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Research Article

Structure and Functional Properties of Arenga Starch by Acetylation with Different Concentrations of Acetic Anhydride

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Abstract

Background and Objective: Arenga starch was extracted from the pith of sugar palm (*Arenga pinnata*), chemically modified by acetylation were produced acetylated arenga starches with different concentrations of acetic anhydride (4, 8, 12, 16% of starch basis). To evaluate the effect of acetylation on the structure and functional properties of chemical modified starches. **Materials and Methods:** The experimental research using material i.e., the arenga starch from the pith of palm sugar (*Arenga pinnata*), acetic anhydride 98%, NaOH, HCl, ethanol 96%, KOH 99.99%, H₂SO₄ 96.1%, KBr, acetone and olive oil. Methods i.e., acetylation of arenga starch, determination of acetyl percentage and degree of substitution, fourier transform infrared (FTIR) spectra, X-ray diffraction, water and oil holding capacity, swelling power and solubility, crude fiber. Data were assessed by one-way analysis of variance and were carried out with Duncan's multiple test ($p \leq 0.05$). **Results:** The percentage of acetyl groups and degree of substitution increased with increasing in concentrations of acetic anhydride. Fourier transform infrared spectra of acetylated arenga starches additionally showed bands of varying intensity attributable to the acetyl groups introduced of the ester group in the sign to 1720.50-1728.22 cm⁻¹. All starch granules were pattern of A-type crystallinity and relative crystallinity of acetylated arenga starches were lower than that native arenga starch. The water holding capacity, oil holding capacity, swelling power and fibre content of acetylated arenga starches increased but solubility decreased with the increasing in concentrations of acetic anhydride. **Conclusion:** Acetylated arenga starches were synthesized with acetic anhydride for use in food.

Key words: Acetylation, acetylated arenga starches, swelling power, crude fiber, chemical modified starches, acetic anhydride, arenga starch, functional properties arenga starch

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Competing Interest: The authors have declared that no competing interest exists.

Data Availability: All relevant data are within the paper and its supporting information files.

INTRODUCTION

Starch, the major storage polysaccharide in plants is widely used in food industry as thickening agent or stabilizer in order to provide some properties such as texture and appearance. In some cases, native starch does not meet the functional properties required in food products. Therefore, starches used in food industry are often modified to overcome undesirable changes in product texture and appearance caused by retrogradation or breakdown of starch during processing and storage^{1,2}.

In the acetylation process, the hydroxyl groups of the anhydroglucose unit of the starch molecule have been transformed to the acetyl groups³. The incorporation of acetyl groups promotes the reduction in the interactions between the outer chains of amylopectin and amylose chains, conferring new features to the polymer. Acetic anhydride is commonly used as an acylating agent and the reaction is activated in the presence of an alkaline catalyst⁴.

The acetylation of the starches and efficiency of the reaction depends on certain factors, as the source of obtaining of the starch, concentration of the reagent, time of reaction, pH and presence of catalyst⁵. According to Singh *et al.*⁶ the acetylation is one of the most well studied and implemented chemical modifications at the industrial level and is based on the esterification of starch with acetyl groups to produce acetylated starches. The acetylated starch has applications which are completed dependent on the percentage of acetyl groups and degree of acetylation or the degree of substitution. The introduction of acetyl groups interrupts the ordered structure of native starch and interferes with the reassociation of amylose and amylopectin molecules in the gelatinized starch, leading to a decrease in the gelatinization temperature, an increase or decrease in the swelling power and solubility along with the storage stability⁷.

Previous studies on acetylated arenga starch have been reported by Rahim *et al.*⁸. They were studied the chemical and functional properties of acetylated arenga starches prepared at different reaction time. Arenga starch has been extracted from the pith of sugar palm trees and its native starch has limited of non and food applications, therefore its needs to be modified with using acetic anhydride to increase range of use. Previous research had never using at different acetic anhydride concentration for the modification of arenga starch. The objectives of this study was to evaluate structure and functional properties of arenga starch by acetylation with different concentrations of acetic anhydride.

