



SYNTHESIS AND CHARACTERIZATION OF NATIVE AND PRE-GELATINIZED CASSAVA STARCHES

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ABSTRACT

Background: Starches and their derivatives have been very useful for domestic and industrial purposes. **Objectives:** Modification of starch intends to improve and expand the utilization of starch in food and non-food applications. **Methods:** The starch was extracted by wet extraction method. Cassava starch was pre-gelatinized by heating the starch solution above 70°C and esterified using phthalic anhydride. The native and modified starches were characterized using Scanning Electron Microscopy coupled with Energy-dispersive X-ray Spectroscopy (SEM-EDS) for morphology and elemental composition; Thermogravimetric analysis (TGA) for thermal stability; Fourier Transformed Infrared Spectroscopy (FTIR) for identification of prominent functional groups; X-Ray Diffractometry (XRD) for the determination of the level of amorphosity. **Results:** The SEM-EDS revealed the surface disruption of starch granules after modification and the elemental composition, XRD showed that the intensity of crystallinity in the native starch has changed to amorphosity in the modified starch, different peaks associated with starch were identified by the FTIR, and the TGA showed the degree of weight loss with increase in temperature. **Conclusions:** Phthalation of the native starch converted its crystallinity to amorphous structure in modified starch.

Keywords: *crystallinity, amorphosity, granules, pre-gelatinization*

1. INTRODUCTION

The various industrial applications of cassava are based on the easy propagation with little cost, high calory, good physicochemical properties, as well the simplicity of its modification [1]. Because of its high demand in industries, there is the need to explore cheaper means of cultivating it to meet global demand. Although, starch is mostly used as food, but it can be chemically or biologically modified into many important and various products, namely, beverages, adhesives, textiles, paper, confectioneries, plastics and pharmaceuticals [2]. Native starches could have limited application because of the reduced functional properties. Therefore, modification is important to improve the functional groups in starch, and to widen its applications especially in industries in modified forms. Modification of starch could be chemical; physical; or enzymatic; it involves changing the physicochemical properties of unmodified (native) starch to obtain more useful derivatives which have an edge over their native forms [3]. It has been reported by Xueju and Qiang (2004) that starch citrate is a resistant starch in food industry [4]. A few proportion of the starch produced globally is used in their crude state, however, chemical and genetic alteration of the function groups improved the production of starch derivatives to serve various puposes in food and allied industries, this has however expanded the application of starch and its derivatives [5]. Modified (acetylated) starches are not easily broken down by enzymatic action [6], however, this makes it a desirable resistant starch which has improved health benefits [7].

Cassava (*Manihot esculenta*) as a perennial and subtropical woody shrub is cultivated annually and valued for its useful tubers [8]. Cassava as an important energy source is a staple food for over 500 million people in Sub-Sahara region, Asia and Latin America [9]. Cassava tuber is useful as primary raw material in textiles, bakeries, and pharmaceutical industries [10]. Cassava plants can be propagated on many soils, even on underutilized highlands. It can also be cultivated in many poor soils where other crops fail to germinate, this allows cassava to be a major player in food security programme [11].

Cassava pulp has about 70% moisture content in its composition, carbohydrate (20-30%), crude protein (1.0-1.8%), crude fiber (1.53.5%), fat (0.35-0.45%), and 8-28 mg HCN/kg of its dry mass [12]. Cassava tuber among other parts remains the chief source of starch; the leaf is rich in protein, vitamins, and minerals. Presently, large production of cassava is being encouraged, and the blending of cassava flour (10%) with wheat flour to form a composite for bread making will reduce the heavy demand already placed on wheat [13]. Nutritionally, cassava in its composition has

potassium (K), iron (Fe), calcium (Ca), vitamins A, B, and B-6, sodium, folic acid, as well as protein [14]. The production and application of cassava and its products have received much attention, the more reason the cultivation is on the rise, and expanding into areas where there was no cultivation of cassava in decades [15]. This study centers on the synthesis, physical and chemical modification of native starch by gelatinization and esterification processes.

