Journal of Food Science and Agricultural Technology

International peer-reviewed scientific online journal

Published online: http://rs.mfu.ac.th/ojs/index.php/jfat

Original Research Article

Functional properties of dual-modified rice starch

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ARTICLE INFO

Article history:

Received 31 July 2018

Received in revised form 8 October 2018

Accepted 10 October 2018

Keywords:

rice starch

hydroxypropylation

cross-linking

ABSTRACT

Dual-modification, hydroxypropylation and cross-linking were conducted to overcome the undesirable properties of native rice starch and to improve its functional properties during processing. The first stage of modification was hydroxypropylation using 6% to 12% of propylene oxide. This was followed by cross-linking using the mixture of 12% sodium trimetaphosphate (STMP) and 0.1% sodium tripolyphosphate (STPP). The level of hydroxypropylation enhanced the subsequent cross-linking and this was indicated by a marked increase in phosphorus content and degree of substitution (DS). This was accompanied by a significant decrease in paste clarity, swelling power, peak viscosity, breakdown and consistency coefficient. The effects of different cross-linking agents: 2% STMP, the mixture of 2% STMP and 5% STPP and the mixture of 12% STMP and 0.1% STPP, on functional properties of rice starch hydroxypropylated with 8% propylene oxide were also investigated. It was found that dual-modified rice starch cross-linked by STMP alone gave the highest phosphorus content (0.192%) and degree of substitution (0.01) resulting in the lowest peak viscosity, breakdown, final viscosity, consistency coefficient, swelling power, solubility index and paste clarity. In addition, the dual-modified rice starch cross-linked with mixed phosphate salts containing a high content of STMP (12% STMP and 0.1% STPP) gave significantly higher phosphorus content (0.161%) and degree of substitution (0.009) compared to that of the mixed phosphate salts containing low STMP content (2% STMP and 5% STPP). It suggests that the higher amount of STMP enhanced the high phosphorus substitution on the starch chains resulting in an increasing rigidity of the rice starch granules.

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Published by School of Agro-Industry, Mae Fah Luang University

ISSN: 2408-1736

INTRODUCTION

Native rice starches have poor freeze-thaw stability, resistance to shear, fair stability to retrogradation and have moderate clarity and soft texture (Raina *et al*., 2006). Many chemical modifications have been used to convert natural starches to derivatives that exhibit specific characteristics. Therefore, it is necessary for a starch to be modified by different methods, such as substitution and cross-linking to increase its usefulness (Wattanachan, et al., 2003; Yeh and Yeh, 1993), whilst hydroxypropylation will improve their freeze-thaw or cold-storage stability. Moreover cross-linking of hydroxypropyl starch imparts viscosity stability and desired short textured properties to the paste. The dual-modification, hydroxypropylation and cross-linking, are widely used methods used to prepare modified starches. The hydroxypropylation will improve paste consistency, clarity and impart freeze-thaw and cold storage stabilities (Wattanachan*, et al*., 2003; Perera and Hoover, 1999). The hydroxypropyl groups introduced in the starch chain have to be capable of disrupting inter and intra molecular hydrogen bonds, hereby weakening the granular structure of starch and leading to an increase in motional freedom of the starch chain in amorphous regions (Choi and Kerr, 2003; Seow and Thevamalar, 1993). The benefits from modification are that cross-linking will reinforce the hydrogen bond in the granule with chemical bonds that act as a bridge between of the starch molecules. As a result, the cross-linked starches are resistant to acidic medium, heat and shear (Yook *et al*., 1993). This dual-modification is particularly desirable for frozen food and other food products to maintain palatable qualities during processing and storage (Jane, 1997).

The amount of cross-linking reagent necessary to give starch products with desirable properties will vary depending on the starch source, the cross-linking reagent, and the level of hydroxypropyl ether substitution. Several previous studies have investigated the effect of the different reaction conditions, such as starch concentration, temperature, pH and concentration of catalyst salt for preparing hydroxypropylated cross-linked starch (Wogguma *et al*., 2014; Wattanachan, *et al*., 2003; Yeh and Yeh, 1993). To the best of our knowledge, few studies have investigated chemical modification of Jasmine rice starch. To improve the functional properties of Jasmine rice starch, the aim of the present work was to modify Jasmine rice starch by dual-modification, hydroxypropylation and cross-linking, and further investigated the effect of the amount of propylene oxide and cross-linking agents on pasting properties, swelling power, paste clarity and flow behaviour.

