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Measurement of starch thermal transitions using differential scanning calorimetry

L. Yu*, G. Christie

CSIRO, Manufacturing Science and Technology, Clayton, CRC for International Food Manufacture and Packaging Science, Melbourne, Australia

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Abstract

Multiple transitions and instability of water contained in starch make it difficult to study the thermal behavior of starch materials using differential scanning calorimetry (DSC). Some key factors that affect the results of thermal behavior determination of starch measured by DSC, such as sample preparation, type of pan and measurement conditions, will be discussed. Maize starches with different amylose content: waxy 0%, corn 27%, G50 50% and G80 80% were used in the experimental work. Three different kinds of pans: autosampler aluminum pan, stainless steel pan with rubber O-ring and high-pressure stainless steel pans were used to demonstrate the effect of various factors on the measured results. Some technologies for improving the measured results are described although they are still under development. A practical guide to studying the thermal behavior of starch using DSC is introduced. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Starch; Thermoplastic starch; Differential scanning calorimetry; Thermal analysis

1. Introduction

In the last 20 years, differential scanning calorimetry (DSC) has been widely used to study the thermal behavior of starches, including gelatinization (Donovan, 1979; Donovan & Mapes, 1980; Eliasson, 1980; Lund, 1984; Shogren, 1992; Stevens & Elton, 1971; Wootton & Bamunuarachchi, 1980; Zobel, 1984) glass transition temperature (Chinachoti, 1996; Maurice, Slade, Sirett & Page, 1985; Slade & Levine, 1987; Stepto & Tomka, 1987; Van Soest, Benes & de Wit, 1996; Zeleznak & Hoseney, 1987) and crystallization (Biliaderis, Page, Slade & Sirett, 1985; Ring et al., 1987). However, the reported results are not consistent and are sometimes controversial because of the complexity of thermal behavior of starches and differing measurement conditions. The thermal behavior of starches is much more complex than that of conventional thermoplastics because the physicochemical changes that occur during heating starch or starch products may involve gelatinization, melting, glass transition, crystallization, change of crystal structure, volume expansion, molecular degradation and motion of water. All these thermal behaviors depend upon the moisture content, and the water contained in starch is not stable during heating. Furthermore, the thermal conductivity of starch is very poor, especially for starch granules, since their bulk density is low. This can also cause unstable results.

Stevens and Elton (1971) first reported the application of DSC to measure the heat of gelatinization of starch in 1971. The experimental works were carried out with starch/water ratios of 1:2 and heating range from 5 to 100°C. There is a clear endothermic peak in the temperature region between 54 and 73°C for different starches and this was defined as the gelatinization temperature. Similar conditions and results were also reported by Wootton and Bamunuarachchi (1980). Donovan (1979) reported that there were two endothermic peaks when heating wheat and potato starches with 27% water to 150°C, and suggested that two kinds of structures or two different environments may be present. Eliasson (1980) observed three peaks when a wheat starch/water mixture with water content in the interval 35–80% was heated to 140°C and concluded that DSC could not explain the second peak. Similar results have been reported by others (Lund, 1984). These studies have given more attention to the peaks at lower temperatures (<150°C), because of a sharp peak appearing in the temperature range 50–75°C. There are a few reports focused on the peaks at high temperatures, particularly the sharp peaks appearing at above 150°C when the moisture content is lower. Shogren (1992) studied the gelatinization of corn starch with 11–50% water and reported that the starch

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* Corresponding author.

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gelatinized (melted) at 190–200°C in the range of water content of 11–30%. Only when the moisture content was above 30% did the amorphous region start to gelatinize at about 70°C.

