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PRELIMINARY STUDIES USING DIFFERENTIAL SCANNING CALORIMETRY OF RADIATION-INDUCED TRANSFORMATIONS IN STARCH AND FLOUR

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Abstract

Differential scanning calorimetry was applied in studies of the effect of gamma irradiation on the potato starch and wheat flour. Essential differences were noticed between endothermal effects observed in concentrated suspensions of the initial and irradiated potato starch and wheat flour heated at a rate of 2.5°C min^{-1}, while only small differences were noticed between gelatinization thermal effects recorded for ca. 20% suspensions of the initial and irradiated potato starch samples heated at a rate 10°C min^{-1}. Moreover, in the case of wheat flour, a decrease of decomposition temperature of the amylose-lipid complex was concluded.

Keywords: amylose-lipid complex transition, differential scanning calorimetry, gamma irradiation, potato starch, starch gelatinization, wheat flour

Introduction

Processes occurring during heating, such as starch gelatinization and glass transition creation and transformation of amylose- and amylopectin-lipid complexes or retrogradation depend on the starch structure: its chain length and number of lateral branches. Differential scanning calorimetry (DSC) has been proved as a useful method for examination of these processes [1–4]. One can expect that chemical and structural changes provoked by gamma irradiation, in particular starch degradation [5–7] and decrease of ordering in starch granules [8–12], would influence those processes. The different nature of viscosity changes found in non-irradiated and irradiated starch gels [13] indicates a possibility to detect some differences also between DSC images of initial and irradiated starch and flour samples.

In this paper the results of preliminary DSC studies on gamma irradiation effect on gelatinization of potato starch and wheat flour are presented. The possibility to observe differences between endothermal effects of gelatinization in irradiated and non-irradiated samples was tested on heating 20% potato starch suspensions with a rate of 10°C min^{-1} and >42 % wheat flour suspensions at a rate of 2.5°C min^{-1}.

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Experimental

Sample preparation and irradiation

Potato starch was extracted in April-May from potatoes of Fauna type (harvested in October and kept at 4°C). A purified sample was dried at 60°C for 18 h. A commercial Polish wheat flour of 'Poznańska' type was used.

Irradiation with gamma rays were carried out in air at ambient temperature with the use of ^{60}Co sources placed in gamma cells installed in Department of Radiation Chemistry in Institute of Nuclear Chemistry and Technology. Native potato starch was irradiated with a dose 20 kGy, applying a dose rate of 1.6 kGy h^{-1} in a gamma cell Issledovatiel. The wheat flour sample was irradiated with a dose of 30 kGy in a gamma cell Mineyola, using a dose rate of 1.7 kGy h^{-1}.

Differential scanning calorimetry

DSC measurements were carried out on a Perkin Elmer DSC-2C calorimeter at temperatures within 30–130°C in an inert gas stream (nitrogen). The instrument was calibrated with gallium (*m.p.*=29.8°C) and indium (*m.p.*=156.6°C). The measurements of ca 20% starch suspensions (3 measurements for each sample) were performed at a heating rate of 10°C min^{-1}, whereas the 42.84–52.40 (by mass) suspensions of potato starch (5 measurements for each sample) and wheat flour (6 measurements for each sample) were heated with a rate of 2.5°C min^{-1}. Covered aluminium pans from TA Instruments were used in the experiments and an empty pan with a double lid was used as the reference pan. Starch and flour suspensions in twice distilled water were located in the pre-weighted DSC pans, which were then hermetically closed and re-weighed. 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 average values of transition enthalpy are given in terms of dry matter content. The enthalpies, peak and onset temperatures were calculated basing on several duplicate measurements by a software developed at the Lund University.

Results

Potato starch gelatinization

Single sharp effect of gelatinization was observed on DSC curves recorded on heating aqueous suspensions of concentration about 20% (20.42–23.35%) with a rate of 10°C min^{-1} (Fig. 1). Under these conditions no significant difference between DSC curves of the initial and the irradiated samples was observed, except that the onset temperature was higher for the irradiated sample. The peaks were observed at 67.8±0.1 and at 68.0±0.1°C, while the onset temperatures at 63.7±0.1 and 64.2±0.1°C in the case of the initial and the irradiated samples, respectively.

