PREPARATION AND PHYSICO-CHEMICAL PROPERTIES OF SUCCINYLATED WATER YAM (*DIOSCOREA ALATA*) STARCH

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Abstract

The starch extracted from water yam tuber was reacted with 7, 12 and 17 g of succinic anhydride to prepare succinylated derivative of the starch. The proximate composition, degree of substitution and the functional properties of the starch was studied, succinylation reaction was confirmed by FT-IR, freeze thaw, syneresis and pasting properties of the starch was also studied. The new band at 1734 cm^{-1} on the FT- IR spectra confirmed the presence of the carbonyl group of succinic anhydride, the degree of substitution (DS) and percentage succinylation ranges between (0.25 - 0.3) and (0.8 - 1.55) respectively.

The proximate composition of the native and succinylated starches were obtained, the results showed that modification had effect on the proximate composition of the starch. Moisture content increased with increase in the degree of modification while others such as ash, fat, protein and fibre content reduced with in increase in degree of modification. Swelling and solubility of all starches increased with increase in temperature, modified starches however have higher values than native. Water absorption capacity increased while oil absorption capacity reduced upon modification. The pasting temperature and set back temperature increased after modification with increase in DS. Freeze thawing decreased on modification, as the number of thawing cycle increased syneresis increased and highest in native starch.

Key words; Succinylation, Substitution, Modification, Syneresis

1.0 Introduction

Yams (*Dioscorea spp*) are annual or perennial plants of great economic importance and nourishment to the people of Africa. The most important species of *Dioscorea (D)* includes: *D. rotundata*, *D. alata, D. cayenensis*, *D. dumetorum*, *D. esculenta* and *D. bulbifera*. *Dioscorea alata* (water yam) is one of the species which serves as a staple food for millions of people in tropical and sub-tropical countries (Hahn, 1995; Coursey, 1967). Yam is an excellent source of starch, which provides calorific energy (Coursey, 1973). The increasing industrial demand for starch necessitated the need to source for it from cheap and available crops.

Starch is a polysaccharide made up of glucose units linked by glycosidic bonds. It is the major polysaccharide of plants stored as discrete semi- crystalline granules in cereals grains, root tubers, stem and piths. It consists of linear amylose and branched amylopectin fractions which are responsible for its crystalline and amorphous properties respectively (Kaur *et al.,* 2007). Starch is widely used in food, paper-making, rubber, packaging materials and plastic industries (Huaigo, *et al.,* 2006). Native starch has limited applications and industrial use due to their inability to withstand extreme processing conditions (Fleche, 2012). In order to get a wider application for starch there is need to improve on its characteristics, which could be achieved by physical, enzymatic and chemical modifications.

Succinylation is a method of chemical modification which involves esterification of pregelatinised starch using succinic anhydride as the esterifying agent, resulting in the introduction of succinyl group on the polymer chain. Succinylation enchances solubilisation of starch in cold water and also retard retrogradation (Mehboob *et al.,* 2015), this work is

aimed at improving the properties of water yam starch by succinylation and make it suitable for use as thickner in the food and cofectionary industries.

2.0 Materials and methods

2.1 Starch Extraction

Water yam tubers were purchased at Oba Awujale market, Ijebu- Ode. The water yams were peeled, cut into cubes and then washed with water to remove dirts. The cubes were blended with water using warring blender for 5 min. the resulting suspension was filtered with a muslin cloth, the filrate was allowed to stand for 4 h to facilitate starch sedimentation and the top liquid was decanted. The sediment was suspended in water, washed and then separated by decantation. The final sediment was packed and dried in an oven at 50^{o} C for 48 h.

2.2 Starch succinylation

The methods of Sathe and Salunkhe, (2010) were used with slight modification. Starch (150 g) was dispersed in 450 ml of distilled water and magnetically stirred for 1 hr. The pH of the slurry was adjusted to 9.0 using 1 M NaOH. Different amount of succinic anhydride (7, 12, 17 g) were used to treat the starch suspension (to obtain starch succinate of three different degrees of substitution) over a period of 2 h while maintaining a pH range of 8.0 – 9.0. At the end of the reaction the pH of the slurry was adjusted to 6.0 using 0.5 M HCl. The mixture was filtered, washed six times with distilled water and then oven dried.

2.3 Determination of degree of modification

Alkali saponification mehtodwas used for the determination of succinyl content. Succinylated starch sample (1 g) was weighed into a conical flask, 50 mL of 75% ethanol was added, and the mixture was refluxed for 30 min while maintaining a temperature of 50^{o}C. After cooling to room temperature, 40 ml of 0.5 M NaOH was added. The flask was covered with aluminium foil and allowed to stand at room temperature for 72 h with shaking occasionally. Saponification occurred with the addition of NaOH and the excess alkali was determined by titrating with 0.5 M HCl, phenolphthalein was used as indicator. Native water yam starch was treated in the same manner to obtain a value for the blank. The percentage of succinyl group and the degree of substitution of the samples were calculated as follow:

$$\text{Percent succinyl} = \frac{\text{blank titre – sample titre) x 0.1x molarity of acid x100}}{\text{weight of sample}}$$

$$\text{Degree of substitution (DS)} = \frac{162 \times \%\text{succinyl}}{1000 - (99 \times \%\text{ succinyl})}$$

2.4 Proximate analysis

Standard Association of Official Analytical Chemistry, (1990) methods were used for determination of moisture, ash, protein, fat, fibre and carbohydrate composition of native and modified starches.

