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EFFECT OF pH ON PHYSICOCHEMICAL CHARACTERISTICS OF THREE TYPES OF MODIFIED GCWS SAGO STARCH.

TONG WOON SHENG

THIS DISSERTATION IS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENT FOR THE DEGREE OF FOOD SCIENCE WITH HONOURS IN FOOD SCIENCE AND NUTRITION

SCHOOL OF FOOD SCIENCE AND NUTRITION
UNIVERSITI MALAYSIA SABAH
2010
DECLARATION

I hereby declare that the work in this thesis is my own except for quotations and summaries which have been duly acknowledge.

16 Apr 2010

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ABSTRACT

This study is to investigate the effect of pH on cold water solubility, swelling ratio, spreadability, morphological and rheological dynamic properties of three types (hydroxypropylation, cross-linking, dual modification) of modified GCWS (Granular Cold Water Soluble) sago starch. These three chemical modifications were combined with alcoholic-alkaline treatment to produce chemical modified GCWS. The physicochemical characteristics were evaluated at pH 2 to pH 9. All modified GCWS samples exhibited good solubility (>50%) across pH 2 to 9. Cold water solubility was found decrease as pH increased, while cold water swelling ratio, spreadability dynamic rheological properties was found increased as pH increased. All modified samples were found to be more solid-like dispersion with G’ value higher than G” value. Though hydroxypropylated, H sample showed similar cold water solubility and swelling ratio (p>0.05) as compared to the control sample; while lower spreadability and G’ and G” value (p<0.05). DM2 was found to have similar (p>0.05) cold water solubility and spreadability as H sample. However, the low degree of cross-linking resulted the swelling ratio, G’ and G” value of DM2 to be higher (p<0.05) than the control. H and DM2 were found rupture with fragmentation across whole pH range like the control sample. The high degree of cross-linking in DM1 caused it to have lowest cold water solubility, swelling ratio, spreadability, G’ and G” value (p<0.05) among all modified samples. On the other hand, the mildly cross-linking in CL brought higher swelling ratio, spreadability, G’ and G” value (p<0.05) as compared to its control. Both DM1 and CL sample were able to retain their granularity throughout pH 2 to 9.
ABSTRAK

EFFECT OF pH ON PHYSICOCHEMICAL CHARACTERISTICS OF THREE TYPES MODIFIED GCWS SAGO STARCH.

Kajian ini dijalankan untuk menyiatkan kesan pH terhadap keterlarutan air sejuk, pembengkakan air sejuk, kebolehsapuan, ciri-ciri morfologi dan sifat dinamik rheologi atas tiga jenis kanji GCWS terubah-suai (hidrosipropilasi, paut-silang, dwi modifikasi). Tiga jenis modifikasi telah dikenakan ke atas kanji sago sebelum rawatan alkohol-alkali untuk menghasilkan kanji GCWS terubah-suai. Ciri-ciri fizikokimia telah diperhatikan pada pH 2 hingga 9. Setiap kanji GCWS terubah-suai mencapai keterlarutan >50% pada pH 2 hingga 9. Keterlarutan didapat menurun apabila pH meningkat. Pembengkakan, kebolehsapuan dan sifat dinamik rheologi didapat meningkat apabila pH meningkat. Semua ampaian kanji GCWS didapat lebih bersifat pepejal dengan nilai G’ melebihi G”. Walauupun dihidripropilasikan, keterlarutan sampel H didapat sama (p>0.05) dengan sampel kawalannya; sementara kebolehsapuan, nilai G’ dan G” didapat lebih rendah (p<0.05) daripada kawalannya. DM2 didapat mempunyai keterlarutan dan kebolehsapuan yang sama (p>0.05) dengan sampel H. Walau bagaimanapun, tahap paut-silang yang rendah pada DM2 mengakibatkan pembengkaan, nilai G’ dan G” lebih tinggi (p<0.05) daripada sampel kawalannya. Sampel H dan DM2 didapat pecah dengan sepian kecil pada julat pH 2 hingga 9. Pemerhatian yang sama juga didapat pada sampel kawalannya. Tahap paut-silang yang tinggi dalam sampel DM1, menyebabkannya mencapai keterlarutan, pembengkaan, kebolehsapuan, nilai G’ dan G” yang paling rendah (p<0.05) antara semua sampel. Sebaliknya, tahap paut-silang yang serderhana pada CL didapat meningkatkan pembengkaan, kebolehsapuan, nilai G’ dan G” berbanding sampel kawalannya. Kedua-dua DM1 dan CL didapat mampu mengekalkan kesempurnaan granul dalam julat pH 2 hingga 9.
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<td>GCWS</td>
<td>Granular Cold water soluble/swelling</td>
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<td>NaOH</td>
<td>Sodium hydroxide</td>
</tr>
<tr>
<td>HCl</td>
<td>Hydrochloric acid</td>
</tr>
<tr>
<td>v/v</td>
<td>Volume of solute in the total volume of solution</td>
</tr>
<tr>
<td>w/v</td>
<td>Weight of solute in the total volume of solution</td>
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<td>M</td>
<td>Molar solution</td>
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<td>STPP</td>
<td>Sodium Tripolyphosphate</td>
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<td>Sodium Trimetaphosphate</td>
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<td>EPI</td>
<td>Epichlorohydrin</td>
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<td>DM</td>
<td>Dual modification</td>
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<td>CL</td>
<td>Crosslinking</td>
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<td>MS</td>
<td>Molar substitution</td>
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<td>DSC</td>
<td>Differential scanning calorimetry</td>
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<td>RVA</td>
<td>Rapid Visco Analyser</td>
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<td>SEM</td>
<td>Scanning electron microscopy</td>
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<tr>
<td>NaCl</td>
<td>Sodium Chloride</td>
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<tr>
<td>N₂SO₄</td>
<td>Nitrogen Sulfate</td>
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<td>POCl₃</td>
<td>Phosphoryl Chloride</td>
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LIST OF SYMBOLS

