UNIVERSITI PUTRA MALAYSIA

PREPARATION AND CHARACTERISATION OF HYDROXYPROPYLATED CROSSLINKED SAGO STARCH FOR APPLICATION IN ACIDIC, FROZEN AND CANNED FOODS

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By

SAOWAKON SUWANLIWONG

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Dedicated to

My parents and my eldest sister

for their love,

understanding,

and encouragement

which have been a constant source of inspiration.

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF PLATES

Abstract of the thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the Degree of Master of Science

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Chairman: **Dr. Sharifah Kharidah Syed Muhammad**

Faculty: **Food Science and Biotechnology**

Hydroxypropylation and crosslinking were carried out to improve the quality of sago starch. The optimum conditions for preparation of hydroxypropylated crosslinked sago starch were found to be an initial reaction with 10-12% propylene oxide at 40°C for 24 hr using 40% (dsb) starch slurry containing 15% sodium sulphate at pH 10.5. This was followed by crosslinking using a mixture of 2% sodium trimetaphosphate (STMP) and 5% sodium tripolyphosphate (STPP). Through hydroxypropylation, it was found that there was a significant increase in molar substitution which will in turn induce the increase in crosslinking and this was seen from the marked increase in phosphorus content and degree of substitution. This was accompanied by a significant decrease in paste clarity, swelling power and solubility compared to that of the native starch. The hydroxypropylated crosslinked

sago starch prepared also exhibited desirable properties in that it exhibited no viscosity breakdown, high acid resistance, high freeze-thaw stability and improved gel texture.

The hydroxypropylated crosslinked sago starch (HPST) was prepared in a larger scale having molar substitution (MS) and degree substitution (DS) values in the range of 0.038 to 0.045 and 0.004 to 0.005, respectively. The properties of HPST in terms of sediment volume, swelling power, solubility and paste clarity were 15.75%ml, 16.7, 8.62% and 5.18 $\%T_{650}$, respectively. The MS value, phosphorus content, paste clarity, swelling power and syneresis after six freeze-thaw cycles of HPST when compared to that of commercially available modified starches which are normally used or incorporated in acidic, frozen and canned foods did not differ significantly. The pasting characteristic of HPST exhibited thin to thick viscosity which is similar ($P>0.05$) to that of commercial hydroxypropylated crosslinked tapioca starch (NAT 8). The acid stability, solubility and freeze-thaw stability of both starches were also similar ($P>0.05$) but the swelling power of HPST was slightly lower ($P<0.05$) than that of NAT 8.

The canning stability of HPST in terms of textural and rheological aspects was very high either in neutral or acidic canning condition at 15 psig (121°C) for 30 min. However, when sterilised longer than 40 min at 121°C, the HPST pastes (6% starch solid) experienced a significant decrease in viscosity and firmness. The HPST paste which consisted of 6% starch solid and 10% sucrose at pH 6.5 exhibited

rapid heat penetration. A sterilisation value (F_o) of 25.48 could be obtained from the sterilisation of HPST paste contained in a can size 300x305 at 121°C for 30 min.

Abstrak Tesis yang Dikemukakan kepada Senat Universiti Puta Malaysia
Sebagai Memenuhi Keperluan untuk Ijazah Master Sains

PENYEDIAAN DAN CIRI-CIRI KANJI TERHIDROKSIPROPILASI-IKATAN SILANG UNTUK APLIKASI DALAM MAKANAN YANG BERASID, DIBEKUKAN DAN DALAM TIN

Oleh

SAOWAKON SUWANLIWONG

Oktober 1998

Pengerusi : Dr. Sharifah Kharidah Syed Muhammad

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Hidroksipropilasi dan ikat-silang telah dilakukan untuk meningkatkan kualiti kanji sagu. Didapati yang syarat optima untuk menyediakan kanji sedemikian adalah dengan memanaskan larutan kanji 40% (yang mengandungi natrium sulfat 15% dan pada pH 10.5) bersama 10-12% propylene oksida pada suhu 40°C, selama 24 jam. Ini diikuti dengan ikat-silang yang menggunakan campuran 2% natrium trimetaposfat (STMP) dan 5% natrium tripoliposfat (STPP). Melalui hidroksipropilasi, terdapat pertambahan penggantian molar yang bererti yang menggalakkan lagi ikat-silang; ini dapat dilihat melalui peningkatan kandungan fosforus dan kadar penggantian. Ini diikuti dengan penurunan bererti kejernihan pasta, kemampuan mengembang dan kelarutannya berbanding dengan kanji tempatan. Kanji terhidrosipropilasi dan terikat-silang yang dihasilkan juga berciri positif dalam erti kata stabil kelikatan, tahan asid, dan stabil masa "freeze-thaw".

