Alcoholic-alkaline treatment of sago starch and its effect on physicochemical properties

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ABSTRACT

Sago starch (Metroxylon sagu) was subjected to an alcoholic-alkaline treatment using varied amounts of sodium hydroxide (NaOH) and a constant amount of ethanol at 35 °C. The cold water-solubility (CWS) of all the sago starches increased with an increase in the concentration of NaOH. For samples with high CWS, the Maltese-cross effect was absent when viewed under a light microscope. These granules were also larger than the native starches and had an indented appearance. The X-ray diffraction pattern changed from a C to a V for starches with high CWS. The amylose content of the treated sago starches increased significantly, whereas the intrinsic viscosity and peak viscosity values for treated starches were lower than the native starches. The gelatinization enthalpy decreased and was not detectable for sago starch with high CWS. It was evident that the alcoholic-alkaline treatment was effective for the production of granular cold water-soluble sago starches.

Keywords: Alcohol; Alkali; Granular cold water-soluble; Sago starch

1. Introduction

Starch is used extensively in the food industry as a thickening and binding agent and in the production of puddings, soups, sauces, salad dressings, diet food preparations for infants, pastry filling and mayonnaise. Starch is also an important raw material for the production of glucose syrup, glucose and other fine chemicals such as gluconic acid and monosodium glutamate. Starch can be found in cereals (corn, wheat, rice), tubers (potato, tapioca) and also stems (sago).

Sago palm, Metroxylon sagu, is one of the oldest species of palms that has been exploited for its stem starch. Tropical Asia has been home to most of the 2,500,000 ha of sago palm cultivated worldwide and has been an important source of dietary fiber in the Asia-Pacific region and the main carbohydrate source in Malaysia (Oates and Hicks, 2002). The rapidly increasing awareness of the importance of sago palm has brought about a considerable amount of research on sago starch and comprehensive reviews on sago starch have been written (Karim et al., 2008a).

In modified starches, food processors have an adaptable tool to meet the specific requirements of a variety of food systems. Native starch has a complex semi-crystalline structure which requires energy to gelatinize it (Jane, 1992). Physical modification, alone or together with chemical reaction, has been applied to change the granular structure and convert native starch into cold water-soluble starch (Jane, 1992). This type of starch modification is relatively new and has been used for microwave-cooked and instant foods such as puddings, instant fillings, sauces and dry mixtures that can be reconstituted with cold or ambient temperature liquids (National Starch and Chemical Corporation Brochure, 1988). Cold-water-soluble granular corn starch for gelled food compositions was first produced by Eastman and Moore (1984), by subjecting slurried granular corn starch to high temperature and pressure in selected aqueous alcohols. Rajagopalan and Seib (1992a) later prepared further granular cold-water-soluble starches by heating starch slurry in a mixture of water–polyhydric alcohol at atmospheric temperature using wheat, corn, potato, tapioca and mung bean starches. Concurrently, Jane and Seib (1991) patented a method for preparing granular cold water swelling/soluble starches by alcoholic-alkali treatments. This process can be used on waxy, high amylose, tuber and normal starches. Alcoholic-alkaline treatment of starches to produce granular cold-water-soluble corn, waxy corn and high amylose corn starches was carried out by Chen and Jane (1994a).
Subsequently, granular cold-water-soluble banana starch was prepared and studied using the alcoholic-alkaline method (Bello-Pérez et al., 2000). The most recent study on granular cold water-soluble corn and potato starch was carried out by Singh and Singh (2003).

The objectives of the current work were to produce granular cold water-soluble (GCWS) sago starch and to study the effect of different concentrations of sodium hydroxide (NaOH) on the percentage of cold water-solubility (CWS) obtained. The morphological, physicochemical, thermal and pasting properties of these starches produced were studied and compared to corn starch.

2. Materials and methods

2.1. Materials

Sago starch was procured from NITSEI Sago Industries Sdn. Bhd. (Penang, Malaysia) whereas corn starch used was from Sigma–Aldrich (S-4126, USA). All chemicals used were of analytical grade. The starch and chemicals were used directly without any further purification.

