

Gelatinization of cornstarch with different amylose/amylopectin content

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Abstract

Gelatinization behaviours of cornstarch with different amylose/amylopectin content (waxy: 0/100, maize: 23/77, Gelose 50: 50/50 and Gelose 80: 80/20) were systematically studied by DSC using stainless steel high pressure pan as functions of water content (9–75%) and temperature (0–200 °C). The number of endotherm and enthalpy of gelatinization depend on amylose/amylopectin, moisture and lipid content. A unique endotherm for the high amylose starch Gelose 80 was detected and labelled as M3. Gelatinization endotherms G, M1 and M2 in different cornstarches showed similar thermal behaviours and variation patterns. The enthalpy of gelatinization was calculated individually and through summarization of all the gelatinization endotherms. The gelatinization enthalpy of amylopectin rich starch is higher than that of amylose rich starch. Total enthalpy of gelatinization increased with increasing amylopectin and water contents.

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1. Introduction

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 (French, 1984). The gelatinization of starch is very important in food processing and has been extensively studied in food science (Hermansson & Svegmarm, 1996; Stevens & Elton, 1971; Tester & Morrison, 1990; Von Eberstein, Hopcke, Konieczny-Janda, & Stute, 1980; Zobel, 1984) for decades, in particularly with higher water content. Recently, starches have been used as important raw materials for biodegradable plastics and its gelatinization process has attracted much attention since it acts as an important and unique characterization in the processing of starch-based materials (Biliaderis, Page, Slade, & Sirett, 1985; Lelievre, 1974, 1976; Russel, 1987; Svensson & Eliasson, 1995). DSC has proven to be an extremely valuable tool to quantify the gelatinization of starch and

has been widely used to study the thermal behaviours of starches (Donovan, 1979; Eliasson, 1980; Lund, 1984; Takahashi, 1982; Shogren, 1992; Tananuwong & Reid, 2004; Tufvesson, Wahlgren, & Eliasson, 2003; Wootton & Bamunuarachchi, 1980; Yu & Christie, 2001). The DSC thermograms give the possibility of analysing transition temperatures as well as transition enthalpies. The enthalpy (ΔH) of a transition was interpreted as corresponding to the amount of crystal order (or double-helical structure) in the starch suspensions that disrupted at heating scans. However, the reported results are not consistent and are sometimes controversial because of the complexity of thermal behaviours of starches, differing measurement conditions and sometimes even using unsuitable facilities. Yu and Christie (2001) have discussed various factors affecting on the measurement results considering pan selection, sample preparation and measurement conditions, etc.

Previous study has shown that gelatinization endotherms and enthalpy depend on starch sources, water content and the ratio of amylose/amylopectin and measurement conditions. The gelatinization of various starches with high water content (>50%) has been well studied since this condition is often encountered in food

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processing. Stevens and Elton (1971) first reported the application of DSC to measure the heat of gelatinization of starch and the experimental work was carried out with a starch/water ratio of 1:2 and a 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 results were also reported by Wootton and Bamunurachchi (1980). Donovan (1979) reported there were two endothermic peaks when heating wheat and potato starches with 27% water to 150 °C, and suggested that two kinds of structure 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 Lund (1984). Shogren (1992) first studied the gelatinization of cornstarch with lower water content (11–50%) and reported that the starch 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.

Cornstarch has particular attractive for scientific interesting since multi-endotherms were detected, and different amylose/amylopectin content was found in the natural resources. Waxy starch is a well studied cornstarch since it contains only one structure of glucan: amylopectin. Previous (Russel, 1987; Takahashi, 1982; Von Eberstein et al., 1980) study has shown that only one endotherm was observed in waxy starch when the water content is higher than 67%. A second endotherm was detected when the water content was about 50% and this endotherm moved to higher temperatures with decreasing water content. More gelatinization endotherms were detected for corn maize starch (containing about 23% amylose) than other starches with different water contents. The gelatinization endotherm at low temperature (60–70 °C) was reported by many authors (Byron, Burros, Young, & Carroad, 1987; Stevens & Elton, 1971) when the system contained excess water (about 70%). Shogren (1992) studied the gelatinization of cornstarch with 11–50% water and detected multi-peaks. The definition of the multi-peaks observed were discussed based on moisture content, defatted cornstarch and some unpublished data. There are few reports about gelatinization of high amylose starch. The highest amylose content in previous studies (Russel, 1987; Von Eberstein et al., 1980) is about 70% and its gelatinization exhibited a broad endotherm with excess water content.