2.5 FT – IR spectroscopy

The IR spectra of starches were obtained using Perkins Elmer Spectrum 100 FT-IR spectrometer in the frequency range 4000 – 650 cm^{-1} at Central University Research Laboratory, University of Ibadan, Nigeria.

2.6 Oil and water absorption capacity

The method of Beuchat, *et al.,* (1975) with modification was used to determined oil and water absorption capacities of the starches. Distilled water (10 ml) /olive oil (10 ml) was added to 1 g of sample in a pre-weighed tube, it was mixed thoroughly for 1 min and allowed to stand for 30 min, with occasional stirring. The mixture was centrifuged at15000 rpm for 15 min, supernatant was discarded and then re-weighed, absorption capacities were expressed as weight gained per initial weight of sample.

2.7 Effect of temperature on swelling power and solubility

Swelling power and solubility was evaluated using the method of Leach, *et al*. (1959), 1 g of starch sample was weighed and transferred into a clean dried test tube and weighed. 10 ml of distilled water was added into the test tube and mixed gently. The resultant slurry was heated at 50ºC, 70ºC, and 90ºC respectively for 30 min in a water bath with agitation every 5 min. The mixture was cooled and centrifuged at 3500 rpm for 15 min. 5 ml of the supernatant was decanted and dried to a constant weight at 100ºC. The residue obtained (after centrifugation) with water it retained was quantitatively transferred to the clean dried test tube used earlier and weighed. Swelling power and solubility were calculated as follow:

$$\text{Swelling power (g/g)} = \frac{\text{weight of wet sediment}}{\text{weight of starch sample} - \text{weight of dry supernatant}}$$

$$\text{Solubility (\%)} = \frac{\text{weight dry supernatant}}{\text{weight of starch sample}} \times 100$$

2.8 Freeze thaw stability

Starch pastes were prepared using aqueous suspension of starches (5%, w/v). The paste obtained were weighed 10 g into centrifuge tubes and subjected to successive freeze- thaw cycling by placing them in freezer at -10^{o}C for 24 h. The frozen pastes were thawed at 25^{o}C for 6 h and centrifuged at 10,000 rpm for 15 min. The weight of the supernatant at the end of each cycle was determined and the per cent of synerisis was expressed as the ratio of the weight of liquid separated to the total weight of the pastes. 5 freeze thaw cycles were performed.

2.9 Pasting properties

Pasting properties were determined with a Rapid Visco Analyzer (RVA). 15 g of starches were dispersed in 25 ml distilled water. A programmed heating and cooling cycle was employed at constant shear rate, where the sample was held at 50^{o}C for 1 min, heated to 95^{o}C in 3 min and then held at 95^{o}C for 2 min. It was cooled to 50^{o}C within 3 min and then held at 50^{o}C for 2 min.

3.0 Results and discussions

3.1 Proximate composition

The results for degree of modification, proximate composition, water and oil absorption capacities are presented in Table 1.The result showed that percent succinylation increased with increase in concentration of the succinic anhydride. This suggests that preparation of starch succinate is favoured by increase in concentration of succinic anhydride since there are more succinyl group to substitute the hydroxyl group on glycosidic ring. The results of the

proximate composition showed that the moisture content ranged between 9.25 and 12.25 %, following modification of the native water yam starch there was an increase in the moisture level of the modified starches even as the degree of modification increases. This is because succinyl group must have enhanced the hydrophilic character of the starch. Ash, protein, fat and crude fiber contents were all reduced after modification, with their values ranging between (5.0-1.50)%, (2.70-0.61)%, (4.0-2.80)% and (0.8-0.24)% respectively. Succinylated water yam starch 3 (SWS_3) had the lowest values which may due to structural changes during modification reaction (Awokoya *et al.,* 2011). Water absorption capacity of starch derivatives was higher than oil absorption capacity as shown in Table 1. As the degree of substitution increases water absorption of the starches also increased. Oil absorption capacity on the other hand reduces on esterification. Increase in water absorption capacity in starches after succinylation has also been reported by Mehboob *et al.* (2015) and Awokoya *et al.* (2011) for corn and cocoyam starches respectively.

Table 1: Proximate composition, water and oil absorption capacity

	NWS	SWSI	SWS2	SWS3
Percent succinyl (%)	-	0.80	1.25	1.55
Degree of substitution (DS)	-	0.25	0.29	0.30
Moisture content (%)	9.25	9.75	10.75	12.25
Ash content (%)	5.00	3.20	2.50	1.50
Protein content (%)	2.70	1.40	0.53	0.61
Fat content (%)	4.00	3.50	3.10	2.80
Fibre content (%)	0.80	0.39	0.31	0.24
Carbohydrate (%)	78.25	81.76	82.82	82.60
WAC (%)	50.00	61.00	64.00	68.00
OAC (%)	40.00	38.00	36.00	45.00

WAC- Water absorption capacity; OAC- Oil absorption capacity Native water yam starch (NWS); Succinylated water yam starch (SWS)

3.2 FT-IR

The infrared spectra of native and modified starches are presented in Figure 1. The band between 3100-3000cm^{-1} is assigned to O-H stretching, the new bands between 1734 cm^{-1} in the starch derivatives indicates carbonyl stretching of ester group which proved that modification actually occurred.

