EFFECT OF HYDROTHERMAL TREATMENT ON THE GELATINISATION PROPERTIES OF POTATO STARCH AS MEASURED BY DIFFERENTIAL SCANNING CALORIMETRY

R. C. Eerlingen, H. Jacobs, H. Van Win and J. A. Delcour[*]

Laboratory of Food Chemistry, Katholieke Universiteit Leuven, Kardinaal Mercierlaan 92, 3001 Heverlee, Belgium

Abstract

Gelatinisation temperatures as a function of moisture content were determined for potato starch. The native starch was then hydrothermally treated at a temperature 3% (Kelvin degrees) below the gelatinisation peak temperature and at moisture levels varying from 20 to 67% (by weight). Gelatinisation temperatures, temperature ranges and enthalpy values were affected for all treated samples. However, two sample populations could be distinguished: those samples treated under 'limited' moisture conditions and other samples treated in the presence of 'extra-granular' moisture. A two-step hydrothermal treatment further increased the gelatinisation temperature, but the effect of the second step was small in comparison to that of the first.

Keywords: DSC, gelatinisation, potato starch

Introduction

In some publications, hydrothermal treatments are called 'annealing' [1–8] when storage is in 'excess' water, while the term 'heat-moisture treatment' [8–15] is used when low moisture levels are applied. Annealing and heat-moisture treatments both cause physical modifications of the starch granules [1–15]. However, according to Stute [8], different effects can be observed for both treatments.

Reported results of studies on heat-moisture-treated (storage at 95 to 110°C in 100% relative humidity for 16 h) potato and corn starches by Sair [9], who found an increase in gelatinisation temperature and an increase in the gelatinisation temperature range, were confirmed by Lorenz and Kulp (storage at 100°C and 18 to 27% moisture for 16 h) [10, 11], Donovan *et al.* (storage at 110 or 120°C and 20% moisture for 140 or 240 min) [8], and Hoover and Vasanthan (storage at 100°C and 30% moisture for one to 24 h) [15], for heat-moisture-

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[*] Author to whom all correspondence should be addressed.

treated wheat, barley, triticale, red millet, potato, arrowroot and cassava starches. It was further shown that the gelatinisation enthalpy decreases after heat-moisture treatment of potato starch [8, 14, 15]. Only a slight [14] or no decrease [8, 15] was observed after heat-moisture treatment of cereal starches.

In 1971, Gough and Pybus [16] reported an increase in Kofler hot-stage gelatinisation temperatures after hydrothermal treatments of wheat starch at 50°C in excess water, but in contrast with what was observed as a result of hydrothermal treatments under limited-moisture conditions, the gelatinisation temperature range was narrowed. Their findings were later confirmed by DSC for wheat starch (treated at 42–47°C for 30 min [1], at 45°C for 24 h [5], at 25 up to 50°C for 24 h [6]), maize starch (treated at 25 up to 50°C for 24 h [6], at 50°C for 24 or 48 h [2, 3]), rice starch (treated at 55°C for 24 h [5]), oat and lentil starch (treated at 50°C for up to 72 h [7]), and potato starch (treated at 50°C for 24 h [5], at 25 up to 50°C for 24 h [6], at 50°C for up to 72 h [7], at 52°C for 14 or 92 h [8]), and by small-angle light scattering [17, 18] for wheat starch. Not only increased gelatinisation temperatures and decreased gelatinisation temperature ranges were noticed but also increased gelatinisation enthalpies [2–5, 7]. Some authors found no changes in gelatinisation enthalpies after annealing of wheat [1] or potato starches [6, 8].

Possible explanations for the effects of hydrothermal treatments on starch properties include:

(i) with respect to crystallinity: development of new crystals in the amorphous regions [2, 3], B- to A-type transitions [8, 9, 14, 15], and crystallite growth or perfection [1, 6, 19] of already-existing crystals. The latter is also observed when synthetic polymers are annealed;

(ii) with respect to the amorphous fraction:

– increase in interactions between the polymer chains, without increase in three-dimensional order (that can be detected by X-ray diffraction) [17]. This could be an increase in interactions between amylose chains or between amylose and amylopectin or lipids [4, 15], resulting in a decrease in the destabilising effect exerted by the amorphous regions on the melting of starch crystallites during gelatinisation [15];

– transformation of amorphous amylose into a helix [10],

(iii) alterations of the interactions between crystallites and the amorphous matrix [8].

In this paper, the term hydrothermal treatment of starch granules refers to their storage at a certain moisture level during a certain period of time at a temperature above the glass transition temperature (T_g) but below the gelatinisation temperature of the starch granules. The purpose of this work was to study the effect of hydrothermal treatments on the gelatinisation properties of potato starch, both at low and high moisture levels at temperatures just below the peak

gelatinisation temperature. To date, most treatments [8–15] have been carried out under specific temperature–moisture conditions, without consideration of the exact gelatinisation temperature of the starch at the moisture level investigated. Therefore, some of the reported results may have been influenced by partial gelatinisation (melting) of the starch granules. We also wanted to determine whether limited-moisture conditions or excess-water levels during the (standardized) hydrothermal treatments cause different effects on the DSC gelatinisation behaviour of potato starch and, if so, under what temperature–moisture conditions this change in effect occurs.

Materials and methods

Potato starch (Meridal G) was obtained from Amylum (Aalst, Belgium). Its moisture content was determined by drying (15 min) with an infrared moisture balance (Cenco, Breda, The Netherlands) and was found to be 15.5%. Proximate total amylose and lipid contents reported for potato starch are 23 to 27% and zero to 0.2%, respectively [20]. According to the supplier, the starch contained less than 0.3% ash and less than 0.2% proteins.

