

## Acetylation of Manihot Esculentus Crantzstarch and Its Potential Application in Pharmaeauticals.

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**Abstract:** *M.esculentus crantz starch* was chemically modified via Acetylation. The product was characterized using Scanning electron Microscopy (SEM), Fourier Transform Infrared (FTIR), and X-ray Diffraction (XRD). Physicochemical characteristics of the native and acetylated starch such as viscosity, solubility, swelling power, emulsifying capacity were also determined. The result showed that the starch from *M.esculentus crantz starch* is composed of a  $\alpha$ -glucose linked together at 1 $\rightarrow$ 4. The acetylated starch had better physicochemical properties than the native starch. The result showed that chemical modification by acetylation may improve the physicochemical properties of polysaccharides resulting in higher efficacy for effective utilization in starch-based industries.

**Keywords:** *Manihot esculentus crantz starch*, Acetylation, excipient, FTIR, SEM. XRD

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### I. Introduction

Modified biomaterials have played major role in the food and pharmaceutical industries over the past few decades. They possess unique properties not found in natural polysaccharides which are suitable for the development of new products [1]. The chemical modification of polysaccharide is the most important route to modify the properties of the naturally occurring biopolymers and to use these renewable resources in the context of sustainable development [2,6]. Acetylation plays an important role in the case of high-amylose starches (55–70% amylose), where cooking at 90–100°C does not disperse these starches, and temperatures of about 160°C are required. Acetylation also lowers gelatinization temperature enough to permit cooking under milder and more economical conditions.

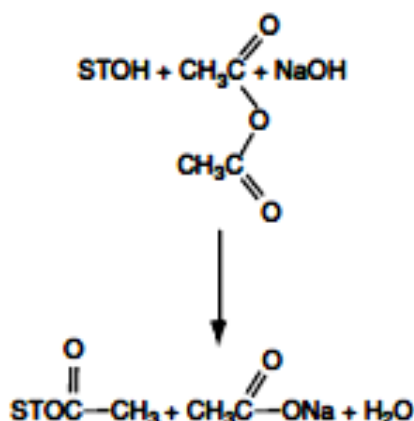


Figure 1: Acetylation of starch (ST) with acetic anhydride under mild alkaline conditions.

While starch acetates are fairly stable chemically under mild to moderately acidic conditions and perform well in most foods, the acetate groups are sensitive to alkaline hydrolysis. At pH 11, starch acetate (1.8% acetyl) is completely deacetylated for 4 h at 25°C. High-processing temperatures at neutral or slightly alkaline pH will tend to promote some deacetylation [6].

It was estimated that 126.6 million tons of cassava was grown in Africa alone. The plant *M.esculentus crantz* belongs to the family Euphorbiaceae. Other modification type of starch and their utilization as excipient in drug formulation have been reported [3,19]. Therefore this study was designed to modify *M.esculentus crantz starch* by acetylation and evaluate the effect of acetylation on some physicochemical and binding properties of

the starch as excipient in pharmaceutical formulation. This research may likely highlights the effect of acetylation on the physicochemical properties of *M.esculentus crantz* starch for possible application as excipient in drug formulation.

## II. Materials And Methods

### Extraction of *M.esculentus crantz* Starch

The tubers of *Manihot esculentus crantz tubers* were purchased from Chobao market, Jos, Plateau State and was identified and authenticated by plant scientist of Department of Plant Sciences, University of Jos, Nigeria. The *M. esculentus crantz* tubers were thoroughly washed and all foreign material removed. The tuber was peeled, weighed and peeled. The tuber was pulverized using a blender. Enough quantity of water was added to the pulp which will then pass through an 180um sieve. The filtrate will be allowed to settle and 0.1N sodium hydroxide will be added to separate the starch and portentous material as well as neutralize the prevailing slight acidity [5,22].

### Preparation of Acetylated Starch

Acetylated starch was obtained using the method reported by [14]. In brief, starch (10g) was dispersed in 50cm<sup>3</sup> of distilled water and then constantly stirred for 30minutes. The slurry was adjusted to pH 8.0 with 3%NaOH. 1.2g of acetic anhydride was added to the slurry. After the addition of the acetic anhydride, the reaction was allowed to proceed for another five minutes. The pH of the slurry was adjusted to 4.5 with 0.5M HCl and filtered through whatman No 1 filter paper. The residue obtained was washed for four times with distilled water to remove completely some acids that may be present in the product and finally air dried at room temperature.

