

# Measurement of electrical conductivity, differential scanning calorimetry and viscosity of starch and flour suspensions during gelatinisation process

Saiwarun Chaiwanichsiri,<sup>1,2</sup> Shigehiko Ohnishi,<sup>3</sup> Toru Suzuki,<sup>4</sup> Rikuo Takai<sup>4</sup> and Osato Miyawaki<sup>1\*</sup>

<sup>1</sup>Department of Applied Biological Chemistry, University of Tokyo, 1-1-1 Yayoi, Bunkyo-ku, Tokyo 113-8657, Japan

<sup>2</sup>Department of Food Technology, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand

<sup>3</sup>Kagawa Prefectural Industrial Technology Center, 587-1 Goto, Takamatsu, Kagawa 761-8031, Japan

<sup>4</sup>Department of Food Science and Technology, Tokyo University of Fisheries, 4-5-7 Konan, Minato-ku, Tokyo 108-8477, Japan

**Abstract:** Electrical conductivity measurements were applied to analyse the gelatinisation process of 12 starch or flour suspensions. The electrical conductivity of starch suspensions was found to increase upon gelatinisation because of the release of ions from starch granules. The initiation temperature of ion release,  $T_i$ , correlated well with the onset temperature in the DSC thermogram ( $R=0.868$ ), while the completion temperature of ion release,  $T_f$ , correlated with the temperature at the start of viscosity increase ( $R=0.865$ ). Thus  $T_i$  and  $T_f$  corresponded to the beginning and ending temperatures of gelatinisation respectively. The electrical conductivity measurement will be used as an on-line technique to monitor the whole process of starch gelatinisation.

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**Keywords:** electrical conductivity; differential scanning calorimetry; viscosity; starch suspension; gelatinisation

## INTRODUCTION

Starch is one of the most important food materials with wide applications. To characterise starches, it is important to know their molecular states, which are represented by amylose/amylopectin ratio, molecular weight distribution, crystallinity and intermolecular interactions among starch polymers and coexisting substances. These molecular states affect the physical properties of starches, such as gelatinisation, retrogradation, pasting property, syneresis, etc, which are very important in determining the functionality of starches in their applications.

Gelatinisation is one of the most important physical properties for characterising a starch. It has been defined as a phase transition of starch granules from an ordered to a disordered state during heating with excess water.<sup>1</sup> To measure gelatinisation, various techniques have been used. X-ray diffraction<sup>2</sup> measures changes in crystallinity. Differential scanning calorimetry (DSC)<sup>3</sup> detects enthalpy changes in the phase transition of starch. Viscosity measurements, typically by Rapid Visco Analyser (RVA)<sup>4</sup> or amylograph,<sup>5</sup> analyse changes in viscosity and pasting or rheological properties during and after gelatinisation.

Swelling power is measured by the ratio of the weight of wet sediment at a certain temperature during gelatinisation to the initial weight of dry starch.<sup>6</sup> By using hot stage light microscopy, loss of birefringence and starch granule rupture ratio can be measured.<sup>7</sup>

By using these techniques, gelatinisation properties have been measured for rice,<sup>4,7,8</sup> potato,<sup>4,9,10</sup> corn,<sup>4,6,11</sup> oat,<sup>12</sup> mung bean<sup>4,13</sup> and lentil<sup>5</sup> starches. Among the techniques for measuring gelatinisation described above, the combination of DSC and viscosity measurement has been most frequently employed because of their ease of use.<sup>4–6,9–11</sup> The relationship between the results from those two techniques, however, is not fully understood, except that the pasting temperature from RVA is always higher than the onset temperature in the DSC thermogram.<sup>4</sup>

In the present paper we have applied the electrical conductivity method as well as DSC and viscosity measurements to characterise the gelatinisation of 12 starch or flour samples. Relationships among the results from electrical conductivity, DSC thermogram and viscosity measurements are discussed in relation to the mechanism of starch gelatinisation.