Hydrothermal treatment

The moisture content of the starch was adjusted by spraying the appropriate amount of water on 25 g of starch to obtain samples with 20, 25, 30, 35, 40, 50 and 67% moisture {by weight, i.e. (water×100)/(water+dry matter)}. After thorough mixing, samples were equilibrated overnight at room temperature in a hermetically sealed container. Moisture contents were then determined as described above. The starch samples were subsequently stored for 16 h at a constant temperature. The storage temperatures (T_{st}) were chosen as a function of the gelatinisation temperatures (T_p) of the native starch at specific moisture contents (Fig. 1 and Table 1). The samples were stored at moisture content 'm' and at a temperature 3% below T_p, determined at specific moisture content 'm', i.e. $T_{st}^m = 0.97 \times T_p^m$ (in K). For potato starch adjusted to, e.g., a moisture content of $m = 25\%$, T_p was 109°C or 382 K (Fig. 1b) and thus, the storage temperature was 0.97×382 K or 97°C.

Starches treated at moisture contents of 30 and 67% were also subjected to a second hydrothermal treatment. Similar to previous conditions, the second T_{st} values were chosen to be 3% below the peak gelatinisation temperatures (determined at 30 and 67% moisture, respectively) of the single-step hydrothermally treated starches.

Polarisation microscopy

Diluted starch suspensions were viewed under polarized light using an Olympus BHS laboratory binocular microscope (Tokyo, Japan).
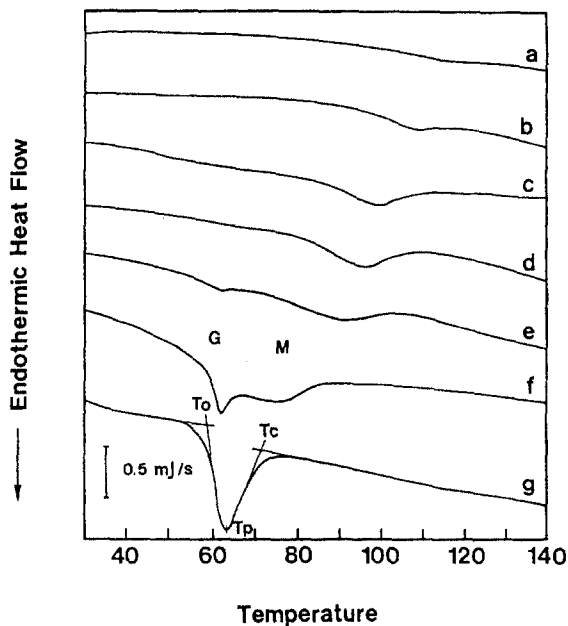
Fig. 1 Gelatinisation thermal transitions (normalized to 5 mg dry matter) for native potato starch at different moisture levels (20, 25, 30, 35, 40, 50 and 67%, i.e. a, b, c, d, e, f and g, respectively)

Table 1 Differences between the storage temperature (T_{st}) applied during hydrothermal treatment and the onset temperature of gelatinisation (T_o) for native potato starch samples at increasing moisture levels

Moisture level/ %	T_o/	$T_{st}=0.97 \times T_o$(K)	$\Delta T^* = T_{st} - T_o$	Relative difference/%, calculated in K
		°C		
20	106(1)[a]	105	−1	−0.3
25	99(1)[a]	97	−2	−0.3
30	89(1)[a]	90	+1	+0.3
35	80(1)[a]	84	+4	+1.1
40	59(1)[a]	52	−7	−2.0
50	59(0)[a]	53	−6	−1.8
67	60(0)[a]	54	−6	−1.7

[a] standard deviation.

DSC

DSC experiments were performed with a Seiko DSC-120 (Kawasaki Kanagawa, Japan). Indium and tin were used as standards. Approximately 7 mg of starch were accurately weighted in an aluminium sample pan. The hydrother-

mally treated starches were analysed as such (at the moisture content applied during the treatment) and at moisture contents of 50 and 67% (w/w). For the latter conditions, starch samples treated at moisture levels above 30% were first air-dried at room temperature. Sample pans were hermetically sealed and heated from 30 to 140°C at a rate of 5°C min^{-1}, with an empty pan as reference. Transition temperatures reported are the onset (T_o), peak (T_p) and completion (T_c) temperatures of the gelatinisation endotherm. The enthalpy (ΔH) of gelatinisation was determined by Seiko software.

When DSC measurements were performed in triplicate and at the same moisture content for the different samples (Tables 2 and 3), mean standard deviations were calculated for T_o, T_p, T_c and ΔH, while in Table 1, where each sample was analysed in quadruplicate and at different moisture contents, the standard deviation for T_o of each sample is shown.

Results and discussion

Gelatinisation of potato starch as a function of moisture content

The gelatinisation transitions of potato starch at different moisture levels are presented in Fig. 1. These results are in agreement with previous findings by Donovan [21]. At a moisture level of 67% (Fig. 1g), a simple, symmetric endotherm can be observed. This endotherm has been denoted as the G endotherm [21]. When the moisture content decreases (below 60% moisture [21]), its size progressively decreases, while a second transition develops (first appearing as a shoulder on the G endotherm), denoted as the M endotherm [21] (Fig. 1f). When the moisture content is further reduced, the M endotherm occurs at higher temperatures and is less intense. At 20% moisture, it is difficult to even detect it. When this was the case, the gelatinisation temperature values were determined by use of the first derivative of the DSC signal (Fig. 1a*).
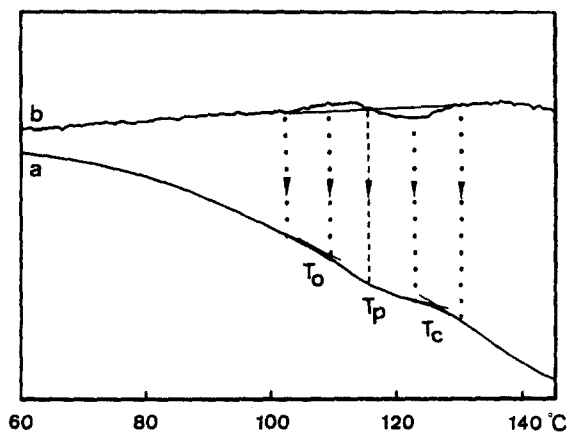

