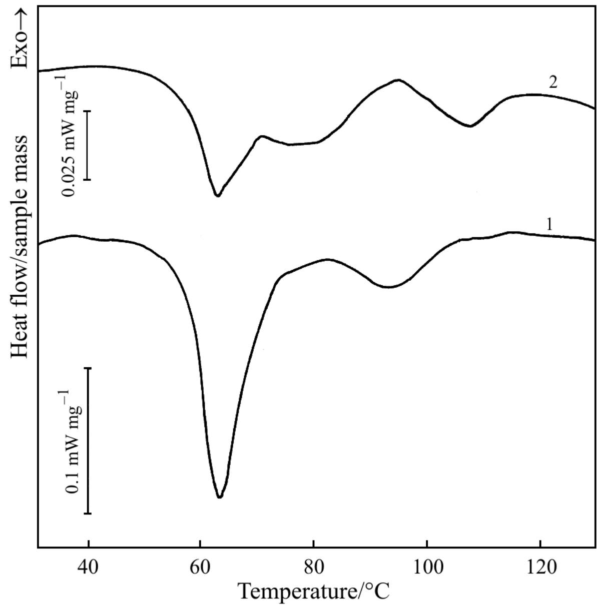

Fig. 1 The examples of DSC curves recorded for wheat flour (initial) during the first heating applying various conditions: curve 1 – heating at 10°C min^{-1}, 27.44% of dry matter (2.873 mg), curve 2 – heating at 5°C min^{-1}, 52.67% of dry matter (5.512 mg)

gether in the Table 1 (points 1–4), while those obtained during cooling are presented in the Table 2 (points 1–4). The examples of DSC curves recorded on heating are shown in Fig. 1. Figure 2 presents a comparison of the selected exothermal effects recorded during cooling.

Double endothermal effects were detected during heating in the DSC curves accordingly to gelatinisation processes taking place in dense suspensions, similarly as described in the previous papers [13, 28–34]. Single gelatinisation endotherm was observed for the watery suspensions. Endothermal amylose-lipid complex transition occurs in the gelatinised samples at the range of higher temperature.

Slightly higher values of peak and onset temperature of gelatinisation endothermal effect were determined for the dense suspensions of the irradiated sample heated at 5°C min^{-1}, as compared to those determined for the non-irradiated one (Table 1, points 3, 4; columns V, VI). Only a negligible increase in both values may be deduced after irradiation in the case of the watery suspensions heated with a rate of 10°C min^{-1} (Table 1, points 1, 2; columns V, VI).

DSC curves recorded during heating in the range of endothermal effect corresponding to the amylose–lipid complex transition were characterised by a high noise level accompanied by weak reproducibility (observed especially in the case of the irradiated sample). Accordingly, only approximate values of the peak temperature as well as onset or beginning temperature of the thermal effect were determined (Table 1, columns VII and VIII, points 1–4).

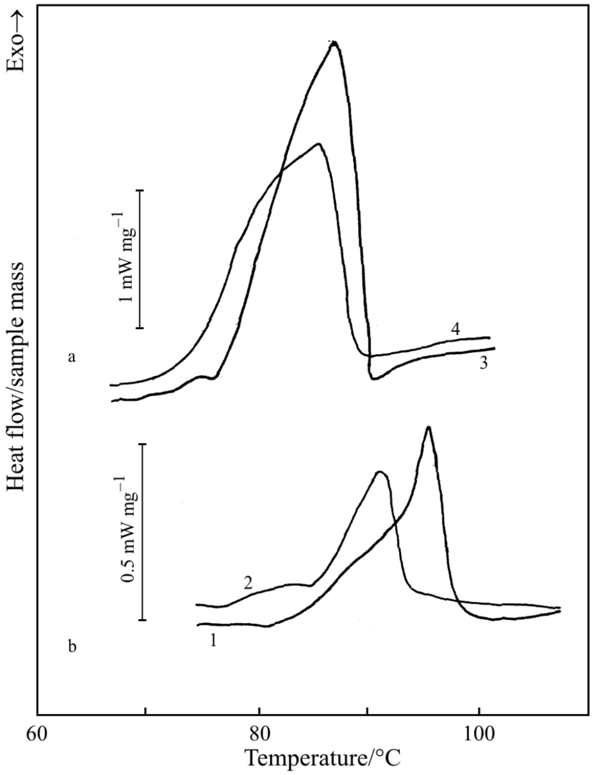

Fig. 2 The examples of exothermal effects detected during cooling of the water suspensions of wheat flour WF3, initial (curves 1, 3) and irradiated with 30 kGy (curves 2, 4): a – cooling at 10°C min^{-1} (initial: 25.73% of dry matter; irradiated: 25.82% of dry matter); b – cooling at 2.5° min^{-1} (initial: 50.0% of dry matter; irradiated: 51.39% of dry matter)