### Powder and Granule Evaluation

The Powder and granule properties were evaluated. The bulk and tapped densities of 30g of the powder or granules was weighed in triplicate into a 100ml measuring cylinder, and the volume occupied by the granules recorded as the bulk volume. The cylinder was then tapped on the wooden platform height of 2.5 cm three times at 2 seconds interval until the volume occupied by the granules remained constant. The data generated was used in computing the Hausner ratio and Carr index or compressibility index. Moisture content was determined using the hot oven method. The particle size distribution of each granulated drug power was characterized by sieve analysis.

### Determination of Physicochemical Properties Of Starch:

#### Viscosity:

The viscosity of a 2% w/v starch suspension was determined using a viscometer (Brookfield, RVDV-II<sup>+</sup>PRO, USA) with a spindle no. RV-02 and a speed of 200 rpm of 200 at 25°C. The readings of viscosity were taken after 30s of rotation. All measurements were performed in triplicate.

#### Swelling index:

The swelling power (by weight) of starch was measured using a method modified from the one reported by Tester and Marison [8,9]. Cassava starch (0.2g) was dispersed in water (20ml). The suspension was heated to 85°C in a water bath for 30min with vigorous shaking every 5min the starch gel was then centrifuged at 2,200 rpm for 15min. The weight of sediment was used to calculate the swelling power, and expressed in percent. The determination was done in triplicate. The swelling power was calculated as follow.

$$\text{Swelling power} = \frac{\text{Weight of sediment}}{(\text{Weight of dry Starch} - \text{Weight of dissolved starch})}$$

#### Solubility

The solubility of starch was determined. Starch sample 10g was suspended in 40ml of distilled water. It was heated to the desired temperature 60°C, 70°C and 80°C for 30minutes with continuous shaking. The mixtures were centrifuged at 100rpm for 15 minutes. An aliquot of supernatants (5ml) were evaporated at 130°C and weighed. The solubility's of the starch were the percentage ratio in mass (g) of the dried supernatant to the initial mass (g) of the dry starch. [22]

#### Microstructure studies by SEM

Morphological features of the native starch and the oxidation of starch was studied with a JSM-5600LV scanning electron microscope of JOEL (Tokyo, Japan). The dried sample was mounted on a metal stub

and sputtered with gold in order to make the sample conductive, and the images were taken at an accelerating voltage of 10KV and at 500x magnification.

**Fourier Transform Infrared (FTIR) and X-ray Diffraction**

The FTIR spectrum of the starch samples were recorded in an FTIR spectrometer (Nicolet Magna 4R 560 MN USA) using potassium bromide (KBr) discs prepared from powdered samples mixed with dry KBr. XRD of *m.esculentus crantz* starch and oxidation of starch were studied using a SIEMEN d-5000, X-ray diffract meter (Siemens, Munich, Germany).

**III. Results And Discussion**

**Table 1: Physicochemical characteristics of the native and acetylated *M.esculentus crantz* starch**

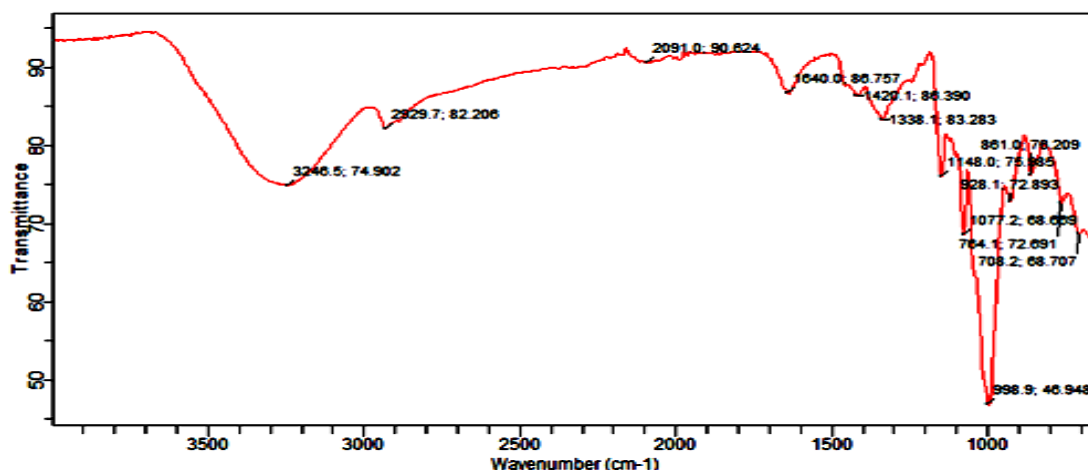
Type	Solubility (%)	Swelling power (%)	Viscosity(M Pa.S)	Emulsifying Capacity(cm <sup>-1</sup> )
Native starch	60°C , 17.7±0.20	5.20±0.00	10.00±0.00	0.013±0.00
	70°C, 21.5±0.01			
	80°C, 39.7±0.20			
Acetylated starch	60°C, 25.5±0.01	11.11±0.00	24.80±0.00	0.092±0.00
	70°C , 38.5±0.01			
	80°C , 57.5±0.02			