DSC has also been used to study the glass transition temperature (T_g) of starch and its products. The results differ from one another significantly. Zeleznak and Hoseney (1987) reported T_g values of 30–90°C for wheat starches with 13–18.7% moisture content, and postulated that the T_g would be below room temperature if the water content was above 20%. Slade and Levine (1987) reported T_g values of 50–85°C for wheat starch containing 55% water. Stepto and Tomka (1987) reported that extruded potato starch containing 15–20% moisture had a T_g of about 25°C. Van Soest et al. (1996) reported the T_g of extruded potato starch with 14% moisture at 5°C and that the T_g for moisture content above 14% could not be measured. Chinachoti (1996) stated that the T_g was not sensitive to measurement by DSC, but still used the technique to improve the results from DMA. Shogren (1992) reported that no T_g was observed for the corn starch on the first scan and suggested that most of the polysaccharide was highly ordered. The T_g of corn-starch containing 25–50% moisture was detected in the temperature range 20–60°C on the second scan. Maurice et al. (1985) proposed that DSC could not be used to study the T_g of starch because the enthalpy of the transition is too weak and most times it is masked by the gelatinization endotherm.

In the present paper, 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, will be discussed. In particular, the effect of various factors on the multiple transitions during gelatinization will be discussed. Maize starches with different amylose content (waxy 0%, corn 27%, G50 50% and G80 80%) were used in the experimental work. Some developing technologies are described, although they are yet to be fully refined. A practical guide to studying the thermal behavior of starch using DSC is introduced.

2. DSC facility and materials

2.1. Differential scanning calorimeter

A Perkin–Elmer Pyris-1 DSC with internal coolant (Intracooler 1P) and nitrogen purge gas was used. Melting point and enthalpies of indium were used for temperature and heat capacity calibration.

Three kinds of pans from Perkin–Elmer were used: autosampler aluminum pans with 30 μl volume (PE No. BO169320), stainless steel pans with rubber O-ring (PE No. 03190218) and high-pressure stainless steel pans (PE No. BO182901).

In order to improve the thermal transmission of starch granules, an ultrasound bath (BRANSON 2200) was used to shake the starch in the DSC pan to pack the starch particles more tightly.

2.2. Materials

Corn starches with different amylose contents (waxy 0%, maize 27%, G50 50% and G80 80%) were used to demonstrate the effect of various factors on the measured results. All materials were supplied by Goodman Fielder. The moisture contents were determined by drying the starches in a vacuum oven at 110°C for 2 h.

3. The effect of various factors on measured results

3.1. Baseline application

Baseline subtraction has been widely used to avoid slope and bend of curves in DSC measurement. The use of

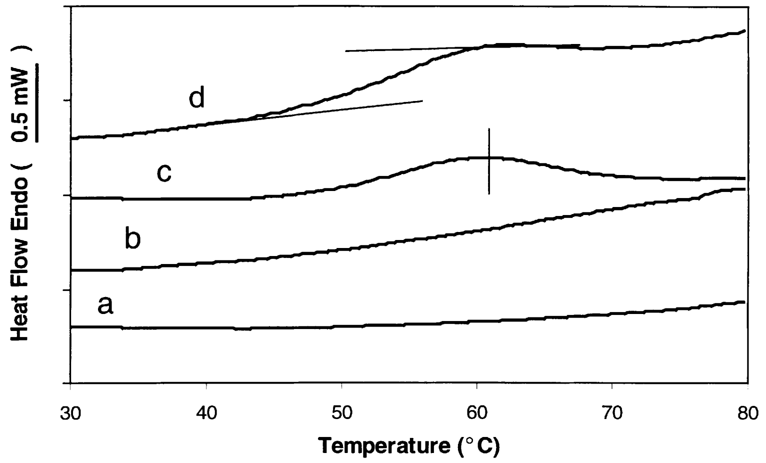

Fig. 1. Effect of water on baseline and measured results: (a) baseline with empty autosampler aluminum pan; (b) endotherm of water (5 mg); (c) endotherm of waxy maize starch (12.7% water) using (b) as baseline; (d) endotherm of waxy maize starch using (a) as baseline.