2.2. Preparation of granular cold water-soluble starches

The method of Chen and Jane (1994a) was used, with slight modification, to prepare GCWS sago and corn starches. Starch (50 g, dry weight basis) was suspended in 200 g ethanol at 35 °C and mechanically stirred. 3 M NaOH solution was added in varying amounts, i.e., 30 g, 45 g, 60 g and 75 g with the effective concentrations being 0.39 M, 0.55 M, 0.69 M and 0.82 M, respectively. The NaOH solution was weighed and added at a rate of 4 g min⁻¹. The mixture was held for 15 min with gentle stirring. An additional 200 g of ethanol was added slowly and the solution was stirred for another 10 min. The slurry obtained was then left at room temperature (25 °C) to allow the starch granules to settle for about 30 min. The supernatant was decanted and the starch washed with fresh ethanol solution. The starch was then re-suspended in ethanol solution and neutralized with 3 M HCl in absolute ethanol. The starch was then washed with 60% and 95% ethanol solutions and dehydrated with 3 M NaOH and 75% ethanol, respectively. The NaOH solution was weighed and added at a rate of 4 g min⁻¹. The mixture was held for 15 min with gentle stirring. An additional 200 g of ethanol was added slowly and the solution was stirred for another 10 min. The slurry obtained was then left at room temperature (25 °C) to allow the starch granules to settle for about 30 min. The supernatant was decanted and the starch washed with fresh ethanol solution. The starch was then re-suspended in ethanol solution and neutralized with 3 M HCl in absolute ethanol. The starch was then washed with 60% and 95% ethanol solutions and dehydrated with absolute ethanol. The starch obtained was oven-dried at 80 °C for 3 h. The dried starch was carefully ground using a bench top grinder (Micro Universal Bench Top Grinder, Retsch, Germany) to a fine powder (<250 μm) and stored in an air-tight container at room temperature. Samples were prepared in triplicates. Henceforth, the abbreviations used to identify the native and treated starches are: NSS for native sago starch, NCS for native corn starch, CSS for control sago starch, 30SS for sago starch treated with 30 g of 3 M NaOH, 45SS for sago starch treated with 45 g of 3 M NaOH, 60SS for sago starch treated with 60 g of 3 M NaOH, 75SS for sago starch treated with 75 g of 3 M NaOH and 75CS for corn starch treated with 75 g of 3 M NaOH.

2.3. Cold water-solubility

The cold water-solubility (CWS) was determined following the method of Eastman and Moore (1984). Determination was done in quadruplicate for each sample.

2.4. Light microscopy

Samples were observed under a light microscope (Olympus BX 41, Tokyo, Japan) fitted with a digital color video camera (Sony Exwave HAD, Tokyo, Japan) with neutral and polarized light using the Image-Pro Express Version 4.0 image analysis system. The sample was dispersed onto a glass slide using 40% ethanol as a hydration medium for observation.

2.5. Scanning electron microscopy

Structural properties of the samples were studied using a scanning electron microscope (Leo Supra 50VP Field Emission SEM, Carl-Zeiss SMT, Oberkochen, Germany) equipped with the Oxford INCA 400 energy dispersive X-ray microanalysis system (Oxford Instruments Analytical, Buckinghamshire, UK). Dried and finely ground samples were placed on double-sided adhesive tape mounted on a specimen holder and coated with a 100–200 Å thickness of gold. Images were recorded on Kodak Plus-X pan films.

2.6. X-ray diffraction pattern

X-ray diffraction patterns of native starch and treated samples were obtained using an X-ray powder diffractometer (D5000 Siemens, Bruker, Germany) equipped with a Cu Kα, target at 40 kV and 25 mA, at a diffraction angle ranging from 2θ = 10° to 30°. A step-scan was set at an angle of 0.05° and a count time of 2 s per step.