\* Correspondence to: Osato Miyawaki, Department of Applied Biological Chemistry, University of Tokyo, 1-1-1 Yayoi, Bunkyo-ku, Tokyo 113-8657, Japan

E-mail: aosato@mail.ecc.u-tokyo.ac.jp

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## MATERIALS AND METHODS

### Materials

Sweet potato, wheat, maize and potato starches were purchased from Wako Chemical, Tokyo, Japan. Japanese rice flour and waxy rice flour were purchased from a local market in Tokyo, Japan. Thai maize flour, glutinous rice flour, rice flour, arrowroot flour, mung bean starch and tapioca starch were purchased from a local market in Bangkok, Thailand.

### Measurement of electrical conductivity

For each of the purified starches, 1 l of  $50 \text{ g kg}^{-1}$  starch suspension was prepared and heated on a hot plate in the temperature range  $20\text{--}95^\circ\text{C}$  under magnetic stirring. The electrical conductivity ( $\text{S cm}^{-1}$ ) of the sample was measured at 5 min intervals during heating using an LCR meter (Hewlett Packard, 4285A, Tokyo, Japan) equipped with a conductivity probe (Hewlett Packard, E 5050A, Tokyo, Japan) in the frequency range from 200 kHz to 20 MHz.

For crude starches and flours, each sample was first washed twice with distilled water and filtered by filter paper (Advantec Toyo, No 2, Tokyo, Japan) to remove low-molecular-weight impurities. Then a  $50 \text{ g kg}^{-1}$  starch suspension was prepared and its electrical conductivity was measured as described above.

### Differential scanning calorimetry (DSC)

The gelatinisation process of each starch sample was thermally measured using a differential scanning calorimeter (Shimadzu, TA-50 WS, Tokyo, Japan). A  $0.2\text{--}0.3 \text{ g}$  sample of  $300 \text{ g kg}^{-1}$  starch or flour suspension was prepared, put into an aluminium sample pan and sealed for DSC analysis. The sample was heated from room temperature to  $95^\circ\text{C}$  at  $3^\circ\text{C min}^{-1}$  and the onset, peak and endset temperatures and gelatinisation enthalpy were measured. The measurements were repeated in triplicate.

### Measurement of viscosity

Air bubbles in a  $5 \text{ g kg}^{-1}$  starch or flour suspension in a beaker (50 ml) were removed under vacuum ( $\sim 30$  Torr) for 30 min. Then the suspension in the beaker was heated on a hot plate under magnetic stirring until the completion of gelatinisation, during which time the change in viscosity was continuously monitored by an on-line vibration viscometer probe (Yamaich Electronics, VM-200, Tokyo, Japan) at a constant frequency of 1 kHz.

## RESULTS

### Electrical conductivity of starch or flour suspensions

Fig 1 shows the frequency dependence of the electrical conductivity of  $50 \text{ g kg}^{-1}$  potato starch suspension measured at 24, 60.5 and  $82^\circ\text{C}$ . No substantial effect of frequency was observed on the electrical conductivity, but the effect of temperature was very serious.

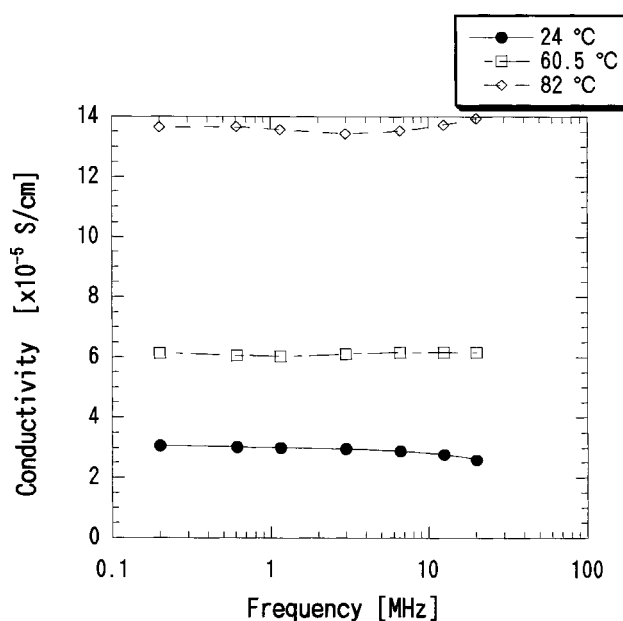


Figure 1. Effect of frequency on electrical conductivity of  $50 \text{ g kg}^{-1}$  potato starch suspension.