**Table 2: Physicochemical properties of drug granules prepared with Acetylated *M.esculentus crantz* starch**

Parameter	Concentration of starch (% w/w)			
	Acetylated starch		Corn starch	
	2	4	6	4
Bulk density(g/cm <sup>3</sup> )	0.44 ± 0.00	0.44 ± 0.00	0.44 ± 0.00	0.54 ± 0.02
Tapped density(g/cm <sup>3</sup> )	0.50 ± 0.00	0.512 ± 0.00	0.51 ± 0.00	0.78 ± 0.01
Hausner ratio	1.16 ± 0.01	1.09 ± 0.01	1.06 ± 0.01	1.47 ± 0.01
Carr's index(%)	12.00 ± 0.15	14.06 ± 0.10	13.60 ± 0.20	14.70 ± 0.20

**Table 3: Physicochemical Properties of drug granules prepared with native *M.esculentus crantz* Starch**

Parameters	Concentration of starch (%w/w)			
	Native starch	4	6	corn starch
	2	4	6	4
Bulk density(g/cm <sup>3</sup> )	0.44 ± 0.00	0.48 ± 0.00	0.46 ± 0.00	0.54 ± 0.01
Tapped density(g/cm <sup>3</sup> )	0.46 ± 0.00	0.46 ± 0.00	0.48 ± 0.00	0.78 ± 0.01
Hausner ratio	1.04 ± 0.01	1.04 ± 0.01	1.06 ± 0.01	1.47 ± 0.02
Carr's index (%)	9.20 ± 0.10	9.20 ± 0.10	10.10 ± 0.10	14.7 ± 0.10