Russel (1987) studied the gelatinization of starches with different amylose/amylopectin content using waxy maize, wheat, potato and amylomaize (amylose content ~70%) starches as raw materials. It was found that the gelatinization temperatures were not affected by the ratio of amylose/amylopectin, but the gelatinization enthalpies of amylomaize, wheat and waxy maize starches ranked in order of amylopectin content in the system containing 57% water. However, the potato starch had the largest

gelatinization enthalpy even through its amylopectin content was similar to that of wheat starch, which was explained by the high proportion of “double helical” structures with only short range order.

In this work, cornstarches with different amylose/amylopectin content (waxy: 0/100, corn: 23/77, Gelose 50: 50/50 and Gelose 80: 80/20) have been systematically studied as a function of water content and measurement conditions. Some arguable endotherms reported previously were carefully retested and confirmed using the latest equipment (PE Diamond-I) and designed experiments. Defatted starch and amylose were prepared from corn maize starch and used to confirm the physical meaning of some endotherms. Stainless steel pans were used in the experimental work to study the thermal properties with high moisture content at high temperature range (up to 350 °C).

2. Experimental

2.1. Materials

Cornstarch with different amylose/amylopectin content was used in the experimental work as model materials. All the starches are commercially available and were kindly supplied by Penford (Australia). Table 1 lists the starches and their characterization. Gelose 50 and Gelose 80 are both cornstarch with amylose content of 50% and 80%, respectively, and are both a kind of genetic products. An infrared heating balance (Model DHS-20) was used to measure moisture content through heating samples to 110 °C for 20 min. Defatted cornstarch was prepared by soxhlet extraction with methanol according to the method of Schoch (1945). Annealed samples prepared through heating the samples to 80 °C and kept at that temperature for 1 h.

2.2. Sample preparation

There are two different ways to add water into starch used in sample preparation. When the water content of a sample needed is high (>50%), the method used is to add water directly into the DSC pan. Starch (about 5–8 g) was weighed accurately into high-pressure stainless steel pans (PE No.B0182901). Water was added to the starch in the DSC pan using a microsyringe, and then sealed with a gold-plated copper seal (PE NO. 042-191758) and

Table 1
List of materials and their characterization

| Starches | Water content (%) | Amylose content (%) | Molecules Weight ^a (MW) |
|--------------|-------------------|---------------------|------------------------------------|
| Waxy | 12.9 | 0 | 20,787,000 |
| Corn (maize) | 12.7 | 26 | 13,000,000 |
| G50 | 12.3 | 50 | 5,115,000 |
| G80 | 12.2 | 80 | 673,000 |

^a Number molecular weight measured by GPC provided by Penford.

reweighed. The mixed materials were equilibrated at room temperature for 24 h before measurement in the DSC. When the water content is low (<50%), another method is used. This method involves pre-mixing starch with water in a glass vial. The mass of a glass vial with cover is weighed first. Starch is then added into the vial that is weighed again to calculate the mass of starch. The water is added using a 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. In order to pick up homogeneous sample the mixed materials were equilibrated in the vial first for 24 h then transferred into a pan. The quantity of the samples in the pan was calculated through measuring empty pan and sealed pan with sample. All the mixtures were also equilibrated for more than 24 h at room temperature before measurement. Whatever the way used, the total moisture content of the mixture was taken as the original moisture content of the starch together with added water. Detailed method and some critical issues have been discussed previously (Yu & Christie, 2001).

2.3. Differential scanning calorimetry

A Perkin-Elmer differential scanning calorimetry (DSC) Diamond-I with an internal coolant (Intercooler IP) and nitrogen purge gas was used in the experimental work. Melting point and enthalpies of indium were used for temperature and heat capacity calibration. The slow heating rate of 5 °C/min was used to minimize any temperature lag due to the large mass of the steel pan.