2.7. Apparent amylose content

The apparent amylose content was determined as described in McGrance et al. (1998) with slight modification. The starch was dissolved in 4 mL of DMSO. After 15 min of heating, the samples were vortexed and returned to the water bath and heated for another 15 min. The values were obtained in quadruplicate.

2.8. Particle size analysis

The Long Bench Mastersizer S (Malvern Instruments) fitted with the QSpec Dry Powder Feeder was used for the determination of number mean diameter. Samples weighing 2 g were prepared in triplicate for this analysis.

2.9. Intrinsic viscosity

Flow time (t) of the samples was measured at 25 °C with a Cannon-Ubbelohde tube (size 75-1762). A 10 mL aliquot of slurry was transferred to the viscometer using a pipette and held for 10 min to equilibrate the temperature of the suspension. This was followed by bringing the liquid level in the tube up to above the upper graduation mark. The flow time (t) was observed for the liquid from the upper graduation mark to the lower graduation mark. The determination was repeated three times. A series of concentrations (c) was obtained for each sample. Flow time for the solvent (90% DMSO), t₀, was also determined in a similar manner. For each dilution the value for specific viscosity, ηsp and ηsp/c was calculated. A plot, ηsp/c (mL/g) against c (g/mL) was drawn and extrapolated to c = 0 to determine the intrinsic viscosity.
heated using a modulation amplitude of 1 in aluminum sample pans using the inverted DSC lid configuration. Samples were weighed at 8 mg (± 0.01 mg) of each were weighed into aluminum DSC pans. The pans were sealed. Samples were heated from 30 °C to 120 °C at a heating rate of 10 °C min−1 under an oxygen-free nitrogen flow rate of 50 mL min−1. The onset (To) and peak (Tp) temperatures and the enthalpy (ΔH) of phase transition, as measured from the endotherm of the DSC thermograms, were determined using the Universal Analysis 2000 (TA Instruments-Waters LLC, New Castle, USA) based on mass of dry solid. The reported values are the means of triplicate measurements.

For the determination of glass transition temperature (Tg), the experiments were also conducted with the DSC in the modulated mode (MDSC). Prior to the determination, the samples were equilibrated at Relative Vapour Pressure (RVP) 0.56 over a saturated NaBr solution at 30 °C for about 8 days. Samples were weighed at 8 mg (± 0.01 mg) and hermetically sealed in aluminum sample pans using the inverted DSC lid configuration. After sealing, the pan was reheated. Samples were heated using a modulation amplitude of 1 °C, from 25 °C to 250 °C at a heating rate of 5 °C min−1. An empty pan was used as the reference pan to balance the heat capacity of the sample pan. The Tg values were determined as the midpoint of the stepwise increase of the specific heat associated with the transition from MDSC thermograms using the Universal Analysis 2000 (TA Instruments-Waters LLC, New Castle, USA). The reported values are the means of duplicate measurements.

2.11. Pasting properties

The pasting profile of the starches (11% (w/w), at a 14% moisture basis) which included the pasting temperature, peak viscosity, trough, breakdown, final viscosity and setback, was determined in triplicate using the Rapid Visco Analyzer (RVA-4, Newport Scientific, Warriewood, Australia). The Rapid Visco Analyzer measures the viscosity in the units "Relative Viscosity Unit (RVU)" and henceforth the pasting properties are determined in RVU. (1000 RVU = 12,000 cP = 12 Pa s). Samples for NSS, NCS, CSS, 30SS, 45SS and 60SS were equilibrated at 50 °C for 1 min, heated to 95 °C over 3.7 min, held at 95 °C for 2.5 min, cooled to 50 °C over 3.8 min and held at 50 °C for 2 min. Paddle speed was set at 960 rpm for the first 10s and then 160 rpm for the rest of the analysis. The pasting curves for 75SS and 75CS were observed by holding the paste formed at 30 °C for 1 h with the same paddle speed as above.

2.12. Statistical analysis

SPSS software (version 12.0 for Windows; SPSS Inc., Chicago, USA) was used to statistically analyze the results obtained. The one-way analysis of variance (ANOVA) was used and the Duncan test (P < 0.05) was used to establish significant pairwise differences.

