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Effect of water content on the gelatinisation temperature of sago starch

A.G. Maaruf[a], Y.B. Che Man[a], B.A. Asbi[b], A.H. Junainah[b], J.F. Kennedy[c,*]

[a]*Department of Food Technology, Universiti Putra Malaysia, 43400 Serdang, Malaysia*
[b]*Food Biotechnology Research Group, Kolej UNITEK Malaysia, 47301 Petaling Jaya, Malaysia*
[c]*School of Chemistry, University of Birmingham, Birmingham, B15 2TT, UK*

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Abstract

Differential scanning calorimetry (DSC) has been used to study gelatinisation phenomena of sago starch. Two endothermic transitions were observed for starch heated in the presence of a limited amount of water (starch/water = 37–50% w/w). These transitions appear to be due to co-operative effects of water-mediated melting of starch crystallites, remaining crystallites and/or amylopectin crystallites. At a water content of 50%, evidence of M_1 endotherm was observed and 85°C represents the effective T_m at the end of melting of native sago starch. The effect of starch concentration on the shape of these two endotherms was studied for sago starch. The experimental data were treated thermodynamically by applying equations describing phase transition of semi-crystalline polymers. The T_m^0 value obtained by extrapolation to $v_1 = 0$ was 390.6 K for sago.

Keywords: Gelatinisation temperature; Sago starch; Water content

1. Introduction

When heated, an aqueous suspension of starch granules undergoes an order–disorder transition known as gelatinisation. This process can be monitored by differential scanning calorimetry (DSC). Single or double endothermic peaks are obtained depending on the water concentration. As the water/starch ratio decreases, a second endotherm begins to develop at higher temperatures. Donovan (1979) pointed out that at high water level, swelling of the amorphous region in a starch granule promoted the transformation of crystalline regions by pulling the crystallites apart in the process of gelatinisation. As water becomes limiting, only part of the crystallites melt with this mechanism while the remaining gives rise to a second high temperature mechanism (Donovan, 1979; Evans & Haisman, 1982; Biliaderis, Page, Maurice & Juliano, 1986; Zeleznak & Hoseney, 1987; Slade & Levine, 1988; Liu & Lelievre, 1991; Liu, Lelievre & Ayoung-Chee, 1991).

Starch gelatinisation is the collapse (disruption) of molecular orders within the starch granule manifested in irreversible changes in properties such as granular swelling, native crystallite melting, loss of birefringence, and starch solubilisation. The point of initial gelatinisation and the range over which it occurs is governed by the starch concentration, method of observation, granule type, and heterogenities within the granule population under observation (Atwell, Hood, Lineback, Variano-Marston & Zobel, 1988).

In its widest sense, the term sago is used to describe starch from the stems of palms, cycads, and from maniac tubers. Sago palm contains a large amount of starch in its trunk and its productivity was calculated to be four times that of paddy rice (Ishizuka, Hisajima & Macer, 1995). Sago starch, produced from pith of sago palm, is a useful resource for commercial raw materials and food stuffs and is an important product in South Asia (Yatsugi, 1986).

Sago starch has been used in cooking for many years. It is especially used in jellies, puddings, and soups. It is used in the form of sago pearls. According to Takahashi (1986), the properties of sago starch are: (1) it is easy to gelatinise, as its gelatinisation temperature is low; (2) it has a high viscosity; (3) it is easily moulded, and (4) gel syneresis is low. Sago starch shows a similar moisture content and granular size to those of potato starch and similar swelling power, solubility, gelatinisation temperature, maximum viscosity, and temperature at maximum viscosity to those of cassava and sweet potato starches but the retrogradation and amylose content are like those of corn starch.

The interaction of water with starch is an important phenomenon occurring in various food processing operations such as baking of bread and cakes, extrusion of cereal-based products, thickening and gelling of sauces and pie fillings (Biliaderis, Maurice & Vose, 1980). The optimisation of these food processing requires a deep

* Corresponding author.