Fig. 1a* Determination of the gelatinisation temperatures by use of the first derivative (curve b) of the DSC signal

Several hypotheses have been formulated to explain the gelatinisation transitions observed with DSC. The increase in gelatinisation temperature with decreasing moisture content has been interpreted by Slade and Levine [22] in terms of the impact of water as a plasticizer on T_g of the partially crystalline, granular starch polymer system. According to these authors, the operative glass transition temperature (T_g^*) is higher than the 'equilibrium' melting temperature of the crystalline regions at low moisture levels. Consequently, because the melting process of the crystallites is restrained, as long as the amorphous regions are in the glassy ('solid-like') state, the effective melting temperature is elevated and observed only after softening of the amorphous regions at T_g^*. Progressive reduction of the (plasticizing) water content leads to an increase in T_g and, as a consequence, to an increase in the observed melting temperature (gelatinisation temperature) [22]. Marchant and Blanshard [17] have suggested that peak multiplicity may be caused by chain reorientation of the starch molecules during slow heating. Biliaderis [23] postulated that the observed thermal profiles may well be the result of several opposing processes, i.e. partial melting, reorganisation (recrystallisation, annealing) and final melting. Donovan and Mapes [21, 24] postulated that peak multiplicity results from the influence of the amorphous regions on the crystallites. According to these authors, hydration and swelling of the amorphous regions destabilize the crystallites, due to the coupling of the amorphous and crystalline regions. As long as excess water is present, the melting of the crystallites occurs cooperatively with the swelling of the amorphous regions. At lower moisture levels, only part of the crystallites is destabilized, while the remainder melts at a higher temperature. This may imply that, as a result of the destabilizing effect of the amorphous regions on the crys-
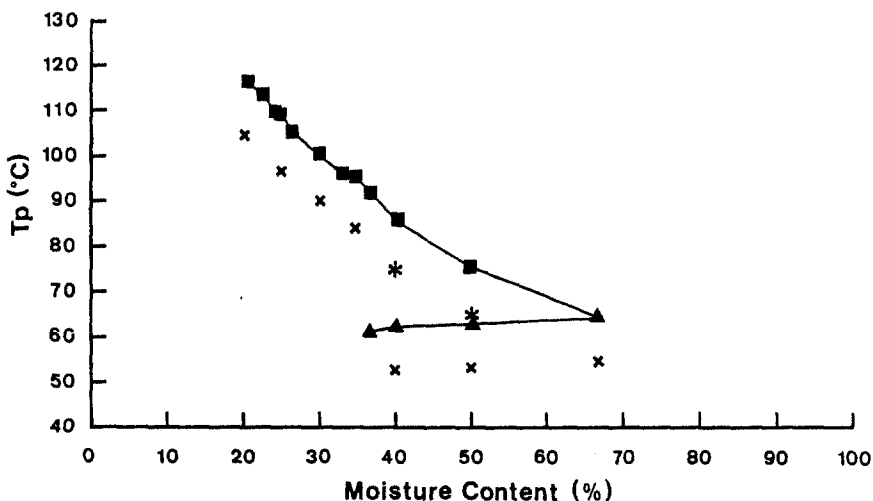

Fig. 2 Gelatinisation peak temperatures (▲, T_p of G endotherm, ■, T_p of M endotherm) for potato starch as a function of moisture content. Symbols (x, ✶) indicate temperature-moisture conditions during hydrothermal treatment of starch

tallites, the observed crystallite-melting temperature is lower than the equilibrium melting temperature. This explanation would then be in contrast with the view of Slade and Levine [22, 25]. Indeed, they postulate that at low moisture levels, the observed melting temperature is higher than the equilibrium melting temperature, because the amorphous regions are only softened at an elevated temperature (T_g increases with decreasing plasticizing water), as explained above. Another explanation is based on the assumed different stabilities of crystalline zones in different granules [26, 27]. At sufficiently higher water levels, i.e. above 65%, each granule absorbs water without restriction, and a single endotherm is observed. Below this water level, there is a competition between the granules for water. The least stable granules melt first. The remaining particles melt at higher temperature because of higher stability and reduction in diluent. Colonna and Mercier [28] have proposed that the first endotherm may be due to loss of three-dimensional order by partial disentanglement in the crystallites, and the second endotherm may be due to a transition from double-helix to coil.

Figure 2 shows the T_p values for potato starch as a function of moisture content. In this graph, T_p values for the G as well as the M endotherms are given. At moisture levels below 37%, only the M endotherm was visible, and consequently, the recorded temperatures are T_p values for the M endotherm.

Effect of hydrothermal treatment on potato starch gelatinisation (at a moisture content of 67%)

As outlined above, in order to avoid starch gelatinisation and treat starch samples in a 'standardized' way, samples were stored at a moisture content 'm' and a temperature 3% below T_p, determined at the specific moisture content 'm', i.e. $T_{st}^m = 0.97 \times T_p^m$ (in K). As long as a G endotherm could be distinguished (Fig. 1), T_p of the G endotherm was considered (67, 50 and 40% moisture). For the samples at lower moisture contents, T_p of the M endotherm was considered instead. The temperature–moisture conditions applied during hydrothermal treatment of the starch are indicated as (x) in Fig. 2. Although all storage temperatures were 3% below T_p, treatments at T_{st} of 90 and 84°C were above T_o (Table 1), because of the broad transition range. Indeed, the sample treated at 84°C showed some loss of birefringence when viewed under polarized light, in contrast with the other samples.