3. Results and discussion

3.1. Cold water-solubility

Cold water-solubility (CWS) measured soluble molecules and highly swollen starch that did not sediment in a moderate centrifugal field despite undergoing high shearing of a dilute suspension of the starch in water at 25 °C (Rajagopalan and Seib, 1992a). The cold water-solubility obtained for the samples is shown in Table 1.

As the concentration of ethanol and the temperature were held constant, the resulting differences in cold water-solubility (CWS) were due to the concentration of NaOH used. The CWS properties increased with an increase in NaOH concentration. For sago starch, the samples that showed a significant increase in CWS were the ones treated with 60 g of 3 M NaOH and 75 g of 3 M NaOH, with values of 63.8% and 91.4%, respectively. Therefore these starches can be referred to as GCWS starches but the same cannot be said for sago starches treated with 30 g of 3 M NaOH and 45 g of 3 M NaOH, as their CWS showed no significant difference from the native starch that was not treated with NaOH. The presence of alcohol not only restricts swelling of starch granules by decreasing the effective water concentration but also acts as a complex-
Fig. 1 – Light micrographs of treated sago starch granules at 20× magnification. (a) 30SS (b) 45SS (c) 60SS (d) 75SS (e) treated corn starch, 75CS and (f) control sago starch, CSS with 40% ethanol as the hydration medium. (Sample description is the same as Table 1).

ing agent to stabilize the dissociated starch chains (Chen and Jane, 1994b). Strong alkali breaks the intermolecular hydrogen bonds of starch thereby enhancing water solubility (Han and Lim, 2004).

On the other hand, corn starch gave a CWS value of only 15.4% although it was also treated with 75 g of 3 M NaOH. Sago starch granules are much larger (15–65 μm) than corn starch granules (5–30 μm) (Murphy, 2000). Large granules were found to swell promptly during the alcoholic-alkaline treatment and the small granules were resistant to swelling under same reaction conditions (Chen and Jane, 1994a). Therefore, the parameters used by Chen and Jane (1994a) for producing GCWS corn starch were not suitable for the production of GCWS sago starch as preliminary experiments had shown that parameters used to produce GCWS corn starch with high CWS caused sago starch to undergo cold gelatinization. Chen and Jane (1994a) produced GCWS corn starch with CWS in the range of 11.7–84.3%. GCWS banana starch gave a range of CWS from 15.2% to 54.3% using the procedure reported by Chen and Jane (1994a). Singh and Singh (2003) prepared GCWS starch using potato starch with CWS ranging from 85.2% to 93.8% also using the method of Chen and Jane (1994a), with slight modifications. Singh and Singh (2003) also used corn starch as comparison and found the value for CWS significantly lower than for potato starch at 63.0%.

3.2. Light microscopy

Fig. 1 shows light micrographs taken of all of the treated samples with 40% ethanol as the hydration medium. Ethanol was used as the hydration medium so as to hinder any disruption or disintegration of the granule from taking place. Fig. 1a–d shows a change in the granule structure, although there is very little difference in the granular structure of sago starch treated with 30 g of 3 M NaOH and 45 g of 3 M NaOH. Fig. 1c (sago starch treated with 60 g of 3 M NaOH) and Fig. 1d (sago
starch treated with 75 g of 3 M NaOH show a more drastic change in the granular appearance. The granules seem to have shriveled. The granules also appear in an agglomerated state. Corn starch treated with 75 g of 3 M NaOH (Fig. 1e) shows similar characteristics to that of sago starch treated with 75 g of 3 M NaOH (Fig. 1d). GCWS starches prepared from wheat, corn, tapioca and hydroxy-propylated cross-linked wheat starch by propan1,2-diol treatment had fractured internally but contained a thin clear outer shell at the surface (Rajagopalan and Seib, 1992b). The typical Maltese-cross birefringence pattern was observed in samples 30SS, 45SS and CSS. However, the intensity of the birefringence is much less in starch which has been treated with 60 g of 3 M NaOH (60SS). Polarized light micrographs of samples 75SS and 75CS showed a loss of the

Fig. 2 – Scanning electron micrographs of (a) native sago starch, (b) native corn starch, (c) CSS, (d) 30SS, (e) 45SS, (f) 60SS, (g) 75SS and (h) 75CS at 1200× magnification. (Sample description is the same as Table 1.)
typical Maltese-cross birefringence pattern; this loss indicates a change in the order of the crystallites in the native starch granules (Jane et al., 1986).