Kanji sagu hidroksipropilasi-ikatan silang (HPST) yang berpenggantian molar (MS) antara 0.038 dan 0.045 serta darjah penggantian (DS) 0.004 dan 0.005 telah disediakan pada skala yang lebih besar. Ciri-ciri kanji HPST seperti isipadu sedimen, kemampuan mengembang, kelarutan dan kejernihan pasta adalah seperti berikut: 15.75%ml, 16.7, 8.62% dan 5.18%T_{650}. Didapati ciri-ciri HPST seperti: MS, kandungan fosforus, kejernihan pasta, kemampuan mengembang dan syneresis selepas enam pusingan freeze-thaw tidak berbeza secara bererti berbanding dengan kanji-kanji komersil yang banyak digunakan dalam makanan berasid, makanan beku dan makanan dalam tin. Pasta HPST menunjukkan ciri-ciri kelikatan dari yang cair hingga ke pekat adalah sama ($p>0.05$) dengan pasta kanji ubi kayu terhidrosipopilasi dan terikat silang (NAT 8). Juga sama ($p>0.05$) bagi kedua-dua kanji ialah kestabilan asid, kelarutan dan kestabilan freeze-thaw; bagaimana pun, kemampuan mengembang HPST adalah rendah sedikit ($p>0.05$) berbanding dengan kemampuan NAT 8.

Dari aspek tekstur dan rheologi, kestabilan kanji sagu hidroksipropilasi-ikat silang yang ditinkan mempamerkan kestabilan yang tinggi sama ada ditinkan dalam keadaan neutral mau pun dalam keadaan asidik pada 15psig (121°C), selama 30 minit. Bagaimana pun, apabila disterilisasi melebihi 40 minit pada suhu 121°C, kelikatan dan kemantapan tekstur pasta HPST (6% pejal) berkurangan secara bererti. Pasta HPST yang terdiri daripada 6% kanji pejal dan gula 10% pada pH 6.5 menunjukkan penusukan haba yang cepat. Nilai sterilisasi (F_o) 25.48 boleh

diperolehi dengan mengsterilisasi pasta HPST dalam tin berukuran 300 x 305 selama 30 minit.

CHAPTER I

GENERAL INTRODUCTION

Sago starch is abundant in Malaysia which is the principle exporter to the world market (Zulpilip et al., 1991). Over the past five years, it was discussed as an inexpensive source of food in Southeast Asia (Stanton, 1993; Magda, 1993). Nowadays, the effort in improvement of sago starch production and starch quality has increased its utilisation as an economically viable feedstock for conversion to industrial sugars, a biomass source for starch hydrolysates and alcohol fermentation (Stanton, 1993; Wang et al., 1996; 1995; Pranamuda et al., 1995; Gorinstein et al., 1994; Haska and Ohta, 1993; Kim and Rhee, 1993). However, the inherent physicochemical properties of sago starch have limited its utilisation as a domestic starch thickener, stabiliser or texture modifier in foods such as starch-based canned products, sauces, custards, pie fillings and frozen desserts.

The disadvantage of the native sago starch is its granules swell with easy rupture during heating and shearing (Yatsuki, 1986; Takeda et al., 1989). Its gel has an undesirable texture and thus it could not be employed in foods that would be subjected to heat processing. Through chemical modifications, however, starches can be altered to increase its usefulness (BeMiller, 1997). Many chemical modifications have been used to convert natural starches to derivatives that exhibit

specific characteristics. In modern foods which are increasingly processed, a vast requirements are needed in the modified food starches (Richmond et al., 1996). Therefore, it is necessary for a starch to be modified by different methods such as substitution and crosslinking to increase its usefulness (Lopez, 1987). Hydroxypropylation and crosslinking are commercially used in dual-modification of starch. The benefits from these modifications are that crosslinking will reinforce starch granules resulting in them to be more resistant in acid, heat and shearing while hydroxypropylation will improve their freeze-thaw or cold-storage stability (Wurzburg, 1986; Tuschhoff, 1986).

The commercially available starch thickeners that form a major part of the total starch sales to the food industry (Pomeranz, 1991) are mainly produced from waxy corn and tapioca. In Malaysia where sago starch is plentiful, food manufacturers have to spend a lot of money per year to import those starches in the native or modified forms to be used as thickeners. As reported in the Import and Export Trade Statistics, Malaysia in 1994 exported 8,413 tonne of sago starch valued at RM (Ringgit Malaysia) 5.6 million, but had to spend about RM 4.5 million for importing only 210 tonne of modified starches (Ahmad Zabri, 1996).

It is therefore the goal of this study to determine if sago starch could be used to substitute some commercially available modified starches by improving its properties through dual-modification: hydroxypropylation and crosslinking. It also aims to alter sago starch properties to be close to the characteristics of commercial starch thickeners being applied in acidic, frozen and canned foods. These foods