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THE EFFECT OF VARIOUS POTATO CULTIVARS AT DIFFERENT TIMES DURING GROWTH ON STARCH CONTENT DETERMINED BY DSC

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Differential scanning calorimetry (DSC) was used to determine the starch content of potato dry matter isolated from various cultivars at different times during growth. When potato dry matter was heated in the presence of excess water, a symmetrical endothermic peak resulted, which was similar to the gelatinization peak of pure starch. From the enthalpy value of potato dry matter and pure potato starch at a moisture content of 70%, the starch content in the potato dry matter can be determined. Starch content increased as growth progressed to a maximum and then decreased. The effect of moisture content and sample mass on gelatinization of dry matter and starch was also investigated. Compared to other starch analysis technique, DSC is a simple and more rapid method.

Keywords: *DSC, gelatinization enthalpy (ΔH), growth times, potato cultivars, potato dry matter, starch content, starch gelatinization*

Introduction

Potato tubers contain 13 to 37% dry matter; 13 to 30% carbohydrates; 0.7 to 4.6% proteins; 0.02 to 0.96% lipids; and about 0.44% ash. In addition, ascorbic acid and other vitamins, phenolic substances and nucleic acids are present [1]. Dry matter and starch content of potato tubers play an important role in the selection of potato for processing. For example, the yield of potato chips and French fries, and the texture of French fries, canned and reconstituted dehydrated potatoes are directly related to the dry matter and starch content of the original potatoes [2]. In fried products, greater starch content in the tuber reduces oil absorption and produces a brittle texture with a characteristic snap [3].

Starch content of plant products is conventionally determined by measuring glucose concentration following enzymatic hydrolysis [4, 5]. For quantitative analysis, the starch has to be fully accessible to amylolytic enzymes. Therefore, grinding must be sufficient to disrupt the cell walls and/or protein network surrounding the starch granules in order for the starch to be fully hydrolyzed to glucose. To overcome problems of ensuring enzyme accessibility and complete hydrolysis, it was decided to explore an alternative method for determining the starch content, to provide effective information for selecting potatoes for processing and to control the quality of potato products.

When starch is heated in the presence of water, DSC curves show first order endotherms indicating that crystallite melting is a major factor in starch gelatinization [6, 7]. DSC provides a simple method for measuring the heat energy required for starch gelatinization. In addition, DSC has been employed to monitor the structure changes in wheat flours [8] and glass transitions in food materials [9]. In the previous study, we investigated the effect of moisture content on the thermal properties of potato dry matter in comparison to isolated potato starch [10]. In the presence of excess moisture (>50%, mass/mass), the curves of potato dry matter exhibited a single endothermic transition at about 69°C. The enthalpy of this endothermic transition was found to be constant between 13 and 14 J g^{-1} based on dry matter mass for a selected potato cultivar. Similar thermal behavior of pure starch was observed in that study. The enthalpy of starch gelatinization was found to be constant also between 16 and 17 J g^{-1} based on starch mass. From that study, we concluded that the endothermic transition in potato dry matter mainly reflected the gelatinization of starch in the presence of excess water.

The objective of the present study was to employ DSC to determine the starch content of potato dry matter, and to investigate the effect of cultivars and growth times on starch content. The effect of moisture content and sample mass of potato dry matter and starch on gelatinization will also be discussed.

Materials and methods

Potatoes

Three common potato varieties were chosen for this study. They are Superior, Shepody and Snowden. Seed tubers were planted on May 17, 2000 for Shepody and

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Snowden, and May 24, 2000 for Superior. Three potato cultivars were grown in the experimental farm of University of Guelph in Cambridge, Ontario, Canada. The first harvest time was 55 days after planting for Shepody and Snowden cultivar, and 48 days after planting for Superior cultivar. About 2 kg tubers were dug for each cultivar. The tuber sizes were very small. Tubers were dug again at 56, 64, 84 and 117 days after planting in the same plot for Superior cultivar due to the maturity. For Shepody and Snowden cultivars, other harvest times were 71, 91, 112 and 124 days after planting in the same plot. The normal harvest time was 124 days for Shepody and Snowden cultivars, and 117 days for Superior cultivar. The different harvest times were mainly due to the different maturity of these three cultivars. After each harvest, potato tubers were washed and subsequently stored at room temperature (22°C) for one day prior to isolation of dry matter and starch.

