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## THE INFLUENCE OF THE GROWTH TEMPERATURE ON STRUCTURAL AND THERMODYNAMIC PROPERTIES OF STARCHES

### Summary

Effects of environmental factors on composition, structure, and physicochemical properties of native starches from different plants have been extensively studied. Among parameters to which attention was paid were environmental factors there is a growth (soil) temperature during plants development (growth temperature) that plays one of the most important role. The application of different physical approaches for a description of the thermodynamic melting parameters of starches allows to determine the cooperative melting unit, the thickness of crystalline lamellae and to evaluate the role of defects in the structural organization of native granules at changes of growth temperature. As example it is considered the influence of growth temperature of plants on the properties of normal potato and sweet potato starches as well as waxy, normal and high-amylose barley starches, i.e. starches with different polymorphous structures of B-, C- and A- types, correspondingly. The nature of calorimetric peaks doubled for some normal and high-amylose barley starches at a decrease in growth temperature is discussed.

### Introduction

The processing of native starches and/or starch containing raw materials is accompanied as a rule, by a gelatinization of starches, i.e. a transformation of granular starch to a viscous-flow state. Since native starch is a semicrystalline substance, from the point of view of modern physics this process can be presented as a melting, this is as the first kind phase transition. The melting temperature of starches extracted even from the same origin can vary from one another [1-5]. Hence, on processing of starches even extracted from the same origins temperature of starch processing should not be constant, otherwise the functional properties of gelatinised starches could vary

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from each other. It implies that melting temperatures of starches and temperatures of their processing must be mutually coordinated.

Differences in melting temperature of starches have complex origin. For instance, genetically controlled factors might be involved, environmental conditions (soil composition, soil temperature (growth temperature), water regime, duration of light day and some others) as well as the reasons caused by varieties in methods of land cultivation might also play an essential role. This research focuses on the influence of environmental conditions, primarily on the soil temperature which influences the melting temperature of starches and on the relationship between the structure of native granules and their thermodynamic properties.

Starch is one of the most abundant substances on the earth. It is found in the leaves of green plants, in the amyloplasts of seeds, grains, roots, and tubers of many crops where it is synthesized in a very condensed and granular form depending on genes and enzymatic activities. The comparison of starch produced in plastids with glycogen in prokaryotes suggests that the biosynthetic pathway has changed during evolution because of selection pressure favoring a semicrystalline product. This property allows plants to store massive amount of fixed carbon generated by photosynthesis [6].

The effects of environmental factors on composition, structure and physico-chemical properties of native starches from different plants have attracted progressively more attention in recent years. Among environmental factors of particular interest there is a soil temperature during plants development (growth temperature). Perhaps, it plays the most important role [7-20]. At the present it has been established that an increase in the growth temperature of cereal and potato starches, irrespectively of the amylose content, leads to increase in melting temperature [7-21].

It is supposed that an increase of melting temperature of starches with increasing of growth temperature may be caused by changes in the double helix length, optimization of registration within crystalline lamellae and/or amorphous region rigidity [8, 10, 21]. It has been hypothesized that elevated growth temperatures directly enhance *in vivo* "annealing" and this is comparable to annealing *in vitro* [8-10, 21]. Until now any firm evidence to support these hypotheses are lacking. The analysis of the works recently published and devoted to a study of the structure formation in starches during their biosynthesis and to an influence of growth temperature on these processes and starch structure, shows that changes in the melting temperatures ( $T_m$ ) for native starches [13-16, 22] as well as for semicrystalline synthetic polymers [23] can be described with the Thomson-Gibbs' equation and equations linking fundamental thermodynamic functions characterizing properties of the surface of starch lamellae. It allows to estimate a role of defects in the structural organization of starch granule. Additionally using the "two-state" model [24] for a description of the melting process for waxy and normal starches, melting cooperative units and the thickness of crystal-

and normal starches, melting cooperative units and the thickness of crystalline lamellae can be determined [13-16, 22]. Collection of the data obtained in these and some other works provides estimation of the influence of growth temperature on the structure and thermodynamic properties of native starches of different polymorphous structure. Besides of it, these data allow to predict properties of new starches as well as to develop better understanding of starch biosynthesis phenomenon, and the relationship between structural and thermodynamic parameters of native starches.