3. Results and discussion

Gelatinization endotherm of various starches with excess water at temperature range between 50 and 190 °C is provided in Fig. 1. It is observed that there is a large gelatinization endotherm appearing at about 70 °C for waxy and maize starch similar to many previous reports (Russel, 1987; Takahashi, 1982; Von Eberstein et al., 1980). This endotherm has been well accepted as the gelatinization of

amylopectin and labeled as G endotherm (Donovan, 1979; Evans & Haisman, 1982; Russel, 1987; Zobel, 1984). Apart from the G endotherm a second endotherm was also detected for maize starch at about 90 °C. Previous study has reported this second endotherm for maize starch, which was considered as the phase transition within an amylose–lipid complex and labeled as M2 (Biliaderis et al., 1985; Jovanovich & Añón, 1999; Raphaelides & Karkalas, 1988). Fig. 1 also provided the thermogram of defatted maize (see curve c in Fig. 1). It is seen that the M2 peak disappeared after the maize was defatted, which confirmed the physical meaning of this endotherm. The thermal transitions of the high amylose content starch (Gelose 50 and Gelose 80) were not as sharp as those of the normal and amylopectin rich starch, instead a very broad endotherm was obtained in the temperature range between 65 and 115 °C. This broad peak is a composite one made up of gelatinization G and a phase transition within amylose–lipid complex M2. These two endotherms can be separated with decreasing water content, which will be discussed later (see Fig. 4). The M2 in the higher amylose starch was also confirmed by defatting Gelose 80 (see curve f in Fig. 1). Apart from this broad endotherm a small endotherm was detected at about 155 °C for the Gelose 80 and labeled as M3. This is a unique endotherm only existing in the high amylose starch. Furthermore, this endotherm still existed after defatting, which indicated it did not relate to the lipid contained in the starch. Based on these results this endotherm has been considered as the melting of amylose and will be discussed in detail later.

With decreasing water content, two new endotherms were detected for waxy starch (see Fig. 2). The first one was observed with about 55% water content, which appeared as a shoulder overlapped with the G endotherm. This one has been called M1 reflecting non-equilibrium melting of crystallites (Russel, 1987) and it disappeared when the water content was lower than about 30%. The second one appeared when the water content was lower than 40%. The temperature of the second one is higher than that of M1 and labeled as Z endotherm. This Z endotherm was also observed previously (Maurice, Slade, Sirett,

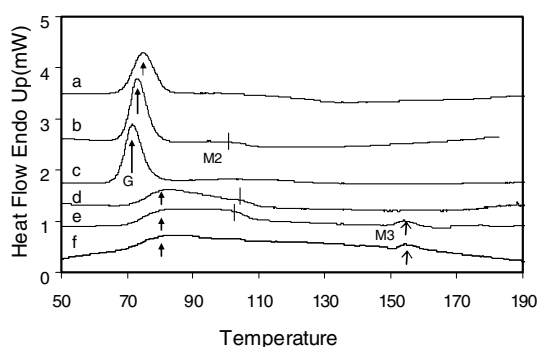


Fig. 1. Gelatinization endotherms of different cornstarch with excess water in the temperature range 50–175 °C: (a) waxy; (b) maize; (c) defatted maize; (d) Gelose 50; (e) Gelose 80; (f) defatted Gelose 80.

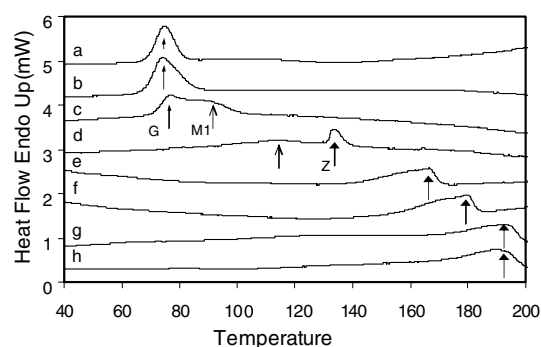


Fig. 2. DSC endotherms of waxy starch with different water content: (a) 74.57%; (b) 64.4%; (c) 54.7%; (d) 40.1%; (e) 29.9%; (f) 20.6%; (g) 13.7%; (h) 9.38%.