Isolation of potato dry matter and determination of dry matter content

Potato dry matter was isolated using freeze-drying fresh potato slices. Potato slices (ca. 5 g, 4×2×1 cm) were prepared from the center of the tuber and lyophilized in a Freeze Dryer 8 (Labconco®, Kansas City, MO, USA). The potato dry matter was then packed in air-tight plastic bags and stored at room temperature (22°C) until further use. Dry matter content was determined from the difference in the mass of potato samples before and after freeze-drying.

Isolation of potato starch and determination of moisture content

Potato starches were isolated as described by Liu [11] with minor modification. Potato tubers were washed, peeled, sliced into 2–3 cm cubes, and soaked in distilled water containing 20 mM sodium bisulphite and 10 mM citric acid for 2 h. The cubes were then disintegrated using a centrifugal juice extractor. The pulp was suspended in distilled water, and the starch milk was collected. The milk was allowed to sediment for a minimum of 30 min, after which the suspended solids were removed by decantation, and the starch sediment was resuspended in water. The starch granules were recovered by filtration using nylon cloth, and washed a minimum of 3 times and finally, ambient air-dried. The dried starch was passed through a 125 micron sieve, packed in air-tight plastic bags and stored at room temperature.

Moisture content of potato dry matter and potato starch was measured by weighing the sample (triplicate) before and after drying at 85°C and 760 mm Hg vacuum for 7 h.

DSC and determination of starch content in potato

The thermal analysis of potato dry matter and starch in the presence of excess water was conducted using a differential scanning calorimeter (2920 modulated DSC, TA Instruments, New Castle, DE, USA). Duplicate samples of potato dry matter (~15 mg) and starch (~20 mg) isolated from different growth times were weighed into high volume pans (Part number: 900825-902, TA Instruments, New Castle, DE, USA). Deionized water was then added to make suspensions with the desired moisture contents. Pans were sealed and equilibrated for 2–5 h at room temperature before heating in the DSC. The measurements were carried out at a heating rate of 10°C min^{-1} from 5 to 130°C. Total sample masses were between 70 and 80 mg depending on moisture content. The DSC instrument was calibrated using indium and an empty pan as reference. The enthalpy (ΔH) of phase transition was measured from the endotherm of DSC curves using software (Universal Analysis, Version 2.6D, TA Instruments) based on the mass of dry solid (dry matter or starch). The integration of the endothermic peak was performed at the same temperature range for dry matter and corresponding starch. Onset temperature (T_o) and peak temperature (T_p) of endotherm were also measured from DSC curves.

Starch content was determined by using the ratio of ΔH of potato dry matter to ΔH of isolated starch ×100. The reported values are the ratios of the mean phase transition enthalpy from duplicate measurements of dry matter to that of isolated starch or commercial potato starch.

Statistical analysis

The statistical analysis was performed using single factor ANOVA for the data. Significant difference was evaluated based on $p \leq 0.05$.

Results and discussion

Thermal properties of potato dry matter and starch isolated from different cultivars and growth times

Thermal behavior of potato dry matter and potato starch upon heating in the presence of excess water

Both potato dry matter and starch show similar thermal behavior when heated in the presence of excess water. As shown in Fig. 1, a single symmetrical endotherm was obtained for potato dry matter and starch isolated from Shepody cultivar harvested at 112 days, at a moisture content of 70%. (All other potato dry matters and starches showed a similar thermal behavior as Fig. 1 when moisture content was about 70%). The endothermic peak indicates that an