Figure 3 shows the gelatinisation thermal transitions in excess water (moisture content of 67%) for the native and hydrothermally treated starch samples. The parameter values are listed in Table 2.

Effect on the gelatinisation temperature

For all samples, the gelatinisation temperatures (T_o, T_p and T_c) were increased by hydrothermal treatment. With regard to the extent of the effect, we can distinguish between two populations of hydrothermally treated samples (Table 2, Fig. 3): those samples stored under limited-moisture conditions (35% or
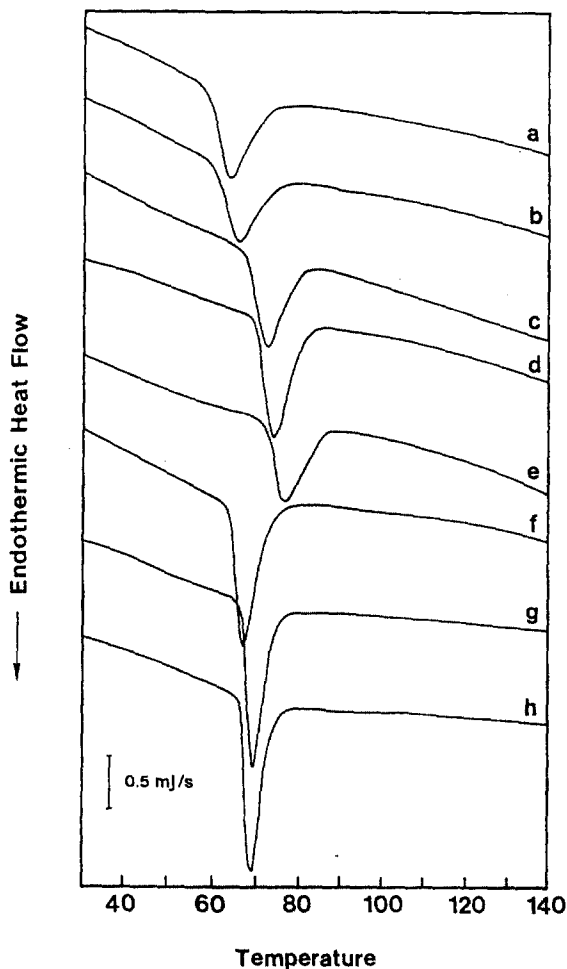
Fig. 3 Gelatinisation thermal transitions (normalized to 5 mg dry matter) for aqueous potato starch (67% moisture): native (a) and hydrothermal treated (at 20%–105°C, 25%–97°C, 30%–90°C, 35%–84°C, 40%–52°C, 50%–53°C and 67%–54°C, i.e. b, c, d, e, f, g and h, respectively)

less) and other samples stored in the presence of extragranular water (40% or more). A progressive increase in gelatinisation temperature was observed with increasing moisture content within both series. Only treatment at 67% moisture did not result in further increases in gelatinisation temperature. A discontinuity was, however, observed between the two series (Fig. 3e–f). Indeed, at a moisture content of 40%, the T_p value was lower than that for samples hydrothermally treated at a moisture level of 35%, although T_p was still higher than that for the native starch sample. Apart from the difference in moisture conditions (limited vs. presence of extragranular water) between the two series, a second

plausible explanation for this discontinuity in the observed effect may be that the second series of samples was treated at a temperature 3% below T_p of the G endotherm, while the first series was treated at a temperature 3% below T_p of the M endotherm, as explained above (Figs 1 and 2).

Therefore, the potato starch samples at 40 and 50% moisture, which showed both the G endotherm as well as the M endotherm, were also treated at a temperature 3% below the T_p of the M endotherm (in line with the samples at lower moisture contents). The temperature–moisture conditions applied are shown as (∗) in Fig. 2. The effects on the gelatinisation temperature were greater after treatment 3% below T_p of the M, instead of the G, endotherm (Table 2). However, the gelatinisation temperature was not higher than that for the samples hydrothermally treated at 35% moisture. In contrast with the treatment at a temperature 3% below T_p of the G endotherm, where an increase in T_p as a function of moisture content was observed, a decrease in T_p with increasing moisture content was observed after treating the starch samples of the second series at a temperature 3% below the M endotherm. Thus, the increase in gelatinisation

Table 2 Gelatinisation parameters for native and hydrothermally treated potato starch, determined at a moisture level of 67%

Treatment	$T_o^a/$	$T_p^a/$	$T_c^a/$	$\Delta T^b/$	$\Delta H^c/$
			°C		mJ mg^{-1}
native	59.5	63.9	72.4	13.0	18.8
20%–105°C[d]	60.8	66.6	74.9	14.1	16.2
25%–97°C[d]	69.2	74.6	82.6	13.4	14.9
30%–90°C[d]	71.1	75.1	82.6	11.5	19.1
35%–84°C[d]	72.6	77.0	85.0	12.4	16.5
40%–52°C[e]	65.0	67.8	74.1	9.1	20.3
50%–53°C[e]	67.8	70.1	75.1	7.3	18.6
67%–54°C[e]	67.5	70.1	75.0	7.5	19.6
40%–75°C[d]	72.8	77.4	83.6	10.8	15.9
50%–65°C[d]	72.4	75.8	80.9	8.5	16.6
30%–90°C+30%–87°C[f]	72.2	76.6	83.5	11.3	19.0
67%–54°C+67%–60°C[f]	70.2	72.3	77.2	7.0	20.8

[a] T_o, T_p and T_c represent the onset, peak and completion temperatures of gelatinisation, with mean standard deviations of 0.3, 0.4, and 0.8°C, respectively.