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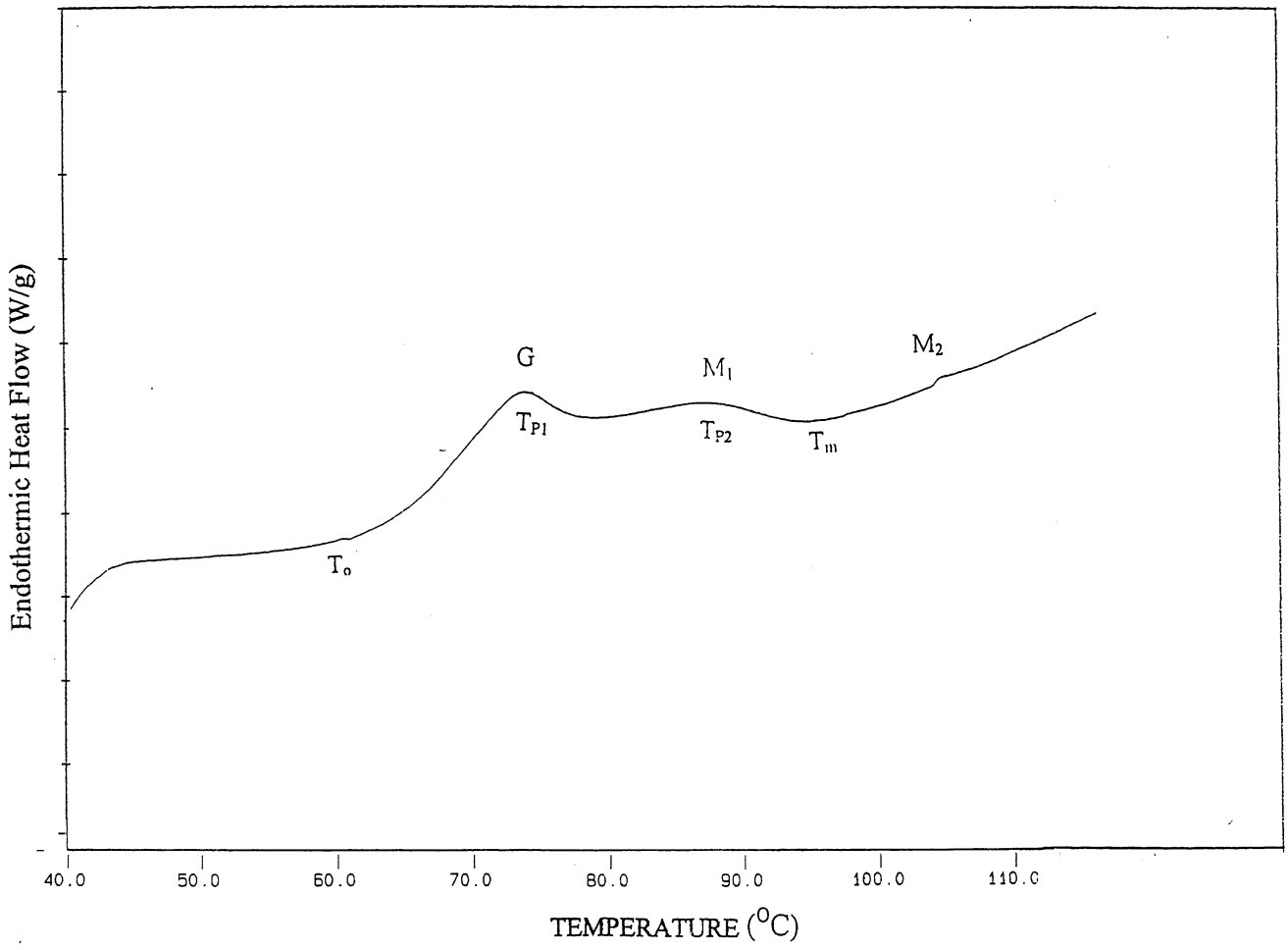


Fig. 1. DSC heat flow curve of sago at a starch/water ratio 4:3 showing designated thermal transition temperature.

knowledge of starch gelatinisation, especially in terms of the rate and temperature relationship because starch is the main dry matter component of these products (Pravisani, Califano & Calfelo, 1985).

