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Thermal Behaviour of High Amylose Cornstarch Studied by DSC

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Abstract

The thermal behaviour of high amylose cornstarches (80% amylose content) was studied by DSC using high pressure stainless steel pans in the temperature range between 0-350 °C. The number of endotherms and the enthalpy of gelatinization were found to depend on moisture content. Up to four endotherms and one exotherm were determined when the moisture content was above 40%. The meaning of each endotherm has been discussed. The enthalpy of gelatinization was calculated based on the summation of all the gelatinization endotherms and found to increase with increasing water content.

KEYWORDS: starch, amylose, thermal behaviour, gelatinization, DSC

1. INTRODUCTION

Starches serve as important ingredients in many fabricated foods. Recently they have been used as raw materials for biodegradable plastics. The starch granule is a heterogeneous material: chemically, it contains both linear (amylose) and branched (amylopectin) structures; physically, it has both amorphous and crystalline regions [1]. Cooking or processing normally causes starch gelatinisation. The definition of gelatinisation is the destruction of the crystalline structure in starch granules [1-2].

In the last 20 years, DSC has been widely used to study the thermal behavior of starches. However, the reported results are not consistent and are sometimes controversial because of the complexity of the thermal behavior of starches and differing measurement conditions. Some key factors that affect the results of thermal behavior of starch as measured by DSC, such as sample preparation, type of pan and measurement conditions, have been discussed in a previous paper [3].

The initial DSC experimental work was carried out with starch/water ratio 1:2 wt:wt and heated from 5 to 100 °C [4]. Stevens and Elton reported a clear peak in the temperature region 54 to 73 °C for different starches which was defined as the gelatinization temperature. Similar conditions and results were also reported by Wootton and Bamunuarachchi [5]. Donovan [6] reported two endothermic peaks when heating wheat and potato starches with water (27 wt%) to 150 °C and suggested two different structures or environments may be present. Eliasson [7] observed three peaks when a wheat starch-water mixture with water contents of 35-80 wt% were heated to 140 °C and considered DSC techniques alone could not explain the second peak. Similar results have been reported by other authors [8]. Shogren [9] studied the gelatinization of cornstarch with water (11-50 wt%) and reported four peaks indicating (1) amylopectin melting; (2) amylose-lipid complex melting; (3) amylose melting; and (4) degradation.

The gelatinization of starches has been extensively studied in food science with many methods being developed. For examples, the estimation of maltose [10]; determination of iodine blue complex [11]; observation of polarizing patterns under microscope [12]; Stevens and Elton [4] firstly reported the application of DSC to measure heat of gelatinization of starch. Since then, it has proven to be an extremely valuable tool to quantify gelatinization of starch; to determine kinetics of gelatinization; and study the effect of chemical modification on gelatinization. However, there are few reports on the thermal behaviors of amylose rich starch [13, 14]. Russell [13] reported that there was one broad endotherm of gelatinization found during heating amylomaize starch (70% amylose) in 57% water. An attempt was made to investigate the process in surplus water conditions but this only exhibited a very broad endotherm between 66°C and 104°C. It was considered the DSC used in the experimental work was not sufficiently sensitive. A similar result was also reported by Von Eberstein [14].

In this paper, we report the thermal behaviors of high amylose (80%) cornstarch studied by DSC using high pressure stainless steel pans between 0-350 °C. In particular, the effect of water content on the gelatinization process was discussed.

2. EXPERIMENTAL WORK

2.1 Materials

High amylose cornstarch G80 from Penford (Australia) was used in this experimental work. The amylose content in the starch was 80% and moisture content 13.35% as measured by an infrared heating balance technique (Model DHS-20) through heating samples at 110 °C for 20 min.

2.2 Differential Scanning Calorimetry (DSC)

A Perkin-Elmer differential scanning calorimetry (DSC) Diamond-I with an internal coolant (Intercooler 1P) and nitrogen purge gas was used in the experimental work. Melting point and enthalpies of indium were used for temperature and heat capacity calibration. Starch (about 7 mg) was weighted accurately into high pressure stainless steel pans (PE No. B0182901). Water was added to the starch in the DSC pan using a microsyringe, the sample reweighed and then sealed with a gold-plated copper seal (PE No. 04191758). The total moisture content of the mixture was taken as the original moisture content of the starch together with added water. The mixed materials were equilibrated at room temperature for 24 hrs before measurement in the DSC. The slow heating rate of 5 °C/min was used to minimise any temperature lag due to the large mass of the steel pan. The scanning temperature range depended on the specimen's water content to avoid bursting the pan's seal by high pressure. Based on our previous experience appropriate temperature ranges are listed in Table 1.

Table 1. Temperature ranges used in the experimental work.