MATERIALS AND METHODS

The laboratorial experiments: The experimental research done in the laboratorial experiments in Faculty of Agriculture Tadulako University. The study duration was 5 months from October, 2017-February, 2018.

Materials: The arenga starch from the pith of palm sugar (*Arenga pinnata*) used in this study was provided dry substance (12% of water content) and purity of the starch 91% from Sigi, Central Sulawesi province, Indonesia. The arenga starch contained 39% of amylose content. Acetic anhydride 98% was analytical grade reagent from Sigma-Aldrich Chemical Co. (St. Louis, MO, USA). The sodium hydroxide (NaOH) pellets 98% and hydrochloric acid (HCl) 37% were purchased from Merck. All the chemicals and reagents for analysis used in this work were of analytical grade purchased at local agent i.e. ethanol 96%, potassium hydroxide (KOH) 99.99%, sulfuric acid (H₂SO₄) 96.1%, potassium bromide (KBr), acetone and olive oil.

Methods

Acetylation of arenga starch: The method described by Phillips *et al.*⁹ with some modifications was to modify by acetylation the arenga starch. The arenga starch (100 g) was dispersed in distilled water (225 mL) and stirred for 60 min at 25 °C. The acetic anhydride of 4, 8, 12 or 16% (starch basis) was added drop to drop to the stirred mixture, while maintaining the pH was kept in an interval of 8.0±8.2 using 3.0% NaOH solution. After adding the reagent the reaction was kept for 45 min. The slurry was then adjusted to pH 5 with 0.5 M HCl, later it was washed free of acid twice with distilled water and once by ethanol to 96%. Finally, product was dried in an oven at 45 °C for 12 h. The acetylation (%), degree of substitution, fourier transform infrared spectra, X-ray diffraction, fiber content, water holding capacity, oil holding capacity, swelling power and solubility were calculated.

Determination of acetyl percentage and degree of substitution: The percentage of acetyl groups (Acetyl %) and degree of substitution were determined by titration according the method described by Sanchez-Rivera *et al.*¹⁰ with few modifications. Approximately 1 g of each sample was added to a glass jar with a lid along with 50 mL of 75% ethyl alcohol. The samples were heated in a water bath at 50 °C for 30 min and, after cooling, 40 mL of 0.5 M KOH was added. The excess alkali was titrated out with 0.5 M HCl using phenolphthalein as

an indicator. The neutralised solution was stirred for 2 h and excess alkali (which may have leached from the sample) was titrated. The average values for the titration of the native starch were used as a blank reaction. Initially, the acetyl (Ac%) was calculated as:

$$\text{Acetyl (\%)} = \frac{(\text{mL blank} - \text{mL sample}) \times \text{MHCl} \times 0.043 \times 100}{\text{Sample weight (g)}} \quad (1)$$

DS is denoted as the average number of sites per glucose unit that receives a substituent group:

$$\text{Degree of substitution} = \frac{(162 \times \text{Acetyl\%})}{4300 - (42 \times \text{Acetyl\%})} \quad (2)$$

Fourier transform infrared (FTIR) spectra: The sample preparation and analysis parameters were performed according to the method by Diop *et al.*¹¹. Tablets were prepared from the mixture of the sample with KBr at a ratio of 1:100 (starch:KBr). The infrared spectra of native and acetylated arenga starches samples were obtained by a Fourier Transform Spectrometer (IR Prestige 21, Shimadzu Corp. Japan) in the range of 5000-400 cm^{-1} .

X-ray diffraction: The X-ray diffraction patterns of native and acetylated arenga starches were recorded using method of Miao *et al.*¹². X-ray diffraction analysis was performed with an X' Pert PRO X-ray powder diffractometer (PanAnalytical, Almelo, The Netherlands) operating at 40 kV and 30 mA with Cu $K\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). The starch powders were packed tightly in a rectangular glass cell (15×10 mm, thickness 0.15 cm) and scanned at a rate of 2°/min from the diffraction angle (2 θ) 3-80° at room temperature. The Relative Crystallinity (RC) of the starch granules was calculated according to the Eq. 3, with as follows:

$$\text{RC (\%)} = \frac{\text{Ac}}{\text{Aa} + \text{Ac}} \times 100 \quad (3)$$

where, Ac is the crystalline area and Aa is the amorphous area on the X-ray diffractogram.