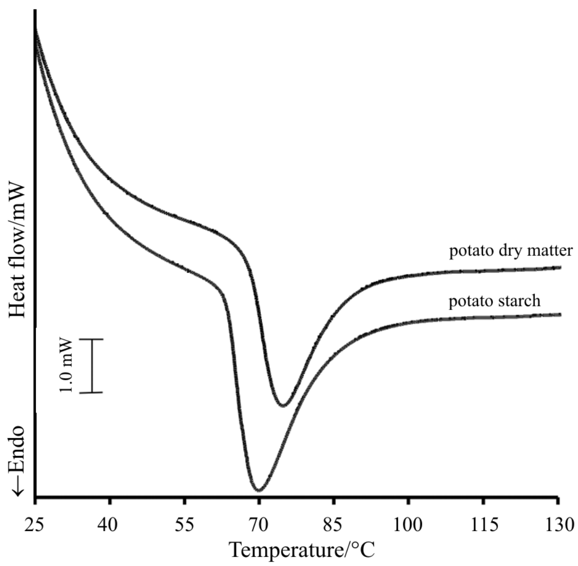

Fig. 1 DSC curves of potato dry matter and starch at moisture content 70% upon heating to 130°C. Labeling refers to samples

order-disorder phase transition (starch gelatinization) of dry matter and starch has taken place upon heating [10]. The enthalpies of gelatinization were 16.3 and 12.2 J g^{-1} for this potato starch and dry matter, respectively. The endothermic transition peak temperature of this potato dry matter was 74°C, about 4°C higher than that of the starch.

Figures 2 and 3 show two series of DSC curves at moisture contents from 61 to 84% for potato dry matter

Table 1 Thermal properties of potato dry matter and starch isolated from Shepody potato harvest at 112 days at various moisture contents

Moisture content/ mass%	ΔH/J g^{-1}		T_p/°C	
	dry matter	starch	dry matter	starch
61.1	11.2	–	76.2	–
65.4	11.4	–	77.0	–
67.1	–	16.1	–	71.9
69.5	–	16.3	–	69.4
70.3	12.2	–	74.6	–
72.1	12.0	–	74.7	–
72.5	–	16.2	–	69.8
76.1	–	16.7	–	69.4
79.9	12.6	–	74.4	–
80.1	–	16.7	–	69.6
83.8	–	17.4	–	69.9

and starch isolated from Shepody cultivar harvested at 112 days. For potato starch, the peak temperatures were between 69.5 and 70°C for moisture content between 69 and 84% (Table 1), but increased to 72°C at 67% moisture content, about 2°C higher than those starch samples with moisture content >69%. In general, a moisture content greater than 65% for this potato starch produced a symmetrical peak in the DSC curve. Starch was considered to be fully gelatinized at this moisture level [11]. With a lower moisture content, the endothermic peak of a pure starch-water system developed a less symmetrical shape and a shoulder appeared

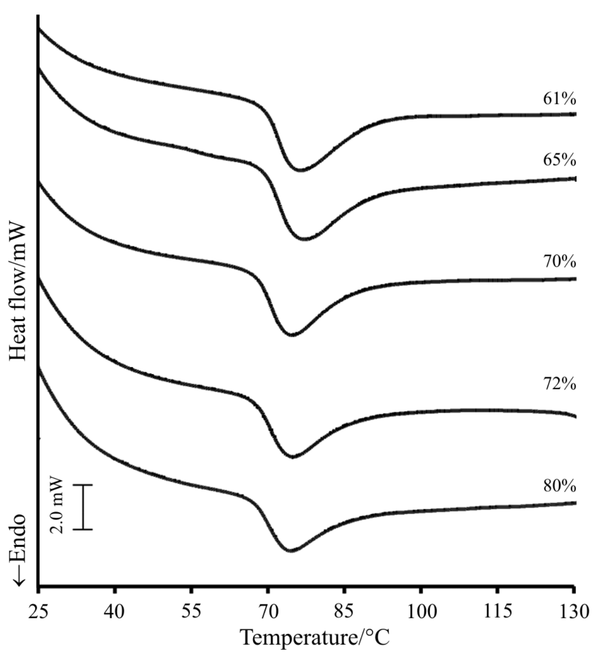

Fig. 2 DSC curves of potato dry matter at different moisture contents upon heating to 130°C. Labeling refers to moisture content in the dry matter