\( k/\text{cm}^3 \) \hspace{2cm} \text{Intensity of light}

\( \text{mL/g} \) \hspace{2cm} \text{Viscosity}

\( \mu \text{m} \) \hspace{2cm} \text{Micrometer}

\( S/\text{m} \) \hspace{2cm} \text{Salinity}

\( ^\circ \text{C} \) \hspace{2cm} \text{Degree Celsius}

\( \text{mL} \) \hspace{2cm} \text{Milliliter}

\( \text{rpm} \) \hspace{2cm} \text{Revolution per minute}

\( g \) \hspace{2cm} \text{gram}

\( L \) \hspace{2cm} \text{liter}

\( \text{Mg} \) \hspace{2cm} \text{milligram}

\( \% \) \hspace{2cm} \text{Percentage}

\( \text{Hr} \) \hspace{2cm} \text{hour}

\( M \) \hspace{2cm} \text{Molar}
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CHAPTER 1

INTRODUCTION

1.1 Background of the study
Pregelatinized starch is a type of starch that is able to swell instantly without forming any lump and without heating it to have thickening effect (Vaclaik and Christian, 2008). Basically there are two types of pregelatinized starch namely the granular cold water swelling starch (GCWS starch) and texturized pregelatinized starch (David and William, 1999). The difference between these two types of starch is that cold water swelling starch granule does not experience rupture, whereas texturized pregelatinized starch granule will rupture after treated with pregelatinized treatment (Zhao, 2007). Pregelatinized starch is widely used in instant food such as soups, puddings, jellies, pie fillings, instant dry mix desserts, sauces, and whipped toppings (Klingler et al., 2006).

Pregelatinized starch can be prepared by various methods, such as drum drying (O’Rourke, 1980), extrusion (Cheng et al., 1977), spray drying (Picheon et al., 1981), alcoholic treatment with high temperature or pressure treatment (Eastman et al., 1984; Rajagopalan and Seib, 1992), and alcoholic-alkaline treatment (Jane and Seib, 1991). Comparison between conventional treated pregelatinized starches and cook up starch showed that there are differences in texture and solubility. Due to the ruptured granule, pregelatinized starch would cause problems such as graininess, less sheen and less flexibility towards processing condition. Consequently, the textures of instant foods made with pregelatinized starch cannot be matched in terms of quality compared to cook up starch (Chen and Jane, 1994a). Thus, further improvement was carried out in order to improve the solubility of the starch while maintaining the granularity of starch. Such improvement method is known as alcoholic-alkaline treatment. The treated starch
swells due to the reaction of starch granule with the alkaline reaction and the degree of swelling is controlled by alcohol (Chen and Jane, 1994b). Alcoholic alkaline treated starch is able to achieve cold water solubility from 50% to 94% (Jane and Seib, 1991).

