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Formation and crystallization of amylose–monoglyceride complex in a starch matrix

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Abstract

The formation of amylose–lipid complexes in a gelatinized potato starch matrix was investigated using potato starch and glycerol monopalmitin. These complexes exist in two forms, with the amounts of each of the forms being dependent on the temperatures and durations of the pre-treatments.

Differential scanning calorimetry (DSC) was used to analyze transition temperatures and melting enthalpies, and thereby determine the amount of the complexes in the samples. X-ray diffraction analysis was used to investigate their crystallinity.

In measurements with DSC, form I started to melt at 88.5°C, and form II at 112.9°C. When complex form II was preheated at 100 or 110°C, its melting point rose to 116.3 and 119.7°C, respectively, because of an annealing effect. The same phenomenon occurred with complex form I: when preheated at 90°C, its melting point rose to 96.8°C. The crystal formation of form II appeared to be slower when treated at 110°C than at 100°C. Their maximum melting enthalpies were reached after about 24 h and 4 h of preheating, respectively. In X-ray diffraction analyses, form II showed a V-pattern, but form I did not. This indicates that form II is more crystalline than form I. It was possible to transform form I into form II when it was heat treated, because form I was then partially or totally melted.

As a comparison, the charged substance cetyltrimethylammonium bromide created complex form I with amylose in the starch matrix, but not form II.

Keywords: Crystallization; Amylose monoglyceride complex; Starch matrix

1. Introduction

Amylose creates inclusion complexes with many compounds. This polysaccharide forms helices around the compounds and then crystallizes. When the complex agents are monoglycerides, fatty acids or linear alcohols, these helices have six D-glucosyl residues per turn (Biliaderis & Galloway, 1989; Helbert & Chanzy, 1994; Raphaelides & Papavergou, 1991; Rutschman & Solms, 1990; Yamashita, 1965). In the case of branched-chain alkyl compounds (e.g. *tert*-butyl alcohol), the helices have seven D-glucosyl residues per turn, and other bulkier molecules (e.g. 1-naphtol) yield helices of eight D-glucosyl residues per turn (Biliaderis & Galloway, 1989; Rutschman & Solms, 1990; Yamashita & Hirai, 1966; Yamashita & Monobe, 1971). The aliphatic part of the fatty acid can be included, but not the polar head, due to both steric and electrostatic repulsion (Godet, Buléon, Tran & Colonna, 1993). In X-ray diffraction studies, complex crystals are found to exhibit the V-amylose structure (Godet et al., 1996; Krog, 1990; Mikus, Hixon & Rundle, 1946; French & Hinkle, 1967).

Starch–lipid complexes have been studied with differential scanning calorimetry (DSC) since the eighties (Eliasson, 1994; Eliasson, Finstad & Ljunger, 1988; Eliasson & Krog, 1985; Biliaderis, Page & Maurice, 1986). If the ligand is glycerol monopalmitin (GMP), two forms of the complex can be identified, each having different DSC peak temperatures (T_p). Form I has a lower T_p (96 ± 3°C when the water content >80% (Biliaderis & Galloway, 1989; Eliasson & Krog, 1985) and is assumed to be formed when rapid nucleation occurs; it is morphologically described by a random distribution of the basic structural elements (i.e. helical segments), having little crystallographic register. Form II is more crystalline and is believed to have a lamellar-like organization of amylose complexes; i.e. the polysaccharide chains are so folded as to have their chain axes perpendicular to the surface of the lamella (Biliaderis, 1992; Biliaderis & Galloway, 1989). This molecular organization seems to be similar to the lamellar stacks shown by amylose–palmitic acid complexes in transmission electron

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microscopy; their thickness was 4.6 nm, which corresponds to the total length of two palmitic acid molecules (Godet, Bouchet, Colonna, Gallant & Buléon, 1996). However, little research has been carried out on time–temperature dependence on formation and crystallization of complexes, and we do not know about any in a starch matrix.

