

MAKALAH PENELITIAN

SOME CHARACTERISTICS OF CROSS-LINKED HYDROXYPROPYL SAGO STARCH^{*})

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ABSTRACT

Sago starch was laboratory hydroxypropylated using 1% propylene oxide in alkaline condition, then cross-linked using 0.000–0.025% phosphorus oxychloride. The dual modified starches with level of cross-linking ranging from 0.0000 to 0.0186 were characterized for amylographic properties, swelling power, paste turbidity, and *in vitro* digestibility using porcine pancreatic α -amylase.

The cross-linking procedure applied to dual modification nearly unchanged the pasting temperature, i. e. at 62.5°C. Cross-linked, hydroxypropyl starches with DS more than 0.0150 had similar amylographic properties which showed high heat and shear stability of the paste. Cross-linking resulted in decrease in the swelling power and the *in vitro* digestibility of the starch.

Hydroxypropylation prior to subsequent modification facilitate the cross-linking with a consequence of lower pasting temperature, higher maximum viscosity, higher swelling power, and lower digestibility.

INTRODUCTION

Sago starch has been mainly a product of local importance throughout the mainland and islands of South East Asia. Modification of starch properties by derivatization is an important factor in the continued and increased use of starch in industry.

Starches commonly used for commercial modification are corn, waxy maize, tapioca, and potato (Rutemberg and Solarek, 1984). Derivatives of other less available starches, such as oil palm and sago may be offered commercially.

Starch granule is not structurally homogeneous from a physical and chemical point of view. Amylose is the main component of crystalline region which more tightly packed. Amylopectin, the branched portion, is packed in amorphous region which the most readily penetrable by water and low

molecular weight water soluble solutes (French, 1984). Functional groups can be introduced in starch molecules by a number of chemical modification techniques. Jane *et al.* (1992) reported that when granular starch was cross-linked, more amylopectin than amylose were found cross-linked.

Proportions of both amylose and amylopectin depend on starch sources (Lineback, 1984). Difference in botanical origin may also relate to difference in accessibility of starch to derivatization with a consequence of difference in reaction condition and in level of modifying agent used to yield similar degree of substitution.

Cross-linking and substitution are two widely used methods for making modified starches. Cross-linked starch is more resistant to acid, heat, and shear than is native starch. Therefore, cross-linked starch is suitable for canned food, surgical dusting powder, and other applications. Hydroxypropylation is one of the substitution methods to improve starch properties for food application. Hydroxypropyl group can be introduced, into starches in order to lower the gelatinization temperature of granular starches, to decrease in retrogradation and gelling tendencies of amylose-containing starches, to increase the water holding capacity of starch dispersions under low-temperature storage condition, thereby extending their usefulness in food or industrial applications (Rutemberg and Solarek, 1984).

Cross-linked as well as cross-linked, hydroxypropylated starches are extensively used throughout the food industry to thicken, stabilize, and texturize food systems. The starches not only play important role in terms of the properties of the final product but are also an important factor in facilitating processing and storage (Wurzburg, 1995).

Yeh and Yeh (1993) found that the procedure used to prepare dual-modified starches affected the product properties. Cross-linking prior to hydroxypropylation reduced the degree of subsequent substitution, but hydroxypropylation increase the degree of subsequent cross-linking.

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This study was to evaluate the properties of sago starch after hydroxypropylation and cross-linking, including their paste properties, for possible future application.

MATERIALS AND METHODS

Materials

Sago starch was purchased from a local market. Water content of the starch was 11.8% which was determined by using a method of AOAC (1970) and amylose content was 24.0% based on the method of Juliano (1971).

Water was glass distilled and all reagents were of analytical grade.

Modification

Hydroxypropyl starch was prepared from sago starch as described by Leegwater and Luten (1971) using 1% propylene oxide in the presence of alkali for good reaction efficiency and sodium sulfate added to repress the swelling tendency.

Cross-linking was conducted using phosphorus oxychloride (POCl_3) by a method described by Wu and Seib (1990). Starch was dispersed in aqueous alkali (pH 10.5) containing sodium sulfate (Na_2SO_4 , 5% based on dry weight of starch). The concentration of starch in the slurry was 35%. The mixture was then heated to 35°C and 0.000%, 0.005%, 0.010%, 0.015%, 0.020%, and 0.025% POCl_3 based on the dry weight of starch was added. The reaction mixture were maintained at 35°C for 60 min. The samples were then neutralized using 1 N HCl to terminate the reaction, and washed with distilled water prior to freeze drying.

