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THE INFLUENCE OF WATER ON THE GELATINIZATION AND RETROGRADATION OF STARCH

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Abstract: The aim of this work was to study the influence of water on the gelatinization and retrogradation of potato and corn starch with using differential scanning calorimeter (DSC). A significant influence of water to starch ratio on the characteristic temperatures of gelatinization was observed. In the case of gelatinization enthalpy, only the lowest water to potato starch ratio differed significantly from the others. In the case of corn starch, there was no dependence of gelatinization enthalpy on water to starch ratio. The water to starch ratio significantly affected the rate of starch retrogradation. Parameters of ΔH_∞ and k of Avrami model decreased with increasing water content, while n increased with increasing water content. Potato starch showed higher values of ΔH_∞ and k, and lower values of n compared to corn starch.
Keywords: starch, potato, corn, gelatinization, retrogradation

INTRODUCTION

Thermal analysis is one of the primary methods of testing gelatinization and retrogradation of starch. It is used both in the characteristics of starch and starch-based products. The processes of gelatinization and retrogradation are relatively well know. However, there is scarce information about the influence of water content on the processes of gelatinization and retrogradation. This applies particularly to retrogradation, because kinetics of this process is extremely important for products, which stability is strongly dependent on starch retrogradation. Thet process occurrs in various conditions of water availability. Therefore, there is a need of a broader study on determination of the effect of water on kinetics of starch retrogradation, both in model and finished products.

The aim of this work was to characterize the influence of water on the gelatinization and retrogradation of potato and corn starch with using differential scanning calorimeter (DSC).

MATERIALS AND METHODS

The influence of water on gelatinization and retrogradation of potato (Trzemeszno, Poland) and corn (Hortimex, Poland) starch with use of differential scanning calorimeter (DSC) was evaluated. Thermodynamic characteristic of starch gelatinization and retrogradation was determined using differential scanning calorimeter DSC F204 Phoenix (Netzsch, Germany). Water-starch dispersion (3:1, 2:1, 1:1) was heated in DSC aluminium pan at temperature range of 25 – 110°C with heating rate of 10°C/min. The empty aluminium pan was used as a reference. On the basis of received thermograms the onset (T_{Og}), peak (T_{Pg}), and endset (T_{Eg}) gelatinization temperatures and enthalpy of gelatinization (ΔH_g) were calculated. After cooling the sample was stored in refrigerator at 4 ±1°C for a given time period. Retrogradation was measured by reheating the sample pan at the same conditions as for gelatinization. The onset (T_{Or}), peak (T_{Pr}), endset (T_{Er}) temperatures, and enthalpy of retrogradation (ΔH_r) were calculated (Singh and Singh, 2001). Temperatures and enthalpy of thermal transitions were determined with use of instrument's software Proteus Analysis (Netzsch, Germany). The changes in enthalpy during storage were described by Avrami equation:

$$\Theta = \frac{\Delta H_\infty - \Delta H_t}{\Delta H_\infty - \Delta H_0} = e^{-k \cdot t^n} \quad (1)$$

where Θ is the fraction of unrecrystallized sample; ΔH_0 *(J)*, ΔH_∞ *(J)*, and ΔH_t *(J)* are retrogradation enthalpies at zero, ∞ and *t* time, respectively, k (s^{-n}) is a rate constant, and n is the Avrami exponent (Ziobro et al., 2013). In order to reduce the number of evaluated parameters it was assumed that $\Delta H_0=0$, that is justified when starch is fully gelatinized during gelatinization. After simplifying the equation takes the form:

$$\Delta H_t = \Delta H_\infty \cdot \left(1 \quad e^{-k \cdot t^n}\right) \quad (2)$$

Calculations were performed with use of Statistica 9.0 (StatSoft Inc., USA).

STATISTICAL ANALYSIS

For statistical evaluation of the obtained results the one-way and two-way analyses of variance at significance level of 0.05 were performed. Significance of differences between the means was estimated by the Duncan's test at significance level of 0.05. All calculations were performed with Statistica 9.0 (StatSoft Inc., USA) statistical software.

RESULTS AND DISCUSSION

Figure 1 demonstrates a typical DSC curves obtained for corn and potato starches with different water content. Different starches gelatinized at different temperatures.

Table 1. Thermal charateristic of starch geltanization (mean value of ten replications±standard deviation).

