For chitosan after chemical-radiation degradation, the first peak is not observed and the peak at $2\theta=20.2^{o}$ is much less intensive. The results show that chemical-radiation degradation of chitosan caused destruction of the crystal structure.

References

[1]. Mao S., Shuai X., Unger F., Simon M., Bi D., Kissel T.: Int. J. Pharm., 281, 45-54 (2004).
[2]. Tian F., Liu Y., Hu K., Zaho B.: Carbohydr. Polym., 57, 31-37 (2004).
[3]. Choi W.S., Ahn K.J., Lee D.W., Byun M.W., Park H.J.: Polym. Degrad. Stabil., 78, 533-538 (2002).
[4]. Kume T., Nagasawa N., Yoshii F.: Radiat. Phys. Chem., 63, 625-627 (2002).
[5]. Tham L.X., Nagasawa N., Matsuhashi S., Ishioka N.S., Ito T., Kume T.: Radiat. Phys. Chem., 61, 171-175 (2001).
[6]. Hien Q.N., Nagasawa N., Tham L.X., Yoshii F., Dang V.H., Mitomo H., Makuuchi K., Kume T.: Radiat. Phys. Chem., 59, 97-101 (2000).
[7]. Bittelli M., Flury M., Cambell G.S., Nichols E.J.: Agric. For. Meteorol., 107, 167-175 (2001).
[8]. Zheng L.Y., Zhu J.F.: Carbohydr. Polym., 54, 527-530 (2003).
[9]. Roberts G.A.F., Domszy J.G.: Int. J. Biol. Macromol., 4, 374-377 (1982).

DSC STUDIES OF GAMMA IRRADIATION EFFECT ON INTERACTION OF POTATO STARCH WITH THE SELECTED FATTY ACIDS AND THEIR SODIUM SALTS

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Differential scanning calorimetry (DSC) appeared to be the appropriate method for detection of gamma irradiation influence on starch interaction with lipids [1-3]. Structural modification of macromolecules and possible changes in the lipid surrounding induced by gamma irradiation, as well as possible modification of the lipid molecules, were found to affect the properties of the inclusion amylose-lipid complexes formed with naturally occurring lipids on heating wheat starch and flour (A-type) [1,2]. Our preliminary DSC studies have also shown differences between the complexes formed by irradiated and the non-irradiated potato starch (B-type) and admixed 1-mono-lauroyl glycerol [3].

Currently, the effect of potato starch irradiation with ^{60}Co gamma rays using a 30 kGy dose was studied on its interactions with two fatty acids (lauric and palmitic) and their sodium salts.

Irradiations with ^{60}Co gamma radiation were carried out in a gamma cell "Issledovatel" in the Department of Radiation Chemistry and Technology, Institute of Nuclear Chemistry and Technology. DSC studies were carried out using a DSC calorimeter of TA Instruments instaled in Vrije Universiteit Brussel (Belgium). DSC studies were carried out during several heating-cooling-heating cycles with a heating and cooling rate of $10^{o}Cmin^{-1}$. The Universal Thermal Analysis Package was applied for data analysis. The suspensions placed in hermetically closed pans were characterized by the surfactant : polysaccharide : water ratio of 1:10:10. This corresponds to 0.498 mmol of lauric acid, 0.390 mmol of palmitic acid, 0.458 mmol of sodium laurate and 0.359 mmol of sodium palmitate per 1 g of starch. DSC studies were carried out during several heating-cooling-heating cycles with a heating and cooling rate of $10^{o}Cmin^{-1}$. Additionally, some complementary studies were continued with a heating and cooling rate of $5^{o}Cmin^{-1}$ applying the smaller lipid to starch ratios. These values correspond to 0.274 and 0.137 mmol of sodium laurate or sodium palmitate per 1 g of starch and 0.274 and 0.68 mmol of palmitic acid per 1 g of starch.