The aim of the present study was twofold: to investigate the effect of heat treatment on the formation and crystallization of complexes, and to optimize yield in a starch matrix by heat treating GMP–starch–water mixtures at different temperatures. DSC was used to analyze transition temperatures and melting enthalpies, and thereby to determine the amount of the complexes in the samples. X-ray diffraction analysis was used to investigate the crystallinity of the complexes. The native potato starch does not contain any lipids (Eliasson, 1994), so that the only starch–lipid interaction in the present experiments resulted with the added GMP. A lamellar phase is formed by GMP in water when it is heated at a temperature above 55°C (Larsson, 1997). It has been shown that monoglycerides in a lamellar phase form complexes with amylose more easily than they do in other liquid crystalline phases (Hoover, 1998).

DSC has been used to show that cetyltrimethylammonium bromide (CTAB) creates complexes with amylose (Eliasson, Finstad & Ljunger, 1988). This surfactant has the same carbon chain length as monopalmitin, i.e. 16 carbon atoms, but it is positively charged. Biliaderis and Galloway (1989) showed that another charged surfactant, lysolecithin, created form I complexes, but not form II complexes. The ability of CTAB to create form II complexes with amylose was investigated in the present work.

2. Materials and methods

2.1. Materials

Native potato starch from Lyckeby-Stärkelsen (Sweden) was used. Its amylose content is about 21% according to producer. Its dry matter was determined to be 89%, by drying the starch at 105°C for 16 h. The glycerol monopalmitin (GMP) used was kindly provided by Niels Krog, (Danisco Ingredients A/S, Denmark), purity >99%. Cetyltrimethylammonium bromide (CTAB) was obtained from Sigma Chemical Company (no H-5882).

2.2. Preparation of amylose–GMP complexes

All samples were prepared in coated aluminium pans from TA instruments. They were prepared in two ways. In the first experimental series GMP, potato starch and double-distilled water were weighed into the aluminium pans in a 0.2:1:3 ratio. Those samples were then heated at 80°C, for periods of between 15 min and 48 h. This temperature was chosen because it is above the temperature of potato starch gelatinization (Svensson et al., 1995), and below the temperature of complex melting (Biliaderis & Galloway, 1989; Eliasson & Krog, 1985).

In the second experimental series, the samples were prepared by first mixing GMP and potato starch (in a 0.2:1 ratio) thoroughly in a test tube. This mixture was put into aluminium pans and water was added; the resulting GMP–starch–water ratio was 0.2:1:3. Those samples were then heated at 90, 100 or 110°C for periods of between 15 min and 24 h.

The heating of the samples was performed in a Heraeus (D-6450 Hanau) oven. Afterwards, each sample pan was directly put on a metal plate at room temperature, i.e. the cooling of the sample only took a few seconds.

2.3. Differential scanning calorimetry

The DSC measurements were performed with a Seiko DSC 6200 instrument. The reference consisted of an aluminium pan containing 8.0 mg aluminium oxide, 90 active, neutral for column chromatography obtained from Merck (Darmstadt, Germany). Data were collected at 0.2 s intervals, with a heating rate of 10°C/min. The melting-transition characteristics of the amylose–lipid complexes (enthalpy (ΔH), onset temperature (T_o) and peak temperature (T_p)) were determined by EXSTAR6000 Thermal Analysis System on a Hewlett Packard computer. The enthalpies were calculated as J per g of starch. The reference consisted of an aluminium pan containing 8.0 mg aluminium oxide, 90 active, neutral for column chromatography obtained from Merck (Darmstadt, Germany).

The time between the heating procedure of the samples and the DSC analysis was between 5 min and 2 h. Non-heated samples were equilibrated for 1 h before analyzed in DSC.

During the DSC-scans the samples were heated from 20 to 150°C in the first experimental series. Samples in the second experimental series were analyzed in the same way, but then also cooled to 20°C (at a cooling rate of 10°C/min) and then reheated to 150°C.

The two ways of preparing the samples were compared by making three samples according to each method. They were then heated at 80°C for 12 h and analyzed by DSC. The melting enthalpy of the complexes was lower with the first preparation method, which indicates that the two methods are not directly comparable. Nevertheless, the peak temperatures were the same.

The tests were performed with single or duplicate samples, except for heating at 80°C for 12 h, when three samples were made, and heating at 100°C for 4 h, when four samples were made. The latter experiments gave standard deviations for T_p of 0.38 and 0.37°C, respectively, and for ΔH, the standard deviations were 0.30 and 0.45 J/g, respectively.