Water and oil holding capacity: Water and oil holding capacity of native and acetylated arenga starches were determined following method described by Larrauri *et al.*¹³ with slight modifications. Twenty-five milliliter of distilled water or commercial olive oil were added to 250 mg of dry sample, stirred and left at room temperature for 1 h. After centrifugation, the residue was weighed water and oil holding capacity were calculated as g water or oil per g of dry sample, respectively.

Swelling power and solubility: Swelling power and solubility of the starch samples were determined the method of Adebowale *et al.*¹⁴ with some modification. The starch (0.25 g) was weighed into a centrifuge tube and it was reweighed (W_1). The starch was then dispersed in 20 mL of water. It was then heated at temperature of 80°C for 30 min in a thermo stated water bath. The mixture was cooled to room temperature and centrifuged at 3000 g for 15 min. The supernatant was decanted carefully and residue weighed for swelling power determination. The weight of dry centrifuge tube and the residue and the water retained was taken as W_2 :

$$\text{Swelling power} = \frac{W_2 - W_1}{\text{Dry weight of the starch}} \quad (4)$$

Aliquots (5 mL) of the supernatant were dried to a constant weight at 110°C. The residue obtained after drying of the supernatant represented the amount of starch solubilized in water. Solubility was calculated as g per 100 g of starch on dry weight basis.

Crude fiber: The crude fiber content of the starch samples were determined the method described by AOAC¹⁵. Approximately 1.0 g samples (W_0) was weighed into fritted glass crucibles and hydrolyzed with boiling 0.128 M H_2SO_4 , followed by boiling in 0.223 M KOH solution in a hot extractor. The residue was washed with preheated distilled water before being transferred to a cold extractor and washed with acetone. The residue and crucibles were oven dried at 105°C overnight and weighed (W_1) before being ignited in a muffle furnace at 450°C for 8 h. The residual ash was first cooled in an oven at 105°C overnight, then cooled to room temperature in a desiccator and finally weighed (W_2). The crude fiber (%) in the samples was calculated with the Eq. 5:

$$\text{Crude fiber (\%)} = \frac{W_2 - W_1}{W_0} \times 100 \quad (5)$$

Statistical analysis: The data reported were done in triplicate and the means were then calculated with the experiments were performed using a completely randomized design. Data were analyzed using a statistical analysis software system (SPSS version 17.0 Institute Inc., Cary, NC). One-way analysis of variance and were carried out with Duncan's multiple test ($p \leq 0.05$).

RESULTS

Acetyl percentage and degree of substitution: Data in Fig. 1 showed that highest percentage of acetyl groups and degree

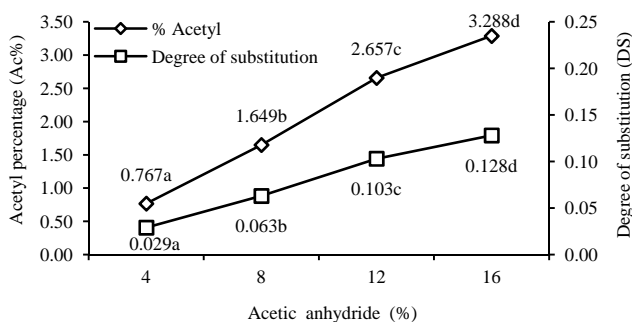


Fig. 1: The percentage of acetyl groups and degree of substitution of acetylated arenga starches at different concentrations of acetic anhydride
 Numbers in the graph followed by a same letter in common are not significantly different at $p < 0.05$

of substitution values were found with increase in the concentrations of acetic anhydride. It can also be explained from the Fig. 1 that the percentage of acetyl groups and degree of substitution increase with increase in the concentrations of acetic anhydride from 4-16%.