Melting of dry solid lauric and palmitic acids are accompanied by endothermal effects with peaks at 45.2 and 65.5°C. Melting of both sodium salts occurs at a considerably higher temperature and is accompanied by double thermal effects with peaks at *ca*. 122 and 135°C. No influence of water presence was noticed on the temperature range of melting of both fatty acids, while melting of both sodium salts occur under such conditions at a considerably lower temperature. During the first heating, melting of lauric acid and sodium laurate in water takes place in a temperature range lower

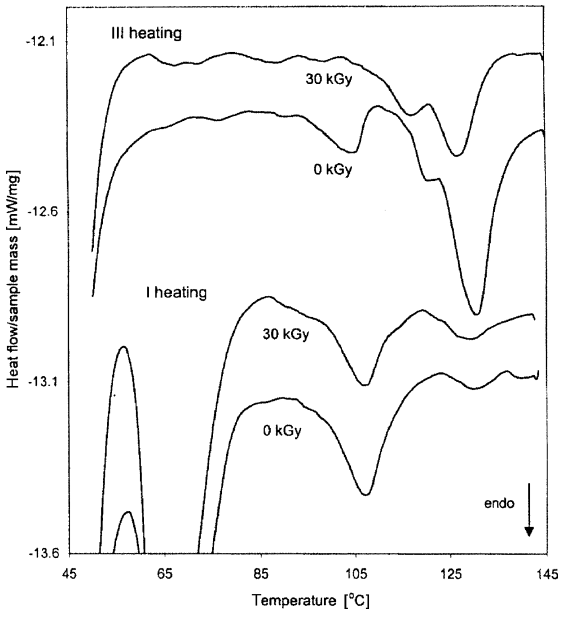

Fig.1. Thermal effects attributted to the melting of amylose-lipid complexes recorded during the first and third heating of the system containing lauric acid admixed to the non-irradiated and irradiated starch (at weight ratio equal to 1:10).

than gelatinization (the example in Fig.1; thermal effect recorded at a temperature below 60°C). Melting of sodium palmitate starts also at a lower temperature but continues during gelatinization while sodium palmitate melts in the same tempera-

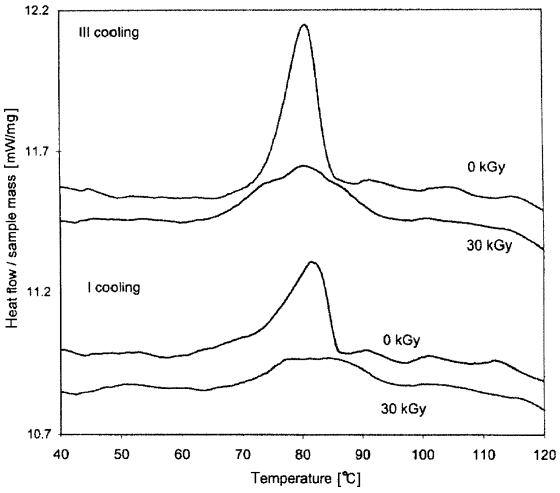

Fig.2. Thermal effects attributted to the crystallization amylose-lipid complex recorded during the first and third cooling of the system containing lauric acid admixed to the non-irradiated and irradiated starch (at weight ratio equal to 1:10).

ture range as starch gelatinizes. Formation of the inclusion complex (exothermal) occcurs during gelatinization of starch (endothermal). Accordingly, the lower total enthalpy was determined on the basis of the second thermal effect than that expected for gelatinization of pure starch present in the system containing simultaneously lauric acid, sodium laurate or sodium palmitate. Transition of the resulting amylose-lipid complex occurs in the range of higher temperatures. In the case of palmitic acid addition, decrease of joint enthalpy of gelatinization and melting of lipid, in relation to the

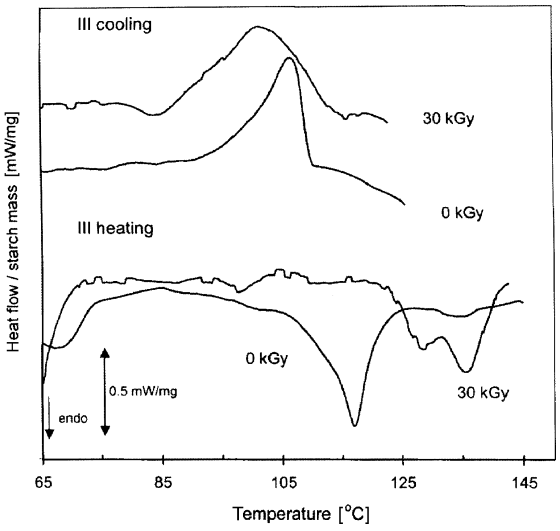

Fig.3, Thermal effects recorded during the third heating and the third cooling of the system containing sodium palmitate admixed to the non-irradiated and irradiated starch (at weight ratio equal to 1:10).

separate enthalpies of both processes was, however, less evident.