Degree of Substitution

The level of cross-linking was analyzed according to Koch et al. (1982). The starch sample was acidified with 0.1 N HCl to form H-cross-linked starch, and then washed with distilled water and dried in a vacuum oven at 40°C. The dried H-cross-linked starch was then titrated with 0.001 N NaOH. The degree of substitution was calculated using the method of Rutenberg and Solarek (1984).

Starch Paste Properties

The pasting behavior of starch sample was examined in a Brabender Amylograph (Brabender OHG, Duisburg).

The standard procedure (Shey and Tripple, 1980) was followed, using 5% starch suspension for all starch samples. The following measurements were taken from an amylograph curve: the pasting temperature, the peak consistency during the heating stage at a rate of 1.5°C per min, the consistency after being held at 95°C for 30 min.

Swelling power of granular starch was determined as described by Swinkels (1988). A mixture of starch (0.75 g) and water (25 ml) was heated in a centrifuge tube at a certain temperature of pasting for 30 min and gently stirred using a magnetic bar. Immediately after centrifuging, the weight of sediment was determined using phenol-sulfuric acid (Dubois et al., 1956). Swelling power was calculated as the ratio of the wet mass of sedimented gel to the dry matter in the gel.

Starch paste obtained from the amylographic examination was cooled to room temperature, and then the turbidity was measured using turbidimeter.

Enzyme

Porcine pancreatic α -amylase, α -1-4-glucan-4-glycano-hydrolase, E. C. 3.2.1.1., 10 mg/ml with specific activity of 1000 I. U. was obtained from Böehring-Mannheim GmbH. The enzyme was diluted with phosphate buffer to obtain 10 μ /ml. Phosphate buffer was composed of 1.02% KH_2PO_4 , 1.065% Na_2HPO_4 , 1% NaCl and 0.4 NaN_3 in distilled water.

Digestibility

Starch digestibility was measured based on the method of Leegwater and Luten (1971). Starch (40 g) dispersed in a 60 ml test tube was heated in a boiling water bath for 30 min with mechanical stirring. The solution was cooled to 37°C, and mixed with 2 ml of the enzyme solution (10 μ /ml likewise brought to 37°C). The mixtures were kept at 37°C and occasionally shaken during 60 min before analysis for reducing power.

The amounts of reducing sugars released by the enzymatic hydrolysis were determined spectrophotometrically with 3, 5-dinitrosalicylic acid (1% in 0.4-M NaOH containing 30% sodium potassium tartrate) according to the method of Bruner (Whistler, 1964). Maltose was used as calibration standard. Percent hydrolysis was calculated as:

$$\frac{\text{mg of maltose from Standard Curve}}{\text{mg of starch (dry basis)}} \times 100$$

RESULTS AND DISCUSSION

Cross-linking of native sago starch with 0.000–0.025% POCl_3 gave modified starches having DS 0.0000 – 0.0059 (Table 1), while cross-linking of hydroxypropylated sago starch with 0.000 – 0.025% POCl_3 resulted in the dual-modified starches with DS 0.0000 – 0.0186 (Table 2).

Table 1. POCl_3 used in cross-linking of sago starch and characteristics of the modified starch

POCl_3 (%)	DS	Pasting temperature (°C)	Maximum Viscosity (BU)	Swelling power (g/g)	Turbidity (Turbidity unit)	Digestibility (%)
0.000	0.0000	70.5	340	30.3	158	38.8
0.005	0.0055	69.4	–	22.3	184	38.2
0.010	0.0055	70.7	–	19.7	316	37.3
0.015	0.0056	71.4	–	18.0	276	36.4
0.020	0.0057	71.1	–	16.7	237	35.5
0.025	0.0059	70.9	–	15.6	263	34.8

Increase in POCl_3 used in cross-linking of the native starch only gave no significant increase in DS of the modified samples. This possibly indicated compactness of the sago starch granules containing 24.0% amylose. As a result, the DS of cross-linking was very low. Previously reported work indicated that hydroxypropyl maize starch containing higher amylose was less substituted (Wootton and Haryadi, 1992). Yeh and Yeh (1993) reported that cross-linking of rice starch containing 14.2% amylose with 0.1% POCl_3 gave the product with low DS (0.0003).

Hydroxypropylation appeared to facilitate the subsequent cross-linking as shown by Table 2 compared to the data in Table 1. Higher DS values were observed when the starch was hydroxypropylated before cross-linking was effected. This was in accordance with the previously reported work by Yeh and Yeh (1993). Kim *et al.* (1992) noted that introduction of hydrophilic group, such as hydroxypropyl group, decreased in associative forces within the starch granule, thereby altered the characteristics of the starch.