### **The influence of the growth temperature on structure and composition of native granules. A general presentation**

It is known [6, 12] that the biosynthesis of two starch polysaccharides (amylose and amylopectin) is under genetic control. Synthases controlling a biosynthesis process are subdivided into two major classes: soluble starch synthases (SSS) which produce amylopectin, and granule bound starch synthases (GBSS) which produce amylose. The ratio of these enzymes during biosynthesis determines the amylose/amylopectin ratio in native starch granules. Since all synthases have individual temperature for their optimal activity, the polymerization degree of synthesized starch polysaccharides and, correspondingly, the structural organization of starch granules can differently depend on environmental conditions, particularly the growth temperature. Furthermore it is well known that temperature and water content in the system are the thermodynamic parameters which control crystallization.

Macromolecules of amylose and amylopectin form starch granules which consist of crystalline lamellae formed by double helices of amylopectin A- chains with polymerization degree of 14 anhydroglucose residue, amorphous lamellae formed by amylopectin B- chains, and an amorphous background formed by amylopectin and amylose macromolecules in unordered conformation. Amylose and amylopectin macromolecules can also form defects located both in crystalline (amylose "tie" chains string type; amylopectin molecular ordered structure) and in amorphous (amylose "tie" and amylopectin chains in unordered conformation) lamellae. For potato and barley starches with B- and A-type polymorphous structure, respectively, an increase in growth temperature does not lead to significant changes in X-ray diffraction patterns irrespectively of amylose content in starches, this is, improvement of the macromolecular packing in the crystalline unit is not observed [7, 13, 16]. For sweet potato starches [7, 14, 15], the transition of crystalline structure from C(A+B)- to A-type is observed at a change of growth temperature from 15°C to 21°C. However, the annealing of C- type sweet potato starches does not induce such temperature [14, 15]. This means that the hypothesis proposed in the works [8-10, 21] according to which elevated growth temperatures directly enhance *in vivo* "annealing" and this is comparable

to annealing *in vitro* is disputable. According to Hizukuri [7], low temperature yields B- type crystalline structure and high temperature favours the A- type.

The question concerning the variations in the thickness of crystalline lamellae remains open and will be consider later.

The analysis of the published data on the amylose content in native granules shows that for maize and rice starches an increase in growth temperature leads to a decrease in the amylose content [17, 25-27] whereas for wheat starch the amylose content slightly increases with temperature [18, 20]. The investigation of barley starches has shown that irrespectively of the starch variety (waxy, normal, high amylose) growth temperature insignificantly changes the amylose content [28] and, similar effect is noted for tuber starches (potato, microtuber) [9, 10]. Environmental influence on the amylose content in sweet potato starch appears to be variable [29].

In contrast to the amylose/amylopectin ratio, level of starch lipids is very sensitive to environmental effects. For example, it is well known that for barley and wheat starches elevating growth temperature results in increase in the amount of starch lipids [8, 12, 18, 20, 28, 30]. For cereal starches insignificant portion of amylose macromolecules complexed with lipids can form both amorphous and crystalline V-type structures from single helices while other portion of starch lipids is free.

The analysis of the data concerning thermodynamic melting parameters of amylose-lipid complexes as well as the results for barley starches published in the works [8, 16, 28] allow to do some remarks about the influence of growth temperature on the formation of amylose-lipid complexes. Taking into consideration that:

- (i) an increase in growth temperature leads to an increase of lipid content in some starches and to decrease in the amylose content in barley starches [8, 28],
- (ii) the magnitude of melting enthalpy for amylose-lipid complexes is proportional to the content of amylose-lipid complexes in starches,
- (iii) the magnitude of melting temperature of amylose-lipid complexes is characteristic for thermostability for amylose-lipid complexes,

one can supposed that in spite of increase in total lipid content in starches, decrease in growth temperature leads to increase in the content of amylose-lipid complexes in starches, at least partly due to a decrease in the amylose content, and decrease in the thermostability of complexes. Since the melting temperature of amylose-lipid complexes depends on nature of fatty acids [31] and its value decreases in the order: linoleic acid < myristic acid < oleic acid < stearic acid < palmitic acid, it can be supposed that at lower growth temperature some fatty acids do not form complexes.