FTIR spectra: The FTIR spectra of native arenga starch (Fig. 2a) showed bands characteristic of the chemical structure of the starch molecules, i.e., stretching of hydrogen bonded hydroxyl groups ($3927.07\text{--}3000\text{ cm}^{-1}$), C-H stretching modes (2931.80 cm^{-1}), O-H bending vibration of adsorbed water molecules (1651.07 cm^{-1}), C-O-H bending, CH_2 twisting, CH bending and C-O-O stretching ($1500\text{--}1300\text{ cm}^{-1}$), C-O-H deformation mode (1249.07 cm^{-1}), coupling mode of C-O and C-C stretching (1157.29 cm^{-1}). The fingerprint feature of the native arenga starch is the broad absorption bands in the

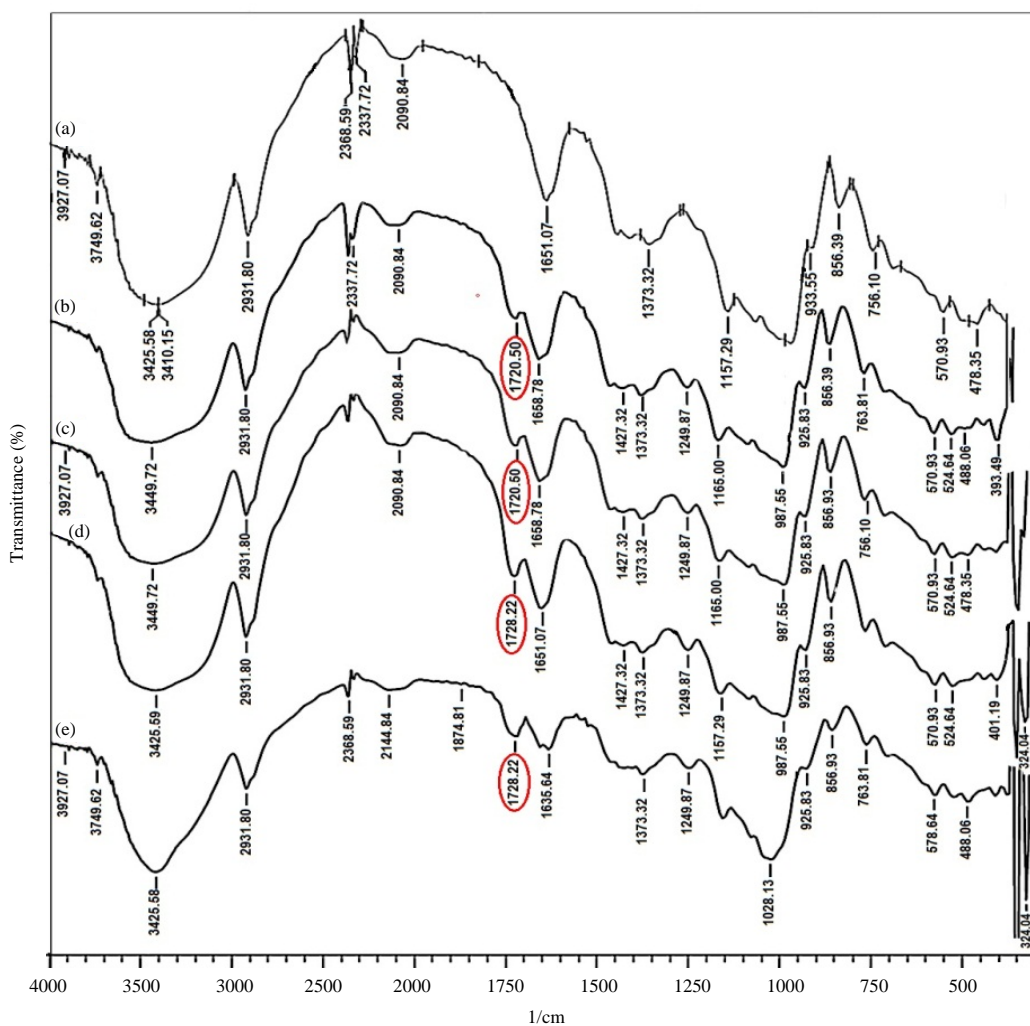


Fig. 2: FTIR spectra of (a) Native arenga starch and acetylated arenga starches at different concentrations of acetic anhydride: (b) 4%, (c) 8%, (d) 12% and (e) 16%

range 1100-990 cm^{-1} , features the C-O stretching in the C-O-C and C-OH in the glycosidic rings, C-H and CH deformation (856.39 cm^{-1}) and C-C stretching (756.10 cm^{-1}).