Differential scanning calorimetry (DSC) is particularly well suited to investigating the phase transitions of starch/water systems because it allows: (1) a study of starch gelatinisation over a wide range of starch/water ratio; (2) determination of gelatinisation temperatures above 100°C, and (3) estimation of transition enthalpies (Biliaderis et al., 1980).

Most research on starch gelatinisation has focused on starches from corn, wheat, and potato. Very few reports are available on starch gelatinisation of starches derived from crops indigenous to the tropical regions, including sago starch. Some studies on the physico-chemical characteristics and the effect of sugars on the thermal and rheological properties of sago starch has been reported (Ahmad, Williams, Doublier, Durand & Buleon, 1999; Ahmad & Williams, 1999). The objective of this study was to investigate gelatinisation/melting of sago starch heated to 120°C at starch/water ratios of 1:1 to 5:3. The significance of the amount of water on the mechanism of starch gelatinisation was further investigated.

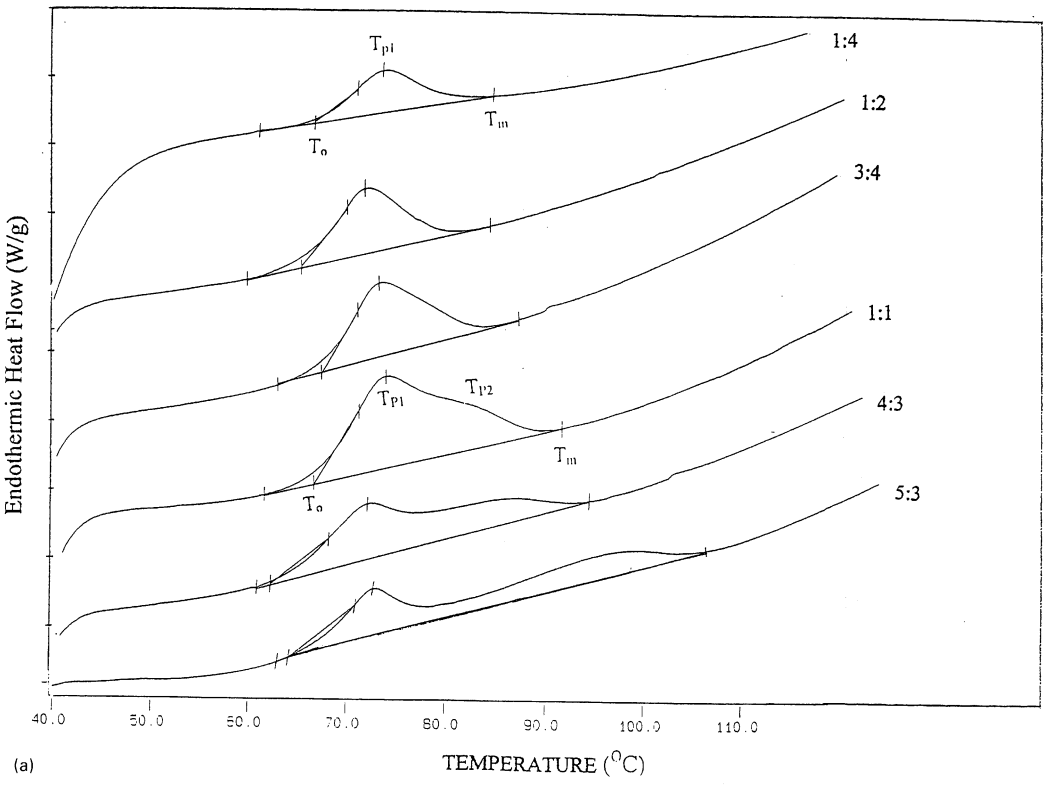
2. Materials and methods

2.1. Materials

Sago starches (*metroxylon sagu*) used were products of PPES Sago Industries (Mukah, Sarawak, Malaysia). Moisture content of the starches was determined by drying 10 replicate samples in an air-oven at 105° to constant weight. These starch samples contained 10.4% moisture ($S_d = 0.05$). Proximate analysis was done by Roslin and Asbi (1995) and indicated that the sago starch contained 0.43–10.16% protein, 22.34–14.05% amylose and 75.56–77.26% amylopectin.