[b] gelatinisation temperature range $(T_c–T_o)$.

[c] enthalpy of gelatinisation, with mean standard deviation of 1.2 mJ mg^{-1}.

[d] hydrothermal treatment at a temperature 3% below T_p of the M endotherm when gelatinising at the specific moisture content.

[e] hydrothermal treatment at a temperature 3% below T_p of the G endotherm when gelatinising at the specific moisture content.

[f] two-step hydrothermal treatment.

temperature with increasing moisture level applied during the treatment in the first series of samples was not observed for the second series of samples.

The maximum effect on the gelatinisation temperature, which could be obtained after a single hydrothermal treatment step, was an increase of ca. 11°C after storage for 16 h at 90°C and 30% moisture (an increase of 13°C was noted after storage at 84°C and 35% moisture; however, partial loss of birefringence was observed for this sample).

Apart from the difference in moisture level between the two series, a second factor may also be involved. Indeed, in a partially crystalline polymer system such as the starch granule, in the rubbery range, kinetics of diffusion-limited relaxation processes, such as crystal perfection, are described by the Williams-Landel-Ferry (WLF) equation [29]:

$$\log\frac{\eta/\rho T}{\eta_g/\rho_g T_g} = \frac{-C_1(T - T_g)}{C_2 + T - T_g}$$

where η is the viscosity (of a diffusion-limited relaxation process), ρ is the density, and C_1 and C_2 are coefficients that describe the temperature dependence of the relaxation process at temperatures above T_g.

The rate of the process therefore increases with increasing relative temperature above T_g of the polymer system ($T-T_g$), as illustrated in Fig. 4 [25]. It has been suggested by several authors [22, 30] that T_g of granular starch is located near T_o (on the time scale of a DSC measurement [22]). However, we have to point out that T_g depends on the operative conditions of moisture content, temperature and time [25]. Therefore, T_g is considered to be essentially the same as T_o on the time scale of DSC measurements, but not on the time scale of the hydrothermal treatment (16 h) [22]. The operative T_g decreases with increasing holding times (longer time scales), as has been demonstrated with synthetic polymers, e.g. polyvinyl acetate [31]. For a specific polymer (with a given T_m/T_g value), T_g is decreased by a constant value, when the timescale is multiplied by a constant factor. Therefore, we expect that since the rate of diffusion-limited relaxation processes (e.g. crystal perfection) increases with increasing relative temperature above the operative T_g ($\Delta T^{**}=T_{st}$–operative T_g), the rate will also increase with increasing relative temperature above T_o ($\Delta T^*=T_{st}-T_o$). Indeed, although all samples were treated at a temperature 3% below T_p at the specific moisture level, ΔT^* was not constant for the different samples (Table 1). We observed an increase in the effect on the gelatinisation temperature with increasing ΔT^*, and thus with increasing ΔT^{**}, in both series of samples. In order to investigate the significance of ΔT^* on the effect of hydrothermal treatments, further experiments will be carried out.

Taking into account the model of Donovan and Mapes [21, 24], one can explain the increase in gelatinisation temperature after hydrothermal treatment as
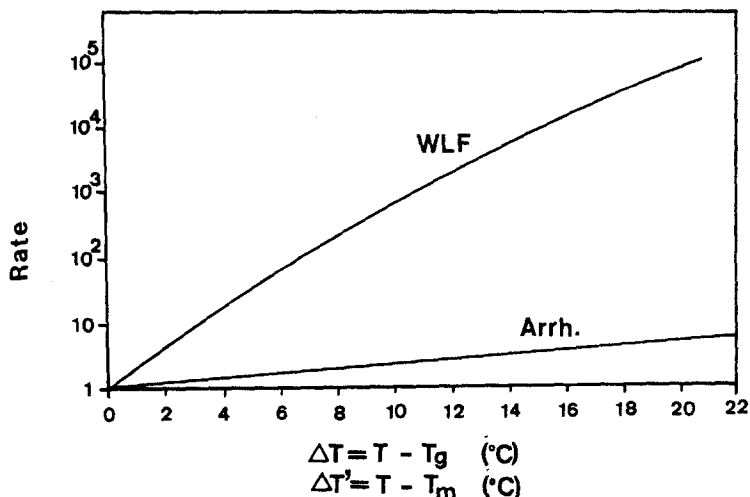
Fig. 4 Schematic presentation of the rate of relaxation processes occurring in the rubbery range, as a function of $(T-T_g)$, as defined by the WLF equation (with its 'universal' numerical constants, from Slade and Levine [25], with permission), in comparison to the rate above T_m as a function of $(T-T_m)$, defined by the Arrhenius equation

an increase of the temperature at which the amorphous regions destabilize the crystallites, resulting in a cooperative melting process. This may be due to stabilization of the amorphous and/or the crystalline fraction. In the case of the models of Biliaderis [23] and Colonna and Mercier [28], an increase in gelatinisation temperature would imply an increase in stability of the crystallites in the granule.

Effect on gelatinisation temperature range

No significant changes in the gelatinisation temperature range could be observed after treatment in limited-moisture conditions, while a decrease was obtained after treatment in excess moisture. The latter is in agreement with previous findings on the impact of annealing on the gelatinisation of starch [1–5, 9] and may indicate a more homogeneous population of crystallites (based on the models of Biliaderis [23] and Colonna and Mercier [28]), e.g. by perfection of the stable structures, possibly in combination with melting of the least stable structures, and/or may indicate increased interactions between the amorphous and crystalline domains, i.e. cooperativity (based on the model of Donovan and Mapes [21, 24]).