Therefore the frequency was fixed at 200 kHz and the electrical conductivity was measured during heating from 20 to  $95^\circ\text{C}$ . The result is shown in Fig 2. The electrical conductivity of the potato starch suspension increased slowly and linearly with an increase in temperature from 20 to  $62^\circ\text{C}$ , then the gradient increased more rapidly beyond  $62^\circ\text{C}$ . This rapid increase in conductivity ended at  $72^\circ\text{C}$ . Similar behaviour was observed for all the other starch and flour samples. The beginning and ending temperatures of the steep increase in electrical conductivity gradient,  $T_i$  and  $T_f$  respectively, were determined from the turning points of the lines in Fig 2 and are listed in Table 1 for all 12 starch or flour samples.

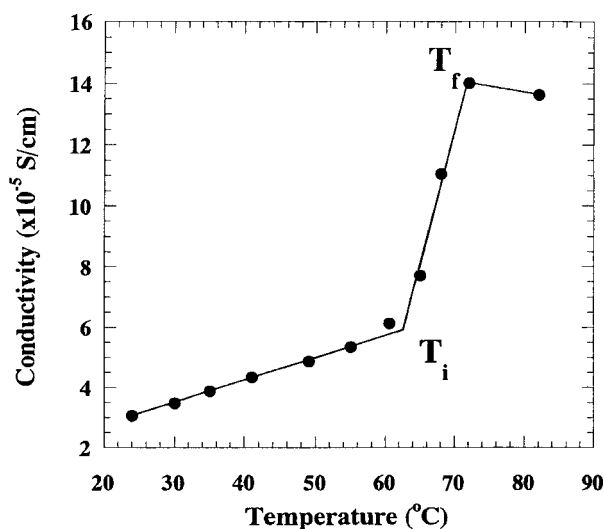


Figure 2. Effect of temperature on electrical conductivity of  $50 \text{ g kg}^{-1}$  potato starch suspension measured at 200 kHz.

Starch origin	Conductivity			DSC		Viscosity $T_{vis}^f$
	$T_i^a$	$T_f^b$	$\Delta T^c$	$T_{onset}^d$	$T_{endset}^e$	
Sweet potato	63.5	76	12.5	68.6	83.5	72.5
Wheat	54	80	26	54.7	69.1	86.4
Maize	63	85	22	62.0	76.7	89
Potato	62	72	10	60.4	74.5	64
Rice	53.1	87.8	34.7	56.1	79.4	76
Waxy rice	57	73	16	58.0	77.1	63.6
Maize (Thai)	64.5	90	25.5	66.4	79.2	92.9
Glutinous rice (Thai)	58	68	10	61.2	75.6	64
Rice (Thai)	57.2	90	32.8	62.2	76.9	90.3
Mung bean (Thai)	67	84	17	72.1	80.8	73.5
Tapioca (Thai)	58.5	67	8.5	62.3	78.2	64.6
Arrowroot (Thai)	58	68	10	63.8	80.4	65.2

<sup>a</sup> Initiation temperature of ion release.

<sup>b</sup> Completion temperature of ion release.

<sup>c</sup>  $\Delta T = T_f - T_i$ .

<sup>d</sup> Onset temperature in DSC thermogram.

<sup>e</sup> Endset temperature in DSC thermogram.

<sup>f</sup> Initiation temperature of rise in viscosity.