2.2. Differential scanning calorimetry

For DSC investigations, a Perkin–Elmer DSC7 was used.



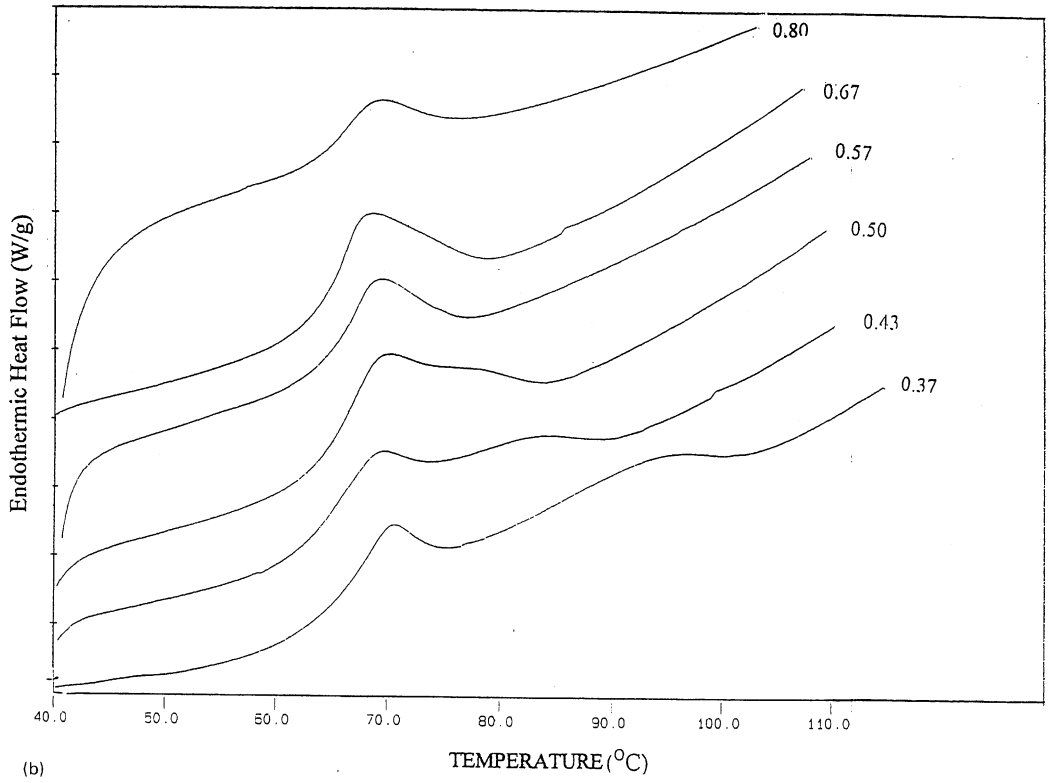


Fig. 2. (a) DSC thermograms of sago starch at various starch/water rations showing T_0, T_{P1}, T_{P2} and T_m (all thermograms are normalised to 1 g of dry starch). (b) DSC thermograms of sago starches heated at different water concentrations; numbers represent volume fraction of water. Percent concentrations of starch (w/w) for these experiments from top to bottom 20.0, 33.3, 42.8, 50.0, 57.2, 62.5 (all thermograms are normalised to 1 g of dry starch).

