A DIFFERENTIAL SCANNING CALORIMETRIC @SC) STUDY ON THE EFFECTS OF ANNEALING AND SAGO STARCH *(Metroxylon sugu)* **SUGARS-EMULSIFIERS ON GELATINIZATION OF**

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ABSTRACT

This study investigated the fleets of annealing, at different temperatures (45-7OC). times (0-24 h) and water:starch ratios (0.6/1-4/1), on the DSC thermal properties profiles associated with gelatinization temperatures of sago starch-water mixtures. The effects of sugars-emulsifiers and of starch mixtures and their interactions were also investigated. DSC data showed an increased gelatinization temperature and enthalpy and a narrower gelatinization temperature range $(T_m - T_o)$ *after annealing of sago starch; the extent of these changes was inversely proportional to the degree of crystallinity of the native starch. For sago starch, the* **G** *transition occurring at about 66-69C and the M, transition occurring at about 75C in excess water became broader and shifed to higher temperatures as the water content was decreased. The effects on the gelatinization temperature and AH, of the addition of sugars-emulsifiers to the starchwater mixture, were observed by comparison with the starch-water results. Sucrose raised the gelatinization temperature by about 6-7C more than did glucose, for sago starch. Emulsifiers (sucrose ester and polysorbate-60), in the presence of sucrose or glucose, did not affect the gelatinization temperature.*

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INTRODUCTION

Annealing of granular starches involves incubation in excess water for a certain period of time at a temperature above the glass transition temperature but below the gelatinization temperature (Maurice *el af.* 1985; Slade and Levine 1988a; Jacobs *er al.* 1995). Annealing, defined **as** the heating of starch in excess water at subgelatinization temperatures, was shown, by the birefringence studies of Gough and Pybus (1971), to narrow the temperature range, raise the peak temperature, and increase the enthalpy for the gelatinization of wheat starch. According to Cooke and Gidley (1992), the difference in ΔH between native and annealed starches suggests that the amount **of** double helices that unravel and melt during gelatinization is higher in annealed (indicated by higher ΔH values) than in native starches. This suggests that the double-helical content of starch granules increase on annealing. Annealing causes structural changes within the starch granule. Presumably, these structural changes affect the amorphouscrystalline relationships within the granule, forcing the granule into more crystalline order (Krueger *ef al.* 1987a).

Maurice *et al.* (1985); Hoseney *et al.* (1986); Slade and Levine (1988a); Yost and Hoseney (1986) all demonstrated that annealing occurs only when starch is heated to a temperature above its glass transition, but not high enough to cause irreversible melting or gelatinization. Annealing of starches has been studied at various starch: water ratios $(1: 1, 1: 3, 1: 5)$ and at temperatures ranging from 50 to 75C (Kuge and Kitamura 1985; Yost and Hoseney 1986; Krueger *er al.* 1987a,b; Knutson 1990; Larsson and Eliasson 1991; Lopez and Lopez 1991; Stute 1992). However, there have been no reports on the response of sago starch to annealing.

DSC was used to study whether the gelatinization process for sago starch is affected by the presence of a combination of sugars and emulsifiers. Gelatinized starch often plays an important role in determining the structural, textural and physical properties of many foods. The proportion of raw and gelatinized starch in ready-to-eat starch-based products may be critical in determining acceptability. Ingredients such **as** emulsifiers or stabilizers are often needed to ensure uniform quality and shelf-life stability of such food products.

Emulsifiers are commonly used in starch-containing foods such **as** macaroni and other pasta foods, processed potato products, or desserts based on pregelatinized starch, in order to improve texture (Krog 1977). It has been suggested that the presence of emulsifiers affects the behavior of starch by modifying the surface of the starch granule, by covering it with a film of either amylose-lipid complexes or of one formed by the emulsifier (Collison and Elton 1961; Eliasson *er al.* 1981). In baked products and other cereal-based foods, emulsifiers function primarily to complex starch (amylose), or as dough conditioners and strengthens or bread and crumb softeners, to increase shelf-life and tenderness. It has been reported that the use of emulsifiers to stabilize the starch complex prevents chilled starch-based foods from sticking to the extruder die during processing of extruded snack products and also helps the rehydration of products such **as** dehydrated potatoes (Anon. **1985).** In starch jellies, emulsifiers can keep starch soft and compressible and can extend starch mold life.

This study was carried out to elucidate the effects of annealing, under different temperature, time and moisture conditions, on the DSC thermal property profiles associated with gelatinization temperatures of sago starch-water mixtures. This study **also** evaluated the potential of sugars (sucrose and glucose) and emulsifiers (sucrose ester (SE) and polysorbate 60 (PS)) and their interactions, to affect the gelatinization of sago starch.