During the subsequent cooling and heating cycles, the processes of crystallization and melting of the amylose-lipid complexes and of free lipid, present in excess in the system, took place.

The differences were noticed between thermal effects recorded for the non-irradiated and irradiated starch during the first cooling and during the subsequent heating and cooling routes. However, only on addition of lauric acid the results correspond well to those obtained previously for the complexes formed in wheat starch with naturally occurred lipids, or in the complexes formed by potato starch with mono-lauroyl-glycerol [1-3]. Transformations of starch lipid complexes occur then at lower temperature in the irradiated than in non-irradiated samples containing lauric acid as well on heating and on cooling (Figs.1 and 2) and are accompanied by a smaller enthalpy. Melting and crystallization processes taking place during the course of thermal analysis induces in both cases ordering in the complex structure (proved by an increase in the enthalpy and temperature of the complex transitions). However, that effect is considerably larger in the case of non-irradiated starch than in the case of irradiated starch.

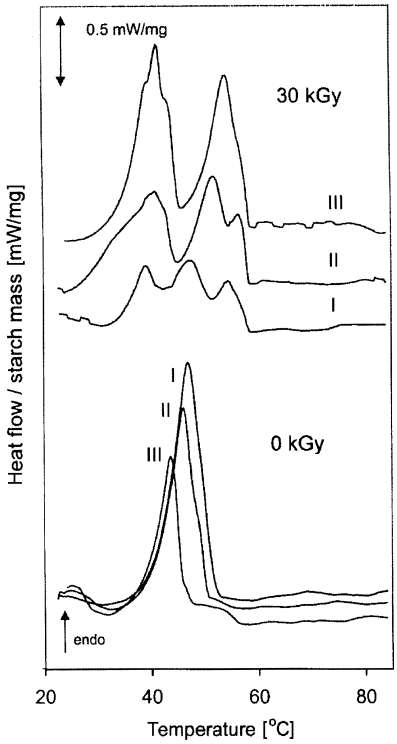

Fig.4. Thermal effects recorded during the first, second and third cooling of the system containing sodium palmitate admixed to the non-irradiated and irradiated starch (at weight ratio equal to 1:10). The enthalpies determined for the first, second and third crystallization of the free-lipid phase in the non-irradiated system are equal to -6.0, -4, 8, -3,7 and the irradiated system -3.8, -7.0, -8.6. The enthalpy determined for melting of this phase during heating was equal to 9.4 and 9.2 both on the third and second heating of these systems.

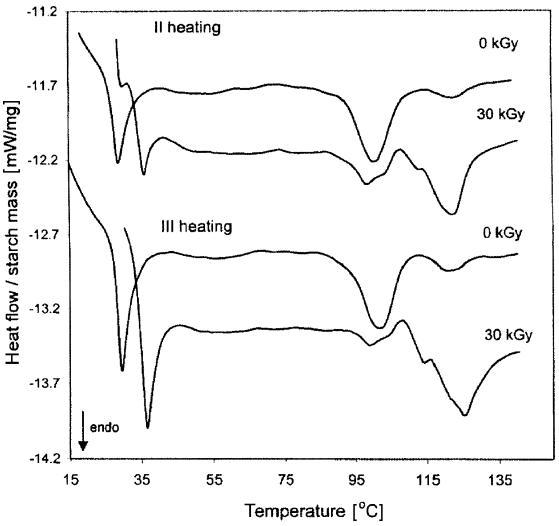

Fig.5. Thermal effects attributed to the melting of amylose-lipid inclusion complexes recorded during the second and third heating of the system containing sodium laurate admixed to the non-irradiated and irradiated starch (at weight ratio equal to 1:10).