## The growth temperature and the relationship between structure and thermodynamic parameters of crystalline lamellae in waxy, normal and high amylose native starches

Environmental factors not always remain constant during plants development so it is very difficult to compare precisely available data on the influence of growth temperature on structure and properties of starches. Changes in structural parameters of starches reflect physicochemical and biochemical processes developing in granules during their biosynthesis. Some suggestions on nature of these changes in starches have been formulated in numerous reports. The differences in structural organization of granules during their biosynthesis can be attributed to the changes in:

1. length of amylose double helix [9],
2. distribution of amylopectin chains length [18, 27, 32-34],
3. ratio between small and large granules, because it is well known that in bimodal starches the melting temperature for small fraction is higher than that for large fraction [35].

The DSC study of native starches under quasi-equilibrium has shown that there is the correlation between the growth temperature of plants and the melting temperature of starches [13-15].

As formerly noted, the melting temperature ( $T_m^{\text{exp}}$ ) of semicrystalline synthetic polymers as well as native waxy and normal starches is determined by Thomson-Gibbs equation [13-16, 22, 23]:

$$T_m^{\text{exp}} = T_m^{\circ} \{1 - 2\gamma_i / (\Delta H_m^{\circ} \rho_{\text{cr}} L_{\text{cr}})\} \quad (1)$$

where  $T_m^{\circ}$  and  $\Delta H_m^{\circ}$  are the melting temperature and the melting enthalpy of a hypothetical crystal with unlimited size (a perfect crystal),  $\rho_{\text{cr}}$  and  $L_{\text{cr}}$  are the density and the thickness of the crystal, respectively and  $\gamma_i$  is the free surface energy of formation of the crystal. Since the values of  $T_m^{\circ}$  and  $\Delta H_m^{\circ}$  for starches are not available, the data reported for the A- and B- type spherulitic crystals can be used instead for estimation of  $T_m^{\text{exp}}$ .

The analysis of the equation (1) shows that  $T_m^{\text{exp}}$  is the function of three variables: the type of polymorphous structure in crystal, the thickness of crystal, and the free surface energy of its formation. The polymorphous structure in native starches can be determined with the X-ray method while the thickness of crystalline lamellae is available from DSC data and equations (2 and 3) [13-16]:

$$v = \Delta H^{\text{vH}} / \Delta H_m \quad (2)$$

$$L_{\text{cr}} = 0.35v \quad (3)$$

where  $v$  is the melting cooperative unit,  $\Delta H^{\text{vH}}$  is the van't Hoff enthalpy,  $\Delta H_m$  is the experimental melting enthalpy of starches, 0.35 nm is the pitch height per anhydroglucose residue in a double helix. According to [13-16, 23], the magnitude of the  $\gamma_i$  could be estimate using equations (1, 4, and 5):

$$q_i = [(\Delta H_m^0 - \Delta H_{\text{exp}}) \rho_{\text{crl}} L_{\text{crl}}] / 2.5 \quad (4)$$

$$\gamma_i = q_i - T_m s_i \quad (5)$$

where  $q_i$  and  $s_i$  are surface enthalpy and entropy of crystalline lamellae, respectively. It is well known that the main contribution in the  $\gamma_i$  is caused by the magnitude of the  $q_i$  which is proportional to the content of defects in crystal. Since the melting of crystal begins from its defects, their increase leads to a formation of crystals with a more "mellow" surface and, respectively, to a decrease in  $T_m^{\text{exp}}$ .