CTAB was mixed with water to give a micellar solution, which was then added to potato starch in the pans. The resulting CTAB–starch–water ratio was 0.2:1:3. Samples were heated either 24 h at 100°C, 24 h at 110°C or 69 h at

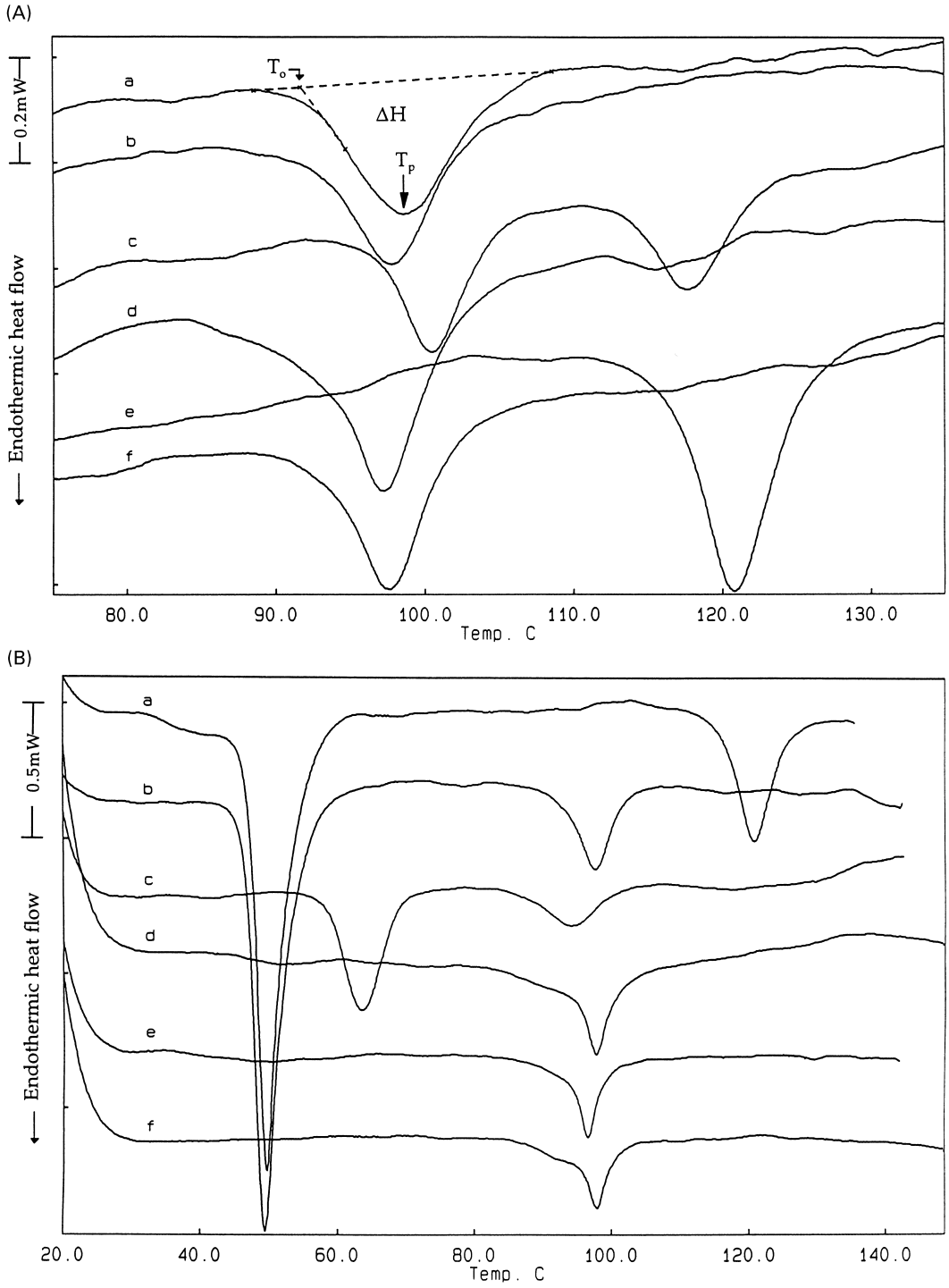

Fig. 1. (A) DSC-scans for heated samples of GMP-starch mixtures (from top to bottom): (a) 1 h at 90°C; (b) rescan of sample (a); (c) 24 h at 90°C; (d) rescan of sample (c); (e) 24 h at 100°C; and (f) rescan of sample (e). (B) DSC-scans (from top to bottom): (a) GMP-starch mixture heated 24 h at 100°C; (b) rescan of sample (a); (c) non-heated CTAB-starch mixture; (d) rescan of sample (c); (e) CTAB-starch mixture heated 24 h at 100°C; and (f) rescan of sample (e).