MATERIALS AND METHODS

Materials

Jasmine, named Khao Dawk Mali 105, rice starch (14.96% amylose) was provided by Bangkok Industrial Co., Ltd.

Preparation of dual-modified rice starch

Rice starch was stabilised by reacting with propyleneoxide, and cross-linked by cross-linking reagent following the procedures modified from Wattanachan, *et al*. (2003). Six grammes of sodium sulphate were added to 60 ml of water and stirred. When the salt was dissolved, 40 g of rice starch (db) were added and the mixture stirred to make up a uniform slurry. Then a 5% sodium hydroxide solution was added with vigorous stirring to prevent starch gelatinization and to adjust the slurry to pH 10.5. The propylene oxide was then added and the slurry, which was at room temperature, was stirred for half an hour. The slurry was then transferred to centrifugal bottles and placed in a shaking incubator at 40°C, with shaking rate at 200 rpm, and held for 24 hr. After completing step one of substitution, the slurry was transferred into a mixing container at room temperature. The pH of that slurry was recorded and then the cross-linking reagent was added with vigorous stirring for half an hour. After that, the slurry was again transferred to the previous centrifugal bottles and the reaction was allowed to proceed for 120 min at 40°C an incubator shaker with a shaking rate of 200 rpm. The starch slurry was then adjusted to pH 5.5 with 10% hydrochloric acid solution to terminate the reaction. The starch was recovered by centrifuge at 2500 rpm for 15 minute was washed with 3 volumes of distilled water. The starch was dried at 40°C to moisture content of 10–12%.

Effet of hydroxypropylation levels

Rice starch was stabilized through it reacting with propyleneoxide with four levels of propylene oxide, which vary from 6, 8, 10 and 12%, and reaction was inhibited by the same cross-linking reagent, with the mixture of 12% STMP and 0.1% STPP

Effect of cross-linking reagent

Rice starch was stabilized through it reacting with propyleneoxide of 8 % (v/w starch solid) and cross-linked by using three different ratios of mixed phosphate salts: 2% sodium trimetaphosphate (STMP) and 0% sodium tripolyphosphate (STPP); 2% STMP and 5% STPP; and 12% STMP and 0.1% STPP.

Pasting properties

The pasting characteristics of rice starch were determined using the Rapid Visco Analyzer (RVA Newport Scientific, Warriewood, NSW, Australia). Water was added to 2.50 g starch (14% moisture basis) of rice starch to give a total water content of 25.0 ml. The stirring speed was 960 rpm for the first 0 second and 160 rpm for 10 second. Temperature and time were set as follows; the sample was held at 50°C for 1 minute, ramped up to 95°C for 4.42 minute held at this temperature for 2.30 minute, cooled to 50oC at 11 minute.

Swelling power and Paste clarity

The swelling power of dual-modified rice starches were determined in accord with the method described by Sasaki and Matsuki (1998). The paste clarity (Transmittance % at 650 nm) of dual-modified rice starch was determined by the method used by Piyachomkwan, *et al*. (2002).

Degree of hydroxypropylation and cross-linking

Hydroxypropyl and phosphorus contents were determined by the method as described by FAO/WHO Expert Committee on food additives (2001). The molar substitution (MS) and the degree of substitution (DS) were calculated in the normal fashion (Rut 1984).

Flow behavior

The rice starch slurry was prepared by weight 4% (db). The flow behavior of gelatinized starches was determined using a rotational rheometer (Haak, RheoStress RS75., Germany) equipped with coaxial cylinder geometry (Z41). It was determined at 60°C and a shear rate in the range of 10-1000 s-1.

Statistical analysis

The experiment plan type Completely Randomized Design (CDR) by Factorial Experimental Design. The data obtained from the study were analyzed using analysis of variance (ANOVA) and the means were separated by Duncan's New Multiple Range Test or the least significant difference.

RESULTS AND DISCUSSION

Effect of hydroxypropylation levels on functional properties of dual-modified rice starch

The dual-modified rice starches had lower pasting temperature than that of native rice starch (Table 1). The granules of dual-modified rice starches were weaken, resulting in faster swelling since hydrogen bonding between hydroxyl groups inside starch granules was reduced by the substitution of hydroxylpropyl group (Watt-anachan, *et al*., 2003). The higher level of hydroxypropyl substitution (Table 2) was reflected in the lower peak breakdown and setback viscosity (Figure 1 and Table 1). The level of hydroxypropylation during the first stage of the dual-modification process enhance the subsequent cross-linking and this was indicated by a marked.