Therefore, taking into consideration mentioned above, i.e. that with the exception of sweet potato starches an increase of growth temperature does not lead to the change in starch polymorphous structure [7, 13-16], some characteristics of crystalline lamellae such as thickness and surface free energy, and entropy, and their changes on varying of the growth temperature should be considered for a better understanding of the mechanism underlying the correlation between melting and growth temperatures.

Table 1

The values of the melting cooperative unit ( $v_{\text{crl}}$ ), the thickness ( $L_{\text{crl}}$ ), the free surface energy ( $\gamma_i$ ), enthalpy ( $q_i$ ) and entropy ( $s_i$ ) of face sides for crystalline lamellae of different starches [10,13-16]. (Thermodynamic parameters characterizing surface faces for crystalline lamellae in starches with asymmetric or doubling DSC-peaks as well as for C-type starches weren't calculated.)

Geno- types	Polymo- rphous structure	Growth tempe- rature, °C	$T_m$ , K	$v$ , anhydroglu- cose residues	$L_{\text{crl}}$ , nm	$\gamma_i$ (J/cm <sup>2</sup> ) 10 <sup>7</sup>	$q_i$ (J/cm <sup>2</sup> ) 10 <sup>7</sup>	$s_i$ (J/cm <sup>2</sup> K)10 <sup>7</sup>
Potato ( <i>Maris Piper</i> )	B	10	333.4	15.7	5.5	4.6	53.9	0.147
	B	16	336.0	14.1	4.9	3.7	39.0	0.105
	B	20	338.6	14.1	4.9	2.8	44.0	0.121
	B	25	343.4	11.6	4.1	1.2	22.4	0.062
Average 13.8±1.7 4.8±0.6								
Waxy barley ( <i>Oderb- rucker</i> )	A	7	316.8	16.0	5.6	17.8	71.3	0.169
	A	10	324.3	13.6	4.7	15.1	59.4	0.137
	A	13	327.5	13.1	4.6	14.0	55.7	0.127
	A	15	328.0	14.7	5.1	13.8	57.6	0.133
	A	16	329.7	14.5	5.1	13.2	53.7	0.123
	A	20	333.0	14.1	4.9	12.1	54.4	0.127
Average 14.6±0.5 5.1±0.4								
Normal barley ( <i>Golden Promise</i> )	A	7	314,7	18,7	6,6	21,2	94,8	0,234
	A	10	320,9	14,0	4,9	18,6	80,2	0,192
	A	13	323,5	14,2	5,0	17,6	76,7	0,183
	A	15	325,5	15,9	5,6	16,8	79,3	0,192
	A	16	327,2	16,9	5,9	16,1	73,8	0,176
	A	20	330,9	17,5	6,1	14,5	75,5	0,184

c.d. tab. 1

Geno- types	Polymo- rphous structure	Growth tempe- rature, °C	T <sub>m</sub> , K	v, anhydroglu- cose residues	L <sub>crb</sub> , nm	γ <sub>i</sub> (J/cm <sup>2</sup> ) 10 <sup>7</sup>	q <sub>i</sub> (J/cm <sup>2</sup> ) 10 <sup>7</sup>	s <sub>i</sub> (J/cm <sup>2</sup> K)10 <sup>7</sup>
Average 16,2±0,8 5,7±0,3								
Normal barley ( <i>Triumph</i> )	A	7	315,0	-	-	-	-	-
	A	10	320,8	12,0	4,2	14,7	55,1	0,126
	A	13	325,0	12,2	4,3	13,4	48,1	0,107
	A	15	326,1	13,7	4,8	13,0	51,8	0,119
	A	16	327,7	13,1	4,6	12,5	45,2	0,099
	A	20	332,0	13,4	4,7	11,1	41,6	0,092
Average 12,9±0,3 4,5±0,1								
High amylose Barley ( <i>Pent- land-field</i> )	A	7	---	---	---	---	---	---
	A	10	320,7	---	---	---	---	---
	A	13	323,6	---	---	---	---	---
	A	15	325,0	---	---	---	---	---
	A	16	332,1	11,5	4,0	10,1	55,4	0,136
	A	20	334,3	12,1	4,2	9,5	51,7	0,126
Average 11,8±0,3 4,1±0,1								
Sweet potato ( <i>Sun- nyred</i> )	C(A+B)	15	327.6	11.9	4.2	---	---	---
	A	21	336.6	14.9	5.2	11.0	63.7	0.161
	A	27	345.2	15.7	5.5	8.7	58.5	0.143
	A	33	351.5	17.0	6.0	6.4	65.9	0.170
Sweet potato ( <i>Ayam- rasaki</i> )	C(A+B)	15	329.7	12.4	4.3	---	---	---
	A	21	337.5	14.8	5.2	10.9	55.9	0.133
	A	27	346.6	15.8	5.5	7.8	52.0	0.127
	A	33	352.3	15.9	5.6	5.7	38.2	0.092