In contrary to the previously examined systems, thermal effect that can be attributed to melting of the amylose-lipid complex occurs at higher temperature during heating of the system containing sodium palmitate and the irradiated starch as compared to that containing the non-irradiated one (Fig.3). However, similarly as in the previous cases, crystallization of the complex was observed at considerably lower temperature in the case of irradiated starch as compared to the non-irradiated one and was accompanied additionally by the endothermal process occurring in a low temperature range (Fig.3). Moreover, the differences were noticed between the route of melting and crystallization of free lipid phase (examples in Fig.4). Therefore, melting occurs at lower temperature in the case of non-irradiated than irradiated starch. This can be attributed to the differences in the structure of the intermediate phase containing lipid and the non-irradiated and those containing lipid and the irradiated starch. Furthermore, after thermal treatment an increase in the enthalpy of crystallization is observed in the system containing the irradiated starch, while a decrease in enthalpy of crystallization occurs in that containing the non-irradiated starch (Fig.4). This points out the weaker interaction between free lipids and non-irradiated starch as compared to the irradiated starch with additional weakening caused by thermal treatment of the irradiated system, in contrary to the strengthening induced in the non-irradiated starch. Simultaneously, no differences were noticed between enthalpies determined for the second and the third melting of this phase in both systems (Fig.4, the caption).

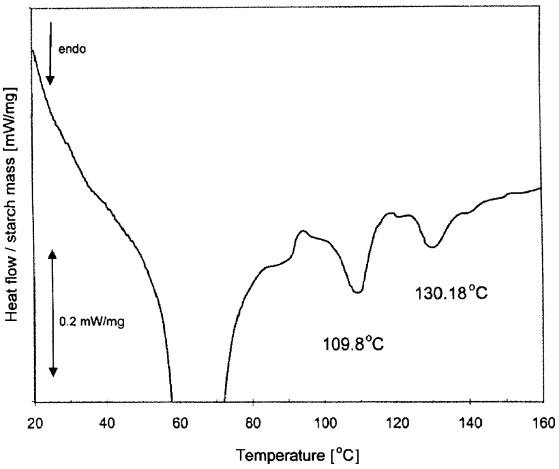

Fig.6. Thermal effects attributed to the melting of amylose-lipid inclusion complexes recorded during the second and third heating of the system containing palmitic acid admixed to the non-irradiated and irradiated starch (at weight ratio equal to 1:10).

Similar results as in the system containing sodium palmitate were obtained in heating the system containing sodium laurate with that difference that exothermal process accompanies melting of the complex formed in the mixtures containing the irradiated starch (Fig.5). This process probably con-

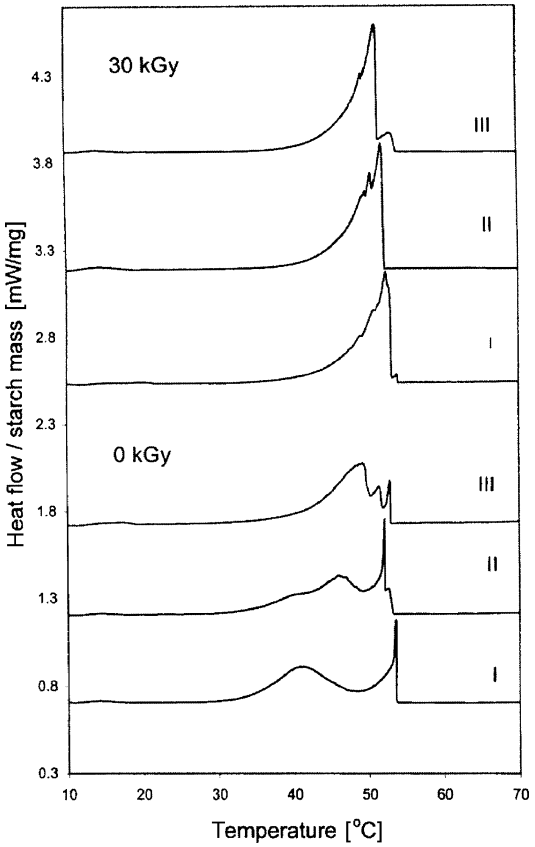

Fig.7. Thermal effects recorded during the first, second and third cooling of the system containing palmitic acid admixed to the non-irradiated and irradiated starch (at weight ratio equal to 1:10). The enthalpies determined for the first, second and third crystallization of the free-lipid phase in the non-irradiated system are equal to -6.0, -4, 8, -3,7 and in the irradiated system -3.8, -7.0, -8.6. The enthalpy determined for melting of this phase during heating was equal to 9.4 and 9.2 both on the third and second heating of these systems.

sist in crystallization of the complex phase during melting (resulting probably in the increased peak temperature) and was not detected in non-irradiated starch. The other difference is that crystallization taking place at the first, second and third cooling of the complexes formed in both irradiated and non-irradiated starch was always accompanied by single exothermal effects with a peak at 89-90°C. A similar conclusion concerning the irradiation effect on weakening the starch interaction with the free lipid phase can be, however, derived as in the system containing sodium palmitate.