Good reproducibility was achieved for exothermal effect of the amylose–lipid complex transition occurring on cooling. The results have indicated a decrease in the peak and onset temperatures of the amylose–lipid complex transition caused by irradiation (Table 2, columns V–VII). Therefore, a decrease in peak temperature equal to ca. 2.1°C and in onset temperature equal to ca. 2.7°C was noticed in the case of the watery suspensions cooled at 10°C min^{-1} (Table 2, points 1, 2, columns V, VI). In the case of the dense suspensions cooled at 2.5°C min^{-1} (Table 2, points 3, 4) a larger decrease equal to ca. 4.3°C was found for both the peak and onset temperatures.

Smaller enthalpy values were obtained for gelatinisation taking place in the irradiated than in the non-irradiated samples. Moreover, the enthalpies of an amylose–lipid complex transition taking place both during heating and cooling in the irradiated samples were smaller than of the transition occurring in the initial ones under the same conditions. The approximate values of

Table 1 DSC results obtained during heating of the reference non-irradiated wheat flour sample and the sample irradiated with a 30 kGy dose applying a rate of 0.47 Gy s^{-1}. ΔH_g, Tp_g, Ton_g are the average values of enthalpy, peak and onset the temperature determined for gelatinisation, ΔH_a, Tp_a, are the average enthalpy and peak temperature determined for thermal effects of an amylose–lipid complex transition, while T_{0a} mean their beginning temperature. ΔH_t is the total value of enthalpy determined for both processes

No.	Dose/kGy	Concentration/ mass%	Heating rate/°C min^{-1}	Tp_g/°C	Ton_g/°C	Tp_a/°C	T_{0a}/°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
the primary DSC analysis										
1	0	25.8–27.4	10	63.4±0.2	58.0±0.2	93.2±1.5	nd (Ton_a=84.8±0.5)	13.8±0.2	11.2±0.8	2.6±0.8
2	30	24.7–27.4	10	63.8±0.2	58.7±0.1	93.5±2.0	nd	11.3±1.0	10.1±1.0	1.2±1.0
3	0	47.8–54.1	5	62.4±0.3	55.4±1.0	105.7±0.3	93.0±1.0	11.9±1.3^{a}	9.6±1.0	2.3±0.4
4	30	49.1–50.3	5	63.9±0.1	56.8±1.5	103.0±1.0	88.8±1.0	9.3±1.3^{a}	8.1±1.0	1.2±0.3
the second DSC analysis performed for the residue obtained after the DSC analysis described at positions 3 and 4 and stored at ambient temperature for 3 days										
5	0	51.1–54.1	5	53.8±0.1	43.8±0.5	113.5±0.8	95.5±2.5 (Ton_a=106.6±2.5)	8.8±0.4^{a,SE}	5.1±0.1	1.7±0.3
6	30	50.5–52.0	5	54.8±1.0	44.0±0.5	110.6±0.5	91.5±2.0 (Ton_a=100.5±2.0)	4.6±0.6^{a,SE}	3.1±0.3	1.5±0.3

^{a}determined as summa of the enthalpy values obtained for both thermal effects, nd – the value was not calculated due to insufficient reproducbility resulting from the irregular profile of the effect. ^{SE}two separated effects were recorded. The values of onset temperature (Ton_a) determined in selected cases for thermal effect of amylose–lipid complex transition are given in brackets.