As can be seen from Table 1 [13-16], the elevation of growth temperature does not lead to any change in cooperative melting unit and the thickness of crystalline lamellae in native potato and barley starches, i.e. in starches related to B- and A- type, respectively, while for sweet potato starches an increase of growth temperature is accompanied by positive correlation with the thickness of crystalline lamellae. According to [13, 16] observed changes in the melting temperatures for potato and barley starches can be caused by accumulation of defects while for sweet potato starches the changes in T<sup>exp</sup><sub>m</sub> can be due to accumulation of defects and increase in the thickness of crystalline lamellae [14, 15]. Indeed, calculations have shown that the decrease in growth temperature leads to the increase in the magnitude of surface entropy for starch crystalline lamellae (Table 1). This phenomenon is evident for potato and barley starches irrespectively of the amylose content in granules but it is insignificant for sweet potato starches. One may suppose that such defects in starch granules are amy-

lose "tie" chains, amylopectin molecular ordered structures, F<sub>2</sub> or F<sub>1</sub> amylopectin sub-fraction [13].

In case of sweet potato starches increase in the thickness of crystalline lamellae can result from: (i) increase in the length of double helices and (ii) change in polymorphous structure in sweet potato starches at an increase of growth temperature, i.e. C (A+B)  $\Rightarrow$  A- type transition in the range of growth temperature between 15°C–20°C [14, 15]. The changes in the structure of crystalline lamellae are presented in Figure 1. As can be seen from Figure 1, an increase in number of defects leads to formation of crystalline lamellae with more "mellow" structure. Apparently due to this reason namely  $\alpha$ -amylase susceptibility of native granules increase with decreasing in growth temperature [7].

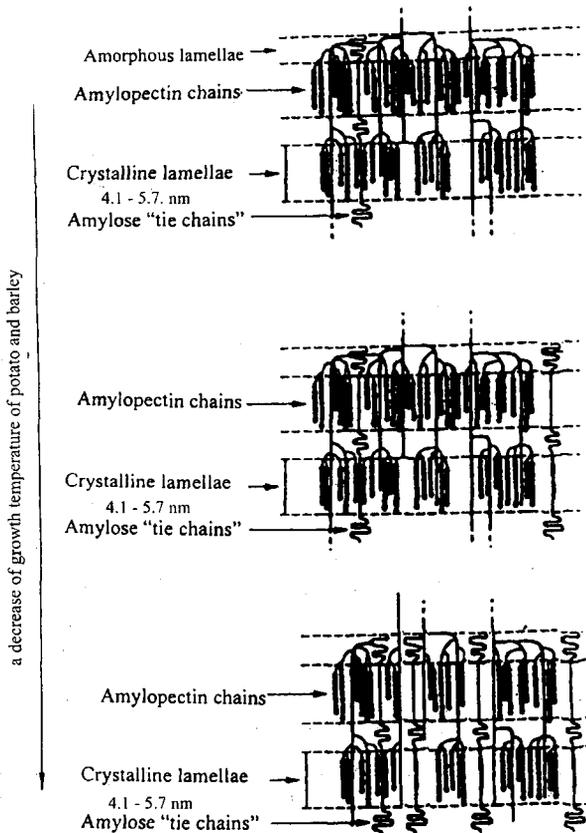


Fig. 1. Schematic presentation of the effects of growth temperature on the amorphous and crystalline lamellae of potato and barley (normal and waxy) starches.