110°C, before the DSC analysis. Moreover, four samples were prepared in the same way, but were then not heated.

2.4. X-ray analyses

A Guinier camera arrangement according to Luzzati, Mustacchi, Skoulios and Husson (1960) was used. As reference sample, tristearin was used, which has a $d = 0.46$ nm. The measurements were performed at 22°C, and the exposure time was 1 h for tristearin and 23 h for the starch samples.

Samples were made by mixing GMP, starch and water in a

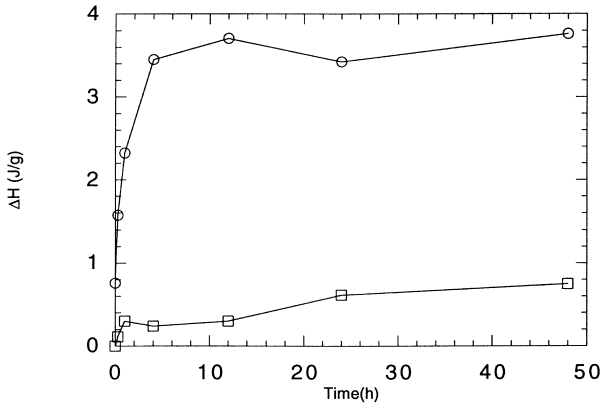

Fig. 2. Melting enthalpies of GMP complexes, heated at 80°C. (—○—) ΔH of complex form I, (—□—) ΔH of complex form II.

0.1:1:3 ratio, in a test tube. The GMP–starch ratio of 0.1:1 was used instead of 0.2:1, because experience from DSC measurements had shown that there had been an excess of GMP.

One sample was heated at 80°C for 4 h, and another one was heated at 100°C for 19 h. These samples were then investigated using X-ray diffraction; they were, moreover, analyzed by DSC. One sample consisted of GMP in water with a ratio of 1:30. It was heated to 80°C and then cooled to room temperature before being analyzed by X-ray diffraction with an exposure time of 24 h. It gave one diffraction line at $d = 0.42$ nm, corresponding well to the short *d*-spacing for the α-form of monopalmitin (Krog, 1990).

3. Results and discussion

3.1. Different forms of amylose–GMP complexes in a starch matrix

Typical DSC thermograms of complex melting are shown in Fig. 1A. From the curves, certain conclusions can be drawn about the crystallization development due to the heating. The onset and peak temperatures were analysed as shown in thermogram (a) in Fig. 1A. The transition enthalpy, ΔH, was calculated from the area of the peak, and was taken to correspond at each treatment temperature to the amount of complex and its crystallinity.

A sample preheated 1 h at 90°C before the DSC scan showed a single endotherm with a T_p of 98.5°C (thermogram (a) in Fig. 1A). This temperature was close to 96.2°C obtained for complex form I for amylose–monopalmitin complexes formed in dilute solution (Biliaderis & Galloway, 1989). It was thus defined as complex form I also in the present system with the starch matrix.

A sample heated at 80°C for 4 h gave only one weak diffraction line, corresponding to a *d*-spacing of 0.46 nm. This indicates that the crystallinity in the sample was very weak. The sample gave an endotherm in the DSC-measurement with $T_o = 88.4$°C and $T_p = 96.3$°C, which indicated the presence of form I complex. An endotherm corresponding to melting of form II could also be seen, but it was very small ($\Delta H = 0.1$ J/g, $T_p = 120.7$°C).