Effect on gelatinisation enthalpy

The impact of the hydrothermal treatments on the gelatinisation enthalpy was less clear-cut (Table 2). There was a tendency for the enthalpy values for the

first series of samples, i.e. samples treated under limited-moisture conditions, to decrease (except for the sample treated at 30% moisture), while for the second series, the values tended to increase. These findings are in agreement with previously published results. A decrease in gelatinisation enthalpy has been observed after treatment of potato starch with limited moisture content (heat-moisture treatment) [8, 14, 15], while an increase of the enthalpy values was noted after annealing of starch [2–5, 7], although some authors noted no significant changes after annealing of potato starch [6, 8]. The decrease in enthalpy values after heat-moisture treatment of potato starch has been explained as resulting from disruption of some double-helices during treatment (when a polymorphic transformation occurs from a B-type to an A+B-type crystalline structure, although this mainly concerns packing differences of double-helices) [15]. However, in the relevant literature, plausible partial gelatinisation during treatment has not been investigated. In our study, partial loss of birefringence was only observed for the sample treated at 84°C and 35% moisture, and X-ray diffraction analysis of the samples showed no change in the B-type crystalline structure.

Effect of hydrothermal treatment on potato starch gelatinisation (at a moisture content of 50%)

The gelatinisation profiles of native and treated starch samples at a moisture content of 50% are shown in Fig. 5. The gelatinisation parameters are listed in Table 3. As was the case for gelatinisation at 67% moisture, an increase in gelatinisation temperature could be observed for all samples after hydrothermal treatment. Here too, a discontinuity in the observed effect, as a function of moisture level during treatment, was observed (between samples treated at or below 35% and samples treated at or above 40% moisture). As was the case for the analysis at 67% moisture, the gelatinisation temperature range clearly decreased for the samples treated at 50 and 67% moisture, while the effect on the other samples was less pronounced. The gelatinisation enthalpy tended to decrease with treatment under limited-moisture conditions, and was only affected to a limited degree for samples treated in the presence of extragranular moisture.

At a moisture content of 50%, peak multiplicity was observed for the native potato starch (Fig. 5a). Although all starch samples (Fig. 5) were analysed at 50% moisture, peak multiplicity could be influenced by hydrothermal treatment of the potato starch granules. Treatment at high moisture levels (50 and 67%) reduced the M endotherm to a great extent, while the G endotherm increased. Hydrothermal treatment at 35% moisture (84°C) resulted in a potato starch sample that showed a less intense G endotherm. This was attributed to partial gelatinisation of the sample during treatment, since T_{st} was above T_o, as mentioned before. The other treatment conditions resulted in samples that showed DSC profiles with both the G and M transitions, as in the case of the untreated potato starch. However, both the G and M endothermic peaks were shifted to higher temperatures.

As a logical extension of the model of Donovan and Mapes [21, 24] this observation can, for all treated samples, be explained as an increase in stability of the amorphous and/or crystalline fractions. For the samples treated at 50 and 67%, the reduction of a second endotherm can be explained as an increase in the cooperative effect ascribed to increased interactions (coupling) between the amorphous and crystalline phases. It can be deduced from the model of Biliaderis [23] that the increase in transition temperatures implies an increase in the stability of the crystallites after treatment (as was concluded before). Furthermore, the reduction of the M endotherm after treatment at 50 or 67% moisture would imply a decreased recrystallisation during the DSC measurement. In-
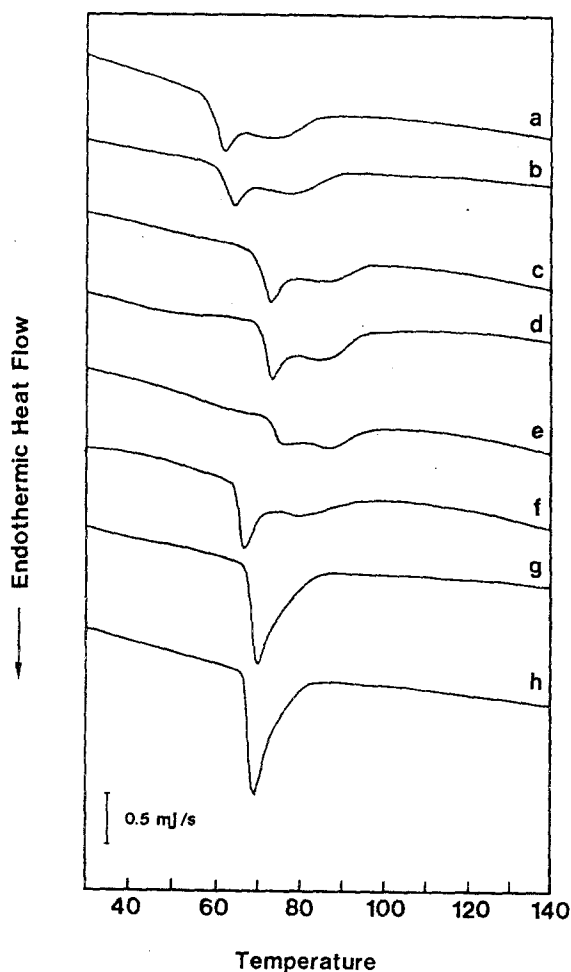
Fig. 5 Gelatinisation thermal transitions (normalized to 5 mg dry matter) for aqueous potato starch (50% moisture): native (a) and hydrothermally treated (at 20%–105°C, 25%–97°C, 30%–90°C, 35%–84°C, 40%–52°C, 50%–53°C and 67%–54°C, i.e. b, c, d, e, f, g, and h, respectively)