On elevation of growth temperature for some normal and high amylose barley cultivars some structural features in behaviour of their starches can be observed. As

can be seen from Figures 2 and 3 [16], at relative low values of growth temperature the asymmetry on DSC-traces or their doubling is observed. Taking into consideration that the DSC-study of these starches was carried out under large water excess (0.3% d.m. dispersions) such shape of DSC-traces is unusual. Usually the same DSC-traces are observed at intermediate water content in a system of native starch-water [35, 36]. At the present nature of this phenomenon remains unexplained.

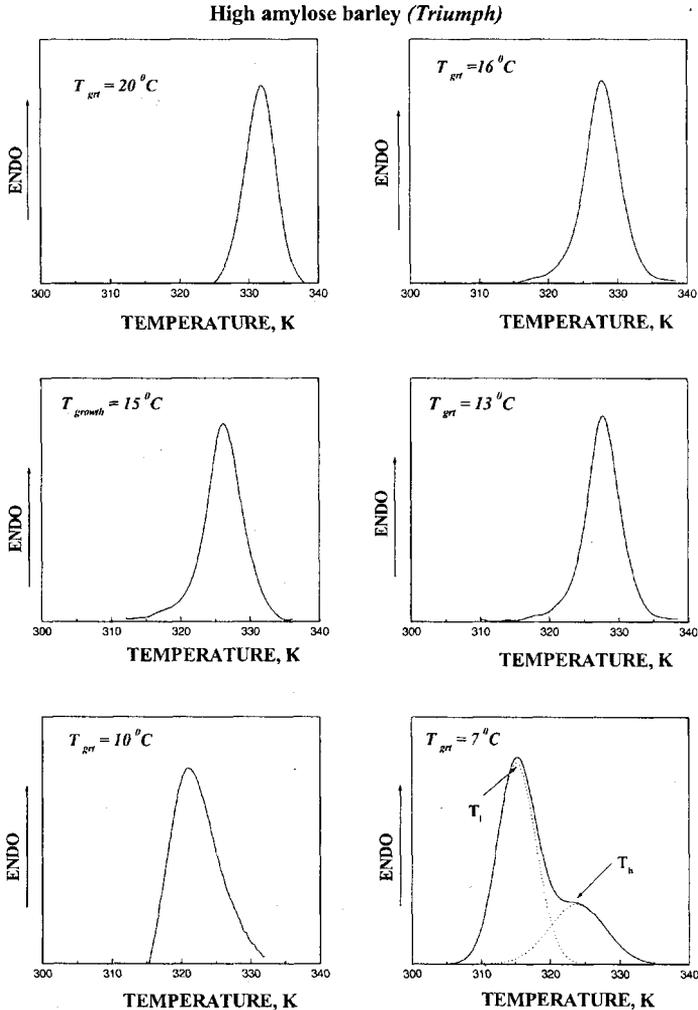


Fig. 2. Excess DSC-traces (—) and results of their deconvolution (-----) for starches ("*Triumph*" variety) grown at different growth temperatures.  $T_l$  and  $T_h$  are the melting temperature of low- and high- temperature structures, correspondingly.