Table 1
Effects of starch/water ration on thermal transition temperatures and enthalpy associated with gelatinisation of sago starch

Starch/water ratio	Volume fraction of water (v_1)	Transition temperature[a] (°C)				Melting temperature range	ΔH (J/g)
		T_0[b]	T_{P1}[b]	T_{P2}[b]	T_m[b]	($T_m - T_0$)	
1:4	0.80	63.6	70.3	–	78.5	14.9	5.044
1:2	0.67	64.2	70.3	–	81.9	17.7	4.453
3:4	0.57	64.1	70.2	–	84.2	20.1	5.141
1:1	0.50	66.4	69.7	77.6	85.2	18.8	2.034
4:3	0.43	66.9	69.1	82.4	91.0	24.1	1.856
5:3	0.37	74.4	68.4	90.9	99.0	24.6	1.617

[a] Values are the average of three replicates. Standard deviation for all samples are ±0.5°C.
[b] T_0 = Transition onset temperature, T_{P1} and T_{P2} = transitions peak temperature, T_m = transition conclusion temperature.

Melting points and enthalpies for indium (m.p. 156.6°C, ΔH_m 28.5 J/g) and *n*-dodecane (m.p. 9.65°C, ΔH_m 218.73 J/g) were used for temperature and heat capacity calibrations. Samples for DSC analysis were prepared using procedures similar to those described by Biliaderis et al. (1980) and Jang and Pyun (1996). Sago starch sample (9–11 mg) containing 10.4% moisture were prepared in Perkin–Elmer aluminium DSC pans (20 μl capacity, Part No. 0219-0062) capable of withstanding at least 30 psi internal pressure after sealing. Sago starch samples were prepared with a range of dry starch to water ratios from 1:1 to 5:3. Starch was weighed (electronic balance — ER 180A) into a tared, aluminium DSC samples pan. Distilled water was added with a microsyringe until all the granules were wetted and uniformly distributed across the bottom of the pan.

Filled pans were left to air dry until the contents reached the desired moisture level and then hermetically sealed using volatile sample sealer accessory (Perkin–Elmer-0219-0061). All samples were analysed within 1 h of sample preparation. In general, triplicate sample pans were heated at 10°C min^{-1} from 20 to 120°C. The volume fraction of water (v_1) in the samples was taken as the total volume of water divided by the total volume of starch and water. Other pairs of pans were subjected to only partial scanning (from 20°C to 57, 63, 72, 85, 87, 89, 92 or 100°C) before cooling and immediately complete rescanning.