Table 2 Average enthalpy values (ΔH_a), the peak and the onset temperature (Tp_a, Ton_a) of the amylose–lipid complex transition determined on the basis of endothermal effects occurring during cooling of the reference initial wheat flour sample irradiated with a dose of 30 kGy applying a dose rate of 0.47 Gy s^{-1}

No.	Dose/kGy	Concentration/mass%	Cooling rate/°C min^{-1}	Tp_a/°C	Ton_a/°C	ΔH_a/J g^{-1}
I	II	III	IV	V	VI	VII
the first DSC analysis						
1	0	25.8–27.4	10.0	77.3±0.1	81.6±0.3	–1.9±0.2
2	30	24.7–26.9	10.0	75.2±0.2	78.9±0.5	–1.5±0.2
3	0	47.8–52.7	2.5	96.3±0.5	98.1±1.0	–2.3±0.2
4	30	49.1–50.3	2.5	92.0±0.2	93.8±0.5	–1.7±0.2
the second DSC analysis performed for the residue obtained after the DSC analysis described at positions 3 and 4 stored at ambient temperature for 3 days						
5	0	51.1–54.1	2.5	99.3±1.0	101.6±1.0	–2.2±0.1
6	30	50.5–52.0	2.5	92.6±1.0	94.5±2.0	–1.7±0.1

total enthalpy and the partial enthalpies of both processes recorded during heating are given in the columns IX–XI of Table 1. The average values of enthalpy of the amylose–lipid complex transition occurring during cooling are presented in Table 2, column VII.

Secondary DSC analyses of gelatinised samples

DSC analyses of the dense samples were repeated (in single heating/cooling cycles) after three days storage at ambient temperature. The results and the description of the experimental conditions are presented in Table 1, points 5, 6 and Table 2, points 5, 6. The examples of DSC curves are shown in Fig. 3.

Small decreases of the water content in the pans (testified by the higher concentration values presented in column III, Table 1) are due to the mass loss resulting from the primary DSC analysis and further storage.

Gelatinisation was observed during heating, accordingly to the retrogradation that took place in the gels. The enthalpy of the process was smaller in the case of the irradiated flour as compared to the non-irradiated one. Moreover, the part of material which gelatinise after retrogradation (as related to that detected during the first DSC analyses) was smaller in the stored gel of the irradiated sample. The enthalpy values obtained during the second heating was equal to ca. 53% and to ca. 38% of these determined during the first heating for the initial and the irradiated samples, respectively (Table 1, column X, points 5, 3 and 6, 4, respectively). Only a negligible difference in the peak and onset temperature of the gelatinisation thermal effect may be deduced (Table 1, columns V, VI).

The well-separated thermal effects of the reversible transition of amylose–lipid complexes were observed both while heating and cooling (Fig. 3). These thermal effects were detected at higher temperature, both in the cases of the initial and the irradiated samples, than during the first DSC analyses carried out under the similar conditions. The transitions occur at lower temperatures in the irradiated sample than in the initial one, during as well heating and cooling. Moreover, one may notice that the difference between the transition occurring during cooling in the initial and the irradiated sample is larger during the present repeated analyses than during the first ones. For example, the peak temperature of the exothermal effect taking place while cooling was detected for the irradi-

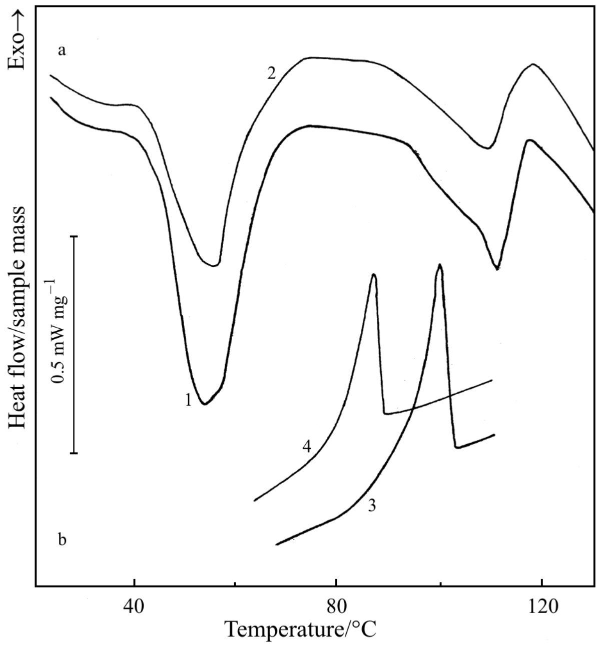

Fig. 3 Examples of DSC curves recorded for the wheat flour WF3, initial and irradiated with a 30 kGy dose (0.47 Gy s^{-1}) three days after the first analysis: curves 1, 3 – initial (49.26 % of dry matter), curves 2, 4 – irradiated (51.39 % of dry matter); a – heating with a rate of 5°C min^{-1} (curves 1,2); b – cooling with a rate of 2.5°C min^{-1} (curves 3, 4)