3.3. Scanning electron microscopy

Fig. 2 shows the scanning electron micrographs of native and treated sago and corn starches. There is very little observable difference in the native sago starch, control sago starch and the 30SS and 45SS treated sago starches. The 60SS treated sago starch showed some indentation in its appearance and some agglomeration of the granules. The 75SS treated sago starch and treated corn starch (75CS) showed similar appearances in that the granules were very much indented and coiled, looking somewhat like they have been wrung. This appearance was similar to that of GCWS waxy barley starch observed by Rajagopalan and Seib (1992b).

GCWS maize starches prepared by Chen and Jane (1994a) using the alcoholic-alkaline treatment showed an indented appearance and were larger than the native granules, which concurs with an experiment on potato starch using the alcoholic-alkaline treatment by Singh and Singh (2003) showing that the granules had an indented appearance and showed internal fragmentation. Large granules were found to swell promptly during the alcoholic-alkaline treatments as compared to small granules which were more resistant to swelling (Chen and Jane, 1994a).

3.4. X-ray diffraction pattern

The X-ray diffraction patterns observed for the samples are tabulated in Table 1. NSS, CSS, 30SS and 45SS displayed a C-type diffraction pattern which is said to be a mixture of A- and B-type patterns (Bilikaderis, 1991). C-type diffraction patterns (showing strong peaks at 2θ = 15.3° and 17.3°) are known to be present in starches with relatively high amylopectin content (Ahmad et al., 1999). Native corn starch displayed an A-type pattern (showing strong peaks at 2θ = 15.3°, 17.4°, 18.2° and 23.5°).

The X-ray diffraction pattern of 60SS, 75SS and 75CS was of the V-type (showing strong peaks at 2θ = 30.3° and 33.3°) although with much lower peak intensities. The majority of the crystalline structure was found to have disappeared in these starches. The V-pattern has a few weak lines that show crystallinity but is relatively amorphous (Willhoff, 1973).

The V-type pattern was observed due to the formation of a single-helix complex with ethanol by the unsubstituted amylose. However, drying of the GCWS starches produced anhydroy V-helices with empty cavities (Rajagopalan and Seib, 1992b). The X-ray diffraction of GCWS corn and high-amylose corn starch produced by the alcoholic-alkaline treatment by Chen and Jane (1994a) showed V-type patterns whereas GCWS waxy maize starch gave an amorphous pattern (Chen and Jane, 1994b). Starches with V-type patterns are water soluble at 25 °C (French and Murphy, 1977). The A-type structures as possessed by corn starches are comparatively more stable and resistant to the alcoholic-alkaline treatment (Lii and Lee, 1993).

3.5. Apparent amylose content

The amylose contents of native sago and defatted sago starch were 30.3% and 33.3%, respectively. Total amylose content of native sago starch as determined by other researchers was in the range of 22–31.7% (Ahmad et al., 1999; Sim et al., 1991). The amylose contents for native corn starch and defatted corn starch obtained in this study were 21.6% and 22.4%, respectively. The amylose content obtained by other researchers for corn starch was in the range of 22.1–32.1 (Singh and Singh, 2003; Chen and Jane, 1994a; Jane et al., 1986). The amylose content of all the samples is shown in Table 1.

However, the amylose content of treated corn starch was significantly lower than that of the native corn starch. The amylose has been reported to leach out during the preparation of GCWS corn starch by aqueous alcohol treatment and alcoholic-alkaline treatment (Chen and Jane, 1994a; Jane et al., 1986). GCWS potato starches also reported a drop in amylose content when compared to native potato starch which was attributed to the fragile nature of the potato starch granules (Singh and Singh, 2003).