Moisture Content	9%	13%	25%	40%	55%	65%	75%
Temperature Range	0-350	0-350	0-320	0-320	0-320	0-310	0-310

3. RESULTS AND DISCUSSION

3.1 Effect of Water Content on Thermal Behaviour

Figure 1 and 2 show the thermograms of the high amylose starch with different water content as determined by DSC. Figure 1 shows the full scale of the thermograms from 50 to 300 °C, in which the large decomposition peak at about 260 °C almost conceals all the other thermograms transitions. The starch samples were carbonized when heated above 260 °C. The formation of carbon black gave a strong indication that not only the chains of the large molecules have been broken down but also the rings of small molecular glucose had been destroyed. The water content slightly decreased the decomposition temperature and made the peak slightly broader. A possible explanation for this observation is that the higher water content caused full gelatinization (destruction of the crystal structure), which resulted in a lower decomposition temperature.

Specific gelatinization endotherms (50-200 °C) are provided in Figure 2. It is noted that the thermal transitions were not sharp, which can be explained by the low heating rate employed [15]. Both the number of specific endothermic transitions and hence the enthalpy of gelatinization (ΔH_G) were related to the system's moisture content. When the water content was low, (9.25%) only one endothermic transition occurred (230 °C) (see Fig.1) that was just prior to the large decomposition peak. It is seen that all the samples tested regardless of moisture content have this endotherm, which results in yellowing of the specimens from the decomposition of the polysaccharide chains without destroying the ring of glucose. According to the definition of gelatinization this endotherm should not be considered as gelatinization. It should be mentioned that the sample with 9.25% moisture was obtained through drying in a dry container with silica gel at room temperature for 24 hours. It is assumed that most of the free water in the starch has been removed during this drying process.

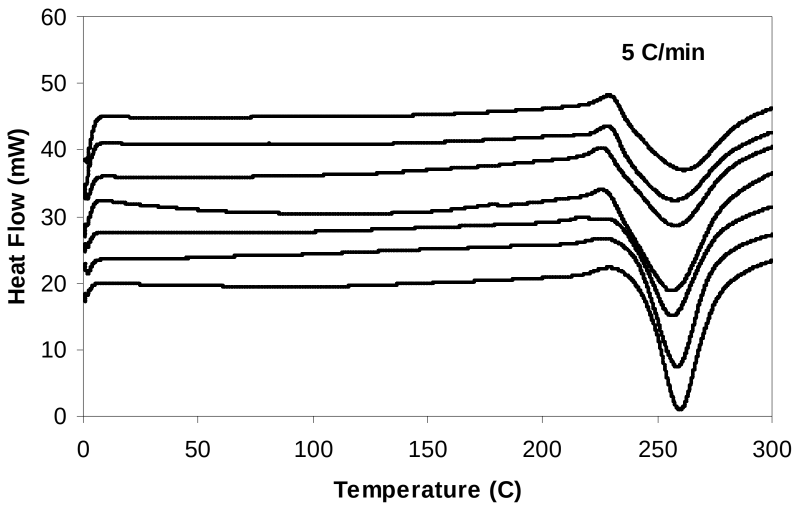

Figure 1: DSC thermograms of high amylose cornstarch with different water contents measured in high pressure pan. The moisture content (from top) are: (1) 74.9%; (2) 64.93%; (3)52.89%; (4) 41.33%; (5) 25.35%; (6) 13.35% and (7) 9.25.

Like most other starches, the high amylose cornstarch also has about 13 wt% moisture in its original state, which exists as internal water (approximately 9 wt%) and free water (approximately 4 wt%). The free water produces the first endotherm of gelatinization at about 150 °C. The temperature of this endotherm decreased with increasing water content. When the water content reached about 25% a new endotherm appeared at 180 °C and the temperature of this new endotherm decreased with increasing water content similar to the first endotherm at 150 °C.

A third endotherm of gelatinization was determined at about 80 °C when the moisture content was above 40 wt%. The enthalpy of gelatinization as determined from this endotherm also increased with increasing water content. When the water content reached 65 wt% the two lower temperature endotherms (at about 80 and 100 °C respectively) began to overlap, but could still be discriminated. These two endotherms may easily be considered as a single broad endotherm if their shifting was not taken into account.

Previous studies [2, 5] have shown that during gelatinisation, the starch granules swell and form gel particles. In general, the swollen granules are enriched in amylopectin, since the linear amylose diffuses out of the swollen granules to make up the continuous phase outside the granules [16]. Waxy starches (amylopectin) usually swell to a greater extent than their normal-amylose counterparts [17], amylose is proposed to act as a restraint to swelling. The high amylose starch used in this work, however, showed some different behaviour, such as the endotherm of amylopectin gelatinization at about 80 °C appears at a higher temperature than that of amylose. A detailed study of this issue will be discussed in a separate paper.