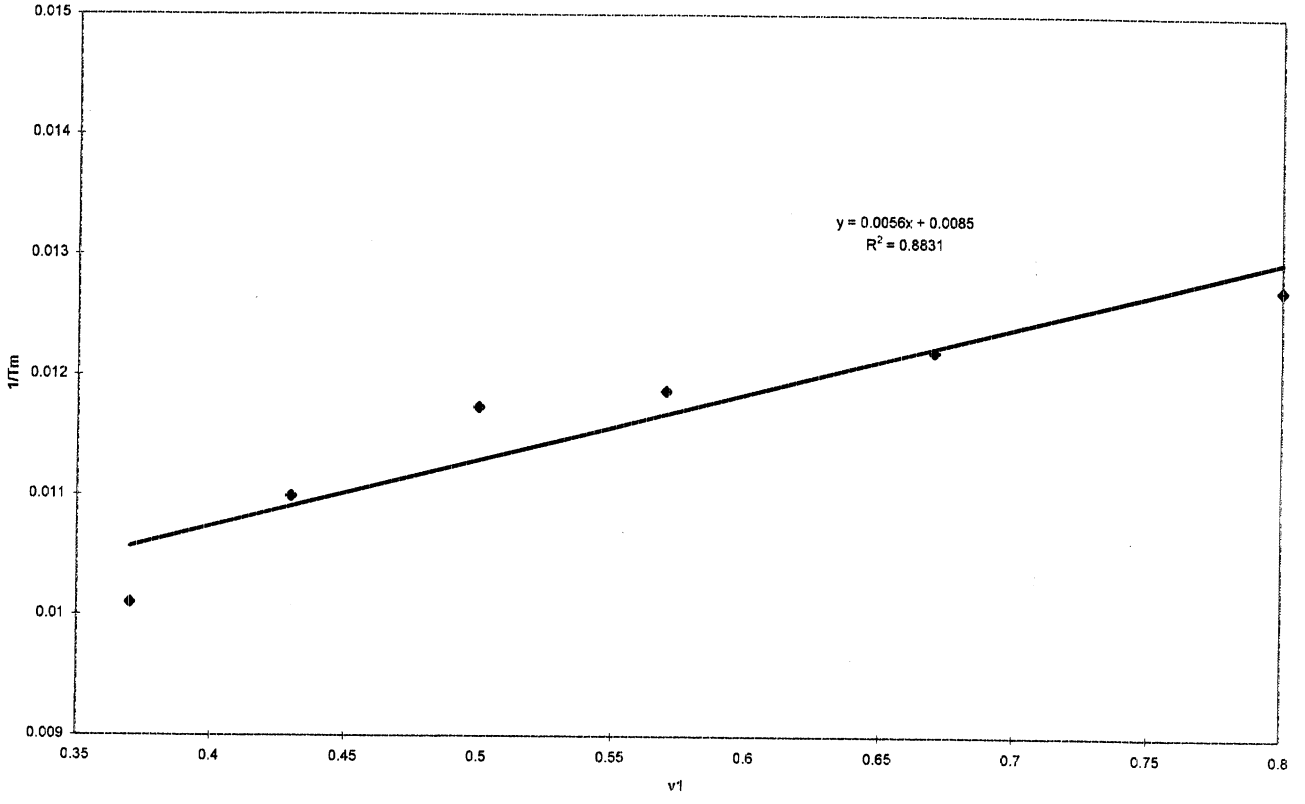


Fig. 3. The reciprocal melting point $1/T_m$ (K), plotted against the volume of water v_1 for sago starch. Line is a linear least square fit of the experimental data.