2. MATERIALS AND METHODS

2.1 Synthesis of Cassava Starch

Cassava tubers were collected from a farm in Ado-Ekiti, Nigeria. The starch was extracted by wet extraction method as described by Wang *et al.* (2006) [16]. The fresh tubers were thoroughly washed with water, cut into small pieces, blended for about two minutes for homogeneity.

The resultant slurry was packed into a muslin cloth and lowered into distilled water inside a bucket. The cloth and the contents were continuously squeezed to expel the starch into the water. The starch was allowed to settle overnight and the supernatant decanted. Further washing of the starch particles was done using distilled water. This process was repeated till the supernatant was clear. The wet starch was spread and air-dried.

2.2 Synthesis of Pre-gelatinized Cassava Starch

Pre-gelatinized starch phthalate was prepared according to the method of Silvia *et al.* (2014) [17]. Pre-gelatinized cassava starch phthalate was prepared in two steps: gelatinization and esterification. Gelatinization was done by heating starch solution above 70°C and drying it into flakes, which were then milled and sieved.

The obtained pre-gelatinized cassava starch was dispersed in distilled water, and reacted with phthalic anhydride solution in ethanol (96%). NaOH (10 M) was used during the reaction in a drop-wise manner to keep the alkaline condition within pH 8-10. Sodium sulphate anhydrous was added during the reaction to absorb excess water. The reaction was carried out at 1000 rpm stirring speed using magnetic stirrer.

The stirring lasted for 30 min, and the solution was allowed to stand overnight to complete the reaction. The solution was then brought to pH 6.5-7 using HCl solution. Ethanol (50%) solution was added into the neutralized solution to wash off the unreacted phthalate. The obtained precipitate was then dried, milled and sieved to obtain pre-gelatinized phthalated cassava starch.

3. RESULTS

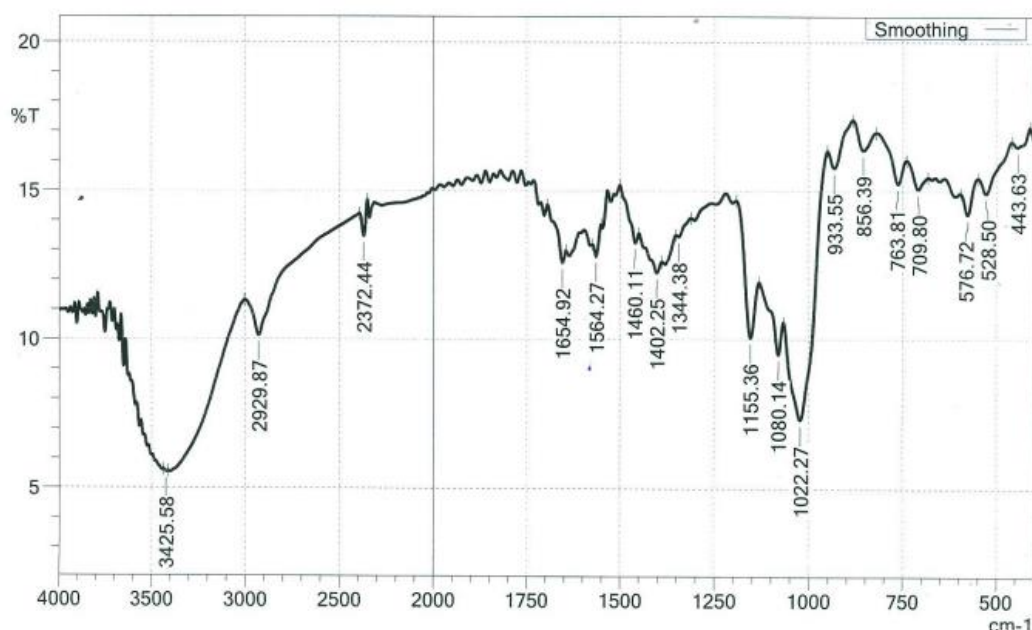


Figure 1a: The figure presents the FTIR spectra of native cassava starch.