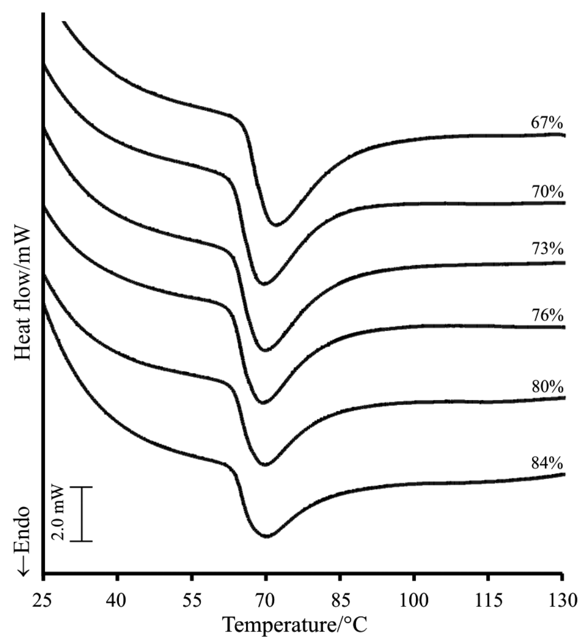

Fig. 3 DSC curves of potato starch at different moisture contents upon heating to 130°C. Labeling refers to moisture content in the starch

[10, 11]. However, a symmetrical peak was observed until moisture content reached 61% for the dry matter-water system. The peak temperatures were essentially constant at 74°C for moisture contents between 80 to 70% in the dry matter, but it increased to 76 and 77°C at moisture contents between 61 and 65%.

The enthalpy of gelatinization varied slightly with moisture content as shown in Table 1. For potato dry matter, the enthalpy was between 11.2 and 12.2 J g^{-1} when the moisture content ranged from 61 to 72%. The enthalpy was 12.6 J g^{-1} when moisture content reached 80%. For potato starch, the enthalpy was between 16.1 and 16.7 J g^{-1} in the moisture content from 67 to 80%. The enthalpy was 17.4 J g^{-1} when the moisture content reached 84%. Enthalpy was slightly higher at higher moisture content due to a solvation effect [11]. Thus, the enthalpy of starch gelatinization is essentially constant at a moisture content of 61 to 72% for potato dry matter, and at a moisture content of 67 to 80% for potato starch. The constant enthalpy of the dry matter indicates that the starch in the potato dry matter is the only factor influencing the magnitude of enthalpy of gelatinization at this moisture range [11]. This provides the basis for the starch content determination. Based on these results, a moisture content of 70% for both dry matter and starch was used to obtain the ratio of their gelatinization enthalpy as starch content in potato dry matter. Measurements done using % starch of the dry matter (as determined enzymatically) ranged from 58 to 70%.

The effect of sample mass on gelatinization properties of potato dry matter and starch at 70% moisture content

Before starch content in potato dry matter was determined, the influence of sample mass on the gelatinization enthalpy at 70% moisture content was assessed. Sample mass did influence the onset temperature and peak temperature of starch gelatinization in potato dry matter isolated from Shepody cultivar harvested at 112 days (Table 2), but did not significantly influence the starch gelatinization enthalpy (p>0.05). A single symmetrical peak was observed as shown in Fig. 4. The transition temperature increased when potato dry matter mass increased. The peak temperature of endothermic transition increased to 76°C and enthalpy decreased to 11.4 J g^{-1} when the mass of dry matter was 25 mg. This result may be due to the thermal lag because of the high volume in the pan. The high volume pan will be overloaded with potato dry matter mass over 25 mg at 70% moisture content. Therefore, volume of sample used should not be too large. It is recommended that 10–20 mg of dry solid mass occupying 1/2 to 2/3 volume of the high volume pan could be used to determine starch content in potato dry matter. Furthermore, a fixed sample mass in that range is also recommended.