Previous studies showed that alcoholic alkaline treatment was affected by various factors such as temperature, concentration of sodium hydroxide and ethanol. Treatment at a lesser concentration of ethanol with a greater concentration of sodium hydroxide and a higher reaction temperature was able to produce GCWS starches with greater cold water solubility (Chen and Jane, 1994a). Further effort on optimization of alcoholic-alkaline treatment on sago starch has identified the optimum condition as 40.7% - 50.5% ethanol and 278.5 - 296.3g sodium hydroxide (Lee et al., 2008). The treated starch under the optimum condition was able to achieved 52.2% cold water solubility, with particle size 25.4μm and retained starch granule. High concentration of sodium hydroxide is able to increase the amylose leaching. On the other hand, excessive sodium hydroxide causes the starch granules to rupture (Lee et al., 2008).

In order to reinforce starch granular structure and increase solubility and swelling of the GCWS starch, attempts was carried out by combining chemical modification such as crosslinking, hydroxypropylation or dual modification prior to alcoholic-alkaline treatment (Teoh, 2009; Lee et al., 2009; Yap, 2009). Teoh (2009) produced hydroxypropylated GCWS sago starch by mixing native sago starch with 8% hydroxypropylation reagent followed by NaOH:Starch ratio 3:1 and 50 % ethanol with 75.15 % cold water solubility. Hydroxypropylation is a substitution reaction of starch where starch is reacted with propylene oxide to form the hydroxypropyl starch which improves the freeze thaw stability, clarity and textural properties of the starch paste (Aziz et al., 2004). Studies showed that the hydroxypropylation weakens the bonding between starch molecules and allows it to swell more readily and more soluble (Lawal et al., 2008). Hydroxypropylation prevents retrogradation, resulting in more fluid paste with improved paste clarity resulting in a product with desired textural properties.
The maximum permitted concentration of hydroxpropylation reagent to be use in hydropropylation reaction is 25 % (FDA, 2009).

Yap (2009) produced cross-linked GCWS sago starch that was able to achieve cold water solubility higher than 60% while retaining granularity. Study found that the mixture of phosphate salts sodium trimetaphosphate (STMP) and sodium tripolyphosphate (STPP) is more efficient than other cross-linking reagent (Wattanachant et al., 2003). Combination treatment of 0.05 % STMP: STPP, 60 % ethanol and NaOH:starch 3:1 had been suggested to achieve highest cold water solubility of 66.2% without rupturing the starch granules (Yap, 2009). Cross-linking was chosen to modify the starch before alcoholic-alkaline treatment as it is able to tolerate higher temperature, higher shear and more acidic conditions (Yoneya et al., 2003). Cross-linking starch is one of the chemical modification techniques by reacting two or more different hydroxyl groups of the native starch with bi or poly-functional chemical reagent (David and William, 1999). The cross-linking reagent reacts and bond covalently with the granular structure to strengthen it (Acquarone and Rao, 2003). Apart from that, cross linked starch would show reduction of paste clarity and improvement in pasting properties (Dumitriu, 2005). The extent of cross-linked starch is able to be verified by the phosphorus content (Deetae, 2008). The maximum permitted concentration of cross-linking reagent should not exceed 0.4% (FDA, 2009).

From previous study, it is found that two combinations of dual modified GCWS sago starch was able to achieve cold water solubility that is higher than 60 % while maintaining starch granule (Pang, 2009). These combinations are 0.07 % cross linking reagent and 9 % hydroxypropylation reagent, as well as combination 0.08 % cross linking reagent and 7 % hydroxypropylation reagent. The treated starch was reacted by 50 % ethanol and NaOH : Starch 1:3 (Pang, 2009).

Dual modification was suggested to be carried out before alcoholic-alkaline treatment because dual modification could improve physiochemical characteristics of
starch. Previous study found that dual modification was able to improve freeze-thaw stability of rice starch (Deetae et al., 2008). Besides that, the dual modified sago starch was showed no viscosity breakdown and no significant difference in pasting characteristics when applied in different pH condition (Wattanachant et al., 2002b).