Formation of the inclusion complex occurs with low efficiency in palmitic acid addition and during the third heating small effects of the complex melting were detected only in the non-irradiated starch (Fig.6). However, a strong interaction were noticed between the starch and free-lipid phase (Fig.7). This concerns probably formation of the so-called surface complex. In fact, the homogeneous residues were obtained after thermal analyses performed with a small palmitic acid content. These interactions were considerably smaller in the irradiated starch as compared to the non-irradiated starch.

Although the differences were noticed between structural properties of the connections formed between the irradiated and non-irradiated starch with all the examined ligands, the effect of irradiation differs depending on the ligand. Moreover, the differences were detected between the influence of thermal treatment on these properties.

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References

[1]. Cieśla K., Eliasson A.-C.: Radiat. Phys. Chem., 68, 933-940 (2003).
[2]. Cieśla K., Eliasson A.-C.: J. Therm. Anal. Calorim., 79, 19-27 (2005).
[3]. Cieśla K., Eliasson A.-C.: DSC studies of gamma radiation effect on the amylose-lipid complex formed in wheat and potato starches. Acta Aliment., in press.

SURFACE TENSION STUDIES OF BINDING CETYLTRIMETHYLAMMONIUM BROMIDE TO GAMMA IRRADIATED AND NON-IRRADIATED POTATO AMYLOPECTIN

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Decrease in molecular weight and the order in starch granules affects gelatinization processes in both A and B types of starch [1-4]. Accordingly, the influence of gamma irradiation was discovered on the interaction of A-type starches with naturally occurring lipids [2,3]. In regard to the structural modification of macromolecules and the formation of short molecular products, differences were also found between the possibilities for binding at ambient temperature of iodine by the irradiated and non-irradiated starch and the structure of the resulting products [4]. Accordingly, gamma radiation is also expected to modify interaction of B-type starches with admixed surfactants: binding of the ligands and the product properties.

Surface tension measurements have appeared useful in studying the interaction of iodine and surfactants with starch polysaccharides [5,6]. This is because that surface tension can be considered as a measure of the monomer surfactant in solution. Therefore, the more the monomer of surfactant in solution, the more the surface tension will decrease before micelles of surfactant start to form. At present, our preliminary results are shown dealing with the effect of irradiation on binding of cetyltrimethylammonium bromide (CTAB) on starch polysaccharides. The method was applied for examination of the process taking place at only slightly elevated temperature enabling to obtain homogeneous CTAB solution.

Waxy potato starch (a pure potato amylopectin) was obtained due to genetic engineering methods and was kindly supplied by Lyckeby Stärkelsen (Sweden). The native dry amylopectin was irradiated with ^{60}Co gamma rays with a 30 kGy dose in a gamma cell "Issledovatel" installed in the Department of Radiation Chemistry and Technology, Institute of Nuclear Chemistry and Technology. Moreover, commercial potato starch was used for the complementary experiments using a Brookfield voscometer. Native dry potato starch or 1% starch gels were irradiated with doses of 10, 20 and 30 kGy.

Axisymmetric drop shape analysis (ADSA) with a Tracker instrument (IT Concept, Longessan, France) installed at the University of Lund (Sweden) was applied for surface tension studies. A syringe with a u-shaped needle was lowered into the sample cell and an air bubble was produced from the syringe. The dynamic surface tension was measured by filming the rinsing buble and analysing the contour of the bubble. The experiments were performed at 27°C (above the Kraft temperature of CTAB). CTAB was gradually introduced to 0.25% polysaccharide gel solutions and the effect of addition each portion of surfactant was studied on their surface tension. The dynamic surface tension was monitored for one hour in each measurement and the equilibrium surface tension was determined as the value when a stable level was reached. The curves representing dependence of equilibrium surface tension on CTAB concentration were then constructed accordingly to the method described by Lundquist *et al*. [6]. Appearance of the free CTAB induces a decrease in surface tension, while stabi-