Figure 2 shows the swelling power of native and dual-modified rice starches. The swelling power of rice starches were considerably reduced (p<0.05) by dual-modification. This implied that hydroxy-propylation will weaken the bonding between starch molecules thus allowing more cross-linking agent to react with starch molecules (Wattanachan, *et al*., 2003; Wu and Seib, 1990). Cross-linking restricted swelling of granule and would also lower solubility by increasing chain binding.

The paste clarity of native rice starch was decreased significantly (p<0.05) after dual-modified rice starches as presented in Figure 2. This was indicated that cross-linking had taken place inside the rice starch granules (Wattanachan, *et al*., 2003). As propylene oxide level increased, the paste clarity of dual-modified rice starches decreased. It also indicated that more cross-linking occurred in dual-modified rice starches. This was supported by a marked increased in the phosphorus content and DS value (Table 2).

The relationship of apparent viscosity and shear rate for native and dual-modified rice starches is presented in Figure 3. It shows that the apparent viscosity decreased with increasing shear rate exhibiting shear thinning (pseudoplastic) behavior. The apparent viscosity and consistency coefficient (k) decreased, while flow behavior index (n) increased with the increasing of propylene oxide level. It suggests that the higher level of hydroxypropylation enhanced the subsequent cross-linking resulting in reduced swelling and increased the rigidity of rice starch granules (Wu and Seib, 1990).

Effect of Cross-linking agent on Functional Properties of Dual – modified Rice Starch

STMP alone or a mixture of phosphate salts (STMP and STPP) was used as cross-linking agent after the rice starch was hydroxypro-pylated with 8% propylene oxide. Pasting parameters were used to compare the efficiency of cross-linking agents (Table 3). The results for pasting temperature did not show any significant difference (p>0.05) when different cross-linking agents were used. STMP alone brought about the lowest peak viscosity, breakdown and setback of rice starch (Figure 4). The mixture of phosphate salts (2%STMP and 5%STPP) showed the higher peak viscosity, breakdown and setback compared with a mixture of 12%STMP and 0.1%STPP. STMP alone and a high amount of STMP in mixed salts gave high phosphorus substitution on dual modified rice starch (Table 4).

Figure 5 shows the swelling power and paste clarity of dual-modified rice starches using different cross-linking agents. The swelling power and solubility of dual-modified rice starch cross-linked with STMP alone was reduced significantly (p<0.05) compared to cross-linking with the mixed salts (STMP: STPP). This indicated that cross-linking with STMP alone gave high phosphorus substitution on starch molecules (Table 3), resulting in restricted granule swelling (Whistler and BeMiller, 1997; Lim and Seib, 1993). Paste clarity was used to compare the efficiencies of the cross-linking agents. The high clarity of native rice starch paste at 21.07 $\%T_{650}$ was decreased significantly (p<0.05) after dual-modification, as shown in Figure 5. Paste clarity of 7.30, 10.2 and 9.93% T650 were obtained from cross-linking with STMP, a mixture of 2%STMP and the mixture of 5%STPP and 12%STMP and 0.1 STPP, respectively. The influence of the ratio of mixed salt (STMP: STPP) on paste clarity was not significantly different (p > 0.05). Dual-modified rice starch cross-linked with STMP alone exhibited the lowest paste clarity because it resulted in the highest phosphorus content (0.192%) and DS value (0.01) as shown in Table 3.

The relationship of apparent viscosity and shear rate for dual-modified rice starches using different cross-linking agents is presented in Figure 6. The flow curves of all samples showed shear thinning behavior. Cross-linking with STMP alone gave the lowest apparent viscosity and consistency coefficient (k = 0.015 Pa.s) and the highest flow behavior index (n = 0.908). The mixture of 12%STMP and 0.1%STPP showed the lower apparent viscosity and consistency coefficient compared with that of the mixture of 2%STMP and 5%STPP. It suggests that the higher amount of STMP enhanced the high phosphorus substitution on the starch chains resulting in increased rigidity of the rice starch granules (Wattanachan, *et al.,* 2003).