The FTIR spectra of acetylated arenga starches (Fig. 2b-e) additionally showed bands of varying intensity attributable to the acetyl groups introduced, i.e., stretching of the C=O of the ester group in the sign to 1720.50-1728.22 cm^{-1} (indicated with arrows).

X-ray diffraction: X-ray diffraction evaluations were performed to check if chemical modification changed the crystallinity of starch molecules. The X-ray diffractograms and relative crystallinity for native and acetylated arenga starches are presented in Fig. 3. All starch granules of native and acetylated arenga starches exhibited peaks at 2 θ approximately 15, 17, 18 and 23°, which were pattern of A-type crystallinity.

Water and oil holding capacity: The data in Fig. 4 showed that water and oil holding capacity of the native and acetylated arenga starches increased with the increase in concentrations of acetic anhydride.

Swelling power and solubility: The data in Fig. 5 showed that swelling power of native arenga starch was lower than that of

modified starches. The solubility of acetylated arenga starches decrease along with the increase in concentrations of acetic anhydride.

Crude fiber: The dietary fiber of native and acetylated arenga starches are presented in Fig. 6. These results showed that the dietary fiber of modified starches were higher than the native arenga starch and dietary fiber of acetylated arenga starches increase with the increase in concentration of acetic anhydride. Acetylation contributed to the increase of dietary fiber.

DISCUSSION

The percentage of acetyl groups and degree of substitution increase with increase in the concentrations of acetic anhydride from 4-16%. These results were similar to the report by Rahim *et al.*¹⁶ which showed that increase in concentrations of butyric anhydride at 5-15% resulted increase in degree of substitution of the butyrylated arenga starches (0.057-0.226). Further, these were supported with the finding by Abba *et al.*¹⁷, the starch was isolated from *Tocca leontopetaloides* tubers, chemically modified by acetylation with varying amounts of acetic anhydride (2.55-26.5 g or 1.57-16.35% of starch basis). Their found that the mean values of percent acetylation and degree