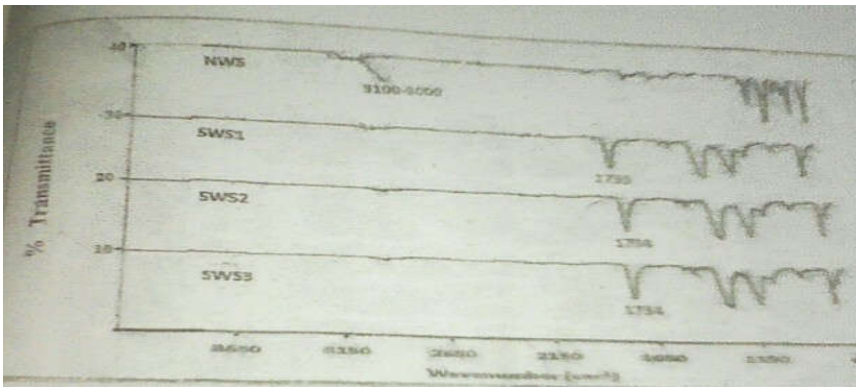

Figure 1: infra-red spectra of native and the succinylated starches.

3.3 Swelling and solubility

The results showed that both swelling power and solubility of the starches were temperature dependent and their values increased with increase in temperature (Table 2), but the modified starches have higher swelling power than the native starch with Succinilated water yam starch 3 (SWS3) having highest values for both swelling power (9.04 %) and solubility (4.48 %). This may be due to structural changes in the starch after modification. Olayinka *et al*., (2011) have also reported increase in swelling power after succinylation of sorghum starches.

Table 2; Effect of temperature on Solubility swelling of native and modified starches

Swelling

Temperature	NWS (%)	SWSI (%)	SWS2 (%)	SWS3 (%)
50° C	2.29	2.45	2.47	3.14
70° C	2.94	3.92	398	3.61
90° C	5.61	7.63	8.97	9.04

Solubility

Temperature	NWS	SWSI	SWS2	SWS3
50° C	0.12	0.18	1.46	1.71
70° C	0.71	0.77	1.84	3.55
90° C	1.11	2.37	2.54	4.48

Native water yam starch (NWS); Succinylated water yam starch (SWS)

3.4 Freeze thaw stability

The retrogradation tendencies of gels preparared from native and succinylated water yam starches were determined by measuring syneresis during storage at 10°C. All starch gels began to retrograde after 24 h indicated by percentage of water separated after thawing. Syneresis was reduced after modification and there was progressive increase in percentage of water separated as the number of thawing cycle increased. The succinylated water yam starch (SWS3) had highest thawing stability since the percentage of water released was much lower than other starches. This may be because succinic groups prevented syneresis during freeze thaw cycle because of its hydrophilic nature (Bhandari *et al.,* 2002). It could be assumed that succinylation of water yam starches had improved the retrogdadation property of the starch.

Table 4 Freeze thaw stability of native and modified starches

	1CYCLE	2CYCLE	3CYCLE	4CYCLE
NWS	65.05	78.40	79.15	82.20
SWS_1	62.25	74.25	73.35	76.20
SWS_2	61.20	72.05	70.65	74.75
SWS_3	60.05	70.80	70.21	70.54

Native water yam starch (NWS); Succinylated water yam starch (SWS)

3.5 Pasting properties

The pasting temperature of the starch was increased after modification with SWS_3 having the highest value. This can be attributed to changes in structure and transition of the amorphous region to crystalline structure (Zavareze and Dias, 2011). There were reduction in peak viscosity and increase in breakdown viscosity of starch as the degree of substitution increased. This may be attributed to structural reorganisation within the granule of the modified starches and the measure of fragility the starch after modification. Set-back values were increased with increase in degree of modification, which is an indication of the starch resistance to retrogradation. The increase in breakdown and set-back values indicated stability of the starch during shearing at high temperature and cooling (Olayinka *et. al.,* 2011)

Table 5 Pasting properties of native and modified starches.

Sample	Pasting temp	setback val	peak viscosity	breakdown val
NWS	81.93	338.00	4000.00	381.50
SWS1	83.50	538.00	3593.50	221.50
SWS2	83.63	668.00	3739.00	407.00
SWS3	85.25	814.00	3814.00	523.50

Native water yam starch (NWS); Succinylated water yam starch (SWS)

4.0 CONCLUSIONS:

The introduction of succinyl group in the starch improved its functional properties; swelling power, freeze thaw stability, water absorption capacity as well as its pasting properties this will make it suitable to be used as thickener in the food and confectionary industries.

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