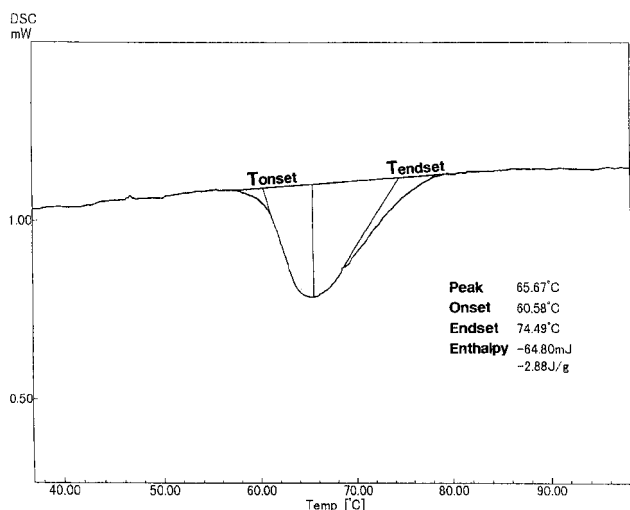
**Table 1.** Parameters ( $^{\circ}\text{C}$ ) representing gelatinisation of various starches

### DSC analysis of gelatinisation

The DSC thermogram of gelatinisation for  $300\text{ g kg}^{-1}$  potato starch suspension is presented in Fig 3. The onset ( $T_{onset}$ ) and endset ( $T_{endset}$ ) temperatures of gelatinisation are  $60.6$  and  $74.5^{\circ}\text{C}$  respectively for this sample. The area between the peak and the baseline on the graph represents the enthalpy of gelatinisation, ie the disruption of the starch granules.  $T_{onset}$  and  $T_{endset}$  for the various starch and flour samples are listed in Table 1.

### Change in viscosity during gelatinisation

Fig 4 shows the viscosity change during heating from  $20$  to  $70^{\circ}\text{C}$  for  $50\text{ g kg}^{-1}$  potato starch suspension. The viscosity observed was not much different from that of water until the temperature reached  $64^{\circ}\text{C}$ , where a sharp increase in viscosity was observed owing to gelatinisation. Similar viscosity curves for the other starch and flour suspensions were observed. The



**Figure 3.** DSC thermogram for  $300\text{ g kg}^{-1}$  potato starch suspension.

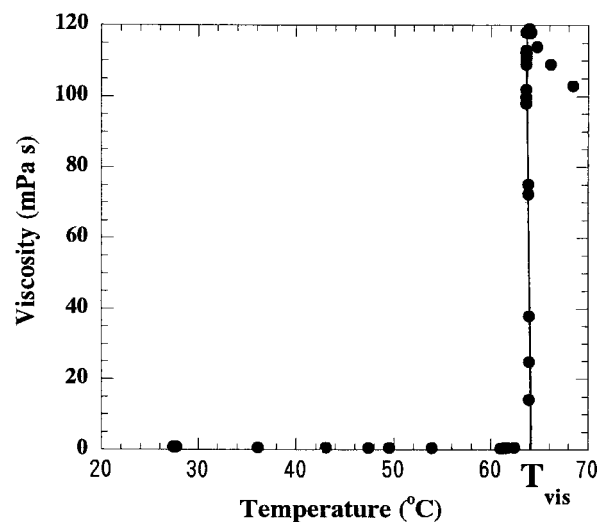
gelatinisation temperature measured from viscosity,  $T_{vis}$ , is given for the various samples in Table 1.

### DISCUSSION

During the gelatinisation process the electrical conductivity of the starch suspension increased as shown in Fig 2. Fig 5 shows the Arrhenius plot of the conductivity in Fig 2 according to the equation

$$\ln(\text{conductivity}) \propto \exp(E_a/RT) \quad (1)$$

where  $E_a$  is the activation energy,  $R$  is the gas constant and  $T$  is the absolute temperature. In Fig 5, two lines with different slopes, corresponding to different activation energies, are observed below and above  $T_i$ . This means that the mechanism of electrical conductivity is different below and above  $T_i$ . Below  $T_i$  the