MATERIALS AND METHODS

Materials

Sago starch *(Metroxylon sugu)* used was obtained from PPES Sago Industries, Sarawak, Malaysia. Sucrose and anhydrous D-Glucose (UNIVAR-Analytical Reagent) were obtained from Ajax Laboratory Chemical, Auburn, Australia. Polyoxyethylene sorbitan monostearate (Polysorbate-60, PS) was obtained from Sigma Chemical, MO; its HLB (hydrophile-lipophile balance) value was **14.7.** Sucrose ester (SE) was donated by Dai-Ichi Kogyo Seiyaku, Kyoto, Japan. This emulsifier is a mixture of the stearic acid and palmitic acid esters of sucrose. It contains approximately **70%** monoester and **30%** dit-tripolyesters, and its HLB value is approximately **15.**

Determination of Moisture Content

Moisture content was determined according to **an** AOAC method **(1984).** Five to ten grams of sample were accurately weighed into a weighed dish (provided with cover). The contents and dish were dried in an oven at $105 \pm$ 2C for **12** h and then removed to a desiccator, cooled and weighed. The moisture content was expressed **as** percentage of removed water:original mass.

Annealing Procedure

The effect of annealing on starch gelatinization **was** examined using a procedure modified from those described by Hoover and Vasanthan **(1 994)** and Seow and **Teo (1993).** Sago starch powder (5.0 mg) was weighed into a tared aluminum **DSC** sample pan, and the water content of a sample was brought to a given water:starch ratio **(0.6/1** to **4/1)** by adding an appropriate amount of distilled water directly to the starch, using a disposable syringe (1 mL), to produce homogeneous slurries. Total sample weight was 9-11 mg, weighed to an accuracy of ± 0.1 mg with an electronic balance (ER 180A, A & D Company, Tokyo, Japan), and any excess water was allowed to evaporate to produce the final weight. The pans were hermetically sealed and then weighed once more to record the final weight. Samples were allowed to equilibrate for 1 h before DSC analysis. Samples at various water contents were heated in a Perkin-Elmer DSC-7 at lOC/min from 20C to a specified annealing temperature **(45** to 70C) and then held isothermally for a specified time (0-24 h), cooled rapidly to 20C, and immediately rescanned at the same rate of 10C/min to 125C. In general, triplicate sample pans were run for all treatments. Enthalpy (ΔH) , onset (T_o) , peak (T_o) and conclusion (T_m) temperatures were calculated automatically with the Perkin-Elmer's **"UNIX"** software.

Effects of Sugars and Emulsifiers

The effects of sugars and emulsifiers on gelatinization of sago starch were examined by modifying the procedure described by Kim and Walker (1992). **A** constant starch:sugar:water ratio of 1:1.5:1.5 was used for DSC. Starch (2.5 mg) and sugar (3.75 mg, on a moisture-free basis) were weighed (to within 0.2 mg) directly into a DSC **aluminum** sample pan on a balance, and then 2.5 mg of SE or PS solution containing 0.6% emulsifier, based on the dry weight of the starch, was added to the starch-sugar mixture using a disposable syringe (1 mL). About 1.25 mg of distilled water was added, the pan was placed back on the balance, and any excess water was allowed to evaporate to produce a final total sample weight of 10.0 m.g.

The mixtures of water and starch at 1:1 and 1:3 were also examined in order to study the effects of water content on gelatinization in the presence of sugars and emulsifiers. The pans were hermetically sealed. The sealed pan with sample was weighed once more to record the final weight. DSC samples were allowed to equilibrate for at least 2 h before analysis. One minute was allowed for temperature equilibration of the DSC sample chamber before starting to increase its temperature from 25 to 150C. Samples were heated in the DSC at a rate of 10C/min.

Differential Scanning Calorimetry @SC)

DSC was done with a Perkin-Elmer DSC-7 (Norwalk, CT). Heat-flow and temperature calibrations were performed using pure indium, with a heat of fusion (ΔH_m) of 28.5 J/g and onset melting temperature of 156.6 C. An empty aluminum pan was used **as** a reference, to balance the heat capacity of the sample pan. Each sample was filled into an aluminum sample pan with lid (Part. No: 0219-0062) which was then hermetically sealed using volatile sample sealer

accessory (P-E: 0219-0061). Various temperatures can be used to characterize starch gelatinization in a DSC thermogram. The onset (T_o) and conclusion (T_n) temperatures (points were the extrapolated endotherm intersects the baseline) and the peak temperature (T_n) (temperature of maximum differential heat flow) were determined.