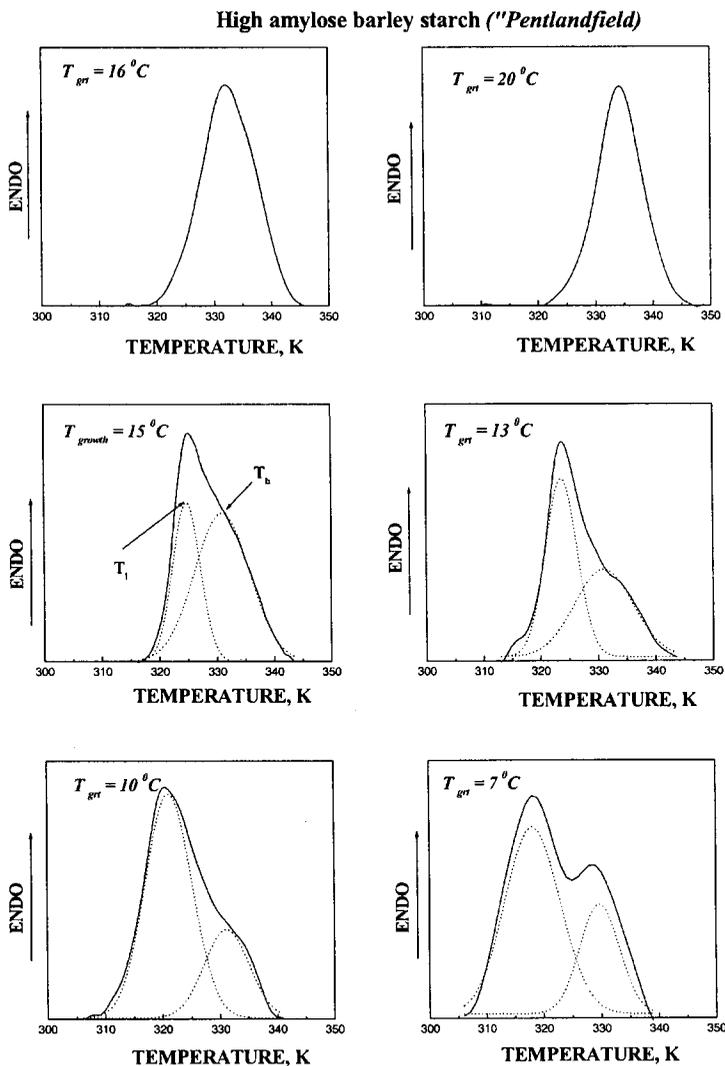


Fig. 3. Excess DSC-traces (—) and results of their deconvolution (-----) for starches ("Pentlandfield" variety) grown at different growth temperatures.  $T_l$  and  $T_h$  are the melting temperature of low- and high- temperature structures, correspondingly.

Generally, change in DSC-trace shapes on decrease in growth temperature could be caused by three reasons:

- 1) change in the ratio of small and large granular size fractions in starches because it is well known that granular size distribution of starches influences the width of starch calorimetric peaks [37]. However, as was supposed in the work [22, 23], this reason is apparently unlikely;

- 2) change in polymorphous structure of starches. However, the X-ray study of the samples showed that the polymorphous structure remains constant irrespective of growth temperature [16];
- 3) accumulation of defects in starch crystalline lamellae on decrease in growth temperature [13, 16].

At the present one assumes that starch granules contain two types of crystallites, which melt at the different temperatures when water content in a system is insufficient [35, 36]. According to [16, 28] a decrease in growth temperature for the barley starches leads to increase in swelling factor and number of defects in granules (Table 2). According to Donovan [35] starch granules contain two types of crystallites distinguishing in the hydration/swelling properties. Supposedly, differences in the hydration/swelling properties result from structural features in starches which are related on DSC- thermograms to B- and A- type starches at intermediate water content [35, 36]. However, the asymmetric or doubling calorimetric peaks are observed also under the water excess (Figures 2 and 3) as starch grew at low temperature [16]. A hypothesis explaining this phenomenon has recently been put forward in the work [16].