Sample	S:W	T_{Og}	T_{Pg}	T_{Eg}	$-\Delta H_g$
	1:1	60.6±0.20[a]	67.0±0.38[a]	82.0±1.30[c]	14.9±0.39[a]
Potato	1:2	61.1±0.14[b]	67.2±0.20[b]	75.7±0.37[a]	15.4±0.71[b]
	1:3	61.5±0.28[c]	67.8±0.32[c]	75.8±0.57[a]	15.8±0.44[b]
	1:1	65.2±0.19[d]	71.9±0.18[d]	90.2±2.48[d]	11.7±0.40[c]
Corn	1:2	66.1±0.22[e]	72.2±0.21[e]	79.5±0.30[b]	11.9±0.58[c]
	1:3	66.4±0.14[f]	72.4±0.23[f]	78.9±0.35[b]	11.7±0.56[c]
One-way ANOVA - p		<0.001	<0.001	<0.001	<0.001

Differences between values signed with the same letters in particular columns are non-significant at 0.05 level of confidence.

According to some authors (Singh et al., 2003) potato starch gelatinizes in the range of 57-78ºC, while corn starch in the range 62-84ºC. According to the others, in turn, potato starch gelatinizes in the range of 60-76ºC, and the corn starch at 57-84ºC (Abdel-Aal, 2009). Potato starch also exhibits somewhat lower peak temperature than corn starch. According to Singh et al. (2003) the difference is 4ºC, while Onyango et al. (2011) estimate it to be 7.6°C. In the case of the examined samples onset temperature (T_{Og}) was in the range of 60.6–61.5ºC for potato starch and 65.2-66.4ºC for corn starch (table 1). The values for potato starch are in accordance with the literature data, while corn starch showed slightly higher values. Peak temperature (T_{Pg}) ranged from 67.0 to 67.8ºC for potato starch and from 71.9 to 72.4ºC for corn starch. Endset temperature of the phase transition varied from 75.7 to 82.0ºC and from 78.9 to 90.2ºC for potato and corn starch, respectively.

For both starches the influence of water/starch ratio on the characteristic gelatinization temperatures was found. In the case of onset temperature, an increase in its value with an increase in water content was observed, which may be associated with transport of heat to the starch granules, that takes more time at higher water content. Thus, at constant heating rate the beginning of phase transition is shifted to higher temperatures. A similar effect was found for the peak temperature. There was an inverse relationship for the end of the transition temperature (T_{Eg}), where the values decreased with an increase in water content. This was probably due to increased availability of water necessary for gelatinization, resulting in accelerated phase transition. Small differences between endset temperatures determined for samples with starch/water ratio of 1:2 and 1:3, and a significantly higher T_{Eg} for the sample with the lowest value of this ratio, suggest that this value strongly reduced water availability for starch and reduced the degree of hydration of amorphous regions of starch granules.

Statistically significant decrease in enthalpy value was observed only for potato starch as compared to the sample with 1:2 and 1:3 starch/water ratio, which indicates an insufficient amount of water. The necessary amount of water depends on the ratio of amylopectin to amylose. Lower content of amylopectin in corn starch than potato starch, causes that for corn starch that amount of water is sufficient, while for potato starch it is below the limit value, resulting in decrease in value of gelatinization enthalpy. Enthalpy values determined for both starches are in accordance with the values presented in literature: 12.5-17.9 $J \cdot g^{-1}$ for potato starch and 12-14 $J \cdot g^{-1}$ for corn starch (Singh et al., 2003; Pycia et al., 2012).

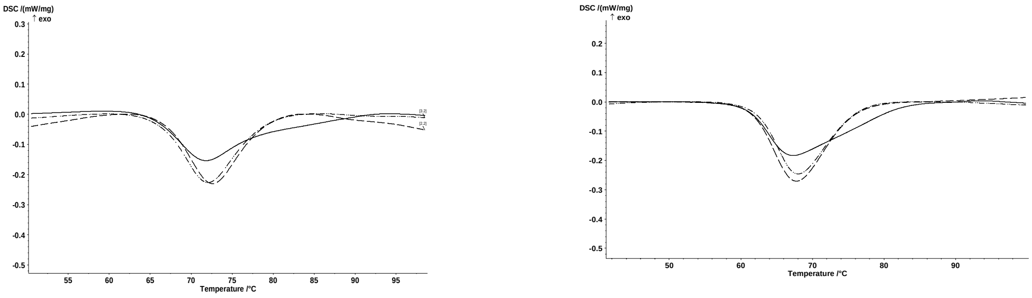

Fig.1 Typical DSC curve of corn (left) and potato (right) starch gelatinization with different starch/water ratio: 1:1 (continuous line), 1:2 (two-point line), 1:3 (dotted line).

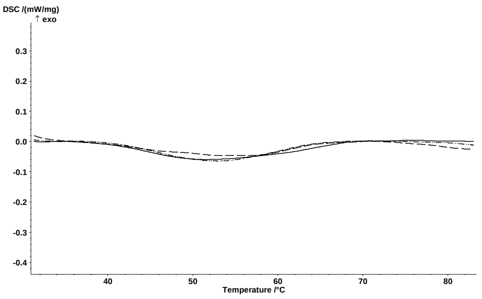

Fig.2 Typical DSC curves (corn starch) of amylopectin geltanization after retrogradation (6 days) with different starch/water ratio: 1:1 (continuous line), 1:2 (two-point line), 1:3 (dotted line).