Table 2. POCl_3 used in cross-linking of hydroxypropyl sago starch and characteristics of the dual modified starch

POCl_3 (%)	DS	Pasting temperature (°C)	Maximum Viscosity (BU)	Swelling power (g/g)	Turbidity (Turbidity unit)	Digestibility (%)
0.000	0.0000	62.5	501	33.3	267	29.6
0.010	0.0150	61.0	404	32.4	295	29.6
0.015	0.0168	61.0	422	32.1	305	29.6
0.020	0.0175	62.2	422	30.1	362	28.4
0.025	0.0186	62.5	490	29.3	750	38.0

Cross-linking procedure employed in this experiment only slightly altered the pasting temperatures. Increase in DS caused decrease in maximum viscosity of the starch paste, decrease in swelling power, increase in turbidity and lower digestibility (Table 1 and Table 2). Pasting temperature of the cross-linked starch at DS 0.0055 (Table 1) and those of the dual-modified starches at DS 0.00150 and 0.0168 (Table 2) seemed to be lower than those of any other related samples. Probably, it was due to the modifying procedure in alkaline condition using low level of POCl_3 facilitating the amorphous fraction of starch granules to gelatinize. Kim *et al.* (1992) reported that alkaline treatment could change starch granular structure causing the starch more easily gelatinize. Further more, the effect of modification at such low level was likely quite small compared to the consequence of the alkaline treatment.

Increase in DS effected increase in the reluctance of the starch to gelatinize as also shown by the amylographs (Figure 1 and Figure 2). Treatment of the pastes of cross-

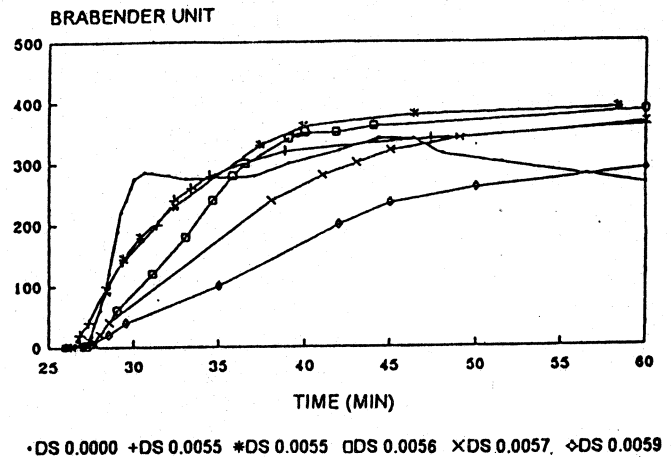


Figure 1. Pasting curves of cross-linked sago starches (DS 0.0000 – 0.0059)

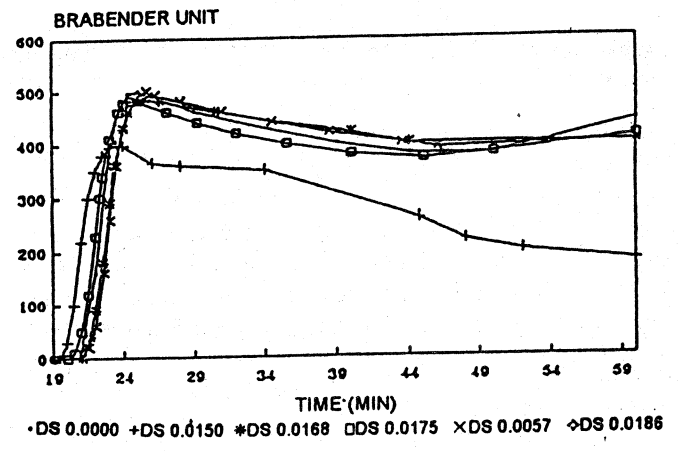


Figure 2. Pasting curves of cross-linked hydroxypropyl sago starches (DS 0.0000 – 0.0186)

linked starches at 95°C for 30 min unchanged the paste viscosity indicating their heat and shear stability. Further increase in viscosity during heat treatment indicated that the cross-linked starches (DS 0.0055 – 0.0059) had not swollen completely to reach the maximum viscosity (Figure 1 and Table 2).

Hydroxypropylation prior to cross-linking made the dual-modified products more easily gelatinize as indicated by lower pasting temperature, high maximum viscosity, and higher swelling power. Probably, decrease in associative bonding in hydroxypropyl starch granules as reported earlier (Kim *et al.*, 1992) caused the starch more easily penetrated by water, therefore they were more susceptible to gelatinization, resulting in significant changes in the pasting properties. The amylographic curves also exhibited that cross-linking enhanced the strength of the swollen hydroxypropyl starch granule.