baseline correction is particularly important for materials containing volatile substances, such as water, because the evaporation of water requires additional energy. This produces a bend in the DSC endotherm, with the curve sloping towards the direction of positive heat flow. Fig. 1 shows the effect of water on the baseline and measured results using an autosampler aluminum pan. Curve a is a baseline with an empty pan, and has the shape of a straight line. Curve b shows the endotherm of pure water. It is seen that the curve was bent at a temperature of 40°C and sloped upward. When heating corn starch containing 13% moisture, a small peak appears at 60°C with an onset temperature at 45°C. Because the bend appears within the same temperature region, the peak could be considered as a change of heat capacity associated with the T_g (see Curve c in Fig. 1). When Curve b is used as a baseline for this measurement, the peak can be clearly identified (see Curve d in Fig. 1) because the effect of water has been removed.

3.2. Sample preparation

Starch, like most other polymeric materials, has poor thermal conductivity; especially granular starch, since the bulk density of starch granules is so low. In order to improve thermal conductivity, the starch sample in the pan is shaken using an ultra-sound bath to pack the granules tightly. Fig. 2 shows the results for waxy starch with 13% moisture heated to 200°C. It is seen that the peaks of the sample with free packing are broad and sometimes a new peak appeared. The peaks of the ultrasound shaken samples improved significantly. Two well defined thermal transitions were obtained. Gently shaking the pan using tweezers can also be used to achieve similar results.

Sample preparation for rigid bulk starch products, such as thermoplastic starch, is another challenge. In order to improve the contact between the sample and the pan, a particular technology has been widely used for conventional polymeric samples. The sample is heated to a temperature above its melting temperature in the pan and then cooled down for further study. Unfortunately, this approach cannot be used with starch products because molten starch does not flow freely. Furthermore, the thermal properties of a starch or its products depends upon its thermal history. Various physicochemical changes could be involved during heating starch or its products, some of which are irreversible.

Some new technologies are currently under development, although they are yet to be fully refined. One involves addition of silicon oil or paraffin oil into the pan as a heat conductor. However, this heat conductor will significantly decrease sensitivity and baseline correction with the heat conductor should be considered. Another method is to gently press flat the sample in the pan. A small autosampler aluminum pan (30 μl) is used. A flat piece is cut from the sample (which should be 0.8 mm thick — that is just greater than the depth of the pan). When the pan is sealed by a crimper, the heat from the crimper will press the two sides of the pan tightly against the flat specimen. A slight mark because of the sample can be seen on the pan surface. Similar methods can also be used for stainless steel pans to study the thermal properties at higher temperatures.

Another method involves granulating the sample under liquid nitrogen conditions, then weighing out the powder sample. However, some potentially misleading results may be encountered with this method. These include change of moisture content upon treatment with liquid nitrogen, and polymer chain orientation (crystallization) under shear stress during granulation.

3.3. Pan selection

Pan selection is one of the key issues in correct measurement of the thermal behavior of starch using DSC. The pan used for studying starch materials must be sealed to avoid moisture leakage. Fig. 3 shows the DSC endotherms of the waxy maize starch containing 15% moisture measured with different pans. It is seen that the autosampler aluminum pan detected a peak at 60°C (see Curve a in Fig. 3), and that the