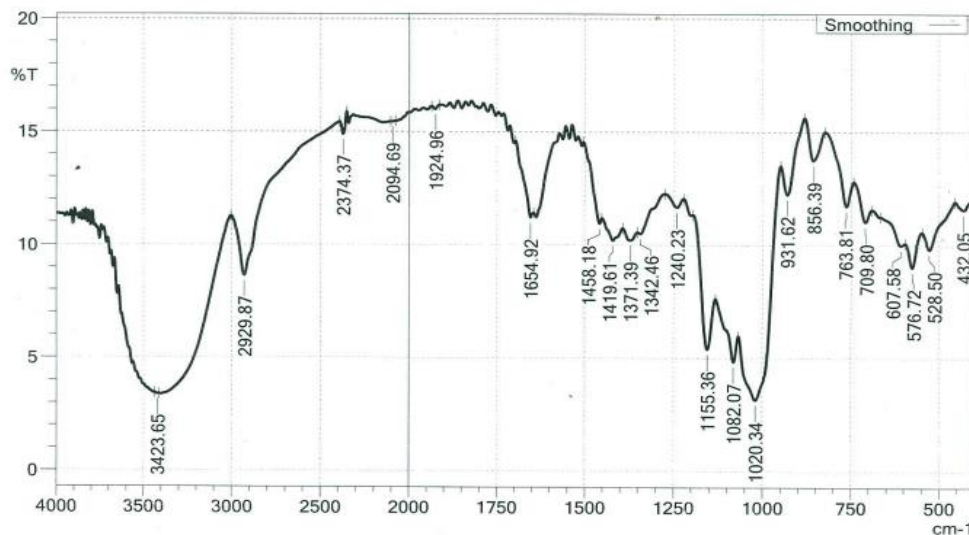


Figure 1b: The figure presents the FTIR spectra of pre-gelatinized phthalated cassava starch.

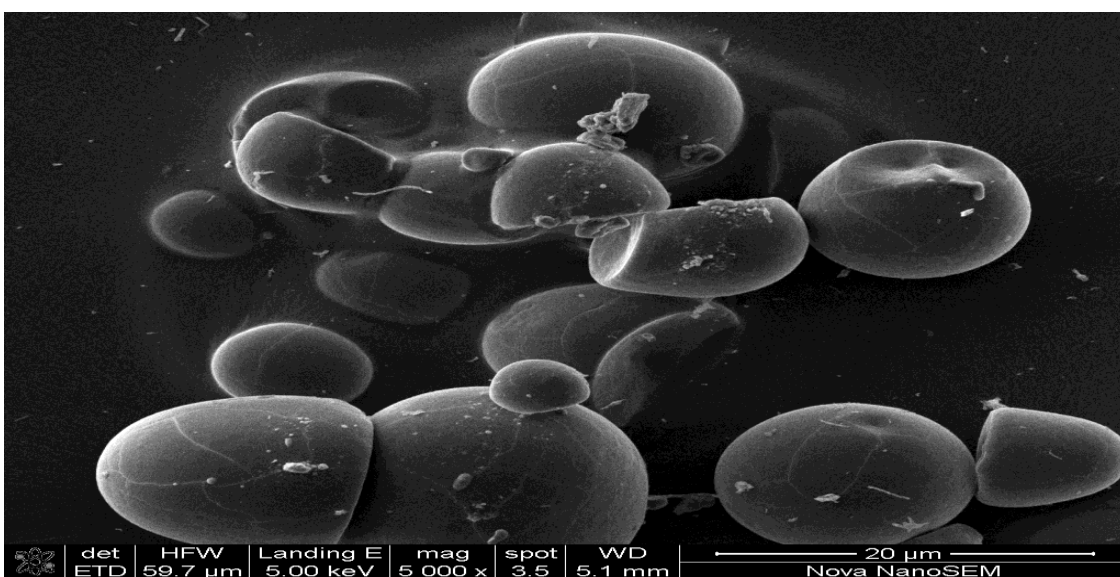


Figure 2a: The figure presents the scanning electron micrograph of native cassava starch.