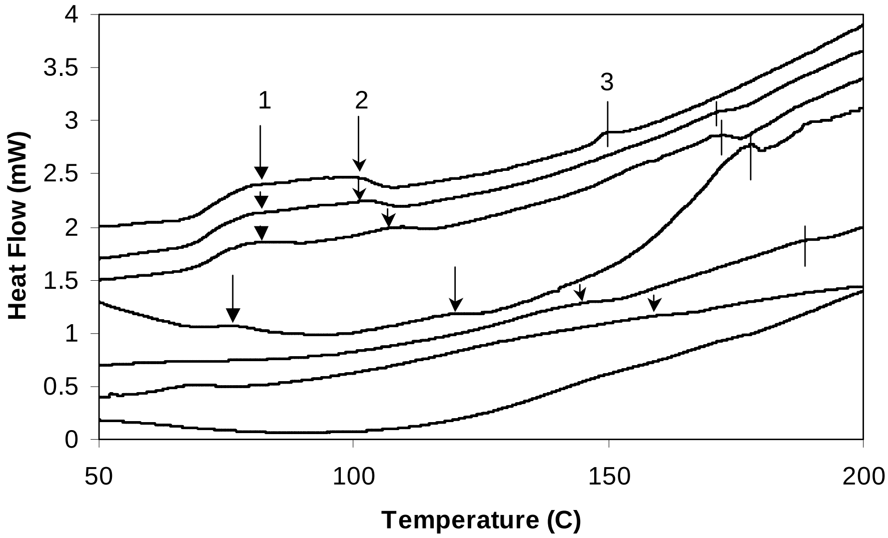

Figure 2: Endotherms of gelatinization for high amylose cornstarch with different water content (moisture contents are the same as those in Fig. 1 respectively).

3.2 Effect of Water Content on Gelatinization Enthalpy

There are numerous reports on measuring the enthalpy of gelatinization for different starches [2,4-7,13,18] but few of them involve high amylose starch. Furthermore, all of the previous reports are based on the calculation of the gelatinization endotherm with high moisture content at lower temperature. In this work the enthalpy of each endotherm of gelatinization with different water content was calculated.

As discussed earlier there are up to three endotherms of gelatinization which have been determined for this high amylose cornstarch. These endotherms are given the number 1, 2 and 3 respectively from lower temperature to higher. Table-2 lists the enthalpies of gelatinization both individual and summated. Since the endotherm-1 and 2 are overlapped in the most cases they were considered as one during measurement of enthalpy, and the endotherm-1 was used to present their onset temperature (T_o) and peak temperature (T_p). It is seen that the total enthalpy is increased with increasing water content. When the water content is lower, the endotherm-2 is a broad weak one with lower enthalpy, and this endotherm becomes sharper with increasing water content. When the water content reached about 25 wt%, endotherm-3 appeared at a higher temperature (about 178 °C), and this endotherm also became sharper, similar to endotherm-2. However, it was found that the enthalpy of endotherm-3 increased with increasing water content initially but decreased sharply when the water content was above 65 wt%. When the water content reached about 40 wt% the lower temperature

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endotherm-1 appeared. The endotherm-1 overlapped with the endotherm-2 when water content was above 55 wt%. The enthalpy of endotherm-1 increased with increasing water content. The endotherm-1 had a larger enthalpy so the total enthalpy increased sharply after it appeared.

Table 2. Gelatinization behaviour with different moisture content

Water Content (%)	Endotherm 1+2					Endotherm 3					Total ΔH (1+2+3) (J/g)
	T_o (°C)	T_{p1} (°C)	T_e (°C)	ΔT (T_o-T_e, °C)	ΔH (J/g)	T_o (°C)	T_p (°C)	T_e (°C)	ΔT (T_o-T_e, °C)	ΔH (J/g)	
9.25											-
13.35	138.3	154.6	164.7	26.4	0.686						0.686
25.35	128.2	139.8	149.6	21.4	1.318	178.5	187.4	192.8	14.3	0.971	2.289
40.33	71.34	76.39	112.7	41.3	1.403	174.5	181.3	185.4	10.9	1.190	2.593
52.89	69.70	80.29	111.1	41.4	6.914	164.4	170.1	175.8	11.4	3.391	10.305
64.93	68.90	80.89	108.7	39.8	10.444	166.2	171.3	175.8	9.6	0.539	10.983
74.90	68.85	80.46	106.1	37.3	11.481	146.7	149.5	158.2	11.5	0.509	11.990

4. CONCLUSION

The thermal behaviour of high amylose cornstarches was studied using DSC with high pressure stainless steel pans scanning over a temperature range between 0-350 °C. The number of endotherms and the enthalpy of gelatinization depended on moisture content. Up to four endotherms and one exotherm were determined when the moisture content was above 40 wt%. Three endotherms of gelatinization were determined and used to calculate the enthalpy of the gelatinization process. This is the first time that the enthalpy of gelatinization has been calculated based on summation of all the gelatinization endotherms with different moisture contents. The total enthalpy of gelatinization increased with increasing water content.

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