The gelatinization temperature range was defined as T_{m} - T_{o} . The amount of energy required for gelatinization (ΔH) was obtained by determining the area under the peak directly from the UNIX software. To obtain the area, a baseline was constructed **as** a smooth line from the beginning to end of a transition. Each reported value is the mean and standard deviation of three measurements.

Data Analysis

Data obtained were taken from a minimum of three replications. A personal computer statistical program, statistical analysis program (SAS) **DOS** version, was used for an analysis of variance (SAS 1995).

RESULTS AND DISCUSSION

Effect of Annealing at Various Water Contents

Moisture content for sago starch was $10.41 \pm 0.05\%$. Annealing caused the entire temperature range of gelatinization to shift to a higher temperature. The breadth of the gelatinization endotherm was narrowed, **as** the shift was greater for the start (T_o) and peak (T_o) temperatures than for the conclusion (T_n) temperature. The annealing process caused **AH** to increase. The effects of water content (during annealing at 55C for 4 h) on T_0 , T_0 , T_m and ΔH of sago starch are shown in Fig. 1 and 2. Substantial decreases in T_o , T_o and T_m were observed after annealing at a water content of 50%. T_0 , T_p and T_m values after annealing were higher **than** those for untreated sago starch by 5.3-ll.lC, 1.2-5.OC **and** 1.9-5.0C respectively, for water/starch ratios from $0.6/1$ to $4/1$. An examination of the data listed in Tables 1 and 2 shows that while $T₀$ shifted to higher temperatures after annealing, T_p and T_m were less affected.

As observed previously by other workers (Gough and Pybus 1971; Lund 1984). annealing considerably narrowed the gelatinization temperature range (T_m-T_n) . It has been explained that this has more to do with relaxation of the amorphous regions than with changes in the crystalline regions (Maurice *er ul.* 1985; Slade and Levine 1988a; Seow and Teo 1993). The unique properties of the starch from sago are reflected in the characteristics (depth, width, and sharpness of transition) of the peak shape. According to Donovan and Mapes (1980). structural relationships within the amorphous regions account for the sharpness of the transition and the temperature at which it occurs. Size and

TABLE **1.** EFFECT OF WATEWSTARCH RATIO AND ANNEALING *(55C* FOR 4H) ON THERMAL TRANSITION TEMPERATURES AND ENTHALPY ASSOCIATED WITH GELATINIZATION OF SAGO STARCH

'Average standard deviation $= 0.5$ **(n=3)**

^hEnthalpy (ΔH) of gelatinization. Average standard deviation = 0.3 (n=3)

TABLE 2. EFFECT OF ANNEALING TEMPERATURE ON THERMAL TRANSITION TEMPERATURES AND ENTHALPY ASSOCIATED WITH GELATINIZATION OF SAGO STARCH AT A WATER/STARCH RATIO OF 0.75:l

'Average standard deviation = 0.4° **(n=3) and** 0.3° **(n=3), respectively**

perfection of the crystallites do not have a significant effect on these characteristics during thermal analysis. The corresponding thermograms for sago starch annealed at $55C$ for 4h at various water/starch ratios are shown in Fig. 3. The thermal transitions associated with starch gelatinization are labeled **as** the G transition and the M_1 endotherm, the former being associated with the glass-to-rubber state transformation and the latter being ascribed to melting of starch crystallites (Maurice *el* al. 1985; Slade and Levine 1988a,b; Seow and Teo 1993).

What appeared to be a relatively small endothermic transition, which became increasingly prominent with decreasing water content, was evident at the leading edge of the broad gelatinization endotherm obtained for the untreated starch. This first transition, occurring at about $66-69C$, appeared to be only slightly affected by water content over the range studied. However, the second or main endothermic peak, occurring at about 75C in excess water, became broader and was shifted to higher temperatures **as** the water content was decreased (Table 1). The gelatinization enthalpy remained substantially the same $(16.8-17.7 \text{ J/g})$ in high-water samples, but decreased significantly when the water/starch ratio was decreased below 1:1, probably due to limited swelling of the amorphous regions of the starch granules (Fig. 2 and Table 1). The enthalpy values after annealing were higher than those for untreated sago starch by 1.0-2.0C for water: starch ratios from $0.6/1$ to $4/1$.