Table 3 Gelatinisation parameters for native and hydrothermally treated potato starch, determined at a moisture level of 50%

Treatment	$T_o^a/$	$T_{p1}^a/$	$T_{p2}^a/$	$T_c^a/$	$\Delta T^b/$	$\Delta H^c/$
			°C			mJ mg^{-1}
native	58.9	63.0	75.6	86.2	27.3	18.6
20%–105°C^d	61.5	65.2	78.6	90.2	28.7	16.7
25%–97°C^d	70.1	73.8	85.2	95.8	25.7	14.7
30%–90°C^d	71.2	74.4	85.8	95.0	23.8	17.6
35%–84°C^d	72.3	77.2	91.3	102.4	30.1	13.0
40%–52°C^e	64.9	67.1	80.1	92.2	27.3	20.0
50%–53°C^e	67.2	69.6	–	84.9	17.7	18.6
67%–54°C^e	67.4	69.6	–	83.1	15.7	18.9
30%–90°C+30%–87°C^f	73.1	75.8	88.2	98.4	25.3	18.2
67%–54°C+67%–60°C^f	68.7	71.0	80.2	87.2	18.5	18.4

^{a} T_0, T_p and T_c represent the onset, peak and completion temperatures of gelatinisation, with mean standard deviations of 0.3, 0.3, and 0.7°C, respectively.

^{b} gelatinisation temperature range (T_c–T_0).

^{c} enthalpy of gelatinisation, with mean standard deviation of 0.7 mJ mg^{-1}.

^{d} hydrothermal treatment at a temperature 3% below T_p of the M endotherm when gelatinising at the specific moisture content.

^{e} hydrothermal treatment at a temperature 3% below T_p of the G endotherm when gelatinising at the specific moisture content.

^{f} two-step hydrothermal treatment.

deed, if during the first transition (G), a partial melting and recrystallisation occurs, whereas during the second one (M), a final melting process occurs, an increased G and decreased M endotherm may be the result of decreased recrystallisation, given that decreased recrystallisation leads to an increased enthalpy for the G endotherm (recrystallisation is an exothermic event) and a decreased final melting enthalpy. On the other hand, based on the hypothesis of Colonna and Mercier [28], the increase in T_p of the G endotherm can be explained as an increase in the stability of the crystallites, while the increase in T_p of the M endotherm, of the samples treated at 20, 25, 30, 35 and 40% moisture, can be due to an increase in length of double-helix formation by the chains. The effects would then be in contrast with observations for the samples treated at 50 and 67% moisture, where no obvious M endotherm is observed at all.

Gelatinisation characteristics of hydrothermally treated potato starch as a function of moisture content

The gelatinisation profiles of hydrothermally treated starches were similar to those of the starting materials (Figs 6 and 1, respectively). However, after treatment, the T_p values were increased, while the T_c values remained more or less
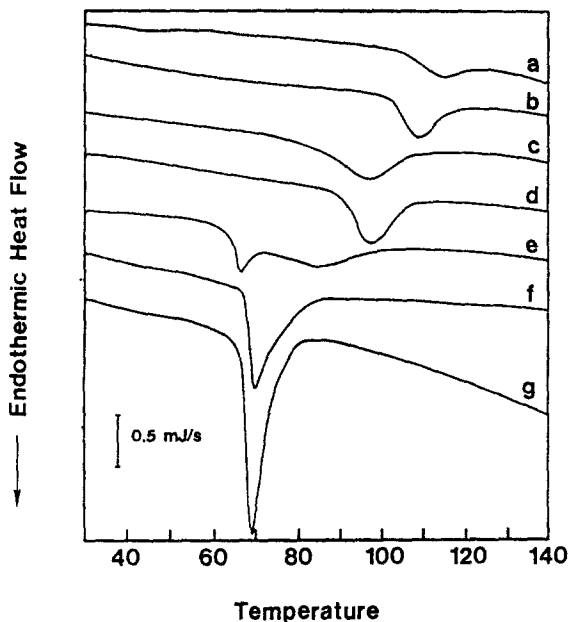
Fig. 6 Gelatinisation thermal transitions (normalized to 5 mg dry matter) for hydrothermally treated potato starch, analysed by DSC, at specific moisture levels (20, 25, 30, 35, 40, 50 and 67%, i.e. a, b, c, d, e, f and g, respectively)

the same for all starches, except for the samples treated at 67% moisture, where an increase in T_c was noted. Also, the transitions were more intense, even when only low moisture levels were present during the DSC measurement (Figs 6a and 1a). A similarity of patterns appeared between Figs 6e (analysis at 40% moisture) and 1f (analysis at 50% moisture), and 6f (analysis at 50% moisture) and 1g (analysis at 67% moisture). A plausible explanation for this may be a better moisture distribution in the granules after treatment.