A sample preheated for 24 h at 90°C resulted in two peaks (thermogram (c) in Fig. 1A). Peak I had a T_p of 100.5°C, i.e. slightly higher than in thermogram (a). The second peak had a T_p of 117.8°C. For amylose–monopalmitin complexes crystallized in dilute solution at 90°C, Biliaderis and Galloway (1989) also obtained two peaks: one at 95.0°C and the other at 112.9°C. Our results are close to theirs, and we thus interpret the second endotherm to represent complex form II.

When a sample was preheated for 24 h at 100°C, it then showed one peak, corresponding to melting of form II (thermogram (e) in Fig. 1A). It had a higher T_p than the one in thermogram (c), 120.8°C.

A difference in crystallinity between the two complex forms could be seen in the X-ray diffraction analyses. A sample heated at 100°C for 19 h gave five diffraction lines, corresponding to *d*-spacings of 11.9, 6.9, 4.6, 4.2 and 0.40 nm. These values are within the range of those of the V_h-pattern reported by Zobel, French and Hinkle (1967). In the DSC-measurement this sample gave rise to two endotherms, where the first one was very small with $\Delta H = 0.4 \pm 0.1$ J/g, $T_o = 91.4$°C and $T_p = 96.0$°C, thus corresponding to the melting of form I complex. The second endotherm had much higher transition energy ($\Delta H = 7.1 \pm 0.8$ J/g), and had $T_o = 116.0$°C and $T_p = 121.6$°C, which correspond to the melting of form II complex (Biliaderis & Galloway, 1989). The strongest diffraction line corresponded to a *d*-spacing of 0.46 nm, which is the same value as for the only diffraction line given by the other sample mainly containing complex form I. That weak diffraction line was probably given because it contained a very small amount of complex form II crystals.

When samples a, c and e were reheated in the DSC, they gave the thermograms b, d and f, respectively (Fig. 1A). These thermograms look similar to each other, and show that form I had been formed during the cooling step. The T_p is lower than in thermogram (a).

Moreover, every sample gave rise to a DSC-peak with $T_p = 49 \pm 1$°C and $\Delta H = 15.4 \pm 1.6$ J/g, corresponding to phase transition of the GMP in excess. This peak is shown in thermogram (a) in Fig. 1B for a sample heated 24 h at 100°C, and in thermogram (b), which is the rescan of sample (a).

3.2. Heat treatment of starch–monopalmitin mixtures

The starch–monopalmitin mixtures preheated at 80°C showed increasing ΔH with time (Fig. 2). This could be due to either formation of more complexes, or formation of more perfect crystalline complexes. However, as T_o did not change significantly during the preheat treatment (see below) the increase in ΔH can to a large extent be attributed to formation of more complexes. After about 12 h a plateau value of about 3.6 J/g was

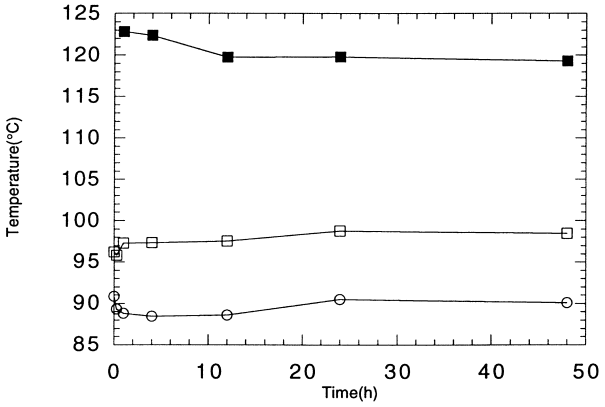

Fig. 3. Melting temperatures of GMP complexes, heated at 80°C. (—○—) T_o of complex form I, (—□—) T_p of complex form I, (—■—) T_p of complex form II.

reached for the enthalpy of form I. Then form II was also formed, but to much smaller extent, its transition enthalpy was less than 0.8 J/g. For amylose–monopalmitin complexes formed in solution the highest ΔH-value for complex form I (18.1 J/g) was obtained at 60°C (Godet et al., 1993). If this value is taken as the highest one for complex form I with 100% amylose, then the value obtained for the starch matrix system (3.6 J/g) corresponds to 20% amylose, i.e. about the amylose content of the starch used. There was no indication that T_o of form I, which was between 88.5 and 90.9°C, was dependent on the heating time (Fig. 3). The T_p increased slightly during long periods of heating and was between 95.8 and 98.8°C. Results from reference samples, which had not been heated, are shown in the diagrams at time = 0 h.