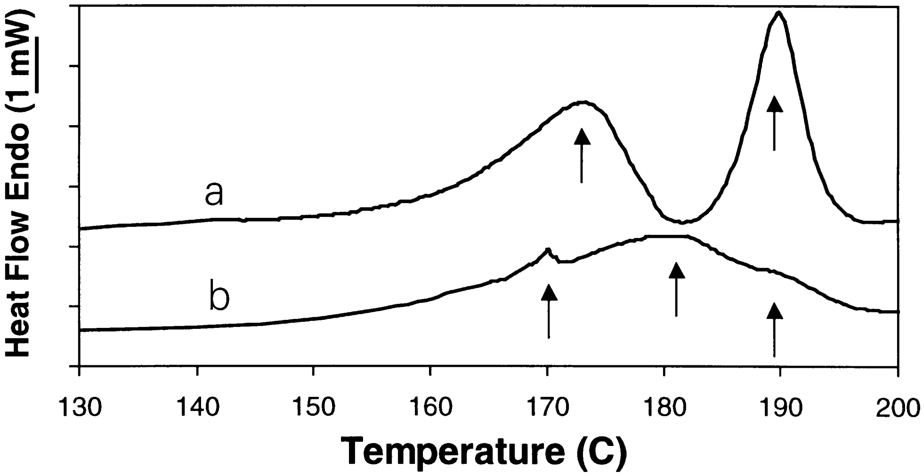

Fig. 2. DSC endotherm of waxy starch with 12.7% moisture (a) with shook sample and (b) without shook sample in stainless steel O-ring pan.

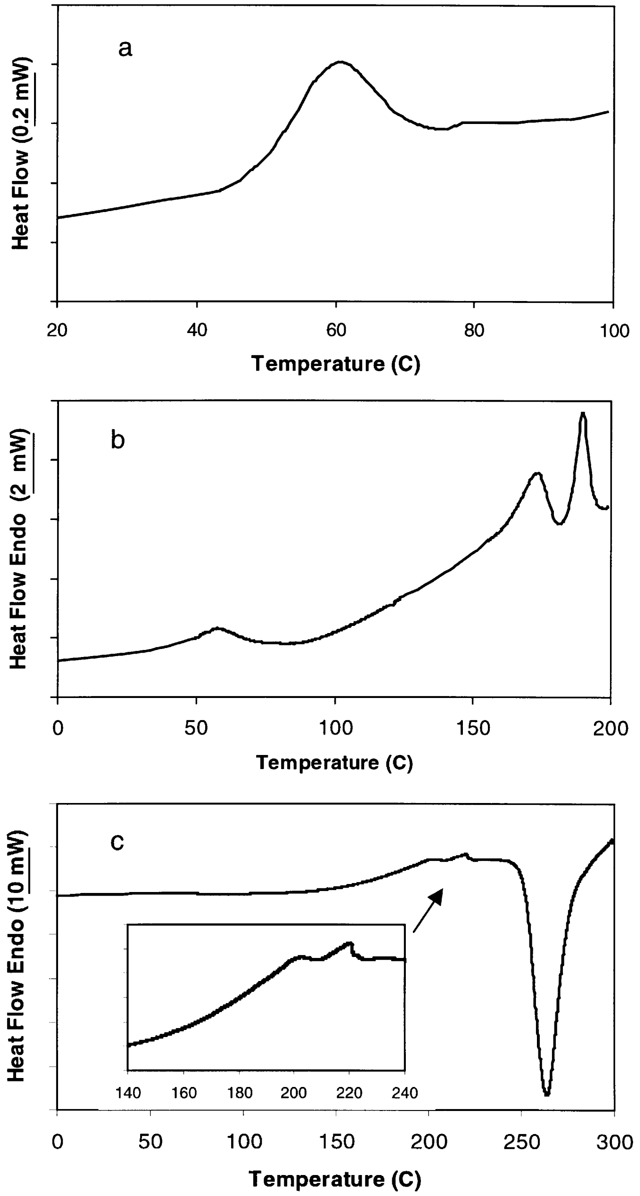

Fig. 3. DSC endotherms of waxy maize starch containing moisture 12.7% measured with different pans: (a) autosampler aluminum pan; (b) stainless steel O-ring pan; (c) high-pressure stainless steel pan.

pan leaked at about 110°C. Two sharp peaks appear in the temperature region of 170–200°C for the stainless steel O-ring pan (see Curve b in Fig. 3), and this pan leaked at about 220°C. The peak at lower temperature (60°C) can also be observed using the stainless steel O-ring pan. A large peak can only be measured using a high-pressure stainless steel pan (see Curve c in Fig. 3) at about 260°C which represented decomposition temperature of starch. Two peaks at higher temperatures (one at 180°C and the other at 190°C) can also be clearly observed if the scale is enlarged in the vicinity of that temperature region using the high-pressure stainless steel pan (see Curve c in Fig. 3). However, the small peak at the lower temperature is hard to measure using this high-mass pan because the pan will absorb the small change in heat capacity.