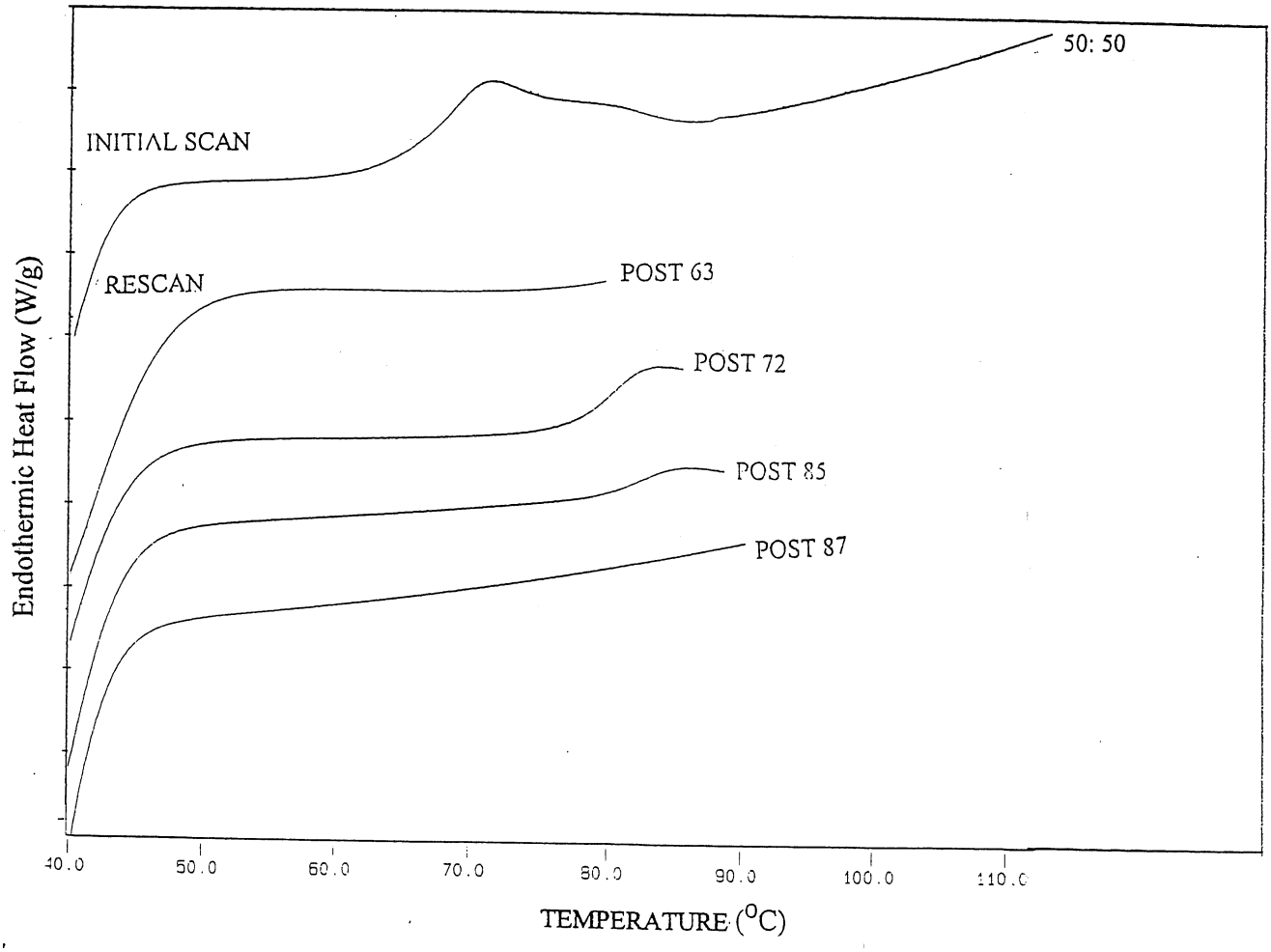


Fig. 4. Perkin–Elmer DSC 7 heat flows curves of sago starch: water mixtures (50:50): top — initial scan at 10°C min^{-1} for native starch; others — rescan at 10°C at 10°C min^{-1} immediately following partial scanning at 10°C min^{-1} from 20°C to maximum temperatures indicated.

The latter sample thermograms were analysed to determine, from the thermal events evident in the complete rescan, what events must have previously occurred during the partial initial scan.

The onset (T_0), peak (T_p) and conclusion temperatures (T_m) associated with the gelatinisation of sago starch were determined as illustrated in Fig. 1. Three major apparent endothermic transitions shown are labelled in the conventional manner as the G, M_1 and M_2 endotherms, the combined area of the G and M_1 endotherms was used to calculate the overall gelatinisation enthalpy (ΔH), which was expressed in J/g dry starch.

3. Results and discussion

In the DSC thermograms, at the leading edge of the broad gelatinisation endotherms, of sago starch at different starch/water ratios (Fig. 2a), what appeared to be a relatively small endothermic transition became increasingly prominent with decreasing moisture content. This first transition, occurring at about 63.6–78.5°C, appeared to be only slightly affected by moisture content over the range studied. However the second endothermic transition (M_1), occurring at about 77.6°C in excess water, became broader and was shifted to higher temperatures as the moisture content was decreased. Peak G has been assigned to a co-operative, water-mediated melting of starch crystallites and M_1 was assigned to the melting of the remaining crystallites (Burt & Russel, 1983) or the melting of the amylopectin crystallites (Shogren, 1992).

With a water content of 43 and 50% and limited amounts of added water, two endotherms (G and M_1) were observed, these results being similar to those of Biliaderis et al. (1980). For water contents greater than 50%, single endotherms ($G + M_1$) were observed at a peak temperature of 70.3°C and reached its maximum average value of approximately 4.9 J/g. At water content below 50%, evidence of M_1 endotherms was observed. When sago starch was heated at high water concentrations, a single endothermic

transition, P_1, was observed (Fig. 2a and b) at about 70.3°C (T_{P1}). As the ratio of starch/water increased, the second endotherms P_2, started to develop at higher temperatures (T_{P2}) and became predominant at low water content.