Heat treatment at 90°C resulted in increasing T_o for complex form I, from 89.5 to 96.8°C; furthermore T_p also increased from 97.4 to 100.5°C (Fig. 4), probably because of an annealing effect. The melting enthalpy of form I

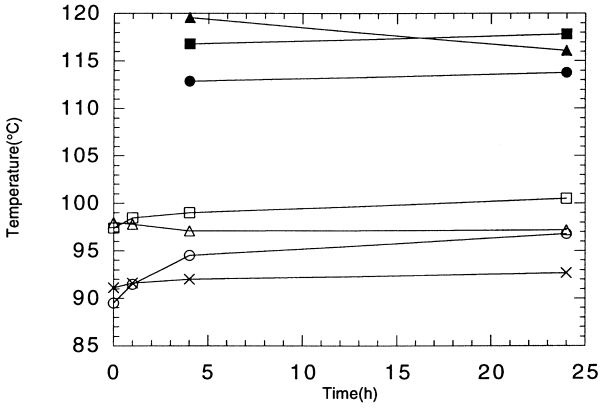

Fig. 4. Melting temperatures of GMP complexes, heated at 90°C. From the first scans: (—○—) T_o of complex form I, (—□—) T_p of complex form I; (—●—) T_o of complex form II, (—■—) T_p of complex form II. From the rescans: (— × —) T_o of complex form I; (—△—) T_p of complex form I, (—▲—) T_p of complex form II.

increased with time during the first hours of heating. However, this enthalpy then decreased while the enthalpy of form II increased (Fig. 5); i.e. form I had partly been transformed into form II. During the rescans, the ΔH were between 3 and 4 J/g, and there was no correlation to the heating time. With the same reasoning as above, for the samples heated at 80°C, it can thus be concluded that at 90°C there is both an increase in the amount of complexes and their perfection. If the ΔH values obtained after 4 h during the first scan are compared with ΔH_1 and ΔH_2 from Biliaderis and Galloway (1989) this calculation gives 20 + 4% = 24% amylose. After 24 h the result is 10 + 9% = 19% amylose. It thus seems that most of the amylose present has been able to form the complex.

Fig. 6 shows the transition enthalpies of the samples heated at a temperature of 100°C. Initially, mainly complex form I was produced. However, after an hour of heat treatment, the more crystalline form II dominated, and a plateau value of about 5 J/g was reached for ΔH of form II after about 4 h. This would correspond to 27% of amylose, calculated as above. After 24 h of heating, no transition of form I could be detected by the DSC. No clear correlation could be seen between the time of heating and the transition temperatures (Fig. 7). The T_p values of form I were between 95.5 and 97.7°C, and the T_p values of form II were between 119.0 and 120.8°C, except the value for 15 min of heating, which was 124.0°C. This T_p value seems to diverge from the main tendency. It is probably because the enthalpy is so small (0.7 J/g) that inhomogeneities in the sample come into play, which could give uncertainty in the peak temperature.

The enthalpy of form II increased more slowly at heating at 110°C than at 100°C, but after 24 h it had reached about the same value as in the heating at 100°C (Fig. 8). Crystal formation seems to be slower at 110°C than at 100°C. The melting enthalpy of form I decreased by increased heating time at 110°C. There is no complex form I at this temperature, since it is melted. When the samples then were cooled, the amylose that still had not formed complex form II, yielded complex form I.

Fig. 9 shows that T_p of form II increased during the heating, from 120.6°C (after 15 min of heating) to 125.0°C (after 24 h of heating).

A comparison of form II at 90, 100 and 110°C of heating (Figs. 4, 7 and 9) shows that T_o and T_p increased with higher heating temperatures, and generally increased with longer heating time. An explanation for this is the annealing effect of heat treatment, which gives the complex crystallites a higher degree of crystallinity (Biliaderis & Galloway, 1989; Biliaderis & Seneviratne, 1990).

During the DSC-rescans of the samples, form I dominates, and only a small enthalpy of form II is observed for some samples. Comparing the rescans, the enthalpies and the peak temperatures seemed to be rather equal, and not dependent on the first heating. However, all samples had then been heated and cooled in the DSC, which means that they had got similar heat treatment before the rescans.

