SOME CHARACTERISTICS OF OIL PALM AND SAGO STARCH ACETATES[1)]

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ASTRACT

Pati kelapa sawit dan pati sagu diasetilasi dengan anhidrid asetat pada suhu 25°C dalam larutan alkali. Tingkat pemberian anhidrit asetat adalah 2,5 - 15,0 %, berdasar berat kering pati. Pati asetat yang diperoleh dicirikan mengenai tingkat substitusi (DS), perilaku pembentukan pasta, kemampuan penggelembungan, dan kedapatcernaannya menggunakan α - amilase pankreas babi.

Hasilnya menunjukkan bahwa makin banyak tingkat pemberian anhidrid asetat menghasilkan pati dengan DS makin besar.

Prosedur modifikasi yang dilakukan menghasilkan turunan pati dengan DS 0,007 - 0,095 untuk pati kelapa sawit, dan DS 0,041 - 0,056 untuk pati sagu. Asetilasi berakibat menurunkan suhu pembentukan pasta, meningkatkan kemampuan penggelembungan, dan menurunkan kedapatcernaannya secara in vitro. Pati kelapa sawit dan turunannya memiliki suhu pembentukan pasta yang lebih rendah dari pada pati sagu dan turunannya. Sifat-sifat pati kelapa sawit mirip dengan sifat-sifat pati sagu dalam beberapa hal.

INTRODUCTION

Starch is a biopolymer occuring naturally in the form of insoluble minute granule. The granule structure is not homogeneous from physical and chemical points of view, depending on the botanical origin and the chemical composition (French, 1984). Therefore, the penetrability of different starches by water and low molecular weight water soluble solutes vary. In the case of chemical reaction involving substitution of the hydroxyl groups in starch molecule, the readiness of different starches to bind substituting compound may consequently vary. Hence, similar condition of chemical convertion of different starch may result in different degree of substitution (DS), and thereby, differently alter physicochemical characteristics of the starch.

Starch derivatization is conducted to modify the cooking and gelatinization characteristics of granular starch, to decrease the retrogradation and gelling tendencies, to increase water holding capacity of starch dispersions at low temperature, to enhance hydrophylic character, to impart hydrophobic properties, and/or to introduce ionic substituents. Chemical modification is an important factor to extend the usefulness of starch. Starches commonly used for commercial modification are corn, waxy maize, tapioca, and potato (Rutenberg and Solarek, 1984). Oil palm (Haryadi et al., 1996) and sago (Flach, 1983) trunks have a great potency as sources of starch in Indonesia. Derivatives of both the starches may be offered commercially.

Acetylation is one of the methods to modify functional propertis of starch to suit industrial applications. The introduction of acetyl group weakens granule structure slightly so that swelling and gelatinization can take place at lower temperature, besides, it stabilizes starch against retrogradation and inter-molecular association. Starch acetate is widely used in food, textile, paper industries, and others (Wurzburg, 1995).

The present study investigates the effect of acetylation of oil palm and sago starches on the characteristics of the modified products. The data are generally required to consider application of the starches.

MATERIALS AND METHODS

Materials

Trunks of 25 years oil palm tree were obtained from the experimental garden of the Faculty of Agriculture, Gadjah Mada University. The trunks were debarked and stored at 4°C until starch extraction was conducted.

Oil palm starch was isolated by the following procedure. The debarked trunks were disintegrated prior to sieving to obtain the parenchymas which were then subjected to blending with water in several batches. The blended parencymas were transferred into cotton bags and squeezed and the filtrate was centrifuged. The residue was blended again to extract residual starch. The washing using a centrifugal separator was repeated twice. The starch was freeze dried.

The oil palm starch contained amylose (37.3%) and water (12.07%). Sago starch purchased from local market, contained amylose (34.4%) and water (11.8%) amylose.

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

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Acetylation

The method of Wurzburg (1964) was followed. Starch (100 g) was dispersed in 500 ml of aquadest and stirred for 30 min using a magnetic bar to obtain a uniform suspension. The pH of the slurry was adjusted to 8.0 with 1 N NaOH and acetic anhydride (2.5, 5.0, 7.5, 10.0, 12.5, and 15.0% w/w, based on dry weight of starch) added slowly to the slurry. The reaction mixture was stirred constantly and the pH of the slurry was monitored beetwen 8.0-8.4. The reaction was allowed to preceed for an additional 5 min after completion of the acetic anhydride addition. The pH of the slurry was finally adjusted to 4.5 with 0.5 N HCl and filtered through Whatman filter paper #4. The residue was then washed five times with aquadest and then freeze dried.

Starch characterization

The starches were analized for DS, pasting behaviour, swelling power, and *in vitro* digestibility. Native starches were included for comparison.

Degree of substitution

DS of the acetylated starches were determined according to Wurzburg (1964). Starch (5 g) was dispersed in 75% aqueous ethanol and warmed for 30 min on a water bath (50°C), cooled to room temperature, and 25 ml of 1 N NaOH added. The stoppered flask was then allowed to stand for 72 hr with occasional shaking at room temperature. Excess NaOH was back titrated with 1 N HCl. The flask was allowed to stand at room temperature for 2 hr and then the titration completed.

Pasting Behaviour

Starch gelatinization curves were obtained by following the method of Shuey and Tripple (1980) using 5% starch suspension for all starch samples in a Brabender Amylograph. The following measurements were taken from an amylograph curve: the pasting temperature, the maximum consistency during the heating stage at a rate of 1.5°C per min, and the temperature at which maximum consistency was attained. Consistency was expressed in Brabender Unit (BU).

Swelling power 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 pasting temperature for 30 min and magnetically stirred. Swelling power was calculated as the ratio of the wet mass of the sedimented gel to the dry matter in the gel.