In order to study fully the thermal properties of a starch sample, more than one type of pan may need to be used. Because the mass and heat capacity of different pans are significantly different, it is not expected that the same result will be obtained using different pans for the same sample. Attempts have been made to unify the temperature measured with different pans through measuring at different heating rate, which will be discussed later.

3.4. Methods of adding water

There are several ways to add water into starch for DSC study. One involves placing the starch sample into different humidity environments to absorb moisture. The mass of a pan is weighed. Starch is added into the pan, which is weighed again to calculate the mass of the starch sample. The pan containing starch is put into a high humidity condition for 24 h to absorb moisture and equilibrate moisture content. The pan is then immediately sealed and weighed again to calculate the additional water content. The advantage of this method is that the moisture content distribution is homogeneous if the equilibration time is long enough. However, this method involves the preparation of controlled humidity environments and it is not easy to verify the quantity of additional water that will be absorbed.

The second method involves pre-mixing starch with water in a glass vial. The mass of a 10 ml glass vial with cover is weighed first. Starch is then added into the vial, which is weighed again to calculate the mass of starch. The water is added using a 10 ml syringe filled with the desired volume, and mixed well using a small spatula. The vial is then sealed and weighed again to calculate the water content. The sample should be equilibrated in the vial for more than 24 h. The advantages of this method are its simplicity and that the content of additional water in the vial can be accurately controlled. However, there is a possibility of moisture loss during movement of the sample from the vial to a DSC pan, especially for samples containing higher moisture contents. Another reason that this method is not suitable for samples containing higher moisture levels is that starch will be precipitated if the content of water is high (>50%). This method is therefore recommended for preparation of samples requiring addition of small amounts of water.

The third method is to add water directly into the DSC pan. The mass of the pan and cover is determined first. Starch is then added into the pan, which is weighed again to calculate the sample mass of the starch. The water is added into the pan using a small 25 μl syringe and mixed gently using a needle. Then the pan is sealed and the quantity of additional water is calculated accurately by weighing the pan containing the sample again. The sample needs to be equilibrated for more than 24 h before measurement. The

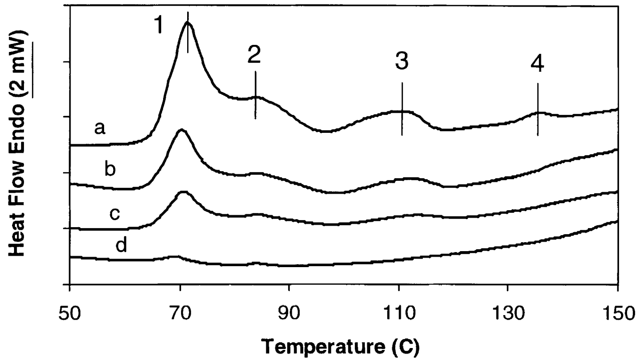

Fig. 4. Effect of sample mass on measured results of corn starch containing 52% water using stainless steel O-ring pan: (a) 26.7 mg; (b) 13.4 mg; (c) 4 9mg; (d) 1.87 mg.

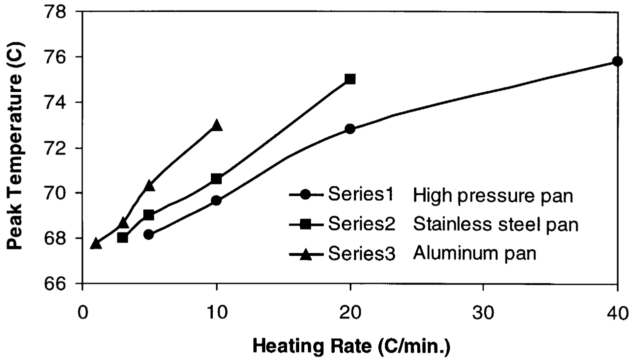

Fig. 5. Effect of heating rates on a peak temperature measured with different pans for corn starch containing 50% water.

advantage of this method is that the amount of water added can be accurately measured and controlled. However, there is a possibility that the distribution of additional water in the DSC pan is not homogeneous even when the sample is equilibrated for more than 24 h, especially for samples containing small amounts of water. A typical result of heterogeneity is the occurrence of new peak. This method is therefore recommended for preparation of samples requiring addition of large amounts of water (>20%).