& Page, 1985; Russel, 1987) and it was suggested that it resulted from annealing of the amylopectin crystallites during heating but without experimental supporting evidence. Fig. 3 shows DSC thermograms of waxy starch annealed at 80 °C that is higher than the G endotherm but lower than the temperature of the Z endotherm. It is observed that the temperature of the Z endotherm decreased after the annealing treatment. Detailed study showed the enthalpy of the Z endotherms were increased after the annealing. This indicated the annealing increased the crystallinity of the sample. The results support that this endotherm Z is the annealing of amylopectin crystallites during heating. The temperatures of both M1 and Z endotherms increased with decreasing water content.

To the best of our knowledge, so far there is no report of systematic studies of high amylose cornstarch. Fig. 4 shows the gelatinization endotherms of high amylose starch Gelose 80 with various water content. With decreasing water content the broad endotherm of Gelose 80 was split into two peaks. This proved that the broad endotherm of high amylose with excess water was a composite of gelatinization and melting endotherms. The endotherm at lower temperature is G since the temperature at which it appeared and variation in behaviour was similar to the G in waxy starch (see Figs. 2 and 5). The second endotherm at the temperature just higher than the G is M2 as

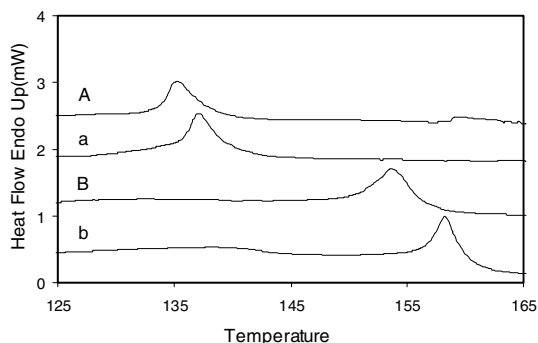


Fig. 3. Effect of annealing on the endotherm Z of waxy starch containing 40% (A, a) and 29.9% (B, b) water: the endotherm of A and B are annealed samples at 80 °C for 1 h.

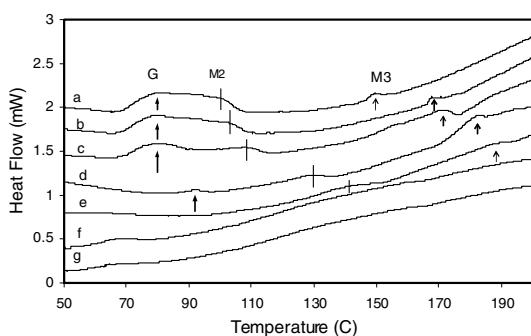


Fig. 4. DSC endotherms of Gelose 80 starch with different water content: (a) 74.90%; (b) 64.93%; (c) 52.89%; (d) 41.33%; (e) 25.35%; (f) 13.35%; (g) 9.25%.

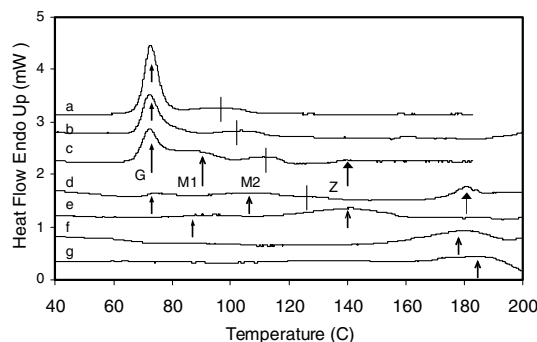


Fig. 5. DSC endotherms of maize starch with different water content. The moisture content (from top) is: (a) 74.57%; (b) 65.3%; (c) 51.8%; (d) 40%; (e) 29.9%; (f) 16.15%; (g) 9%.

discussed above. The endotherm M2 moved to higher temperature with decreasing water content and disappeared when the water content was lower than 25%. The temperature of the unique endotherm M3 for Gelose 80 also increased with decreasing water content and disappeared when the water content was lower than about 25%. This endotherm M3 has been interpreted as the melting of amylose based on comparison with lower amylose and defatting samples (see Fig. 1). Similar behaviour for pure amylose from potato was also observed (data not published).