Enzyme

Porcine pancreatic α-amylase, α-1-4-glucan-4-glycano-hydro-lase, E. C. 3.2.1.1., 10 mg/ml with specific activity of 1000 I. U. was obtained from Boehringer-Mannheim GmbH. The enzyme was diluted with phosphate buffer to obtain 10 /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 expressed as percent hydrolysis was measured based on the method of 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 prior to analysis for reducing power.

The amounts of reducing sugars liberated by the treatment with the enzyme were determined spectrometrically with 3, 5-dinitro- salicylic acid (1% in 0.4-*M* NaOH containing 30% sodium potassium tartrate) at 540 nm according to the method of Bruner (Whistler,

Table 1. The amounts of acetic anhydride used to prepare oil palm starch acetate and the characteristics of the modified staches

Aceticanhydride (%)	DS	Pasting temperature (°C)	Swelling power (g/g)	Maximum consistency (BU)	Maximum consistency temperature (°C)	Digestibility (%)
0.0	0.000	70.0	13.5	210	78.0	64.6
2.5	0.007	68.5	17.5	215	75.0	57.2
5.0	0.082	66.7	18.3	215	73.5	55.2
7.5	0.086	65.5	21.3	220	72.0	55.3
10.0	0.088	65.5	25.0	220	70.5	51.9
15.0	0.095	61.8	26.9	225	67.5	50.8

A blank with pure starch was conducted concurently and the DS calculated as follows:

$$\% \text{ Acetyl} = \frac{(\text{ml blank} - \text{ml sample}) \times \text{normality of HCl} \times 0.43 \times 100}{\text{Weight of sample (g) dry basis}}$$

$$DS = \frac{162 \times \% \text{ Acetyl}}{4300 - (42 \times \% \text{ Acetyl})}$$

1964). Maltose served as reference standard. Digestibility was calculated as:

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

RESULTS AND DISCUSSION

The effects of graded levels of anhydride used to acetylate oil palm and sago starches on DS, pasting properties and digestibility of the modified starches were as shown in Table 1 and Table 2, respectively.

Higher amount of acetic anhydride used to acetylate both native starches gave higher degree of substitution. The pasting temperature decreased with increasing acetyl content which was consistent with the earlier reported work (Wurzburg, 1995).

The starch acetates with higher DS showed more progresively decrease in pasting and maximum temperatures, increase in swelling power and maximum consistency, but decrease in *in vitro* digestibility (Table 1 and Table 2).

The reaction procedure gave oil palm starch acetates with DS ranging from 0.007-0.095. The acetylation not only reduced the pasting and maximum consistency temperatures, but also increased in maximum consistency and swelling power.

Ginting *et al.* (1996) studied the pasting characteristics of oil palm starch acetates and reported that acetylation took place more easily compared to the results shown in Table 1. Therefore, the resulted starch acetates at the same DS as those presented in Table 1 had lower pasting and maximum concistency temperatures and higher maximum consistency. This probably was ascribed to the drying procedure applied to the isolated native oil palm starch involving application of cabinet dryer at 50-60°C which might have caused irreversible structural change of the oil palm strach granules and subsequently facilitated the starch to bind the modifying group. Coinciding with this occurrence, Hoover and Vasanthan (1994) reported that anealing of native oat starch at 50°C for 0.5-72 h caused the starch less compactly packed, and therefore, the swelling factor decreased.

The tendency of alterations of sago starch properties by acetylation was similar to those encountered by the oil palm starch. The introduction of acetyl substituents took place more readily in oil palm starch than that in sago starch as indicated by higher DS obtained from the same level of acetic anhydride addition (data in Table 1 compared with those shown in Table 2). The acetylation procedure gave sago derivatives with DS ranging from 0.041-0.085 (Table 2). The difference in the readiness to bind the acetyl group was probably due to the difference in starch granular compactness.

The native oil palm starch contained 37.3% amylose, while the native sago starch sample contained 34.4% amylose. Higher amylose containing starch might not always neccesarily comprise more crystalline region as starch of different botanical origin might have different in tightness of granular packing. The less compactly packed starch granules are more penetrable by water and modifying agent (French, 1984), as a result the starches are more easily substituted.

Most of starch use is at gelatinized state, hence starch digestibility was measured at that state. The gelatinized parent oil palm starch showed more suceptible to amylolitic degradation than the sago starch did. This might also indicated that the oil palm starch granule was more tightly packed than the sago starch was.

Acetylation decreased the _in vitro™ digestibility of the starch derivatives (Table 1 and Tabel 2). The introduction of a functional group on one anhydroglucose unit was believed to protect neighboring units from enzymic attack. It was generally assumed that degradation of chemically modified starch with α-amylase decreased digestibility with increasing level of modification (Rutenberg and Solarek, 1984). However, at such level of substitution most of the unhydroglucose units in the starches remained unchanged and as a consequence the starches retained the nutritive values

Table 2. The amounts of acetic anhydride used to prepare sago starch acetate and the characteristics of the modified staches

Aceticanhydride (%)	DS	Pasting temperature (°C)	Swelling power (g/g)	Maximum consistency (BU)	Maximum consistency temperature (°C)	Digestibility (%)
0.0	0.000	69.0	19.1	180	76.5	62.3
2.5	0.041	68.5	25.6	260	76.0	57.8
5.0	0.056	68.5	26.0	260	75.5	56.7
7.5	0.060	65.5	25.8	262	75.0	55.0
10.0	0.077	67.0	25.0	264	74.0	53.4
15.0	0.085	66.0	27.0	272	73.5	53.4

associated with the native starch as indicated by their digestibility.

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