**Fig2 : FTIR of acetylated *M.esculentus crantz* starch**

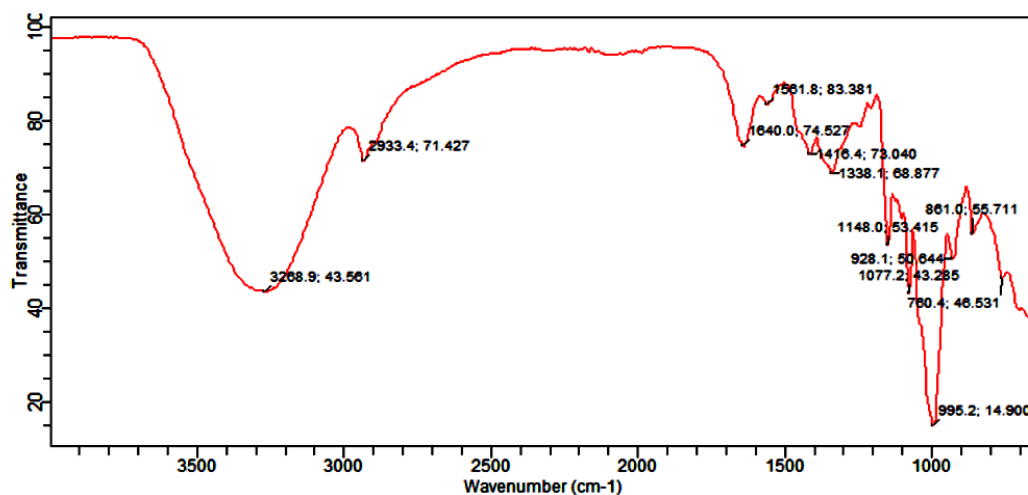


Fig3: FTIR of Native *M.esculentus crantz* starch

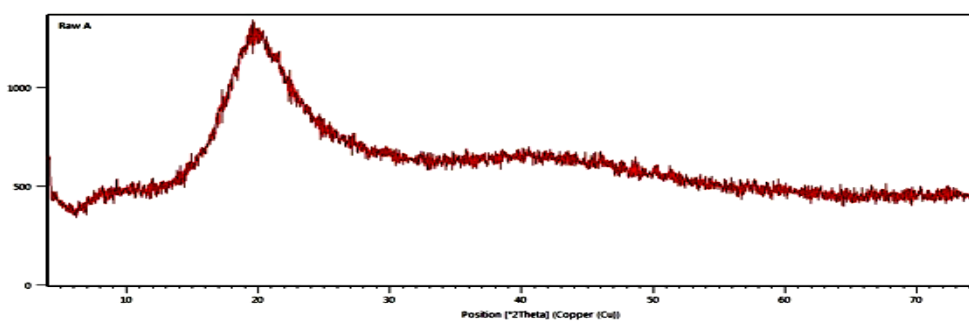


Fig4 : X-ray Powder diffractograms of Native *M.esculentus crantz* starch

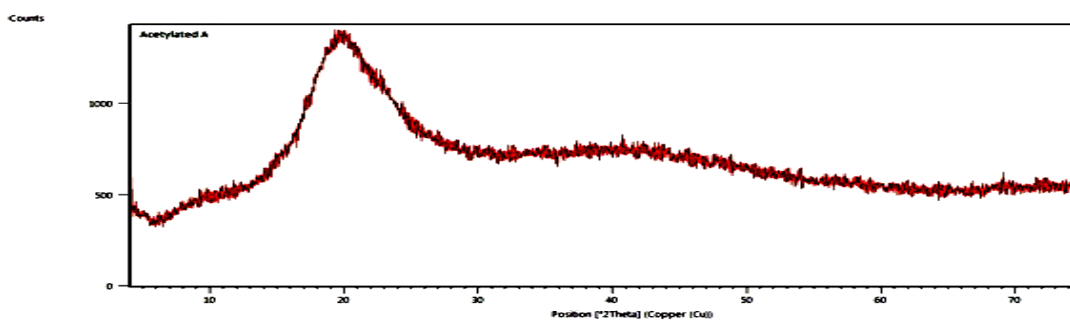


Fig 5: X-ray Powder diffractograms of Acetylated *M.esculentus crantz* starch

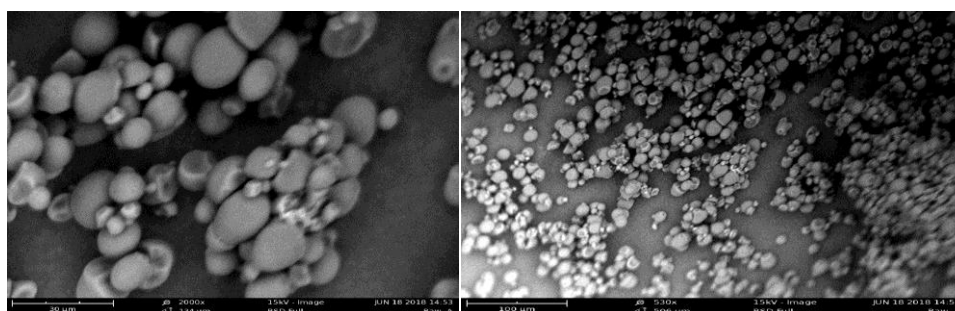
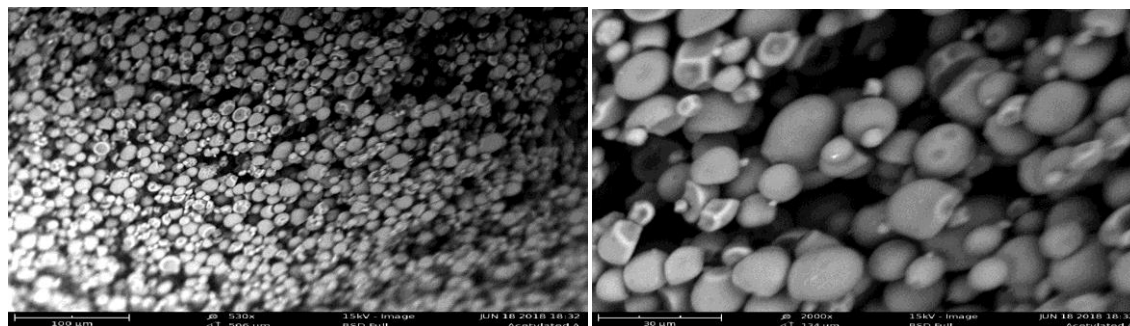