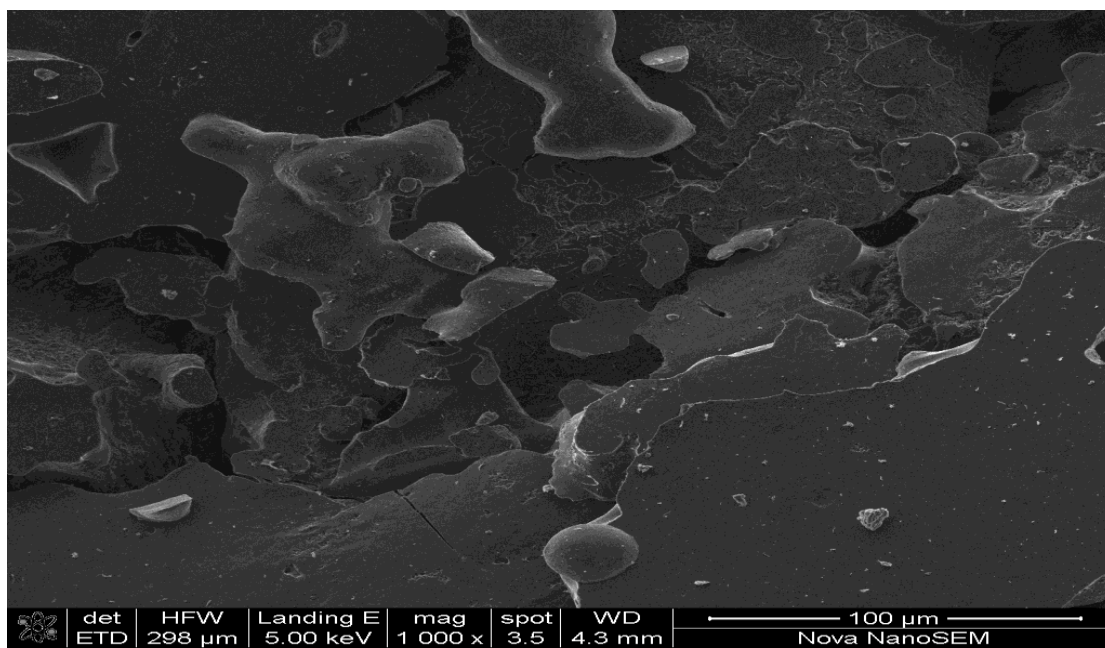


Figure 2b: The figure presents the scanning electron micrograph of phthalated cassava starch.

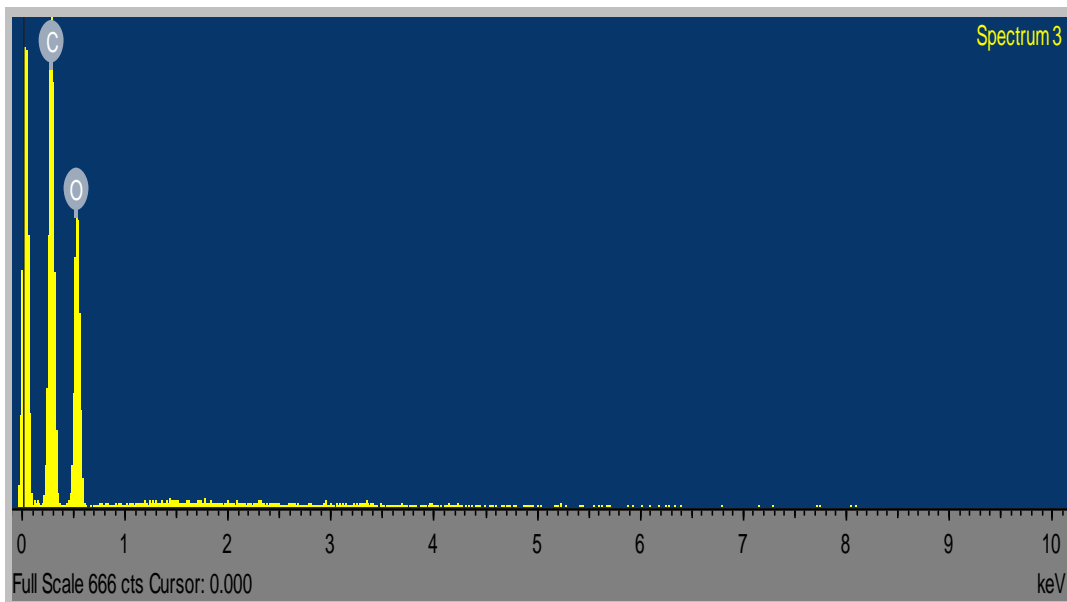


Figure 3a: The figure presents the EDS of native cassava starch.