The enthalpy of gelatinisation (ΔH) remained largely the same (4.5–5.1 J/g) in high moisture samples but decreased significantly when the starch/water ratio was increased beyond 4:3 due probably to limited swelling of the amorphous regions of the starch granules (Table 1). ΔH has been used as an indicator of degree of molecular order for comparative purposes (Cooke & Gidley, 1992). A possible explanation is that chain lengths associated with the molecular order in sago starch are shorter than for the wheat (9.7 J/g), potato (16.2 J/g) or tapioca (16.9 J/g) starches examined by Cooke and Gidley (1992) and that this leads to lower values of both the enthalpy and temperature of melting.

Although the P_1 occurred essentially at a constant temperature (68.4–70.3°C), it was of interest to observe a progressive shift of the P_2 endotherm as the volume fraction of water (V_1) was decreased (Fig. 2b and Table 1). This concentration-dependant shift of both T_{P2} and melting point T_m suggested a thermodynamic treatment of these results by employing equations that characterise other polymer systems. Similar theoretical treatments of starch gelatinisation data have also been used by Lelievre (1973) and Donovan (1979).

The Flory analysis is useful in that it provides a basis for comparison of the thermal stability of starch materials and allow estimations of the apparent T_m under various moisture levels (Biliaderis, 1992). According to the Flory equation (Flory, 1953), the following relation holds between melting point of a polymer and the diluent concentration:

$$\frac{1}{T_m} - \frac{1}{T_m^0} = \frac{R}{\Delta H_u}\frac{V_u}{V1}(v_1 - \chi_1 v_1^2) \quad (1)$$

where ΔH_u is the enthalpy of fusion per repeating unit (glucose), V_u/V_1 is the ratio of the molar volume of the repeating (glucose) in the chain to that of the diluent (water), R the gas constant, T_m^0 (K) the true melting point of the undiluted polymer, v_1 the volume fraction of the diluent and χ_1 the Flory interaction parameter. The melting point (T_m) of the heated starch/water mixtures was taken as the melting point of the most perfect crystallites at the upper temperature limit of the endotherm according to Flory (1953). For an ideal solution, $\chi_1 = 0$, hence Eq. (1) gives a linear relationship between v_1 and $1/T_m$. The intercept at $v_1 = 0$, therefore, gives the reciprocal of the melting point of the most perfect crystallites of the undiluted polymer, ($1/T_m^0$). Plot of $1/T_m$ against v_1 for sago starch is given in Fig. 3. Linear regression analysis of the experimental data shows significant correlation ($R^2 = 0.883$). The T_m^0 values obtained by extrapolation at $v_1 = 0$ were 390.6 K (117.6°C) for sago. Corresponding values of 210°C for wheat (Lelievre, 1973) and 168°C for potato (Donovan, 1979) starches have been reported previously. Differences in the T_m^0 values may be related to various factors in which the granular organisation and its inherent crystallinity are probably the most important.

The composite diagram of PE DSC 7 heat flow curves for sago starch, shown in Fig. 4, demonstrated conclusively that initial heating to at least 85°C was required (for a heating rate at 10°C min^{-1} to a final sample water content 50%) to complete the non-equilibrium melting process associated with gelatinisation and pasting of native sago starch. Partial initial scanning to temperatures ≥63°C, but <85°C, resulted in only partial melting, as evidenced in the rescans by a peak of the melting profile, compared with the thermal profile of the complete melting process shown at the top of Fig. 4. This peak decreased in area with increasing maximum temperature (in the range 63–85°C) of the partial scan but only disappeared completely (yielding a featureless thermogram, as evidence by the flat baseline, from 20 to 100°C) after initial heating to ≥85°C. It was concluded that 85°C represents the effective T_m at the 'end of melting' for native sago starch heated at 10°C min^{-1} with 50% total water content.

4. Conclusions

During gelatinisation of sago starch, multiple (one or two) endothermic transitions are observed by differential scanning calorimetry (DSC), which become increasingly prominent with decreasing water content. Gelatinisation temperature of sago starch is low and it is easy to gelatinise. The influence of various food ingredients on sago starch gelatinisation will be studied under conditions resembling those employed in the preparation of various heat-processed foods.

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