Table 2 Thermal properties of potato dry matter–water (Shepody cultivar harvested at 112 days) system at 70% moisture content with different sample mass

Dry solid size/ mg	Moisture/ %	T_o/ °C	T_p/ °C	ΔH/ J g^{-1}
5.0	69.9	64.6	69.7	14.0
4.9	70.1	64.5	70.0	14.1
10.0	70.1	65.0	71.0	13.4
10.0	69.9	65.4	71.2	13.0
14.9	70.0	66.1	72.4	12.8
15.1	70.1	66.5	72.6	12.2
20.9	69.9	67.0	73.8	12.1
20.0	70.3	66.9	74.0	12.5
25.0	70.0	68.7	75.8	11.4
24.8	70.5	68.9	76.0	11.9

For isolated potato starch, the transition temperature and enthalpy were essentially consistent with different masses at 70% moisture (Table 3). There was no significant difference (p>0.05) on gelatinization enthalpy as a function of starch mass at this moisture level.

Table 3 Thermal properties of starch-water (starch isolated from Shepody potato cultivar harvested at 112 days) system at 70% moisture content with different sample mass

Dry solid size/ mg	Moisture/ %	T_o/ °C	T_p/ °C	ΔH/ J g^{-1}
4.0	69.8	64.5	68.0	16.1
4.2	70.1	64.1	67.8	16.4
7.9	69.8	63.9	67.5	16.0
8.4	69.5	63.5	67.2	16.0
12.4	69.3	63.8	68.1	16.9
12.2	69.3	63.9	68.2	16.8
15.8	70.0	63.8	68.6	17.1
16.2	70.0	63.7	68.5	16.8

Effect of different potato cultivars and growth times on gelatinization enthalpies of dry matter and starch

The gelatinization enthalpy of potato dry matter and isolated starch was influenced by growth times and cultivar of tubers (Table 4). The gelatinization enthalpy of dry matter and starch was the lowest at the earliest harvest time for three cultivars. The enthalpy increased slightly when tuber growth time increased. Gelatinization enthalpy of isolated starch slightly increased as growth time progressed for Superior and Snowden potatoes. The value of starch gelatinization enthalpy was higher than the corresponding potato dry matter enthalpy. The lower gelatinization enthalpy of

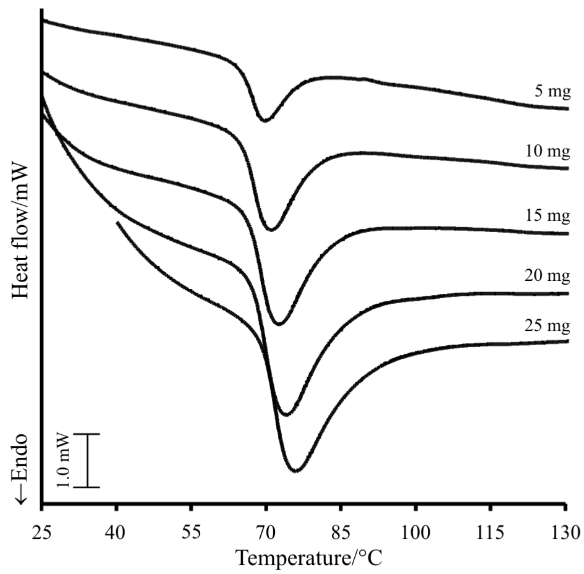

Fig. 4 DSC curves of potato dry matter at moisture content 70% with different sample mass upon heating to 130°C. Labeling refers to dry matter mass in the DSC pan

potato dry matter is mainly due to the lower starch content in the sample of dry matter compared to pure starch. Therefore, in this study the ratio of gelatinization enthalpy of dry matter to isolated starch is used as the indicator of starch content in potato dry matter. Compared to the other two cultivars, Shepody potato showed a slightly lower gelatinization enthalpy in isolated starch. Different molecular structure and the interaction with water of the starches from these potato cultivars at different growth times could be the major cause of different gelatinization enthalpy. Further investigation of this subject is planned.