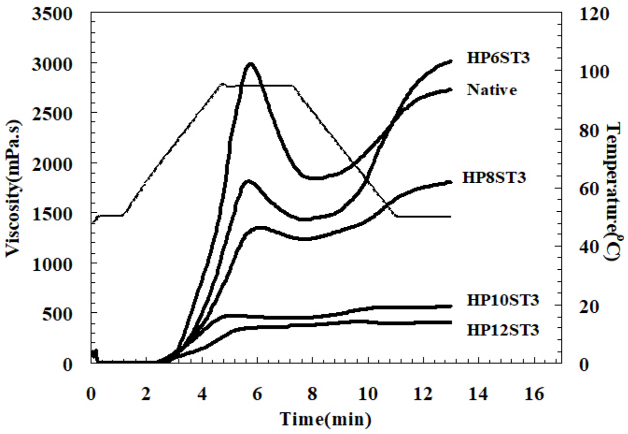

Figure 1 Amylograph of native and dual-modified rice starches hydroxypropylated with propylene oxide of 6% (HP6), 8% (HP8), 10% (HP10) , and 12% (HP12) and cross-linked with the mixture of 12% STMP and 0.1% STPP(ST3).

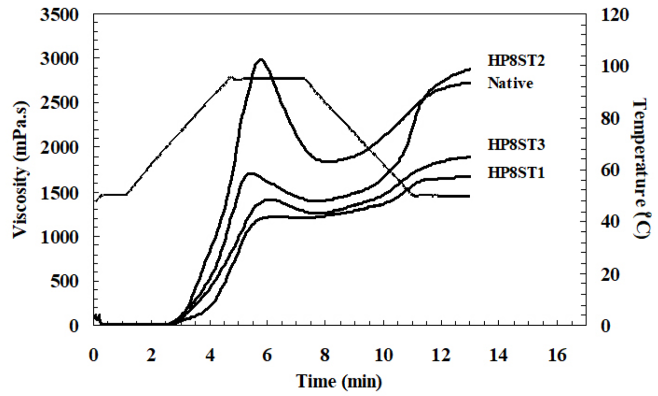

Figure 4 Amylograph of native and dual-modified rice starches hydroxypropylated with propylene oxide of 8% and cross-linked with of 2% STMP (HP8ST1), the mixture of 2% STMP and 5% STPP (HP8ST2) and the mixture of 12% STMP and 0.1% STPP (HP8ST3).

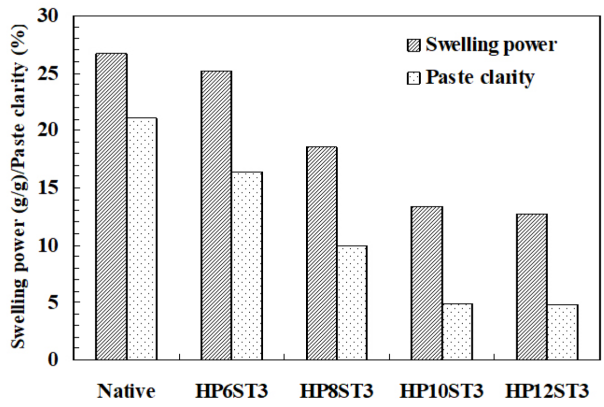

Figure 2 Swelling power and paste clarity of native (NS) and dual-modified rice starches hydroxypropylated with propylene oxide of 6% (HP6), 8% (HP8), 10% (HP10) , and 12% (HP12) and cross-linked with the mixture of 12% STMP and 0.1% STPP(ST3).

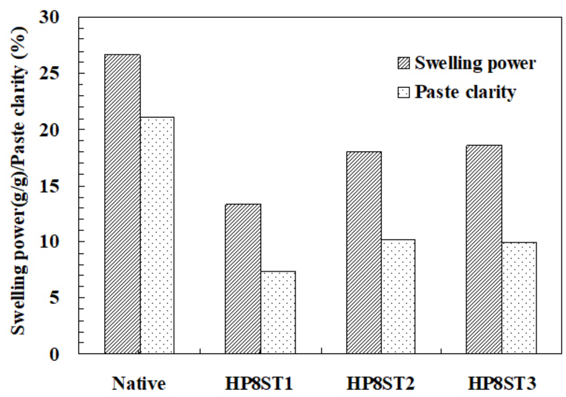

Figure 5 Swelling power and paste clarity of native and dual-modified rice starches hydroxypropylated with propylene oxide of 8% and cross-linked with of 2% STMP (HP8ST1), the mixture of 2% STMP and 5% STPP (HP8ST2) and the mixture of 12% STMP and 0.1% STPP (HP8ST3).