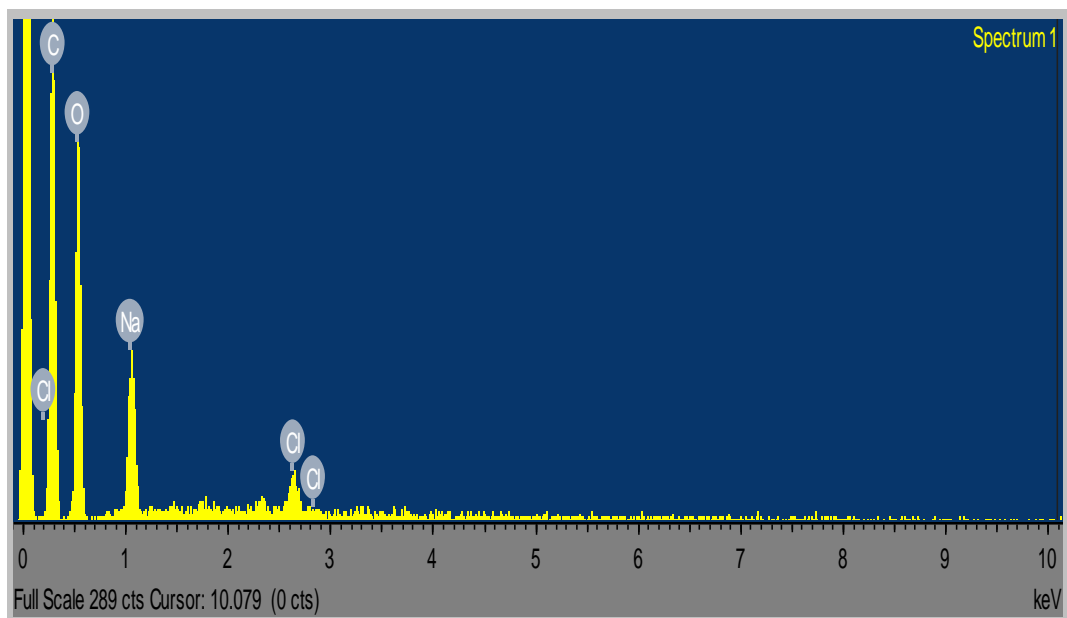


Figure 3b: The figure presents the EDS of phthalated cassava starch.