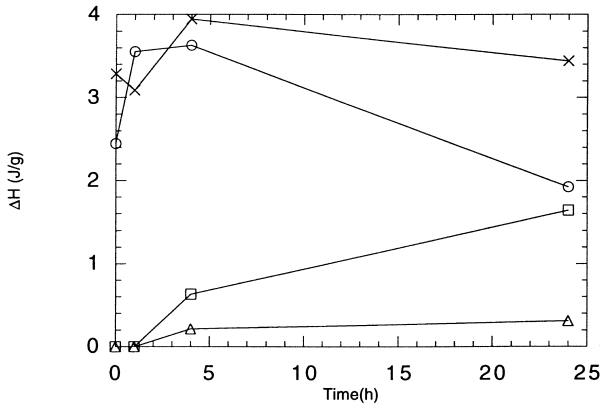

Fig. 5. Melting enthalpies of GMP complexes, heated at 90°C. From the first scans: (—○—) ΔH of complex form I, (—□—) ΔH of complex form II. From the rescans: (— × —) ΔH of complex form I, (—△—) ΔH of complex form II.

The highest value of the melting enthalpy of form II (5.2 J/g) was higher than for that of form I (3.9 J/g) even though the amount of material in the samples was the same. This could be explained by the higher degree of crystallinity of form II.

Three samples that had been heated to 150°C and then cooled to 20°C in the DSC were then kept at room temperature (20°C) for 75 days. DSC analyses thereafter showed that still only complex form I was present, except for a very small endotherm corresponding to form II (with $\Delta H =$ 0.09 J/g). Form I was stable and had not been transformed into the more crystalline form II during this time. The mean values were: $T_o = 91.3$°C, $T_p = 98.0$°C and $\Delta H = 3.5$ J/g, which correspond rather well to the values of second scans from other DSC analyses in this work.

The results show that heat treatment is necessary for the formation of form II. The heating temperature needed in this system seems to be at least 80°C, when a small amount complex form II is formed, but 90°C is needed to yield more.

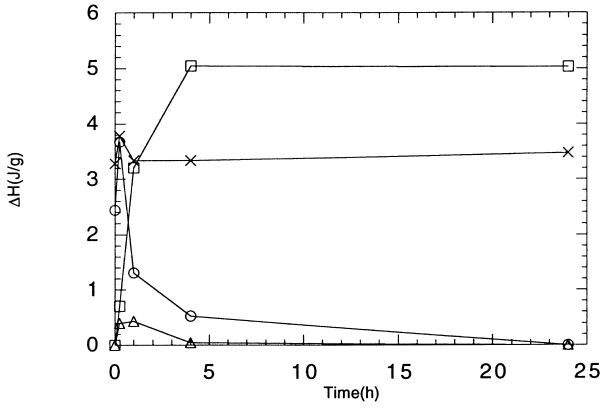

Fig. 6. Melting enthalpies of GMP complexes, heated at 100°C. From the first scans: (—○—) ΔH of complex form I, (—□—) ΔH of complex form II. From the rescans: (— × —) ΔH of complex form I, (—△—) ΔH of complex form II.

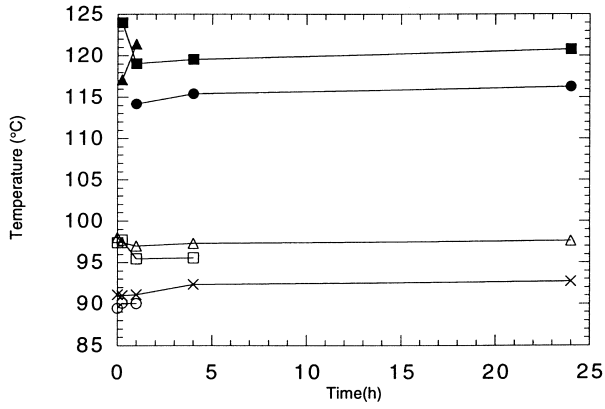

Fig. 7. Melting temperatures of GMP complexes, heated at 100°C. From the first scans: (—○—) T_o of complex form I, (—□—) T_p of complex form I, (—●—) T_o of complex form II, (—■—) T_p of complex form II. From the rescans: (— × —) T_o of complex form I, (—△—) T_p of complex form I, (—▲—) T_p of complex form II.

