Characteristics of Cross-Linked Oil Palm Starch[1]

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ABSTRACT

Oil palm starch was cross-linked with 0.005-0.025% phosphorus oxychloride ($POCl_3$) in alkaline solution. The modified starches were analyzed for degree of substitution (DS), amylographic properties, swelling power, paste turbidity, and in vitro digestibility using porcine pancreatic α-amylase. The results suggested that the cross-linking procedure afforded modified starches with DS of 0.0134-0.0184. Increase in the use of $POCl_3$ resulted in a higher DS of the starch derivative. Starting at the use of 0.015% $POCl_3$ the DS tended to level off. Cross-linking caused the starch more stable to heat and shear, decreased the swelling power, and increased in the paste turbidity. The solubility and digestibility of starch with a DS of 0.0134 were slightly increased, while starches with higher DS were less soluble and less digestible.

INTRODUCTION

The production of palm oil has tremendously increased since the 1970s, especially in Malaysia and Indonesia (Nishino, 1988; *in* Tomimura, 1992). Oil palm tree are usually replanted in every 25 years of its economic life span. In Indonesia, in 2010, more than 1 million ha of oil palm plantation area will comprise 25 year's old trees (Manalu *et al.*, 1994). It is estimated that the amount of trunks available is at the rate of 84 ton/ha (Megat Ayub, 1985; *in* Tomimura, 1992).

The trunk after debarking comprises 71-76% vascular bundles and 24-29% parenchymas. The parenchymas contains 55% starch (Tomimura, 1992). Extraction of the parencymas from the upper part of the trunk yielded 11.16% starch (Kapti Rahayu Kuswanto *et al.*, 1995). The starch extracted might be used in food industry.

Cross-linking is a widely used method for making modified starch. 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 (Rutenberg and Solarek, 1984). These starches are also an important factor in facilitating processing and storage (Wurzburg, 1995).

The objectives of this study was to evaluate the properties of oil palm starch after cross-linking by using $POCl_3$, including their paste properties, for future application.

MATERIALS AND METHODS

Materials

Oil palm starch was isolated from the trunk parenchymas of 25 years oil palm tree. The starch contained water (12.07%), amylose (37.3%), protein (0.41%), fat (0.003%), ash (0.6%), and phosphorous (0.08%) (Kapti Rahayu Kuswanto *et al.*, 1995).

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

Cross-linking Reaction

Cross-linked oil palm starches of five different degree of substitution (DS) were laboratory prepared with 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 0.005%, 0.01%, 0.015%, 0.020%, and 0.025% $POCl_3$ based on the dry weight of starch was added. The reaction mixtures 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 before freeze drying.

Starch characterization

The starches were analyzed for degree of substitution, paste propeties, and *in vitro* digestibility. Native oil palm starch was included for comparison.

Degree of substitution

The level of cross-linking was analyzed according to Koch *et al.* (1982). The modified starch sample was acidified to form H-cross-linked starch using 0.1 *N* HCl. Sodium ions bound to phosphate groups were replaced by hydrogen ions during acidification. H-cross-linked starch was 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 method of Rutenberg and Solarek (1984).

Starch Paste Properties

The pasting behavior of starch sampel was examined in a Brabender Amylograph. The standard procedure (Shuey 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 and solubility of granular starch was determined as described by Swinkles (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 the sedimented gel to the dry matter in the gel. Solubility was calculated as the percent of starch dissolved in the continuous liquid phase.

The turbidity of starch paste obtained from the amylographic examination, which had been cooled to room temperature, was evaluated 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 Bõehringer-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.

In vitro digestibility

Starch digestibility was measured based on the method described by Leegwater and Luten (1971). Starch (40 mg) dispersed in 8 ml of water 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 saccharides released by the treatment with pancreatin were determined spectrometrically 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

A preliminary experiment to cross-link oil palm starch have been conducted with the concentration of $POCl_3$ being around 0.1% similar to the level applied to modify rice starch containing 14.2% amylose (Yeh and Yeh, 1993). Amylographs of the cross-linked starch pastes showed that all the starches were so resistant to gelatinization that no maximum viscosity reached. This indicated that the degree of cross-linking was too high. A microscopic examination confirmed that the treated starches hardly swelled. Since the use of starch, particularly in food industry, is mostly at gelatinized state, and according to Wurzburg (1995), cross-linking is usually developed only to minimize granule rupture during the cooking process. Therefore, further work employing these levels of $POCl_3$ addition was abandoned.