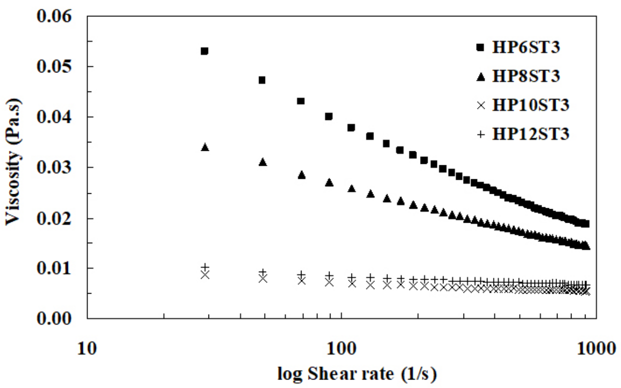

Figure 3 Relationship of viscosity and log shear rate of dual-modified rice starches hydroxypropylated with propylene oxide of 6% (HP6), 8% (HP8), 10% (HP10) , and 12% (HP12) and cross-linked with the mixture of 12% STMP and 0.1% STPP(ST3).

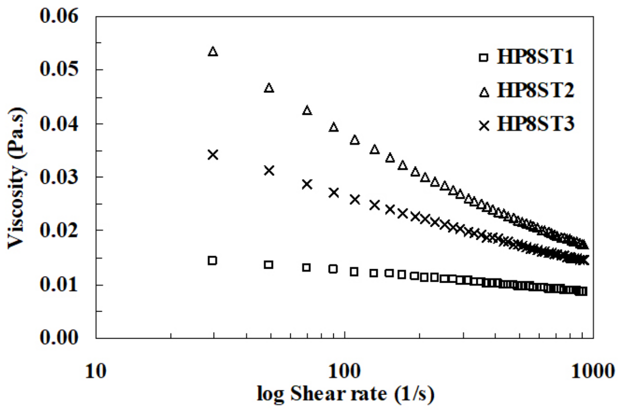

Figure 6 Relationship of viscosity and log shear rate of dual-modified rice starches hydroxypropylated with propylene oxide of 8% and cross-linked with of 2% STMP (HP8ST1), the mixture of 2% STMP and 5% STPP (HP8ST2) and the mixture of 12% STMP and 0.1% STPP (HP8ST3).

Table 1. Pasting properties of native and dual-modified rice starches hydroxypropylated with propylene oxide of 6% (HP6), 8% (HP8), 10% (HP10) , and 12% (HP12) and cross-linked with the mixture of 12% STMP and 0.1% STPP(ST3).

Sample	Pasting Temperature (°C)	Peak (mPa.s)	Breakdown (mPa.s)	Setback (mPa.s)
Native	$68.55^{a} \pm 0.00$	$2950.00^{a} \pm 49.50$	$1097.50^{a} \pm 58.69$	$879.00^{b} \pm 1.41$
HP6ST3	$66.49^{b} \pm 0.95$	$1879.60^{b} \pm 99.39$	$336.20^{b} \pm 50.28$	$1454.90^{a} \pm 175.80$
HP8ST3	$66.48^{b} \pm 0.73$	$1362.33^{c} \pm 117.59$	$122.89^{c} \pm 28.32$	$494.78^{c} \pm 86.35$
HP10ST3	$66.77^{b} \pm 0.81$	$542.25^{d} \pm 87.14$	$26.25^{d} \pm 1.50$	$131.25^{d} \pm 13.65$
HP12ST3	$64.41^{c} \pm 1.00$	-	-	-

Note: Each value is mean of duplicate ± SD.

The different superscripts in the column denote the significant differences (p<0.05).

Table 2. Hydroxypropyl and phosphorus content, molar substitution (MS) and degree of substitution (DS) of native and dual-modified rice starches hydroxypropylated with propylene oxide of 6% (HP6), 8% (HP8), 10% (HP10) , and 12% (HP12) and cross-linked with the mixture of 12% STMP and 0.1% STPP(ST3).