Fig. 5 shows the DSC thermograms of maize starch with various water contents. With decreasing water content, the endotherm G almost remained at the same temperature when the water content was higher than 40% and moved to higher temperature when the water content was lower than 40%. The endotherm M1 moved to higher temperature with decreasing water content. When the water content decreased to about 50% four endotherms were observed. Based on the results discussed above these four endotherms were identified as G, M1, M2 and Z, respectively. The endotherm G disappeared when the water content was lower than 30%. It has noted that the gelatinization endotherms G, M1 and M2 in different cornstarches show similar thermal behaviours and variation patterns even through the temperatures of each endotherm are different. The temperature difference could result from a complex issue involving molecular weight, molecular weight distribution, interaction between amylose and amylopectin, or other level of microstructure difference etc. This phenomenon probably is a unique characteristic for natural polymers.

The gelatinization enthalpies were calculated individually and through summarization of all the gelatinization endotherms. Since some gelatinization endotherms overlapped under measurement conditions a mathematical curve fitting technique was used to separate the peaks. The conventional mathematical deconvolution (origin 7.0 software) was performed to fit peaks. Fig. 6 shows a typical example of the deconvoluted peaks from the mathematical curve fitting technique. Table 2 lists the individual and summed enthalpies of maize starch as an example.

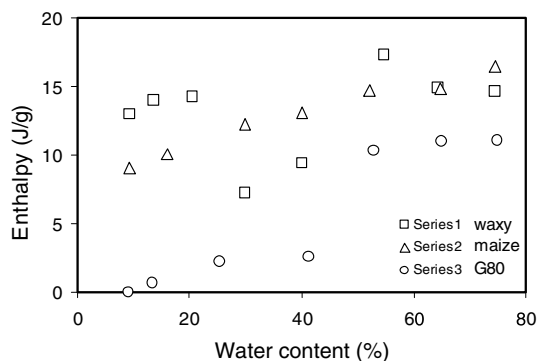


Fig. 7. Effect of water content on the summarized gelatinization enthalpy of cornstarches with different amylose/amylopectin content.

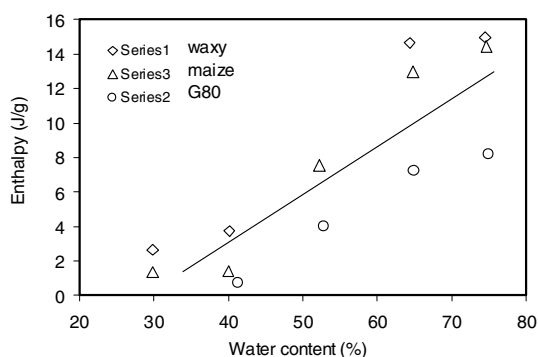


Fig. 8. Effect of water content on the enthalpy of endotherm G for various cornstarches.

The broad endotherm for high amylose starch with excess water content was split into two endotherms through reducing the water content. This proved that the broad endotherm of high amylose with excess water was a composite of gelatinization and melting endotherms. The endotherm at lower temperature is G since the temperature at which it appeared and variation in behaviour was similar to the G in waxy starch. The second endotherm at the temperature just higher than the G is M2. A unique endotherm for the high amylose starch Gelose 80 was detected and labelled as M3 and has been interpreted as the melting of amylose based on comparison with lower amylose and defatting samples.

Gelatinization endotherms G, M1 and M2 in different cornstarches showed similar thermal behaviours and variation patterns. The enthalpy of gelatinization was calculated individually and through summarization of all the gelatinization endotherms. The gelatinization enthalpy of amylopectin rich starch is higher than that of amylose rich starch. The total enthalpy of gelatinization is increased with increasing amylopectin and water content in general.