ated flour at a temperature ca. 6.7°C below and the onset at a temperature 7.1°C below these determined for the initial sample (Table 1, columns V, VI points 5 and 6), while the corresponding values both equal to 4.3°C were found on the basis of primary analyses carried out under the similar conditions (Table 1, points 3 and 4). The peak and beginning of endothermal effect was recorded during heating for the irradiated sample at 2.9 and 4.0°C below that found out for the initial sample (Table 4, points 5, 6, columns V, VI) as compared to 2.1 and 2.7°C, respectively, determined on the basis of the primary DSC analysis. Moreover, an onset temperature for the irradiated sample was determined at 6.1°C below that found for the initial one.

Primary DSC analysis of suspensions stored at depressed temperature

Dense suspensions were kept for 21 days at temperature of –20°C before measurements, while watery suspensions were stored at 4°C for 3 days and at –20°C for 21 days afterwards.

It was noticed in the previous experiments that the differences between the temperature of the amylose–lipid complex transition occurring in the initial and the irradiated samples were bigger when thermal effects were recorded during cooling then while the foregoing heating. Therefore, in the present series of measurements the transition was observed apart from the primary heating and cooling also during the next heating and cooling processes.

Thermal effects with an irregular profile were recorded. Particularly weak reproducibility for the amylose–lipid complex transition was obtained for thermal effects recorded during the first heating, when superposition with thermal effect of gelatinisation occur. Only the peak temperatures were determined, therefore, for thermal effects of both gelatinisation and complex transition taking place both during heating and cooling. Our results together with experimental conditions are presented in Table 3.

No differences may be deduced between the peak temperatures of thermal effects corresponding to gelatinisation taking place in the watery suspensions of the initial and the irradiated samples, while for dense suspensions an increase in gelatinisation temperature may be concluded after irradiation.

Amylose–lipid complex transition occurs in both samples at a higher temperature during the second heating (Table 3, points 1–3, columns V, VI), than during the first one. The transition occurs at a lower temperature in the irradiated samples than in the initial ones during the first cooling, the second heating and the second cooling. No explicit conclusion may be drawn concerning this transition occurring during the first heating on the basis of the presented data.

The differences between the transition taking place in the irradiated and non-irradiated samples were larger during the second cooling than during the first one. The peak temperature of thermal effects of the transition occurring in the watery suspensions of the irradiated sample was ca. 3.3°C lower during the first cooling and ca. 5.1°C lower during the second cooling than that of the transition taking place in the non-irradiated sample under the same conditions. The appropriate values determined on the basis of thermal effects recorded for dense suspensions were equal to ca. 1.7 and 3.3°C.

Apart from testing the possibility to observe the differences between the transition-taking place in the irradiated and non-irradiated samples after storage, this procedure was applied in purpose to check whether the exothermal process would be observed in the low temperature range (20–45°C). Such a process was noticed previously for the dense wheat flour suspensions stored before measurements at similar temperature [13]. No exothermal effect was, however, noticed at presently applied conditions during the first heating, alike in the case of the DSC analyses of the fresh suspensions.

Table 3 Average values of the peak temperature recorded during a double heating–cooling cycles with heating and cooling rate of 10°C min^{-1}. Points 1, 2 – the suspensions were stored before the DSC analyses for 3 days at temperature of 4°C and then for 21 days at temperature of –20°C. Points 3, 4 – the suspensions were stored at –20°C for 21 days

No.	Dose/kGy	Concentration/ mass%	Tp_g/°C	Tp_a/°C			
				Heating cycles		Cooling cycles	
			I heating	I heating	II heating	I cooling	II cooling
I	II	III	IV	V	VI	VII	VIII
1	0	21.3–23.1	63.3±0.3	93.6±1.0	98.9±1.4	76.9±2.0	76.8±2.0
2	30	21.22–24.2	63.0±0.2	92.7±0.3	98.1±0.6	73.6±0.1	71.7±0.8
3	0	49.1–49.2	63.6±1.0	107.6±0.1	111.5±1.5	91.3±0.2	91.7±0.1
4	30	48.9–50.0	65.7±0.1	nd	110.1±0.4	89.6±0.4	88.4±0.1

nd – not determined

Discussion

Gelatinisation of flour [13, 21–23] depends on the structure of the starch granules, but also on the presence and properties of other than polysaccharide components, alike proteins and lipids. The possible influence of the particular radiation-induced products on gelatinisation processes in flour was discussed in details in the preceding study [13] together with the evaluation of the possible conclusions arising from studies carried out using the particular methods.