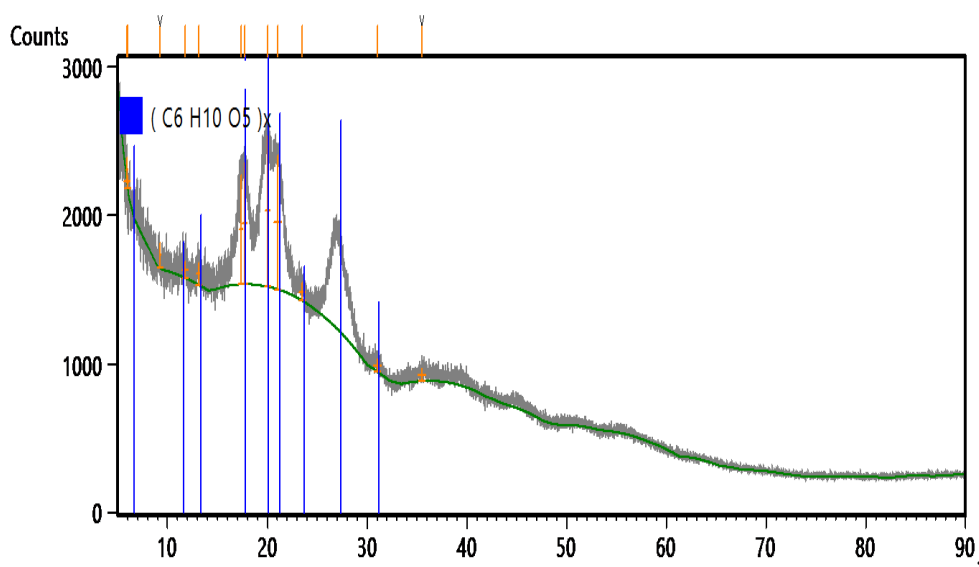


Figure 4a: The figure presents the XRD of native cassava starch.

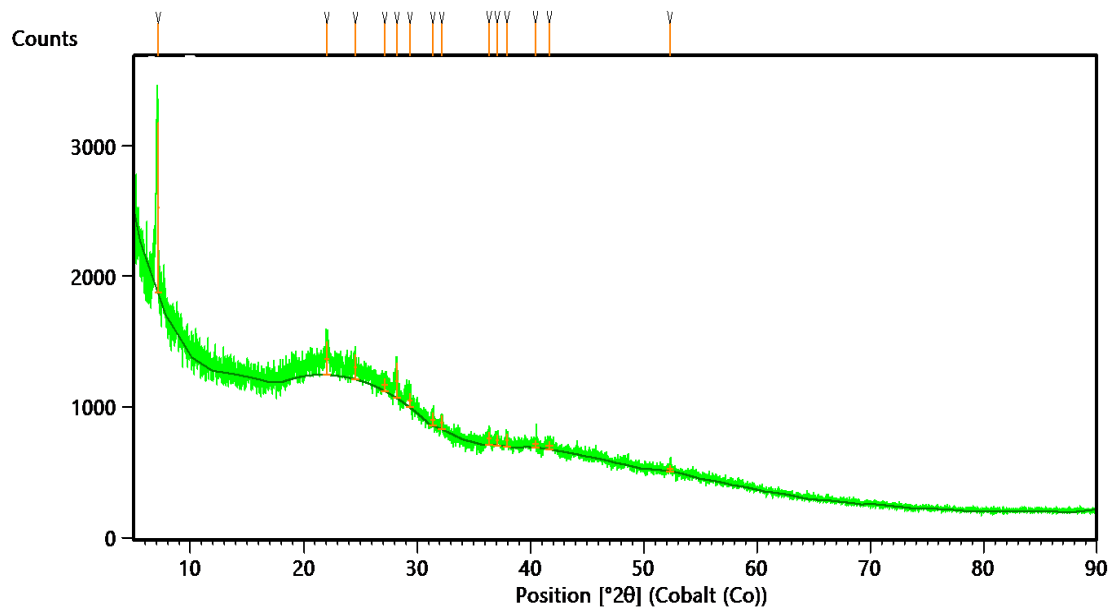


Figure 4b: The figure presents the XRD of Phthalated cassava starch.

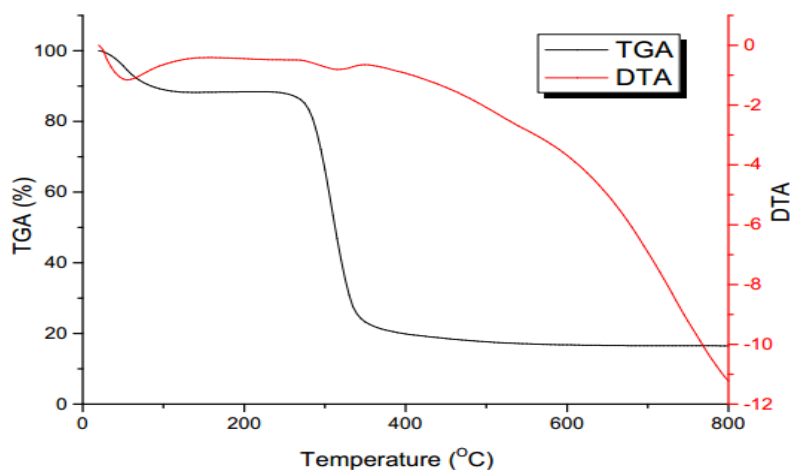


Figure 5a: The figure presents the TGA and DTA of native Cassava starch.