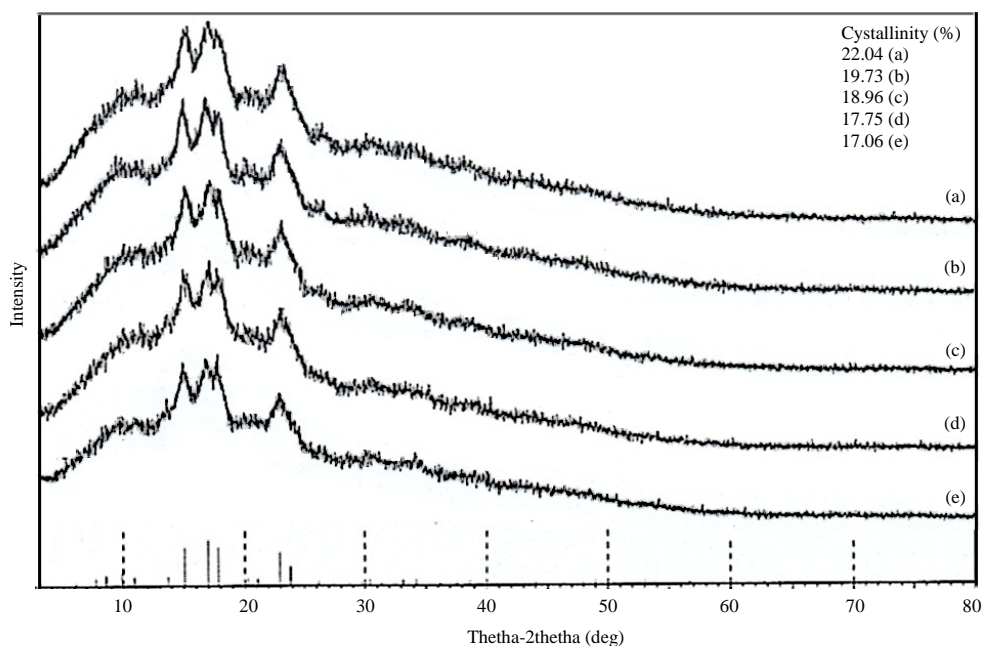


Fig. 3: The X-ray diffractograms and relative crystallinity of (a) Native arenga starch and acetylated arenga starches at different concentrations of acetic anhydride: (b) 4%, (c) 8%, (d) 12% and (e) 16%

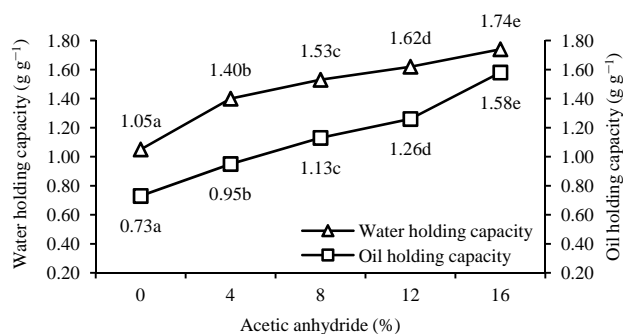


Fig. 4: Water and oil holding capacity of native and acetylated arenga starches at different concentrations of acetic anhydride

Numbers in the graph followed by a same letter in common are not significantly different at $p < 0.05$

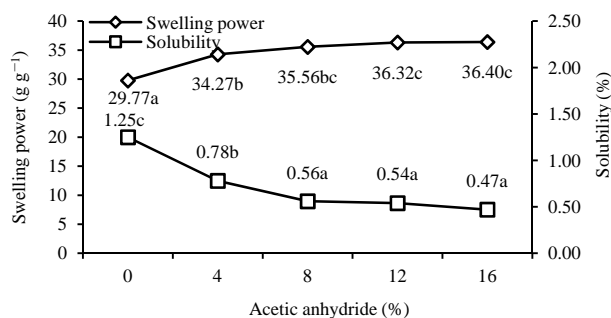


Fig. 5: Swelling power and solubility of native and acetylated arenga starches at different concentrations of acetic anhydride

Numbers in the graph followed by a same letter in common are not significantly different at $p < 0.05$

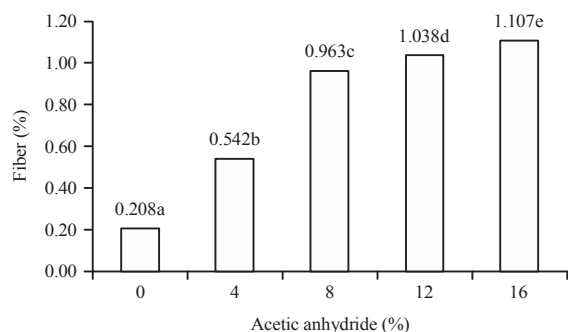


Fig. 6: Dietary fiber of native and acetylated arenga starches at different concentrations of acetic anhydride

Numbers in the graph followed by a same letter in common are not significantly different at $p < 0.05$

substitution of the acetylated starches obtained from addition of varying amounts of acetic anhydride were found increase with increase in the amounts acetic anhydride.

The acetylation of starch molecule promoted the introduction of the acetyl groups in the native arenga starch, resulting acetylated arenga starches exhibiting improved resistance to retrogradation with degree of substitution 0.029-0.128 (Fig. 1) allowing food application. Depending on the values degree of substitution, acetylated arenga starches in the presence of 4-8% of acetic anhydride were classified as low degree of substitution (< 0.1), whereas treatment with 12-16% of acetic anhydride resulted in an acetylated starch with medium degree of substitution (0.1-1.0). A low and medium degree of substitution with (0.01-0.20) acetylated starch has been used in the food industries such as film forming, binding, adhesion, thickening, stabilizing and texturing¹⁸⁻²¹.