Two maxima were observed in the endothermal effect of the concentrated suspensions (42.84–44.64%) of the initial sample, connected with two steps gelatiniza-

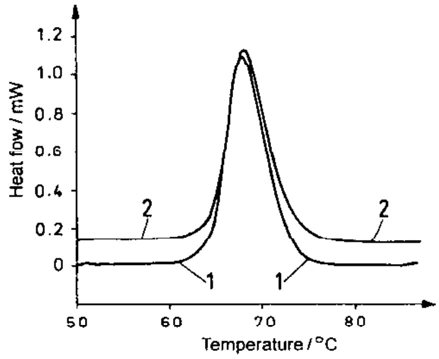

Fig. 1 Comparison of DSC curves recorded at a heating rate of 10°C min^{-1} for low concentration aqueous suspension of initial and irradiated potato starch: 1 – initial (20.42%, 1.904 mg of dry mass), 2 – irradiated with 20 kGy (22.72%, the values of ordinate were standarized for 1.904 mg of dry mass, while 2.208 mg mass portion was used in the experiment)

tion processes (Fig. 2). Besides of the sharp peak at 64.3±0.1°C (the onset was found at 61.2±0.1°C), a shoulder is noticed at higher temperatures. Both the peak and the onset temperatures were higher in the case of the irradiated sample, as compared to those of the initial one, and equal to 63.9±0.1 and to 66. 9±0.1°C. Moreover, in the case of the irradiated sample, a decrease in the height of the first maximum, accompanied by disappearance of boundaries between two endothermal effects, was observed. A comparison of selected DSC curves is shown in Fig. 2.

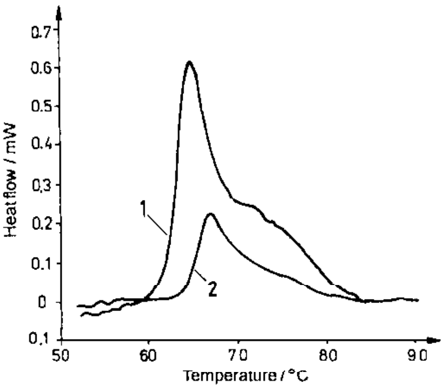

Fig. 2 Comparison of DSC curves recorded at a heating rate of 2.5°C min^{-1} for concentrated aqueous suspensions of potato starch: 1 – initial sample (45.13%, 2.870 mg of dry mass), 2 –sample irradiated with a dose of 20 kGy (45.22%, 3.218 mg; the values of ordinate were standarized for 2.870 mg of dry mass)

It may be concluded that the enthalpy of gelatinization decreases after irradiation. The enthalpy values found for the initial and the irradiated samples on the basis of the results obtained for diluted suspensions at heating rate 10°C min^{-1} were calculated as 19.0±0.3 and as 17.2±0.3 J g^{-1}, respectively. The enthalpy values found for the concentrated suspensions of initial and the irradiated samples (heated with 2.5°C min^{-1}) were calculated as 17.3±1.0 and 13.9±1.0 J g^{-1}, respectively.

Wheat flour gelatinization

43.44–52.40% aqueous suspensions of initial wheat flour and a sample irradiated with a dose of 30 kGy were examined with a heating rate 2.5°C min^{-1}. Examples of DSC curves of irradiated and non-irradiated flour are shown in Fig. 3.

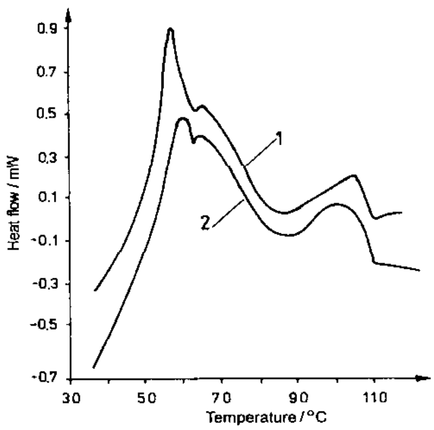

Fig. 3 Comparison of DSC curves recorded at a rate of 2.5°C min^{-1} for suspensions of non-irradiated wheat flour (1), and irradiated with a dose of 30 kGy (2). The concentration of the initial flour suspension was 46.67% (3.567 mg of dry mass) and that of the irradiated flour was 48.22% (3.037 mg of dry mass, the values of ordinate were standarized for 3.567 mg)

Two steps gelatinization processes were observed, like in the case of concentrated starch suspensions. The gelatinization was followed by endothermal transition of the amylose-lipid complex. Similarily, as in the case of potato starch, the occurrence of two gelatinization processes, easily detected in the case of the initial sample, was not so evident in DSC curves of the irradiated sample suspensions of identical concentration. A negligibly higher peak and onset temperatures were found for the gelatinization effect of the irradiated flour. The mean values of the peak temperature were determined on the basis of 6 measurements as 59.1±0.5 and at 59.9±0.5°C for non-irradiated and irradiated samples, respectively. The respective onset temperature values were 50.2±0.5 and 51.2±0.5°C.