**Figure 4.** Change in viscosity of  $50\text{ g kg}^{-1}$  potato starch suspension during heating.

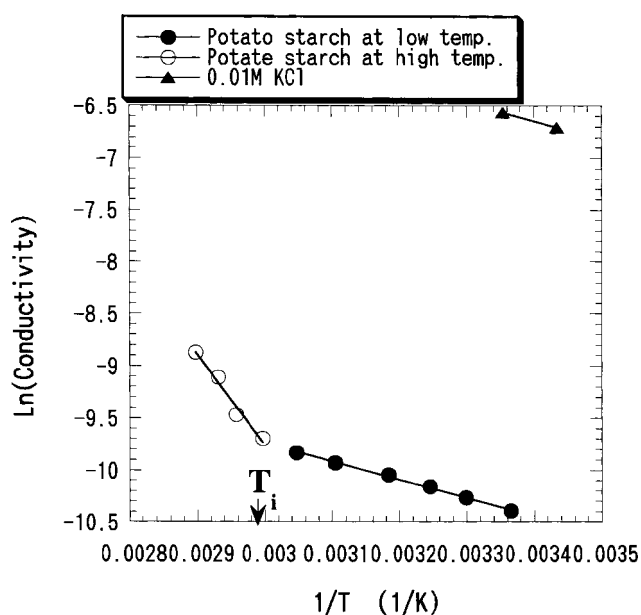


Figure 5. Arrhenius plot for electrical conductivity of 50g kg<sup>-1</sup> potato starch suspension measured at 200kHz.

activation energy calculated from the slope of the line was 14.5 kJ mol<sup>-1</sup>. In Fig 5 the electrical conductivity data for 0.01 M KCl<sup>14</sup> are also shown. From these data the activation energy for the electrical conductivity of KCl solution was calculated to be 14.8 kJ mol<sup>-1</sup>, which is very close to that for potato starch suspension below  $T_i$ . Therefore the increase in electrical conductivity below  $T_i$  is considered to be related to ion transfer or molecular diffusion of ions in the background solution. Above  $T_i$ , however, the slope of the Arrhenius plot increased and the apparent activation energy became 71.6 kJ mol<sup>-1</sup>.

This may be due to the fact that the starch granules started to swell at  $T_i$  and the ions inside granules began to be released. When the temperature of the suspension reached  $T_f$ , the granules swelled enough to collapse and all the ions inside appeared to be completely released into the suspension.

As for the ions inside starch granules, it has been reported that starches contain phosphates which are bound to amylopectin through ester binding.<sup>9</sup> A good correlation has been reported between phosphate and mineral contents of potato starches among varieties.<sup>15</sup> Counter-cations to phosphates are reported to be mainly potassium followed by magnesium and calcium.<sup>9,15</sup> These cations are free ions and thus may be responsible for the change in electrical conductivity of starch suspensions undergoing gelatinisation.

Changes in electrical conductivity during the gelatinisation of starch have also been investigated in the literature.<sup>16,17</sup> In these cases, however, the electrical conductivity of the starch suspension decreased with gelatinisation. This seems to be due to the large difference in background ion concentration. The electrical conductivity level of these systems is larger by more than two orders of magnitude as compared with the present case, so that the ion release during

gelatinisation was not distinguishable. Wang and Sastry<sup>16</sup> added sodium chloride to their sample to increase the electrical conductivity because of the need for ohmic heating, and Karapantsios et al<sup>17</sup> used crude flour samples. In these cases, gelatinisation caused a decrease in unbound water content<sup>16</sup> to reduce the electrically accessible water,<sup>17</sup> which caused a decrease in electrical conductivity. In the present case we used pure water with purified samples or repeatedly washed flour samples. Therefore the background ion concentration was very low, so that the ion release from starch granules was easily distinguishable during gelatinisation.

Results from the electrical conductivity, thermal analysis and viscosity measurements are compared to analyse the mechanism of starch gelatinisation. Fig 6 compares  $T_{\text{onset}}$  from DSC with  $T_i$  from electrical conductivity. The good correlation ( $R=0.868$ ) observed in this figure shows that the initiation of ion release from starch granules strongly relates to the beginning of the thermal event in gelatinisation.