The overall gelatinization enthalpy, up to a water:starch ratio of 1.3:1, was also unaffected by the annealing treatment, but there appeared to be a significant increase in ΔH at higher starch concentrations. Krueger et al. (1987a) reported that the enthalpy change during starch gelatinization is almost entirely related to the melting of the crystalline domains, and that it can be used as a good approximation of the degree of crystallinity, whereas the gelatinization temperature can be regarded **as** a measure of the perfection of the crystallites.

Effects of Annealing Temperature

Annealing of sago starch at temperatures of 45 or 55C shifted T_o to higher temperatures, but T_p , T_m and ΔH remained practically unchanged (Fig. 4 and Table 2). The biphasic gelatinization endotherm remained intact, although there appeared to be a trend toward a merger of the two *peaks* into a single endotherm, as the first transition became increasingly sharper. As expected, T_o of **sago** starch annealed at *55C* was higher **than** that annealed at 4%. However, after annealing at 65C or 70C for **4** h or 1 h, respectively, only a single endotherm, occurring at a higher temperature and with a smaller ΔH , was obtained.

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Generally, at temperatures above *65C,* enthalpy decreased further, indicating accelerated melting, so that only the most perfect crystallites, i.e., those that melt at the highest temperatures, survived. For annealing above *632,* the endotherm became much sharper and more symmetrical. T_0 and T_p increased and occurred at much higher temperatures, **as** observed in sago and potato starches.

Effects of Annealing Time

The transition temperatures (T_0, T_n, T_m) and enthalpy (ΔH) of gelatinization, for sago starch subjected to an annealing temperature of *55C* for different time periods at a water:starch ratio of 2:1 are shown in Table 3. The T_0 , T_p and T_m of sago starch increased with increasing annealing time. The increase was most pronounced for T_0 and least for T_m . Similar observation have been made by Hoover and Vasanthan **(1994)** and Larsson and Eliasson **(1991)** for wheat, oat, potato and lentil starches. At the end of 24 h, the increase in T_o for sago starch **was 12.1c.**

Transition temperature $(C)^b$ and Enthalpy (ΔH) (J/g)	Annealing time (h)						
	0,0	0.5	1.0	4.0	6,0	12.0	24.0
$T_{\rm O}$	60.2	64.7	64.8	66.0	69.8	70.7	72.3
$T_{\tt P}$	73.9	76.3	77.0	77.9	79.2	81.3	82.8
T_m	78.2	81.4	81.6	82.1	83.7	84.3	86.2
T_m - T_O	18.0	16.7	16.8	16.1	13.9	13.6	13.9
ΔH°	15.5	15.7	15.6	17.3	18.0	18.3	18.9

TABLE 3. THE INFLUENCE OF ANNEALING" TIME ON THE THERMAL CHARACTERISTICS OF SAGO STARCH

'healing tempaxme = *55C;* **water/stmh ntio** = **211.**

 ${}^{\text{b}}T_{\text{O}}$, T_{P} and T_{m} represent the onset, peak and conclusion temperatures of gelatinization. Average standard deviation = **0.5 (n=3)**

'Enthalpy (ΔH) of gelatinization. Average standard deviation = 0.4 (n=3)

Annealing decreased the transition temperature range (T_m-T_o) and increased the ΔH of sago starch. At the end of 24 h, the decrease in $T_m - T_0$ amounted to 4.1C. The reason for the decrease in the gelatinization temperature range (T_m-T_o) on annealing has been a subject of controversy. It has been suggested that the decrease in $T_{m} - T_{0}$ could be due to alterations of the coupling forces between the crystallites and the amorphous matrix (Stute 1992), perfection of starch crystallites (Maurice *ef al.* 1985; Slade and Levine 1988a; Larsson and Eliasson 1991), more crystalline orientation (Krueger *ef al.* 1987a) or to interactions between amylose and amylopectin chains (Knutson 1990).

In sago starch, the G transition became increasingly more distinct and narrower with increasing time of annealing, as T_0 was shifted to higher temperatures, an effect similarly observed by Hoover and Vasanthan (1994) and Seow and Teo (1993). Since the M_1 endotherm was more or less unaffected, the overall effect was a narrowing of the gelatinization temperature range (T_m-T_o) caused primarily by changes in the lower-temperature (G) endotherm. The thermal transitions associated with gelatinization of sago starch annealed at *55C* for different times are shown in Fig. 5. In this study, it was found that annealing increased the enthalpy of gelatinization, and that annealed (or partially annealed) sago starch samples varied in gelatinization characteristics. Increases in ΔH were evident only after annealing had been in progress for 4, 6, 12 or 24 h. At the end of 24 h, the increase in ΔH was 3.4 J/g.