Moreover, it may be stated, that the transition temperature of the amylose-lipid complex decreases after irradiation. The mean peak temperature of the endothermal effect of this transition was determined as 105.4±1.0 and at 101.8±1.0°C for the initial and the irradiated samples, respectively.

It was difficult to calculate exactly the gelatinization and amylose-lipid complex transition enthalpies, because of the indistinct boundaries of both small and broaden effects. Decrease, resulting from irradiation may be, however, deduced, in the gelatinization enthalpy and in the total enthalpy of two processes, calculated from the beginning of gelatinization to the end of amylose-lipid complex transition. The average values of total enthalpy 13.7±0.8 and 11.2±0.8 J g^{-1} were found for the initial and the irradiated samples respectively. The values of gelatinization enthalpy, obtained on the way of integration in the partial area were equal to 11.0±1.0 and 8.2±1.0 J g^{-1} for the initial and the irradiated sample. The respective values of amylose-lipid complex decomposition enthalpies were equal to 2.7±0.4 and 3.0±0.8 J g^{-1}.

Discussion

The differences between endothermal effects of gelatinization occurring in suspensions of irradiated and non-irradiated potato starch and wheat flour were observed by DSC. These differences, i.e. decrease of gelatinization enthalpy after irradiation and broadening of endothermal effects give evidence on decrease of ordering in starch grains, found previously by X-ray scattering [8–12].

The obtained results were found to depend on conditions of the DSC experiment. Essential differences were noticed in the shape as well as in the peak and onset temperature of endothermal effects observed in concentrated suspensions of the initial and irradiated potato starch and wheat flour heated at a rate of 2.5°C min^{-1} , while only small differences were noticed between gelatinization thermal effects recorded for ca. 20% suspensions of the initial and irradiated potato starch samples heated at a rate 10°C min^{-1} .

The occurrence of two gelatinization maxima is a well known phenomenon observed in suspensions of high concentration of starch [2–4], probably due to the occurrence of two different kinds of crystalline regions in the presence of small amount of water. The gelatinization of the regions with lower degree of orientation, predominant in the sample, occurs at lower temperatures and is accompanied by a sharp thermal effect. The gelatinization of regions indicating higher orientation level occurs at higher temperatures and is accompanied by a shoulder observed at higher temperatures on the DSC curves. It can be concluded, on the basis of the gelatinization endotherm shape, that the destruction of the first type regions, in consequence of irradiation, is faster than the destruction of the regions of the second type. The decrease of total gelatinization enthalpy of potato starch and wheat flour is accompanied by the decrease in the height of the first maximum of thermal effect of gelatinization. Moreover, an increase in peak and onset temperatures of gelatinization effect is observed in the case of potato starch.

A decrease of transition temperature of the amylose-lipid complex in wheat flour indicates also the presence of structural transformations occurring in starch grains under the effect of irradiation.

References

1 A.-C. Eliasson, Thermochim. Acta, 246 (1994) 343.
2 I. Larsson and A.-C. Eliasson, Starch/Starke, 43 (1991) 227.
3 E. Svensson and A.-C. Eliasson, Carbohydr. Polym., 29 (1995) 171.
4 J. Lelievre and Hua Liu, Thermochim. Acta, 246 (1994) 309.
5 J. Raffi, J. P. Agnel, C. J. Thiery, C. M. Frejaville and L. Saint-Lebe: J. Agric. Food Chemistry, 29 (1981) 1227.
6 T. Hayashi and S. Aoki, J. Agric. Food Chem., 33 (1985) 14.
7 Y. Ghali, N. Ibrahim and H. Aziz, Starch/Starke, 31 (1979) 325.
8 K. Cieśla, T. Żółtowski and L. Yu. Mogilevski, Starch/Starke, 43 (1991) 11.
9 K. Cieśla, E. Gwardys and T. Żółtowski, Starch/Starke, 43 (1991) 251
10 K. Cieśla, T. Żółtowski and L. Yu. Mogilevski, Starch/Starke, 44 (1992) 419.
11 K. Cieśla, T. Żółtowski and R. Diduszko, Food Structure, 12 (1993) 175.
12 K. Cieśla, Zeszyty Naukowe PŁ – Inżynieria Włókiennicza i Ochrona Środowiska Nr2/16 (1993) 343.
13 K. A. Korotchenko, M. A. Nadzafova and V. A. Sharpatyi, Izv. Vyssh. Uchebn. Zaved., Pishch. Teknol., (1982) No. 1, 76.