Fig 7 compares  $T_{\text{endset}}$  with  $T_f$ . No correlation was observed in this case. This was rather unexpected, showing that the end of the thermal event and the completion of ion release in gelatinisation are independent of each other. In Fig 8 the gelatinisation temperature measured by viscosity,  $T_{\text{vis}}$ , is compared with  $T_f$ , showing a good correlation ( $R=0.865$ ). This suggests that the completion of ion release corresponds to the collapse of starch granules, which causes a drastic increase in viscosity.

From these results a mechanism is conceptually shown in Fig 9 to explain the relationship between gelatinisation and ion release from starch granules. The beginning of ion release corresponds to the beginning of gelatinisation, which is the beginning of the breakdown of the starch crystalline structure detected by  $T_{\text{onset}}$  in DSC measurement. The comple-

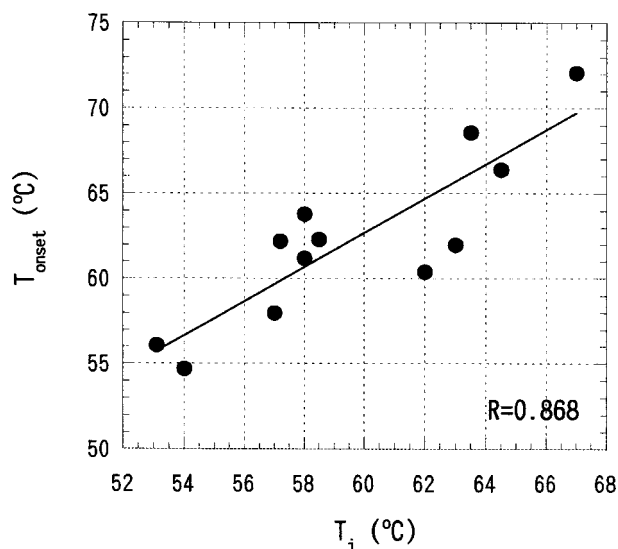
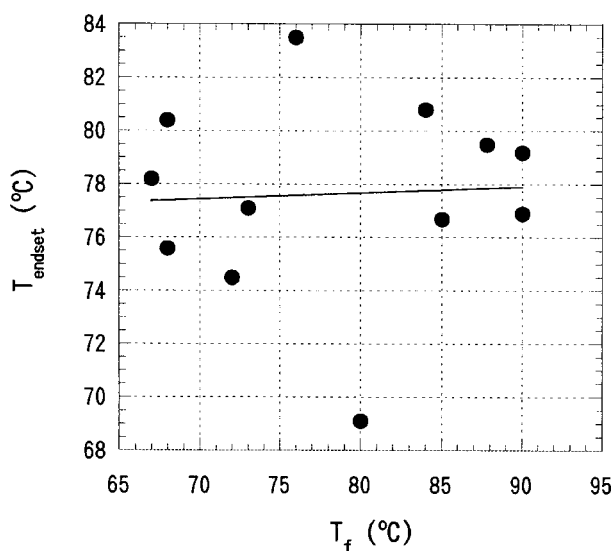


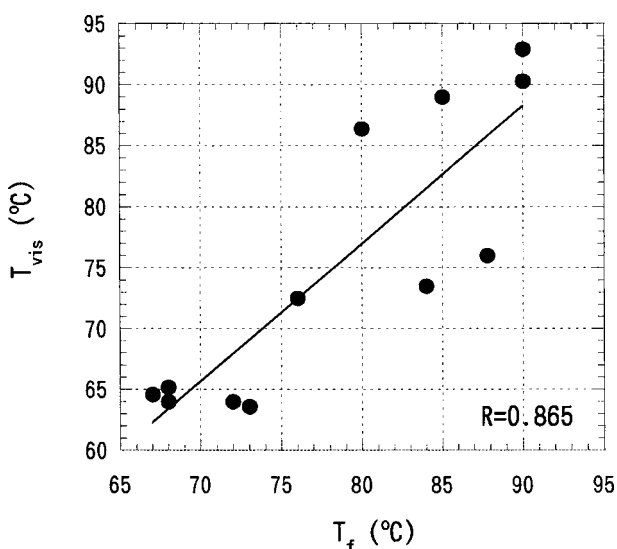
Figure 6. Correlation between initiation temperature of ion release from starch granules ( $T_i$ ) and onset temperature in DSC thermogram ( $T_{\text{onset}}$ ) for various starch and flour suspensions.