These study were agreed with the finding by Bartz *et al.*⁴ reported that the bands characteristics of the native barnyardgrass starch. The intensity of those bands increased with the acetylation level, whereas the intensity of the band assigned to the stretching of OH of starch ($3900-3000 \text{ cm}^{-1}$) gradually decreased as a consequence of the increasing number of OH which were replaced by acetyl groups. FTIR spectra of different DS of acetylated rice starches showed some new absorption bands at $1742, 1435, 1375, 1240 \text{ cm}^{-1}$ assigned to carbonyl C=O, CH₃ antisymmetry deformation vibration and CH₃ symmetry deformation vibration and carbonyl C=O stretch vibration, respectively. The extent of the incorporation of acetyl groups in the starch molecule may be visualized by an increase in the peak intensity of carbonyl C=O at 1741.7 cm^{-1} and the structures of acetylated arenga starches at band^{7,22} of 1720 cm^{-1} .

The acetylated indica rice starches and had the similar X-ray diffraction patterns as native starch exhibited peaks at $2\theta = 15, 17, 18$ and 23° , which were characteristic of A-type crystallinity²³ and native wheat starch had several strong peaks at $2\theta = 15, 17, 18$ and 23° . The crystal structure of the native and modified arenga starches were changed inconspicuous. These results suggested that acetylation did not change the crystalline pattern of acetylated arenga starches at different concentrations of acetic anhydride up to 16% in this case. There were no inspected changes in the X-ray diffraction patterns between the native and acetylated arenga starches but there was a reduction of the overall relative crystallinity of the acetylated arenga starches compared to the native arenga starch. The relative crystallinity of native and acetylated arenga starches with different concentrations of acetic anhydride were 22.04, 19.73, 18.96, 17.75 and 17.06%, respectively. The relative crystallinity of acetylated arenga starches were lower than that of native arenga starch. These were similar to the results of Bartz *et al.*⁴ that the relative

crystallinity of the acetylated barnyardgrass starches were lower than that of native starch and decreased with rise in iodine levels as catalyst. With the increase in the proportion in acetic anhydride, the relative crystallinity became gradually lowered and the diffraction peak also reduced in turn.

Acetylation improved the water and oil holding capacities as a result of incorporation of acetyl groups on the starch molecules which enhanced binding capacity more than the native arenga starch and also acetylated arenga starches indicated that either hydrophilicity or hydrophobicity tend to improve after acetylation. Similar observations were observed by Yadav and Patki²⁵ in acetylated chick pea starch, water and oil absorption capacities increase with the increase concentration of acetic anhydride (6, 8 and 10% w/w). Their reported the enhanced capacity to absorb water or oil may be attributed to the insertion of acetyl group that facilitated access of water to amorphous domain by hydrogen bond distribution, steric hindrance, inter-granular and intra-granular disorganization.

According to Lawal²⁶ reported the water and oil absorption capacities of native and acetylated new cocoyam starches were lower than the native new cocoyam starch. Lawal²⁶ found that both hydrophilic and hydrophobic capacities tendency of the starches improved after acetylation. Improvement in water and oil absorption is a result of introduction of functional groups on the starch molecules, which facilitate a more enhanced, binding capacity than the native new cocoyam starch.

Then, swelling power of native arenga starch was lower than that of modified starches. Olatunde *et al.*²⁷ reported that the swelling capacity of native banana starch (1.38 g g^{-1}) was lower than that of acetylated banana starch (2.14 g g^{-1}). The swelling power was reported that the acetylated arenga starches increased with the increase in concentrations of acetic anhydride from 4-16% of starch basis. This phenomenon was probably caused by a weakening of intermolecular association force due to introduction of acetyl groups that reduced the hydroxyl groups after acetylation⁸. These were similar to the results of Kulkarni *et al.*²⁸ that swelling power of starch acetates of *Lagenaria siceraria* increased with the increase in amounts of acetic anhydride (1.02, 1.53 and 2.04 g). Their found that the swelling power was reported to have correlation with the amylose content, crystallinity and intermolecular hydrogen bonding. On heating crystallinity of the starch acetate changes due to replacement of hydrogen bonds by water, which caused an increase in the swelling of starch acetate granule.