Sample	Hydroxypropyl content (%)	MS	Phosphorus content (%)	DS
Native	$0.1876^{e} \pm 0.0000$	$0.0052^{e} \pm 0.0000$	$0.015^{e} \pm 0.000$	$0.001^{e} \pm 0.000$
HP6ST3	$0.3215^{d} \pm 0.1030$	$0.0088^{d} \pm 0.0028$	$0.083^{d} \pm 0.002$	$0.004^{d} \pm 0.000$
HP8ST3	$0.6211^{c} \pm 0.0111$	$0.0171^{c} \pm 0.0003$	$0.161^{c} \pm 0.004$	$0.009^{c} \pm 0.000$
HP10ST3	$0.7967^{b} \pm 0.0101$	$0.0220^{b} \pm 0.0003$	$0.259^{b} \pm 0.009$	$0.014^{b} \pm 0.001$
HP12ST3	$0.9729^{a} \pm 0.0068$	$0.0269^{a} \pm 0.0002$	$0.283^{a} \pm 0.007$	$0.015^{a} \pm 0.000$

Note : Each value is mean of duplicate ± SD.

The different superscripts in the column denote the significant differences (p<0.05).

Table 3. Pasting properties of native and dual-modified rice starches hydroxypropylated with propylene oxide of 8% and cross-linked with of 2% STMP (HP8ST1), the mixture of 2% STMP and 5% STPP (HP8ST2) and the mixture of 12% STMP and 0.1% STPP (HP8ST3).

Sample	Pasting Temperature (°C)	Peak (mPa.s)	Breakdown (mPa.s)	Setback (mPa.s)
Native	$68.55^{a} \pm 0.00$	$2950.00^{a} \pm 49.50$	$1097.50^{a} \pm 58.69$	$879.00^{b} \pm 1.41$
HP8ST1	$66.10^{b} \pm 0.07$	$1238.75^{d} \pm 36.09$	$10.25^{d} \pm 4.11$	$476.75^{d} \pm 37.66$
HP8ST2	$66.37^{b} \pm 0.46$	$1709.3^{b} \pm 13.61$	$307.33^{b} \pm 9.07$	$1476.67^{a} \pm 32.72$
HP8ST3	$66.63^{b} \pm 0.62$	$1422.00^{c} \pm 96.35$	$138.17^{c} \pm 21.02$	$557.20^{c} \pm 57.12$

Note : Each value is mean of duplicate ± SD.

The different superscripts in the column denote the significant differences (p<0.05).

Table 4. Hydroxypropyl and phosphorus content, molar substitution (MS) and degree of substitution (DS) of native and dual-modified rice starches hydroxypropylated with propylene oxide of 8% and cross-linked with of 2% STMP (HP8ST1), the mixture of 2% STMP and 5% STPP (HP8ST2) and the mixture of 12% STMP and 0.1% STPP (HP8ST3).

Sample	Hydroxypropyl content (%)	MS	Phosphorus content (%)	DS
Native	$0.1876^{c} \pm 0.0000$	$0.0052^{c} \pm 0.0000$	$0.015^{d} \pm 0.000$	$0.001^{d} \pm 0.000$
HP8ST1	$0.5602^{b} \pm 0.0000$	$0.0154^{b} \pm 0.0000$	$0.192^{a} \pm 0.009$	$0.010^{a} \pm 0.001$
HP8ST2	$0.5567^{b} \pm 0.0034$	$0.0153^{b} \pm 0.0001$	$0.053^{c} \pm 0.002$	$0.003^{c} \pm 0.000$
HP8ST3	$0.7967^{a} \pm 0.0101$	$0.0220^{a} \pm 0.0003$	$0.161^{b} \pm 0.004$	$0.009^{b} \pm 0.000$

Note : Each value is mean of duplicate ± SD.

The different superscripts in the column denote the significant differences (p<0.05).

CONCLUSIONS

The dual-modified Jasmine rice starch which was done under selected conditions, found that the mixture of STMP and STPP was more efficient in cross-linking than STMP alone. Greatly altered Jasmine rice starch was obtained by hydroxypropylation with 10-12% propylene oxide, following by cross-linking with a mixture of STMP and STPP. Under these conditions of dual-modification, the hydroxypropylated cross-linked Jasmine rice starch would have the desirable starch properties which is resistant to heat and shear

ACKNOWLEDGEMENTS

The authors would like to express their sincere thanks to graduated school, Prince of Songkla University for supporting this research.

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