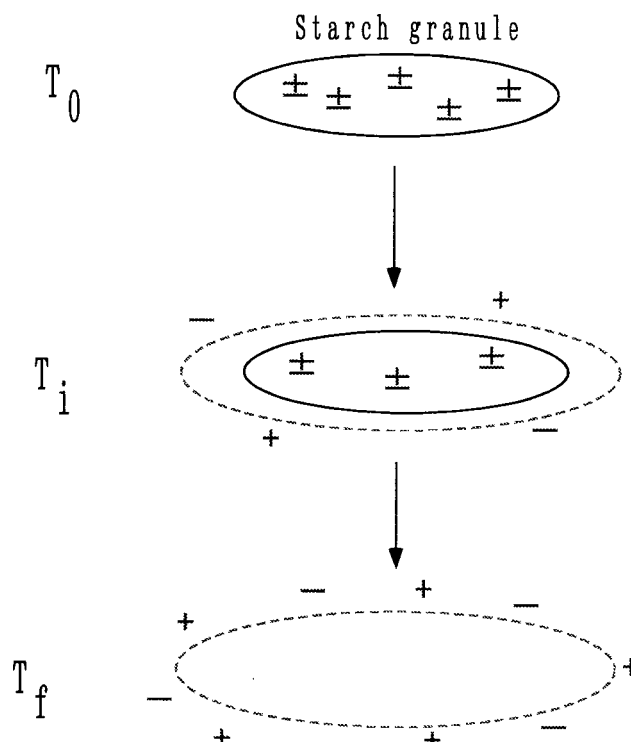
**Figure 7.** Correlation between completion temperature of ion release from starch granules ( $T_f$ ) and endset temperature in DSC thermogram ( $T_{endset}$ ) for various starch and flour suspensions.

tion of ion release corresponds to the completion of gelatinisation, which means the complete disintegration of the crystalline structure. At this stage, free ions as well as starch polymers are leached out from starch granules, causing the drastic increase in viscosity. This stage might be realised with some time lag after the stage corresponding to  $T_{endset}$  from DSC analysis, because of the need for molecular diffusion of starch macromolecules and ions. This may explain the lack of correlation between  $T_{endset}$  and  $T_f$  in Fig 7.

In Table 1, results from the electrical conductivity, thermal analysis and viscosity measurements were compared for 12 different starch samples. From these, especially from  $T_i$  and  $T_f$ , potato, waxy rice, glutinous rice (Thai), tapioca (Thai) and arrowroot (Thai) showed lower gelatinisation temperatures, while



**Figure 8.** Correlation between completion temperature of ion release from starch granules ( $T_f$ ) and initiation temperature of rise in viscosity ( $T_{vis}$ ) for various starch and flour suspensions.



**Figure 9.** Conceptual diagram of gelatinisation in relation to ion release from starch granules ( $T_0$ , before gelatinisation;  $T_i$ , beginning of gelatinisation;  $T_f$ , completion of gelatinisation).

maize, maize (Thai), rice and rice (Thai) showed higher gelatinisation temperatures. This is consistent with literature data.<sup>4</sup> The starch group with the higher gelatinisation temperatures was also characterised by larger differences between  $T_i$  and  $T_f$  ( $=\Delta T$ ; Table 1). As for the difference in gelatinisation temperature between normal and waxy rice, normal rice contains a higher amount of amylose. The higher amylose content causes a higher gelatinisation temperature<sup>4,6,8</sup> because of the formation of amylose–lipid complexes.<sup>12,18</sup>

In conclusion, electrical conductivity measurements were proved to be effective as a method to monitor the whole process of starch gelatinisation. By using this method, the relationship between data from DSC and viscosity became clarified and a mechanism for gelatinisation in relation to ion release from starch granules was proposed. The electrical conductivity method is convenient and expected to be used in on-line applications.

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