1.2 Rationale
This study is a continuous effort to further characterize the properties of the modified GCWS sago starch which consists of combination of chemical modification (dual modification, cross-linking and hydroxypropylation) and alcoholic-alkaline treatment that was carried out in the laboratory previously. Studies on cold water solubility and starch microscopic structure of modified GCWS sago starch were done previously (Pang 2009; Teoh, 2009; Yap, 2009).

GCWS starch has been widely used in various types of food systems which can be acidic or alkaline. Based on FDA (2009), pH of the common foods are in the range of pH 2 to 9. For instance, pregelatinized starch was used in production of reduced fat cream cheese which was coagulated in the mild acidic condition. Cream cheese is usually stored under refrigerated condition (Finocchiaro, 1997). Cream cheese usually have the pH value of 4.10 - 4.79 (FDA, 2007). GCWS starch also has been applied in instant pudding (O'Rouke, 1980). The pH value of lime flavor pudding can be as low as 2.60 (FDA, 2007). Besides that, modified GCWS starch also has potential to be applied with egg to produce custard, and egg usually has pH value of 8 (FDA, 2007). Thus it is important to understand the behavior of the modified GCWS starch in the range of pH 2 to 9. Wattanachant et al. (2002b) found that chemical modified starch was able to resist wide range of pH. However, there is no any study on pH effect towards physicochemical properties of these modified GCWS starch. The result of the study allows us to determine suitability of modified GCWS sago starch in the potential industrial processing condition and food system which could be either acidic or alkaline.
Based on the earlier studies, different chemical modified starch have different characteristics. For instances, cross-linked starch would have higher stability towards swelling, heat shear and acidic condition (Yoneya et al., 2003). The hydroxypropylated starch would have improved clarity of starch paste, greater viscosity, reduced syneresis and freeze-thaw stability (Wu and Seib, 1990). Mean while, dual modified reaction is able to improve paste consistency, smoothness and freeze-thaw stabilities (Sing et al., 2007). Therefore, we anticipated different chemical modified GCWS starch would behave differently when compared to GCWS sago starch that was solely produced by alcoholic-alkaline treatment.

In Malaysia, sago palm is inexpensive and not agriculturally intensive as rice. Presently, commercial production of sago flour in Malaysia occurs mainly in Sarawak and small parts of Johor. In Sarawak, the planting area of sago is estimated above 50,000 hectare which is the fourth largest area for crops in Sarawak. Sarawak is also one of the biggest exporters of sago. Sago brings above RM50 million in exports earning in latest year for Sarawak (Aziz, 2002; DOA, 2009). This value is expected to rise in coming year, therefore by understanding the new application of sago starch it would able to boost up the starch industry by diversify the usage of sago starch and increase the value of the sago starch.

1.3 Objective
To study the effect of pH on cold water solubility, cold water swelling, spreadability, morphological study and rheological dynamic properties of three types (hydroxypropylation, cross-linking, dual modification) of modified GCWS (Granular cold water soluble) sago starch.
CHAPTER 2

LITERATURE REVIEW

2.1 Sago starch

Sago starch is extracted from the sago palm which is a hepaxanthy (once flowering), monocotyledonous plant which belongs to the species of the genus *Metroxylon* sub family of *Calamoideae*, and family of *Palmae*. Sago palms usually are 6-14m tall and hapaxantic which mean the sago palm will die after it flowered once (Singhal *et al.*, 2008). The extraction of sago starch usually can be done in two methods which are the traditional method and the modern method (Karim *et al.*, 2008; Nishimura and Laufa, 2002).

The traditional extraction usually involves four major processes which start with harvested mature sago palm. It follows by cutting sago palm into partitioned logs. Followed by pounding or crushing of the sago pith and lastly is the washing of sago piths for starch extraction (Nishimura and Laufa, 2002). The fibrous pith will be rasped by a sharpened piece of hardwood. The rasped pith will mix with water and streams through the sieve, to filter the fibre out. The starch will settles on the bottom of the vessel (Flach, 1997).