A decrease in the enthalpy of gelatinisation taking place both in the dense and the watery suspensions found after irradiation at present was similar to the previous result concerning wheat flour [13, 35] and wheat as well as potato starches [14, 35, 36]. It can be concluded that the smaller gelatinisation enthalpy determined for the irradiated sample as compared to the non-irradiated one corresponds mainly to the smaller content of the crystalline phase in the irradiated starch than in the non-irradiated one. It supports the opinion [13] that the endothermal effect observed by DSC is connected to the decrease in ordering by the crystalline part of starch. In fact, relatively small decrease in gelatinisation enthalpy corresponds well to small decrease in crystallinity [6, 9] but not to essential decrease in macromolecular ordering [7–9, 13].

It was previously displayed that the specific conclusions concerning the influence of γ-irradiation on the gelatinisation temperature depend on the methods applied for studies and the condition applied in measurements (concentration, heating rate) due to the kinetic restrictions [13]. The present results, in comparison with the previous ones [13], indicate additionally that the conclusions resulting from experimental data obtained under selected conditions may differ also for particular flour batches. Indeed, the influence of irradiation on gelatinisation temperature found in the present study corresponds well to our results obtained for the potato starch sample used in [14] and wheat starch sample used in [36], whereas differs rather from those obtained for the previously examined wheat flour batch (dense suspensions). In particular, an increase in the gelatinisation temperature after irradiation can be concluded at present for the dense suspensions heated with a rate of 5 and 10°C min^{-1} on the basis of the lower peak and onset temperatures determined for the irradiated than for the non-irradiated samples. The previously examined wheat flour has revealed a decrease in the temperature of gelatinisation taking place in a dense suspension during heating at 10°C min^{-1} after sample irradiation, while a negligible increase in that temperature might be deduced for the same processes occurring during heating at 2.5°C min^{-1}. Therefore, finding of the other parameter which may describe irradiation effect on gelatinisation temperature (as, for example, an apparent activation energy [13]) seems to be the more important.

Rather small differences were detected between the peak and onset temperatures of gelatinisation process occurring in watery suspensions of the initial and the irradiated wheat flour during heating at 10°C min^{-1}, alike in the case of both wheat and potato starch [14, 36]. After irradiation a relatively small increase in temperature of gelatinisation taking place in fresh suspensions can be concluded, while no differences may be deduced for the process occurring in the suspensions stored before measurements at a low temperature.

The smaller gelatinisation enthalpy determined for the irradiated (dense) gelatinised sample after three days of storage at ambient temperature than for the non-irradiated one subjected to the identical treatment, indicates a smaller amount of the crystalline fraction formed in the irradiated sample. Moreover, the amount of the former crystalline material, which recrystallized under these conditions, was smaller in the irradiated sample than in the initial one. It shows that irradiation decreases the recrystallization (retrogradation) ability of the dense flour gel. It well corresponds to the decreased capability for creation of the crystalline oriented regions in the presence of water, concluded for the irradiated flour on the basis of smaller gelatinisation enthalpy values and on the basis of SAXS data [7–9]. It conforms also to the reduced ability for absorbing water vapour from atmosphere and for forming the crystalline regions in a solid-state, found by WAXS method for potato starch [6, 9, 18]. This disordering is caused by a decrease in the polysaccharides chain length resulting from irradiation.

Essential influence of radiation on the amylose–lipid complex transition was detected. The differences between the amylose-lipid complex transition occurring in the initial and the irradiated samples were easier detected by DSC analysis during subsequent cooling than while preceding heating. Smaller differences were, however, discovered between the temperature of the transition ongoing in the initial and the irradiated samples during the first heating, in comparison with the previous study [13]. It is connected with a smaller reproducibility of the present data.

The lower temperature of the transition taking place in the irradiated flour as compared to that occurring in the non-irradiated one indicates the lower stability and consequently the lower complex symmetry after irradiation. Smaller enthalpy values determined for the irradiated sample as compared to the non-irradiated one suggest that irradiation reduces ability to form amylose–lipid complexes. The reduced ability for creation of this type of complexes and the modified structure of the resulting complexes after irradiation is probably caused by modification of starch macromolecules (especially decrease in the chain length and in crystalline ordering) and possible transformation of lipid molecules.