3.3. Potato starch–CTAB mixtures

Non-heated samples with CTAB showed transition peaks with $T_o = 87.6 \pm 0.9$°C, $T_p = 93.8 \pm 0.7$°C and $\Delta H = 2.7 \pm 0.7$ J/g. It is shown in thermogram (c) in Fig. 1B, where the peak with $T_p = 64$°C corresponds to gelatinization of potato starch. The peak values from the rescans of these samples ($T_o = 94.3 \pm 0.6$°C, $T_p = 97.8 \pm 0.4$°C and $\Delta H = 5.4 \pm 0.8$ J/g) were higher than in the first scan (thermogram (d) in Fig. 1B).

None of the DSC-scans from samples with CTAB showed any peak in the region of the peak temperatures of form II complexes with GMP. Every heated sample showed one DSC peak, and the peak values did not seem to be dependent on duration or temperature of the heat treatment. The values were: $T_o = 93.8 \pm 0.7$°C, $T_p = 96.6 \pm 0.6$°C and $\Delta H = 5.3 \pm 0.2$ J/g, which corresponds to the transition of amylose–CTAB complexes (Eliasson et al., 1988). These temperatures are below the heating temperatures. The onset

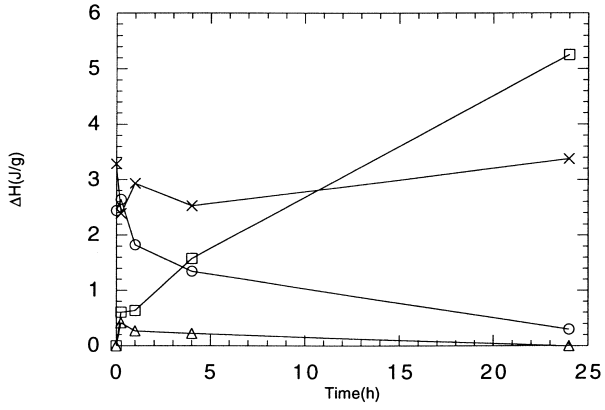

Fig. 8. Melting enthalpies of GMP complexes, heated at 110°C. From the first scans: (—○—) ΔH of complex form I, (—□—) ΔH of complex form II. From the rescans: (— × —) ΔH of complex form I, (—△—) ΔH of complex form II.

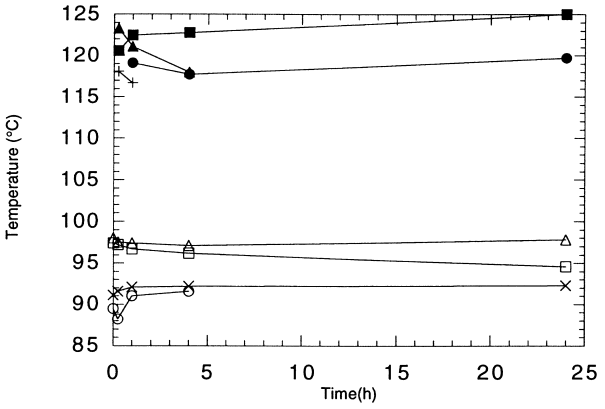

Fig. 9. Melting temperatures of GMP complexes, heated at 110°C. From the first scans: (—○—) T_o of complex form I, (—□—) T_p of complex form I, (—●—) T_o of complex form II, (—■—) T_p of complex form II. From the rescans: (— × —) T_o of complex form I, (—△—) T_p of complex form I, (— + —) T_o of complex form II, (—▲—) T_p of complex form II.

and peak temperatures were slightly higher compared to the first scan ($T_o = 95.0 \pm 0.6$°C, $T_p = 98.2 \pm 0.4$°C). However, the transition enthalpy was the same, $\Delta H = 5.2 \pm 0.2$ J/g. Thermogram (e) in Fig. 1B shows a sample heated 24 h at 100°C, and thermogram (f) shows the rescan of e. The peak values of heated samples were similar to the values from the DSC-rescans of non-heated sample.

Acknowledgements

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