The acetylated arenga starches showed lower solubility compared to native arenga starch (Fig. 5). The solubility of acetylated arenga starches decrease along with the increase

in concentrations of acetic anhydride. These observation were similar to the results of Rahim *et al.*¹⁶ reported that solubility of butyrylated arenga starches decreased with increasing degree of substitution. According Lee *et al.*²⁹ the solubility of acetylated indica rice starches were lower than that of native indica rice starch. Colussi *et al.*⁷ reported that the acetylated rice starches showed lower solubility compared to native rice starch. This decreased solubility of acetylated rice starches can be attributed to the introduction of bulky acetyl groups in the starch molecules, which impart greater hydrophobicity than the hydroxyl groups in the starch molecule, due to the lower binding affinity with the water.

The butyrylated arenga starches were contains resistant starch content¹⁶. Nugent³⁰ reported that resistant starch obtained from modified starches by various types of chemical treatments and has characteristics similar to dietary fiber. It resists to hydrolysis and digestive enzymes. The starch cannot be digested in the small intestine but can be fermented by the gut microflora in the colon. Therefore, resistant starch is also classified as dietary fiber. The dietary fiber of native and acetylated arenga starches are presented in Fig. 6. These results showed that the dietary fiber of modified starches were higher than the native arenga starch and dietary fiber of acetylated arenga starches increase with the increase in concentration of acetic anhydride. Acetylation contributed to the increase of dietary fiber. According to Carolina and Ilmi³¹, chemical modification using different concentration of acetic anhydride (3, 4 and 5%, in 300 g of canna) and two types of canna used in this study were red and white canna. Their found that dietary fiber modified starches were higher than the native starches and also observed that dietary fiber of acetylated red and white canna starches increase with the increase in concentrations of acetic anhydride.

IMPLICATION AND RECOMMENDATION OF RESEARCH RESULTS

The application of research results can be used by government and stakeholders in the production of modified starch as a functional and multipurpose food. The study developed a method of chemical starch modification that can be applied to small industrial and large industries scale. This modification can be applied to all sources of starch and can be done by farmers and communities and industries so that the impact on the income increase of farmers and the community. The acetylated arenga starches produced has been high swelling power so that it can replace some or all of the wheat flour in the manufacture of food products such as noodles, bread and cookies. The acetylated arenga straches also has been good hydrophobic and hydrophobic properties so it can be used as the main materials of functional food.

The research are only limited to the process of modification arenga starch by acetylation with analysis the functional characteristics are also limited. Future research is expected to examine the development of dual modifications with analysis of functional characteristics such as prebiotic and glycemic indexes *in vitro* and *in vivo*.

CONCLUSION

Acetylated arenga starches were synthesized with acetic anhydride for use in food, with the maximum percentage of acetyl groups and degree of substitution of 3.288 % and 0.128, respectively. The FTIR spectroscopy showed that the characteristic absorption intensities of esterified starch increase with the increasing in concentrations of acetic anhydride. The X-ray diffraction confirmed that the crystal structure of acetylated arenga starches was destroyed. Incorporation of acetyl groups to starch molecule can accomplished by the reaction of arenga starch with acetic anhydride, improving the hydrophilic and hydrophobic properties of the starch and producing acetylated arenga starches with potential for application as food functional development

SIGNIFICANCE STATEMENT

This study reports that a method of chemical starch modification that can be applied to small industrial and large industries scale, the acetylated arenga straches also has been good hydrophobic and hydrophobic properties so it can be used as the main materials of functional food. This study will help researchers to uncover critical areas of modified starch as a functional and multipurpose food. Thus, a new theory regarding the acetylated arenga starches produced has been high swelling power so that it can replace some or all of the wheat flour in the manufacture of food products such as noodles, bread and cookies

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