Increase in the transition temperature (indicated by an increase in peak and onset temperature of thermal effects) after thermal treatment followed by retrogradation suggests that such acting improve the amylose–lipid complex structure both in the initial and in the irradiated sample. It is probably partially due to the known fact that the complexes between starch and lipids may be created during thermal treatment of the gelatinised samples. It might be supposed, consequently, that thermal treatment causes reinforcement of the links between a polysaccharide chain and a lipid molecule. The smaller increase in temperature of transition discovered for the irradiated sample than for the initial one indicates that smaller improvement of the complex structure occurs under the applied treatment in the irradiated flour than in the initial one. In result, it is easier to detect differences between thermal effects corresponding to the amylose–lipid complex transition recorded during the second DSC analysis carried out after three days from the primary measurement.

The physico-chemical changes following in granules after a prolonged storage in water at a low temperature (4, –20°C) lead to observation of smaller thermal effects of amylose–lipid complex transition and consequently to deterioration of reproducibility of DSC data. Thermal effects of amylose–lipid complex transition were still observed, however, at a lower temperature in the case of the irradiated samples than in the case of the non-irradiated one during the first and the second cooling and the second heating. The transition was observed at an essentially higher temperature during the second heating than during the first one, just as in the case of the second analysis carried out after retrogradation. Moreover, it might be noticed that the transition occurs in the irradiated sample at a lower temperature during the second than during the first cooling, while it takes place at the same or a slightly higher temperature in the non-irradiated sample. In result, the difference between exothermal transition recorded for the irradiated and non-irradiated samples are larger during the second than during the first cooling conducted in the same DSC course.

The comparison of the results obtained for fresh suspensions during the first DSC course with those obtained during the second one after three days of retrogradation indicates that the appropriate treatment of the sample may lead to enlargement of the irradiation effect on the amylose–lipid complex structure. Therefore, it seems possible to elaborate the procedure enabling to extend differences between the irradiated and non-irradiated samples and to use observation of the transition of the amylose–lipid complex by DSC for testing irradiated foods in the future.

Conclusions

Differences were observed between endothermal effects of gelatinisation and amylose–lipid complex transition occurring in both dense and watery suspensions of non-irradiated and irradiated with 30 kGy wheat flour heated at 10 and 5°C min^{-1} and cooled at 10 and 2.5°C min^{-1}. The differences were found when DSC measurements were carried out for the fresh suspensions as well as in the case of suspensions stored before the measurements at temperatures of 4 and –20°C and during the second analyses performed for a gelatinised samples after 3 days from the primary experiments.

Smaller enthalpies of gelatinisation and of the transition of amylose–lipid complex were determined for the irradiated than for the non-irradiated samples. The altitude of differences between peak and onset temperature of both thermal effects recorded for the initial and the irradiated flour samples depend on the conditions applied during the DSC measurements (concentration, heating rate) and of preceding treatment of the samples with regard to their influenced physico-chemical properties.

Retrogradation occurs easier in the dense suspensions of the non-irradiated wheat flour than in the dense suspensions of the irradiated sample.

Thermal effects of the reversible amylose–lipid complex transition were recorded always at a lower temperature in the case of the irradiated samples than in the case of the non-irradiated ones, both during heating and cooling of the dense and watery suspensions. The differences between this transition taking place in the non-irradiated and the irradiated wheat flour were larger during the second DSC analysis performed after 3 days for the gelatinised samples than during the first DSC course. It is due to the fact that such treatment improves complex structure of the irradiated sample less than that of the non-irradiated one. These differences were also larger during the second cooling processed as the following step in the same DSC analysis than during the subsequent first cooling. A prolonged storage of the suspensions at a depressed temperature reduces possibility to detect of irradiation effects on the amylose–lipid complex.

Acknowledgements

Thanks are due to Mr. Wojciech Głuszewski from the Institute of Nuclear Chemistry and Technology for performing γ-irradiation.

The financial support of the Swedish Institute (fellowship of Dr. Krystyna Cieśla), enabling to perform DSC experiments at Lund University is kindly acknowledged.

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Received: January 20, 2004
In revised form: July 14, 2004