3.6. Particle size

The particle size analysis results obtained are given in Table 1. The mean diameter of native sago starch was 29.4 μm. This concurred with the results from literature where the size of sago granules ranges from 5 μm to 65 μm with the average being 30–31 μm (Ahmad et al., 1999; Takahashi, 1986; Swinkles, 1985). From the results, we find the size of the treated starches increasing although not significantly up to 45SS. The mean diameter for 60SS and 75SS was significantly larger. From the microscopic observation in Fig. 2, it was seen that for 60SS and 75SS the granules were forming clusters or were being agglomerated, therefore the larger size.

Corn starch had a mean diameter of 13.6 μm which is within the granule range of 5–30 μm (Murphy, 2000). The mean diameter for 75CS was significantly higher than that of 75SS and this could be due to a higher affinity to agglomerate as corn starch has smaller sized granules.

3.7. Intrinsic viscosity

Intrinsic viscosity, [η] of a polymer solution is influenced directly by the friction or resistance to displacement of the macromolecules to flow and thus indirectly by their size and shape as well as interactions (Tanglertpaibul and Rao, 1987). The results of the intrinsic viscosity of the samples studied are given in Table 1.

The intrinsic viscosity value obtained for native sago starch, 114.2 mL/g, is slightly lower than the value of 125.3 mL/g reported by Lee (2003). The [η] of the native sago starch was higher than that of native corn starch. The [η] value for common corn starch at 22 °C was reported as 105 mL/g by Kapoor and Bhattacharya (2000). In a study of the [η] of potato starches and bean starches, the [η] values of the potato starches were considerably higher than those of bean starches, concluding that the molecules within a potato starch granule have a higher average molecular weight or size than bean starch (Kim et al., 1997). Similarly, because the [η] of sago starch is higher than the [η] of corn starch, it is likely that sago starch...
has a higher molecular weight than corn starch. Sago starch has a larger diameter than corn starch as discussed in Section 3.6, therefore one of the reasons for the higher [\(\eta\)] for sago starch. The [\(\eta\)] values for amylose and amylopectin sago starch ranged from 310 to 460 mL/g and 210 to 250 mL/g, respectively (Ahmad et al., 1999).

The [\(\eta\)] values of the alcoholic-alkaline treated starches were lower than the native starches. This could be due to the degradation of amylopectin. Treated starches with a higher CWS gave a lower [\(\eta\)] value which could be due to a change in the internal structure. The higher the concentration of NaOH used, the lower the [\(\eta\)]. Karim et al. (2008b) found that with increasing alkaline treatment time the [\(\eta\)] decreased which has been related to the changes in molecular weight of amylose and, to a lesser extent, amylopectin.

### 3.8. Thermal properties

Thermal properties of all the samples were measured using the Differential Scanning Calorimeter and the results obtained are presented in Table 2.

The \(T_0\) (onset temperature) and \(T_p\) (peak temperature) of the treated starches were significantly lower than that of the native sago starch except for 45SS which recorded a higher \(T_0\). A change in the internal structure of the starch granules can cause the starches to gelatinize at a lower temperature (Jane et al., 1986; Chen and Jane, 1994b). The native sago starch also has a significantly higher gelatinization enthalpy compared to the treated native starches except for CSS which is not significantly lower. The lower gelatinization enthalpy values of the treated starches could be due to chain lengths, associated with the molecular order, being shorter than in the native sago starch. This was previously found to be a possible reason for native sago starch having lower enthalpy and melting temperatures compared to wheat, potato and tapioca starches (Maaruf et al., 2001).