Another method involves adding excess water then evaporating some off. The disadvantages of this method are the time requirements and that the system may not be homogeneous if the additional water content is too low or too high after evaporation.

3.5. Effect of sample mass

It is well known that there is a balance between sensitivity and resolution that is controlled by the sample mass. A large sample mass will increase sensitivity but decrease resolution. For most conventional polymeric materials, 3–5 mg of sample is recommended. The mass of starch sample used for DSC is generally higher because the transition enthalpies are lower. For example, the heat of fusion of polypropylene is about 80 kcal/g (Miller, 1989), whereas the measured energy of gelatinization of starch has been reported to be as low as 4 J/g (Lund, 1984). The increased mass will decrease resolution, which can result in peak broadening and overlap between two neighboring peaks. The poor thermal conductivity of starch granules also reduces the height of measured peaks because the peaks become broader. Fig. 4 shows an example of the effect of sample mass on the results. It is seen that when the mass of sample is lower than 3 mg, only one peak is measurable for corn starch containing 20% water. Two separate peaks can be measured when the mass of the sample is between 5 and 20 mg. When the mass is too high (>30 mg), the two peaks overlap. Therefore, 10–20 mg of sample is recommended.

3.6. Effect of heating rate

The DSC thermal response for macromolecules is a result of kinetic events, where the measured parameters are functions of the heating or cooling rate. The temperature of measured peak depends on the heating/cooling rate because the relaxation of the polymer chains is time-dependent, and because of the poor thermal conductivity of polymeric materials. Measured results using different types of pan may not be same, because the thermal conductivity, heat capacity and mass of different types of pans differ, which affect the kinetic events. Generally, the pans with larger mass and poorer conductivity will delay the measured peak more.

As mentioned earlier, some studies may require more than one type of pan. In practice, DSC measurement using aluminum pans is normally carried out at 10°C/min. However, measurement using larger mass pans (such as high-pressure stainless steel pans) has to be carried out at lower heating or cooling rates (<5°C/min). Attempts have been made to unify the transition temperatures measured using different pans through varying the heating rate. Fig. 5 shows the effect of heating rate on a peak temperature measured with different pans for corn starch containing 50% water. It is seen that increasing the mass of the pan and decreasing heating rate will reduce the peak temperature. An important point is that, using this kind of master curve, a particular peak can be identified even when measured with a different pan or different heating rates. Thus it is possible to discuss "a particular peak" for multiple transitions measured with different pans.

3.7. Effect of moisture equilibration time

As discussed above, starch samples need to be equilibrated for a certain time if they require addition of water. The equilibration time required depends upon the amount of additional water. The less water that is added, the more time is needed for equilibration.

However, after equilibrating the sample for a long time, some transition enthalpies may be lost or changed — for example, because of the diffusion of water into starch and/or different motion of water in different regions. This is a complex issue and will be discussed in a separate paper.

4. Summary

The thermal properties of starch are much more complex than for conventional thermoplastics. This is because of the multiple transitions and instability of water contained in starch of starch thermoplastics. Some key factors that affect the determination of thermal behavior of starch measured using DSC have been discussed. It is seen that various factors, such as sample preparation, type of pan and measurement conditions, must be carefully considered. Otherwise, misleading results may be obtained, such as: (i) a peak missing because of a large pan mass; or (ii) the appearance of false peak due to poor conductivity of the starch or insufficient equilibration; or (iii) confusing a peak with a glass transition endotherm because of water evaporation.

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