Impact of two-step hydrothermal treatment on the gelatinisation properties of potato starch

In order to find out whether the gelatinisation properties of potato starch could be influenced to a greater extent, two hydrothermally treated samples (at 30 and 67% moisture) were treated a second time at the specific moisture content and at a temperature 3% below T_p of the sample obtained after the first hydrothermal-treatment step (i.e. 87°C for the sample treated at 30% moisture, and 60°C for the sample treated at 67% moisture). The gelatinisation profiles of these samples are shown in Fig. 7, and the parameters are given in Tables 2 and 3. For both treatments investigated, a two-step process further increased T_o, T_p and T_c. However, the increase was only marginal (1–2°C), in comparison
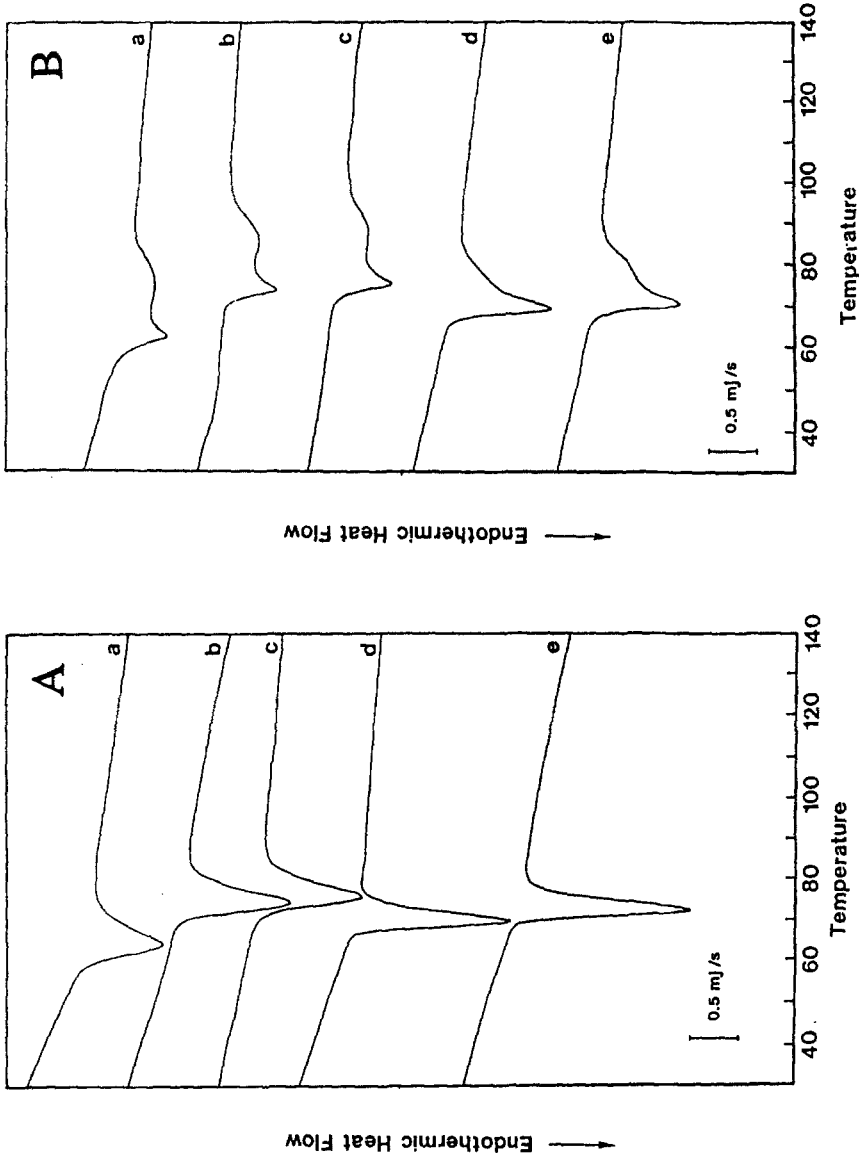
Fig. 7 Gelatinisation thermal transitions (normalized to 5 mg dry matter) for aqueous potato starch (67% moisture, Fig. 7A and 50% moisture, Fig. 7B): native (a), hydrothermally treated at 30% in a single step at 90°C (b), and in a two-step procedure at 90 and 87°C (c), and hydrothermally treated at 67% in a single step at 54°C (d), and in a two-step procedure at 54 and 60°C (e)

with the increase after the first step (ca. 11°C for the treatment at 90°C and 30% moisture, and 6°C for the treatment at 54°C and 67% moisture). The enthalpy values did not change significantly after the second step.

Conclusions

In this study, potato starch was hydrothermally treated at varying moisture levels (20–67%) and at temperatures 3% below the gelatinisation T_p determined at the specific moisture content. The treatments greatly affected the DSC gelatinisation properties of the starch. The treated samples could be divided into two series: starch samples treated at low moisture contents (up to 35%) and samples treated at moisture contents of 40% and higher. An increase in the gelatinisation temperature with increasing moisture content applied during the treatment was observed for both series, but a discontinuity occurred between the two series. The temperature range was decreased for the second series; the enthalpy values tended to decrease for the first series of samples, while they tended to increase for the second series. Thus, it seems that as long as no extragranular water is present (up to ca. 35% moisture), the effects resemble the effects that have been described for so-called heat-moisture treatments, while at higher water levels, the effects resemble those of the so-called annealing treatments. Apart from the difference in relative moisture content (limited or presence of extragranular moisture) between the two series, a second plausible explanation for the discontinuity between the two series was that the difference between T_{st} and T_o (taking the latter as indicative of T_g) was not constant. Further studies have to be carried out in this area.

Although hydrothermal treatments involving storage at a temperature 3% below T_p have been carried out before [5], this storage temperature caused some gelatinisation of one sample, because of the broadness of the gelatinisation transition. Therefore, in further experiments, it may be more appropriate to store the samples at a temperature some percentage below T_o instead of T_p.

Under the experimental conditions, the maximum effect on the gelatinisation temperature obtained in a single hydrothermal-treatment step, without loss of birefringence, was an increase of more than 11°C after storage of potato starch for 16 h at 30% moisture and 90°C. The effect on the gelatinisation temperature of a second hydrothermal-treatment step was small in comparison with the effect after the first step.

The influence of hydrothermal treatment on crystalline structure and rheology will be the subject of future research.

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