There was no gelatinization endotherm observed for the treated starches 60SS, 75SS and 75CS. GCWS corn and potato starches showed an absence of gelatinization endotherm after alcoholic-alkaline treatment which confirmed the changed nature of the GCWS starches (Chen and Jane, 1994a; Singh and Singh, 2003). This shows that the alcoholic-alkaline method disrupts most of the crystalline structure of starch granules and makes the remaining crystalline structure unstable compared to the crystalline structure of native starch. Gelatinization is a process where the intra- and intermolecular bonds within the starch granules are broken. Therefore any change in the degree of hydrogen bonding will cause a change in the heat required to gelatinize a starch. Hydration and swelling experienced by the amorphous regions of starch granules placed in water induces mobility of polymer chains, which in turn enhances the melting of the crystallites, allowing the granules to be disordered quickly (Biliaderis et al., 1980). Water acts as a plasticizer for the amorphous region, depressing the glass transition temperature and inducing crystallites to melt at lower temperatures (Krueger et al., 1987).

Glass transition temperature (\(T_g\)) values of the native starches and treated starches are shown in Table 2. The \(T_g\) of native sago starch is not significantly different compared to CSS, 30SS and NCS but is significantly lower than 45SS. Treated starches 60SS, 75SS and 75CS have significantly lower \(T_g\) compared to the other starches.

A comparative study of granular and pregelatinized starches showed that a higher degree of crystallinity gave rise to high value for \(T_g\). Crystallites act as tie points that restrict the movement of the polymer back bone and are not involved in the glass transition. Therefore, in starch granules with a higher degree of crystallinity, there follows an inhibition of

### Table 2 – Thermal properties and glass transition temperatures of native sago and corn starch and treated starches.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(T_0) (°C)(^a)</th>
<th>(T_p) (°C)(^a)</th>
<th>(T_g) (°C)(^b)</th>
<th>(\Delta H) (J/g dry starch)(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NSS</td>
<td>70.0 ± 0.3(^d)</td>
<td>75.5 ± 0.2(^c)</td>
<td>165.5 ± 0.3(^b)</td>
<td>24.8 ± 2.4(^b)</td>
</tr>
<tr>
<td>NCS</td>
<td>66.3 ± 0.2(^a)</td>
<td>71.0 ± 0.1(^a)</td>
<td>166.3 ± 0.6(^b)</td>
<td>16.5 ± 1.0(^a)</td>
</tr>
<tr>
<td>CSS</td>
<td>68.7 ± 0.3(^b)</td>
<td>74.3 ± 0.3(^b)</td>
<td>165.8 ± 0.0(^d)</td>
<td>24.7 ± 3.6(^a)</td>
</tr>
<tr>
<td>30SS</td>
<td>68.3 ± 0.3(^b)</td>
<td>74.9 ± 0.2(^b)</td>
<td>166.5 ± 1.0(^b)</td>
<td>19.7 ± 1.0(^c)</td>
</tr>
<tr>
<td>45SS</td>
<td>69.4 ± 0.2(^b)</td>
<td>74.5 ± 0.6(^b)</td>
<td>169.7 ± 0.6(^d)</td>
<td>16.7 ± 0.3(^c)</td>
</tr>
<tr>
<td>60SS</td>
<td>–</td>
<td>–</td>
<td>83.4 ± 2.2(^a)</td>
<td>–</td>
</tr>
<tr>
<td>75SS</td>
<td>–</td>
<td>–</td>
<td>84.0 ± 1.0(^d)</td>
<td>–</td>
</tr>
<tr>
<td>75CS</td>
<td>–</td>
<td>–</td>
<td>83.3 ± 1.6(^d)</td>
<td>–</td>
</tr>
</tbody>
</table>

\(T_0\), onset temperature; \(T_p\), peak temperature; \(T_g\), glass transition temperature; \(\Delta H\), gelatinization enthalpy.

Means within a column with different letters are significantly different at \(P \leq 0.05\). (Sample description is the same as Table 1.)

\(^a\) Values are means ± SD (\(n = 3\)).