Table 2

Thermodynamic characteristics of low- and high- temperature structures in barley starches ("Triumph" and "Pentlandfield" varieties) and relevant proportions<sup>a</sup>

Barley variety	Growth temperature, °C	Low temperature structure			High temperature structure		
		T <sub>l</sub> , K	ΔH <sub>l</sub> , kJ/mol	Proportion, %	T <sub>h</sub> , K	ΔH <sub>h</sub> , kJ/mol	Proportion, %
<i>Triumph</i>	7	315.2	1.6	69.9	323.9	0.7	30.1
<i>Pentlandfield</i>	7	314.9	0.8	63.7	326.6	0.5	36.3
	10	321.1	1.3	72.2	331.1	0.5	27.8
	13	323.6	1.1	52.6	330.99	1.0	47.4
	15	324.7	0.7	34.8	330.9	1.3	65.2

<sup>a</sup>The low- and high- temperature structure content in starches were determined as relative enthalpic contributions (%) of each structure to the overall melting enthalpy of the samples.

Taking into consideration that

- (i) an amount of defects in crystalline growth rings located closer to a surface of granules is apparently larger than in crystalline growth rings located nearer to hilum [22, 38, 39],
- (ii) such defects are accumulated at low growth temperature and induce a decrease of melting temperature [13, 22],

one can assume that observed asymmetry or doubling of calorimetric peaks results from increase in crystalline lamellae with large defect content. At the first approximation the melting of crystalline lamellae containing defects and crystalline lamellae "without" defects can be considered as the melting of two independent structures. When differences in the content of these structures are not too significant the peak doubling can be observed only under the intermediate water content in the starch-water systems. While these differences became significant the peak doubling can be observed under the water excess. At this case, using deconvolution procedure for asymmetric calorimetric peaks, determination of the content of structures in native granules becomes available.

Results of deconvolution are presented in Figures 2 and 3. The low-temperature endotherms can be attributed to the melting of the crystalline lamellae containing the largest number of defects and having the largest swelling factor while the high-temperature endotherms can be related to the crystalline lamellae with the smallest number of defects and swelling factors. The analysis of the results shows that the asymmetry of calorimetric peaks on the DSC-thermograms of barley starches under the water excess is observed when the difference in the content of the low- and high-temperature crystalline structures is approximately of 30-40%. Certainly such explanation of results is only hypothetical and requires additional structural investigations.

### Concluding remarks

The application of different physico-chemical approach for the description of melting process of starches, grown under various temperature provides estimation of the thickness of crystalline lamellae, thermodynamic parameters characterizing the surface of starch crystalline lamellae as well as an influence of growth temperature and the amylose content on number of defects in starches with different polymorphous structure. It is apparent that decrease in growth temperature on development of starch granules containing of B-, A- and C (A+B) -type crystalline structures leads to the formation of starch crystals with decreased melting temperature whereas the thickness of crystalline lamellae remains constant. Such behaviour can be explained by the accumulation of defects located in crystalline and amorphous lamellae. The increase in number of defects can be due to decrease in growth temperature and increase in the amylose content this is it can lead to appearance of peak doubling on DSC-traces .

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## WPLYW TEMPERATURY WZROSTU NA STRUKTURALNE I TERMODYNAMICZNE WLAŚCIWOŚCI SKROBI

### Streszczenie

Badano wpływ czynników środowiskowych na skład, strukturę i właściwości fizykochemiczne natywnych skrobi z różnych roślin. Wśród parametrów, na które zwrócono szczególną uwagę była temperatura gleby w trakcie wzrostu roślin i ona wydaje się być najistotniejszym parametrem. Różne sposoby opisu termodynamicznych parametrów topnienia skrobi pozwalają wyznaczyć kooperatywne jednostki topnienia, grubość lamelli krystalicznych i oszacować rolę defektów strukturalnych w organizacji natywnych gałeczek spowodowanych zmianami temperatury wzrostu. Przykładem może być wpływ temperatury wzrostu roślin na właściwości skrobi ze zwykłych i słodkich ziemniaków oraz woskowych, zwykłych i wysokoamylozowych odmian jęczmienia, tzn. skrobi o różnych polimorficznych strukturach odpowiednio typu B, C i A. Omówiono naturę pików kalorymetrycznych skrobi z niektórych normalnych i wysokoamylozowych odmian jęczmienia rosnących w obniżonych temperaturach. ☒