Fig6: Scanning electron micrographs of Native *M.esculentus crantz* starch



**Fig7: Scanning electron micrographs of Acetylated *M.esculentus crantz* starch**

The viscosity, swelling power and solubility compared favorably with other commercial starches previously studied by other authors [4,10,11]. Swelling is a primary mechanism in diffusion controlled release dosage form [5,8]. The viscosity, swelling power, emulsifying capacity, and solubility for acetylated starch;  $24.00 \pm 0.00\%$ ,  $11.11 \pm 0.00\%$ ,  $0.092 \text{cm}^{-1}$  and at  $80^\circ\text{C}$   $57.5 \pm 0.02\%$  respectively were higher than the native starch  $10.00 \pm 0.00\%$ ,  $5.20 \pm 0.00\%$ ,  $0.013 \text{cm}^{-1}$  and at  $80^\circ\text{C}$   $39.7 \pm 0.20$  respectively (Table 1). The result shows that the acetylated starch when used as a binder /disintegrant could absorb sufficient moisture to swell and cause tablets to disintegrate and burst and free up sufficient energy to release drug content. [8,12]. It was reported that introduction of carboxyl and carbonyl groups reduce the bond strength between starch molecules (amylase and amylopectin) and thereby increase the swelling power and solubility of the starch granules. [14]. This facilitates access of water to amorphous areas, enhancing the viscosity [12,15]. The superior solubility and swelling power of the acetylated starch compared with the native starch may be due to the presence of hydrophilic substituting groups ( $-\text{CH}_3\text{COO}-$ ) which allow the retention of water molecules because of their ability to form hydrogen bonds [12]. The increase in the viscosity of the acetylated starch may be due to the steric hindrance exhibited by the bulky carbonyl groups which obstruct the proper alignment of starch chain for maximum retrogradation [12]. Adding bulky functional groups reduces the tendency of the starch to recrystallize and make the starch less prone to damage by heat and bacteria [8,12]. NaOH increases the reactivity of starch toward chemical reaction as compared to the untreated starch. Thus it means that etherifying or esterifying reagents are able to penetrate the swelled starch structure more easily and thus substitution of the hydroxyl group of the anhydrous glucose unit becomes easier [7,13].

#### FTIR spectroscopy

The infrared spectra of the native and acetylated starch (fig8). show a broad band between  $3600$  and  $3000 \text{cm}^{-1}$  which was assigned to O-H stretching and it is due to hydrogen bonding involving the hydroxyl groups in the starch molecules. The band at around  $2922 \text{cm}^{-1}$  is assigned to  $\text{CH}_2$  symmetrical stretching vibrations and the band around  $1600$  and  $1420 \text{cm}^{-1}$  there is strong absorption peaks for asymmetric and symmetric vibration of  $\text{COO}^-$  in the spectrum of the oxidation of starch. This band confirms the introduction of  $-\text{CH}_3\text{COO}-$  group into the starch molecule [16,17,18].

The X-ray diffractogram of the starch samples shows presence of numerous weak peaks, confirming its complete amorphous nature. The result of (XRPD) confirms that the starch exhibits only an amorphous portion. The biological and botanical source of a pharmaceutical material serves as a determining factor in the granule shape, size and morphology. As a result, these characteristics not only help to differentiate various materials but also give an indication of the processing parameters [4,13]. The flow properties of the powders and the formulated granules were evaluated and the results were as presented in Table 2. The powder flow properties suggest that native *M.esculentus crantz* starch powder had poor flow characteristics and may require modification to improve the flow of the powder. The tapped density which is indicative of the powder packing properties was higher than the bulk density for all the powder used. *M.esculentus crantz* starch powder gave the lowest bulk and tapped densities compared to the modified starch. Acetylated starch had improved physicochemical properties which further enhanced the flow properties and compared favourably with the standard starch used.

#### IV. Conclusion

Acetylated *m.esculentus crantz* starch was prepared and characterized. The new carbonyl groups were detected by FTIR, SEM and XRD. A high viscosity, swelling power, solubility and Emulsifying capacity were observed for aqueous solutions of the acetylated starch compared to the native starch. The study confirms that acetylation improves the properties of the native starch. It is more attractive because the starch from

*M.esculentus crantz* is a natural, abundant, non-toxic, low cost and regional raw materials. This material may be utilized as binder or disintegrant in solid dosage formulation.

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