Effects of Sugars and Emulsifiers

This study examined the effect of emulsifiers on the gelatinization temperature of sago starch with the presence of sugars. The effects on the gelatinization temperature and enthalpy, of the addition of various sugars and emulsifiers to the starch-water mixture, may be observed by comparison with the starch-water results. The type of sugar and emulsifier is known to affect starch gelatinization. Different starches have different gelatinization temperatures and enthalpies. Krog (1973) reported that the addition of **an** emulsifier affects the rheological behavior of starch during gelatinization. The effects of certain emulsifiers have been attributed to the formation of insoluble amylose-lipid complexes (Van Lonkhusyen and Blankestijn 1974).

The addition of the same sugar or emulsifier to different starches (at different water levels) may not result in the same response. In the present study, sucrose and glucose were found to increase the gelatinization temperatures of sago and potato starches. T_o , T_p , and T_m were all increased with the addition of either sugar. Sucrose (disaccharide) delayed the sago starch gelatinization temperature by 5.9-7.3C more than did glucose (monosaccharide). The extents of delay were different for potato starch.

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Bean and Osman **(1959)** found that disaccharides retard starch swelling more than do monosaccharides. In our study, T_0 , T_p and T_m decreased with increasing water level (starch:water ratios from 1:1 to 1:3). These transition temperatures decreased by **1.5-3.5C** and **1.9-3.3C** for sago starch in the presence of sucrose and glucose, respectively, **as** shown in Table **4.** For sago starch in the presence of sugar (sucrose or glucose), emulsifiers (SE and PS) did not affect gelatinization temperature. As before, T_o , T_o and T_m decreased with increasing starch:water ratio.

The gelatinization enthalpies and transition temperature ranges $(T_m - T_o)$ for sago starch in the presence of emulsifier are given in Table *5.* The effect of the additives was to increase the gelatinization enthalpy but decrease $T_m - T_o$, with increasing starch:water ratio. The DSC thermograms of sago starch in the presence of sugars-emulsifiers are shown in Fig. 6. In a few previous investigations, DSC has been used to study gelatinization in the presence of emulsifiers, and the gelatinization enthalpy has been reported to increase (Hoover and Hadzier **1981),** decrease (Kugimiya and Donovan **1981;** Gough *ef al.* 1985), or to be unaffected (Eliasson *et al.* 1981). When increased ΔH values are observed, this might be due to phase transitions of the emulsifier, whereas unaffected ΔH values might be explained by the fact that the level of addition is too low to cause **an** effect detectable by DSC.

Generally, no significant differences (P > **0.05)** were observed in the gelatinization temperature and enthalpy values for most treatments in which SE or **PS** were added to starch-sucrose or starch-glucose mixtures. Buck and Walker **(1988)** reported that, when SE was added at **1** or **3%** to starch (corn or wheat) and/or starch-sugar (sucrose, dextrose, or fructose) combinations, SE had no significant effect on gelatinization temperatures, except for that of the wheat starch-sucrose combination. In that case, the peak temperature increased with increasing SE concentration.

Although emulsifiers, themselves, did not affect the DSC-measured gelatinization temperatures for most treatments, some interactions between the emulsifier and sugar were observed. No significant differences in the endothermic T_m and transition ranges $(T_m - T_o)$, between the starch-sucrose and starchglucose combinations, were seen. However, their overall trends were significantly different **(PcO.05)** in the presence of emulsifiers, suggesting that **sugar**emulsifier interactions might have occurred.

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^b0.6 % based on dry starch weight, SE = Sucrose ester, PS = Polysorbate **b0.6 %based on** *dry* **starch weight, SE** = **Sucrose ester, PS** = **Polysorbate** Values are average ± standard deviation based on triplicates **Values are average** f **standard deviation based on triplicates T_Q**= **onset**, T_p = **peak** and T_m = **conclusion temperatures** T_0 = onset, T_P = peak and T_m = conclusion temperatures

1,IIand marestarch/waterratiosofl:l, 1:l.S and 1:3,respectively.

I, II and III are starch/water ratios of 1:1, 1:1.5 and 1:3, respectively.

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TABLE 5. GELATINIZATION TEMPERATURE RANGE AND **ENTHALPY VALUES OF SAGO STARCH, IN** THE **PRESENCE OF SUGAR AND EMULSIFIER, AT VARIOUS STARCH/WATER RATIOS**

V,,,-T0 = **Gelatinization temperature range SE** = **Sucrose** *ester,* **PS** = **Polysorbate**

Values are average f standard **deviation based on triplicates**

1,II and III are starch/water ratios of 1:1, 1:1.5 and 1:3, respectively

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