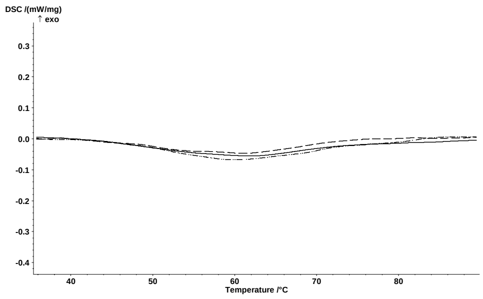

Fig.3 Typical DSC curves (potato starch) of amylopectin geltanization after retrogradation for starch/water ratio 1:3 with different time of storage: 5 days (continuous line), 9 days (two-point line), 21 days (dotted line).

Table 2. Avrami equation parameters describing changes in enthalpy of retrogradation.

Sample	S:W	dh	k	n	R^2
	1:1	9.28	0.44	0.37	0.88
Potato	1:2	8.43	0.23	0.47	0.95
	1:3	7.43	0.16	0.59	0.94
	1:1	8.20	0.32	0.37	0.93
Corn	1:2	7.02	0.06	0.71	0.94
	1:3	6.47	0.02	0.88	0.97

Retrogradation is a characteristic phenomenon, during which a large amount of hydrogen bonds are formed between starch chains during cooling of starch paste (Singh et al, 2003). During the retrogradation process amylose forms a double helix consisting of 40-70 molecules of glucose, and amylopectin crystallizes by grouping the side-chain branches. According to Singh et al. (2003) and Subaric et al. (2011) starch retrogradation enthalpy have lower value by about 60-80% compared to the starch gelatinization enthalpy.

Similarly, the temperature associated with the thermal transition of the crystalline starch is from 10 to 26 °C lower than the corresponding temperature of gelatinization. Lower phase transition temperatures for retrogradated starch as compared to fresh starch result from formation of small crystals during storage, which disintegration involves smaller amount of energy.

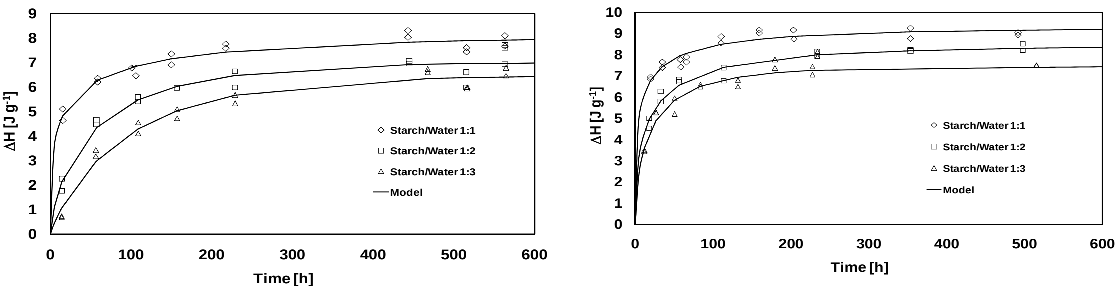

Fig.4 The relationship between the enthalpy of transition and the storage time for corn (left) and potato starch (right).

Figures 2 and 3 illustrate examples of DSC curves for samples stored for varying periods of time, while Figure 4 shows dependence of the enthalpy on storage time. Retrogradation kinetics is often described by Avrami model, which is based on the assumption, that there is a linear relation between changes in physical parameters of the analyzed system (e.g. its enthalpy) and the number of emerging crystallites (Ziobro et al., 2013). Parameters of the Avrami model are summarized in table 2. Increase in the water to starch ratio in both cases caused a decrease in values of ΔH_∞ *(J)* and retrogradation rate constant, and an increase in the value of *n*. Comparing the two studied starches a higher rate constant and lower value of index *n* can be seem for potato starch.

CONCLUSION

A significant influence of water to starch ratio on the characteristic temperatures of gelatinization was observed. In the case of gelatinization enthalpy, only the lowest water/starch ratio for potato starch differed significantly from the others. In the case of corn starch, there was no dependence of gelatinization enthalpy on water to starch ratio. The water to starch ratio significantly affected the rate of retrogradation. Parameters of Avrami model decreased and increased with increasing water content, respectively for ΔH_∞ and *k* and for *n*. Potato starch was characterized by higher values of ΔH_∞ and *k*, and by lower values of *n* as compared to corn starch.

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