Gel turbidity is a simple measure of starch retrogradation occurring after cooling of gelatinized starch (Swinkels, 1988). Yet, the increase in turbidity with increase in DS (Table 1 and Table 2) might indicate that the swelling of starch granules was progressively less as the starches more cross-linked as shown by their swelling power and their amylographic pattern (Figure 1 and Figure 2). Smith (1982) noted that ungelatinized starch slurry generally appears opaque, and then the dispersion gradually becomes clear when the starch gelatinizes. Opacity is often an indication of unswollen granules or under-cooking.

Modification effected the *in vitro* digestibility of gelatinized starch samples. Starch derivatives with higher level of cross-linking (DS) were more resistant to α -amylolysis. The cross-linking showed a significant effect on the digestibility of sago starch. Different result due to cross-linking has been reported that cross-linking had only a small effect on the digestibility of wheat starch (Wootton and Chaudhry, 1979).

Hydroxypropylation before cross-linking made the dual-modified starches more difficult to digest. But, the effect of cross-linking on the digestibility of hydroxypropyl sago was small, which was in a good agreement with those previously reported work (Wootton and Chaudhry, 1979).

The digestibility of cross-linked, hydroxypropyl sago starches at DS 0.00150 – 0.0168 were similar to that of the uncross-linked hydroxypropyl sago starch sample. Again, an explanation offered for this was possibly due to the alkaline condition applied during the chemical reaction resulting in the starch granular structure more susceptible to enzyme attack; and the effect of alkali was more prominent than the consequence of cross-linking.

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REFERENCES

- AOAC, 1970. Official methods of analysis of the Association of Official Analytical Chemists. AOAC, Washington.
- Dubois, M., Gilles, K. A., Hamilton, J. K., Reber, P. A. and Smith, F., 1956. Colorimetric method for determination of sugars and related substances. *Anal. Chem.* 28: 350.
- French, D., 1984. Organization of starch granules. *In: Starch chemistry and technology*. R. L. Whistler, J. N. BeMiller and E. F. Paschall (eds.), pp. 184 – 248.
- Kim, H. R., Hermansson, A. M. and Ericksson, C. E., 1992. Structural characteristics of hydroxypropyl potato starch granules depending on their molar substitution. *Starch/Starke* 44: 111 – 116.
- Koch, V. H., Bommer, H. D. and Kopper, J., 1982. Analytische untersuchung von phosphatevernetzten starcken. *Starch/Starke* 34: 16 – 21.
- Jane, J., Xu, A., Radosavljevic, M. and Seib, P. A., 1993. Location of amylose in normal starch granules. I. Susceptibility of amylose and amylopectin to cross-linking reagents. *Cereal Chem.* 69: 405 – 409.
- Juliano, B.O., 1971. A simplified assay for milled rice amylose. *Cereal Sci. Today* 16: 334 – 340.
- Leegwater, D. C. and J. B. Luten, 1971. A study on the *in vitro* digestibility of hydroxypropyl starches by pancreatin. *Starch/Starke* 23: 430 – 432.
- Lineback, D. R., 1984. The starch granule organization and properties. *Baker's Dig.* 17.
- Rutenberg, M. W. and D. Solarek, 1984. Starch derivatives: Production and uses. *In: Starch chemistry and technology*. R. L. Whistler, J. N. BeMiller and E. F. Paschall.
- Shuey, W. C. and Tripple., H., 1980. The amylograph handbook. AACC.
- Smith, P. S., 1982. Starch derivatives and their use in foods. *In: Food carbohydrates*. D. R. Lineback and G. E. Inglett (eds.), pp. 237 – 269.
- Swinkels, J. J. M., 1988. Starch terminology: Definitions and discription of important terms of the starch chemistry and starch technology. AVEBE, Foxhol.
- Whistler, R. L., 1964. *Methods in carbohydrate chemistry*. Vol. 4, Academic Press, New York.
- Wootton, M. and Chaudry, M. A., 1979. Enzymic digestibility of modified starches. *Starch/Starke* 31: 224 – 228.
- Wootton, M. and Haryadi, 1992. Effects of Starch and preparation condition on substituent distribution in hydroxypropyl starches. *J. Cereal Sci.* 15: 181 – 184.

Wu, Y. and P. A. Seib, 1980. Acetylated and hydroxypropylate distarch phosphates from waxy barley: Paste properties and freeze-thaw stability. *Cereal Chem.* 67: 202 – 208.

Wurzburg, O. B., 1995. Modified starches. *In: Food polysaccharides and their application.* A. M. Stephen (Ed.) pp. 67 – 98.

Yeh, A. I. and S. L. Yeh, 1993. Some characteristics of hydroxypropylated and cross-linked rice starch. *Cereal Chem.* 70: 596 – 601.