Cross-linking with 0.005-0.025% $POCl_3$ resulted in modified starches having DS 0.0134-0.0184 (Table 1). Beginning with addition of 0.015% $POCl_3$, the reaction resulted in the cross-linked starches with DS tending to level off. This possibly indicated compactness of the starch granules containing high amylose (37.3%) which were difficult to modify. As a result, the level of cross-linking was very low. Previously reported work indicated that hydroxypropyl maize starch containing higher amylose was less substituted (Wootton and Haryadi, 1992). In accordance with this result, Yeh and Yeh (1993) reported that cross-linking of rice starch containing 14.2% amylose with 0.1% $POCl_3$ gave the product with DS 0.03%.

Increase in DS resulted in increase in the reluctance of the modified starches to gelatinize as shown by the amylograph (Figure 1). Treatment of the pastes of modified starches at 95°C for 30 min (Figure 1) unchanged the paste viscosity indicating their heat and shear stability. Further increase in viscosity during the heat treatment indicated that the cross-linked starches had not swollen completely to reach the maximum viscosity.

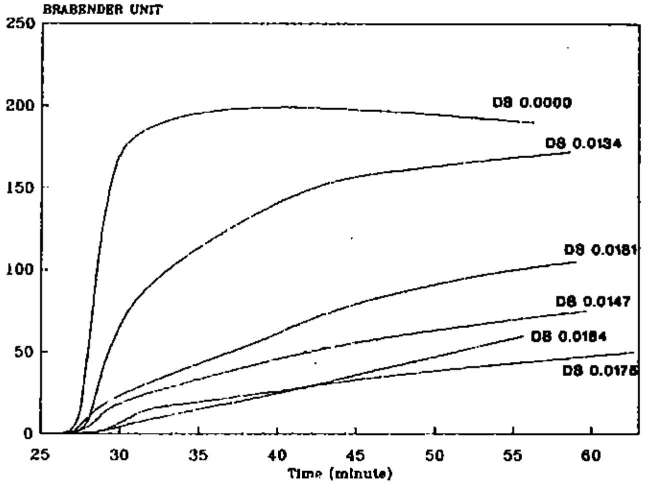

Figure 1. **Amylographs of native and cross-linked oil palm starch (DS 0.00134-0.0184)**

Solubility of the cross-linked starch with DS 0.0134 was higher than that of the unmodified sample (Table 1). This possibly was due to the cross-linking procedure in alkaline condition using very low level of $POCl_3$ (i. e. 0.005%) facilitating the amorphous fraction of starch granules to disolve in water. It was previously reported that alkaline treatment could change starch granule structure (Kim *et al.*, 1992), and consequently the starch gelatinized more easily in alkaline condition (Takahashi and Wada, 1992). Furthermore, the effect of modification at such low level was likely quite small compared to the consequence of the alkaline treatment. Higher level of cross-linking resulted in lower solubility.

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

Table 1. **$POCl_3$ used in cross-linking of oil palm starch and characteristics of the modified starch**

$POCl_3$ (%)	DS	Pasting temperature (°C)	Swelling power (g/g)	Solubility (%)	Turbidity (Turbidity unit	Digestibility (%)
0.000	0.0000	71.5	23.6	2.7	434	37.9
0.005	0.0134	71.6	18.2	3.8	658	36.8
0.010	0.0147	71.6	14.0	2.8	1368	39.1
0.015	0.0175	72.9	14.1	3.3	1105	39.5
0.020	0.0181	70.8	14.3	3.3	1578	33.6
0.025	0.0184	73.0	13.3	3.3	1592	33.0

Starch digestibility was examined at gelatinized state, based on the fact that most of starch use is at that condition. The starch with DS 0.0134 was more digestible than that of the unmodified starch as shown in Table 1. This phenomenon was likely similar to that of starch solubility, showing that starch at such level of cross-linking was more soluble than the starches with higher DS (Table 1). The alkaline condition during the cross-linking reaction likely enhanced the starch susceptibility to α-amylase attact, and this effect was more intensive than that of the cross-linking at such very low level.

Starches with DS hinger than 0.00134 were more resistance to α-amylolitic digestion (Table 1). However, at such low level of cross-linking most of the unhydroglucose units in the starches were unchanged resulting products retained the nutritive values associated with the native starch as indicated by their digestibility.

CONCLUSION

Cross-linking of starch extracted from oil palm trunk using 0.005-0.025% $POCl_3$ gave the modified products with DS 0.0134-0.0184. The use of $POCl_3$ more than 0.015% resulted in the cross-linked starch with tendency of DS to level off. Increase in DS caused the starch more difficult to paste. Cross-linked starch at DS 0.005 was more soluble and more digestible than the native starch. While at higher DS the starch was less soluble and less susceptible to enzymic digestion.

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