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References

- Biliaderis, C. G., Page, C. M., Slade, L., & Sirett, R. R. (1985). Thermal behavior of amylose-lipid complexes. *Carbohydrate Polymers*, 5, 367–389.
- Byron, C., Burros, L. A., Young, P., & Carroad, A. (1987). Kinetics of corn meal gelatinization at high temperature and low moisture. *Journal of Food Science*, 52(5), 1372–1380.
- Donovan, J. (1979). Phase transitions of the starch-water system. *Biopolymers*, 18, 263–275.
- Eliasson, A.-C. (1980). Effect of water content on the gelatinization of wheat starch. *Starch/Stärke*, 32, 270–272.
- Evans, I. D., & Haisman, D. R. (1982). The effect of solutes on the gelatinization temperature range of potato starch. *Starch/Stärke*, 34, 224–231.
- French, D. (1984). Organization of starch granules. In R. Whistler, J. N. Bemiller, & E. F. Paschall (Eds.), *Starch: Chemistry and technology* (pp. 183–256). Orlando: Academic Press.
- Hermansson, A. M., & Svegmärk, K. (1996). Development in the understanding of starch functionality. *Trends Food Science & Technology*, 7(11), 345–353.
- Jovanovich, G., & Anón, M. C. (1999). Amylose-lipid complex dissociation: A study of the kinetic parameters. *Biopolymers*, 49, 81–89.
- Lelievre, J. (1974). Starch gelatinization. *Journal of Polymer Science*, 18, 293–296.
- Lelievre, J. (1976). Theory of gelatinization in a starch water solute system. *Polymer*, 17, 854–858.
- Lund, D. B. (1984). Influence of time, temperature, moisture, ingredients and processing conditions on starch gelatinization. *CRC Critical Review in Food Science and Nutrition*, 20(4), 249–257.
- Maurice, T. J., Slade, L., Sirett, R. R., & Page, C. M. (1985). Polysaccharide-water interactions – thermal behavior of rice starch. In D. Simatos & S. L. Multon (Eds.), *Properties of water in food* (pp. 211–227). Dordrecht, Netherlands: Martinus Nijhoff.
- Raphaélides, S., & Karkalas, J. (1988). Thermal dissociation of amylose-fatty acid complexes. *Carbohydrate Research*, 172, 65–82.
- Russel, L. P. (1987). Gelatinisation of starches of different amylose/amylopectin content. A study by differential scanning calorimetry. *Journal of Cereal Science*, 6, 133–145.
- Schoch, T. J. (1945). The fractionation of starch. *Advances in Carbohydrate Chemistry*, 1, 247–276.
- Shogren, R. L. (1992). Effect of moisture content on the melting and subsequent physical aging of cornstarch. *Carbohydrate Polymer*, 19, 83–90.
- Stevens, D. J., & Elton, G. A. H. (1971). Thermal properties of the starch water system. *Starch/Stärke*, 23, 8–11.
- Svensson, E., & Eliasson, A.-C. (1995). Crystalline changes in native wheat and potato starches at intermediate water levels during gelatinization. *Carbohydrate Polymer*, 26, 171–176.
- Takahashi, K. (1982). Application of differential thermal analysis to examination of thermal behaviour of starch. *Journal of The Japanese Society of Starch Science*, 29, 56–67.
- Tananuwong, K., & Reid, D. S. (2004). DSC and NMR relaxation studies of starch-water interactions during gelatinization. *Carbohydrate Polymers*, 58, 345–358.
- Tester, R. F., & Morrison, W. R. (1990). Swelling and gelatinisation of cereal starches. II. Waxy rice starches. *Cereal Chemistry*, 67, 558–563.
- Tufvesson, F., Wahlgren, M., & Eliasson, A.-C. (2003). Formation of amylose-lipid complexes and effects of temperature treatment. *Starch/Stärke*, 55, 61–71.

- Von Eberstein, K., Hopcke, R., Konieczny-Janda, G., & Stute, R. (1980). DSC investigation of starch: Part I. Feasibility of thermal methods to characterize starches. *Starch/Stärke*, 32, 397–404.
- Wootton, M., & Bamunuarachchi, A. (1980). Application of differential scanning calorimetry to starch gelatinization. *Starch/Stärke*, 31, 126–129.
- Yu, L., & Christie, G. (2001). Measurement of starch thermal transition using differential scanning calorimetry. *Carbohydrate Polymer*, 46, 179–184.
- Zobel, H. F. (1984). Gelatinization of starch and mechanical properties of starch pastes. In R. Whistler, J. N. Bemiller, & E. F. Paschall (Eds.), *Starch: Chemistry and Technology* (pp. 285–309). Orlando: Academic Press.