Starch content of potato dry matter isolated from different cultivars at different times during growth by DSC

Table 4 presents the starch content obtained from DSC for potato dry matter and starch isolated from three cultivars at different growth times. In each cultivar, starch content was lower at earlier growth periods (i.e. <60 days), but to varying degrees. Starch content was 59% of the dry matter for Shepody cultivar at 55 days, but increased to a maximum of about 84% at 91 days and then decreased as growth time continued. For Snowden, starch content was about 70% of the dry matter at 55 days and increased to a maximum about 73% at 71 days and then decreased slightly. For Superior cultivar, starch was about 61% of the dry matter at 48 days, increased with time to 72% at 64 days and remained constant until 84 days, then decreased. These results were consistent with previous studies [12, 13] on starch content as a function of tuber growth time. At the earlier growth period, Snowden potato dry matter had the highest starch content (70%), and Superior and Shepody potato dry matter had lower and similar starch content (about 60%). At normal harvest time, Shepody potato dry matter showed the highest starch content (75%). Superior potato dry matter had the lowest starch content (65%). Starch content varied with potato cultivar at different times during tuber growth. Starch granule development and structure of the starch molecules may well be different among these different cultivars at different growth times. Further investigation is needed.

Starch contents of potato dry matter determined by enzymatic hydrolysis [14] showed a similar trend to the DSC method, but slightly lower values [15]. However, the difference between the DSC method and enzymatic method varied with the cultivars and

Table 4 The enthalpies of gelatinization of potato dry matter and starch isolated from different cultivars at different times during growth

Cultivar	Growth time/days	Gelatinization enthalpy (ΔH/J g^{-1})*		Starch content/%
		dry matter	starch	
Shepody	55	9.7±0.8	16.5±0.7	58.8
	71	12.2±0.4	16.0±0.3	76.3
	91	13.1±0.0	15.6±0.0	84.0
	112	12.3±0.3	16.3±0.5	75.5
	124	12.6±0.3	16.8±0.3	75.0
Snowden	55	11.8±0.1	16.9±0.1	69.8
	71	12.5±0.0	17.2±0.3	72.7
	91	12.2±0.2	17.8±0.1	68.5
	112	12.0±0.1	18.1±1.0	66.3
	124	12.5±0.0	18.0±0.1	69.4
Superior	48	10.1±0.2	16.5±0.3	61.2
	56	11.5±0.3	17.1±0.6	67.3
	64	12.4±0.1	17.2±1.4	72.1
	84	12.6±0.1	17.3±0.2	72.8
	117	11.7±1.0	18.0±0.5	65.0

*Value denotes mean ± standard deviation times during tuber growth. Incomplete hydrolysis of starch in potato dry matter may be the main reason for the difference. Data in Table 4 indicate that in general the DSC method, using potato dry matter, is valid as a means to determine starch in potato dry matter. The DSC method requires about 20 mg dry matter and takes about 20 min to complete, depending on heat rate, whereas the enzyme method requires 100 mg dry matter and takes over 2 h to complete.

Thus, the advantage of the DSC method is that it is rapid, and requires a small amount of sample. A disadvantage is that unlike enzyme methods it is not an absolute method and so requires isolated potato starch.

Conclusions

The enthalpy of gelatinization varied with potato dry matter and starch isolated from different cultivars at different times during growth. The enthalpy was essentially independent of moisture content between 61 to 72% for potato dry matter, and 67 to 80% for potato starch. The effect of sample mass on gelatinization enthalpy at 70% moisture content was very small for potato dry matter and starch. Thus, starch content in potato can be determined by measuring the enthalpy of gelatinization from DSC curves at 70% moisture content of the potato dry matter and isolated starch. Starch content of the three cultivars differed and was lower at shorter growth times. The highest level was found between two and three months after planting. Starch content decreased thereafter for all three cultivars, but to varying degrees among the three cultivars.

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