The modern extraction is more or less similar to the traditional method which it involve machinery and able to extract in a bigger scale. The bark of the sago palm was removed and the debarked section will be fed into the mechanical rasper to rasp the pith into finer pieces. The rasped product will mix with water and form starch slurry to pass through series of centrifugal sieves to separate the coarse fibres. The further
purification was done by using nozzle separator through sieve bends and a series of cyclone separators to produce very pure starch (Singhal et al., 2008).

The sago palm usually grow optimally under humid tropical lowlands which at the altitude of 700m and the temperature of the environment of 25°C, relative air humidity of 70%, the inditental light 800 k/cm² per day and salinity should not exceed 1/8 of the salt concentration of the sea water. These are the optimum conditions for sago palm to grow. Therefore sago starch commonly can be found in countries such as Malaysia, Indonesia and Papua New Guinea (Aziz, 2002).

The starch granule are made up by two major type of polymer which known as amylose and amylopectin. There are some other minor constituents such as lipids, proteins, phosphate and ash which it did play a role in affect the functional properties of the starch in starch application (David and William, 1999). Sago starch is different compare to other types of starch by its size of granule, swelling power, gelatinization, retrogradation and the synerisis of the starch (Wattanachant et al., 2002).

2.1.1 Structure and organisation
Sago starch contains 27% amylase and 73% amylopectin, in its polymer structure. The amylose and amylopectin moeclules was arranged readily and made up starch granules which contain crystalline and non crystalline regions in alternating layers (Fennema, 1996). The amylose content of the sago starch is higher if the starch is extracted from the upper part of the lower part of the trunk compare to the starch that is extracted from the upper part of the trunk (Tomoko et al., 2000). The grain size distribution of sago starch is about 16 – 25.4µm. The grain size will increase up to 40 µm as the age of the trunk getting old until initiation of the inflorescence. The sago starch had bigger average granule size compared to other starch bases such as waxy maize, waxy barley, tapioca, wheat, corn and rice (Satin, 2000). The molecular weight for amylose is ranged between $1.41 \times 10^6$ – $2.23 \times 10^6$ and the amylopectin molecular weight is $6.70 \times 10^5$ – $9.23 \times 10^6$ (Colonna et al., 1984); (Roger et al., 1993). The
chemical composition of sago starch can be shown in Table 2.1. The amylose and amylopectin ratio play important role in affecting the viscosity, shear resistance, gelatinization, textures, solubility, tackiness, gel stability, cold swelling and retrogradation of the starch (Satin, 2000).

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Dry weight basis (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amylose</td>
<td>27</td>
</tr>
<tr>
<td>Amylopectin</td>
<td>73</td>
</tr>
<tr>
<td>Lipids</td>
<td>0.1</td>
</tr>
<tr>
<td>Protein</td>
<td>0.1</td>
</tr>
<tr>
<td>Ash</td>
<td>0.2</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>0.02</td>
</tr>
</tbody>
</table>

*Source: (Singhal et al., 2008)*

Amylose is one of the essential linear polymer compose made up almost the whole α-1,4 linked D-glucopyranose (Fennema, 1996). The simplified amylose polymer can be shown as in Figure 2.1. Usually amylose exist in long helical structure which it have molecular weight about $1.41 \times 10^6 - 2.23 \times 10^6$ (Karim et al., 2008). The interior of the helix structure contains hydrogen atoms which are hydrophobic; the exterior of the helix structure consists of hydroxyl groups (David and William, 1999). The amylase forms a 3-dimensional network when the molecules associate upon cooling which this phenomenon responsible for the gelatinization of the starch pastes (Vaclaik & Christian, 2008).
Figure 2.1: α-1, 4, linkages of amylose

Source: (David and William, 1999)

Amylopectin is the major component of starch (comprising 70–80%) and is a much larger branched molecule in which about 5% of the glucose units are joined by α1-6 linkages (Jobling, 2004). The structure of amylopectin can be shown as in Figure 2.2. The highly branched amylopectin will packed together in the form of double helices and it forms many small crystalline areas containing the dense layers of starch granules and alternate with less dense amorphous layers (Fennema, 1996).

Figure 2.2: Amylopectin

Source: (Tester, Karkalas and Qi, 2004)
References


De L. M. 1999, Biodegradable polystyrene foaming products. US patent 6,090,863