\(^b\) Values are means ± SD (\(n = 2\)).
different from the untreated native sago starch. The pasting treated samples, CSS, 30SS and 45SS, were not significantly

Table 3. Pasting temperature is the temperature at which

3.9. Pasting properties

The differences in pasting behavior of the native sago and corn starch as well as the treated starch are presented in

Table 3. Pasting temperature is the temperature at which starch granules start to swell. The pasting temperature of the treated samples, CSS, 30SS and 45SS, were not significantly different from the untreated native sago starch. The pasting temperature of sample 60SS was lower at 52.6 °C. As the CWS for this sample was high (63.8%) the swelling of the granules took place at a faster rate when heat was employed. A lower pasting temperature indicates that the crystalline structure of the treated samples has decreased (Chen and Jane, 1994b). This concurs with the X-ray diffraction and DSC results.

The peak viscosity (a measure of the thickening power of starch) of native sago starch is significantly higher than all the other starches. It is interesting to note that CSS which was only treated with ethanol showed a significantly lower peak viscosity of 171.8 RVU than the native starch. The peak viscosities for 30SS and 45SS were 221.5 RVU and 242.0 RVU, respectively. The difference could be due to the addition of 3 M NaOH, causing the starch granules to change its crystalline structure.

Samples 75SS and 75CS hydrated instantly to 160.0 RVU and 180.0 RVU, respectively. The final paste viscosities of 75SS and 75CS after being stirred for 1 h at 30 °C were 231.1 RVU and 271.1 RVU, respectively. Fig. 3 shows that the viscosity of these starches had yet to reach a plateau. There is a possibility that the solubilized starch polymers and the insoluble granule fragments have begun to reassociate therefore causing the viscosity of these starches to continue to increase. The final paste viscosities of NSS and NCS are lower than 75SS and 75CS, respectively. The final paste consistency of GCWS wheat starch was lower than its native form whereas GCWS tapioca starch had a value higher than native tapioca starch (Rajagopalan and Seib, 1992b). The apparent viscosity of GCWS banana starch pastes was higher than the native starch (Bello-Pérez et al., 2000). Sample 60SS has a very low viscosity which could be due to the shear thinning taking place during the stirring of the sample at temperatures of 90 °C. The starch granules of 60SS are thought to be fragile as they had a CWS of 63.8%.

When the paste cools, the solubilized amylose and amylopectin polymers reassociate and a rise in viscosity referred to as setback is noticed (Thomas and Atwell, 1999). The setback value of 60SS was significantly lower than the native sago starch. This shows that in 60SS, the solubilized starch polymers and insoluble granule fragments has a lower tendency to reassociate than the native starch. The reassociation of the solubilized starch polymers and insoluble granule fragments is known as retrogradation (Thomas and Atwell, 1999). However, a significantly higher setback value was observed for 30SS and 45SS. The presence of a small amount of 3 M NaOH and ethanol had brought about a significant change in the structure of the sago granules.

4. Conclusions

In summary, alcoholic-alkaline treatment brought about changes in the physicochemical, morphological, thermal and pasting properties in sago and corn starches which varied with the concentration of NaOH used at constant concentration of ethanol and temperature. The cold water-solubility properties increased with the increase in NaOH concentration. An effective concentration of 0.69 M NaOH and above showed great distortion and caused indentation in the granular structure which were still intact. The X-ray diffraction pattern of the sago and corn starch changed from a C to a V after being treated with 60 g and 75 g of 3 M NaOH. The amylose content of the alcohol-alkaline treated sago starch showed an increase in comparison with native sago starch but the corn starch showed a significant decrease in amylose content. The particle sizes of the sago samples treated with 60 g and 75 g of 3 M NaOH were significantly higher than the native starches which was explained as being due to the agglomeration of the starches. The intrinsic viscosity results indicate that some degradation had taken place in the alcohol-alkaline treated starches. Samples 60SS, 75SS and 75CS showed no thermal gelatinization enthalpy and a lower Tg indicating a disruption in the crystalline structures of the treated starches. The treated samples showed a much lower peak viscosity than the native starches. The viscosity of samples 75SS and 75CS were found to increase with the possibility of retrogradation occurring.

References