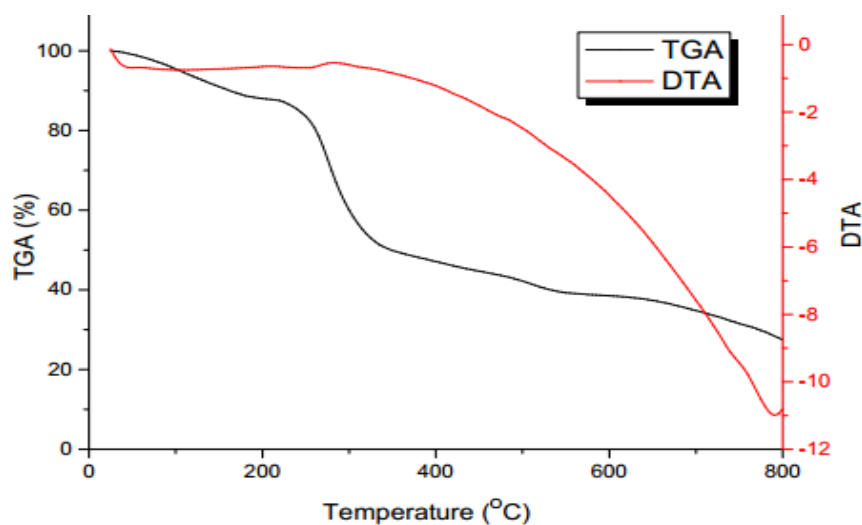


Figure 5b: The figure presents the TGA and DTA of Phthalated Cassava starch.

4. DISCUSSION

FTIR spectroscopy was used to verify the change in the chemical structures of starch molecules resulting from phthalation. The FTIR spectra of native starch and phthalated starches are presented in Fig.1a and 1b respectively. In spectrum of native starch, the peak at 3425.58 cm^{-1} and 2929.87 cm^{-1} correspond to O-H and C-H stretching, while the

peaks at 1654.92 cm^{-1} and 1460.11 cm^{-1} correspond to O-H and C-H bending [18]. Phthalated starch showed some absorption bands at 1924.96 cm^{-1} , 1371.39 , and 1240.23 cm^{-1} assigned to C=O, CH_3 symmetry deformation vibration and carbonyl C–O stretch vibration, respectively. These new absorption indicated that phthalated starches were formed during esterification process.

The surface morphology of native and modified starches were verified using Scanning Electron Microscopy (SEM) (Hitachi SU8030 FE-SEM Tokyo, Japan). The micrograph of the native starch granules is presented in Fig. 2a. It has a round and globular shape with truncated end on one side, the surface of the native starch granules is smooth with no evidence of any fissures or pores. The result agrees with the submission of Aviara *et al.* (2014) who reported that the surface of starch granules are often times spherical, with a few exception, having indented shapes similar to egg that was cut at various positions [19]. Lawal (2011) reported oval or elliptical granular shapes for the starch granules synthesized from pigeon pea [20]. The micrograph of the phthalated starch is presented in Fig. 2b, the surface of the granular structure was disrupted, displaying a film-like and an irregular surface, in contrast to the native starch micrograph (Fig. 2a). This disruption could be traced to the intermolecular hydrogen bonds that were damaged during the phthalation process. The result is similar to the report of Adenike *et al.* (2014) who reported that bitter yam has larger, more fibrous, irregular aggregate shape after acetylation [21]. In addition, Yixiang *et al.* (2004) reported that there was a loss of starch granule structure of maize after acetylation [22]. Similarly, Agbo and Odo (2010) reported that distortions were observed in the morphological structure of acetylated and oxidized starches of *Icacina* [2].

The EDS of the native and phthalated cassava starches are presented in Fig. 3a and 3b. The spectrum of native cassava starch showed the presence of carbon (C) and oxygen (O) as elemental composition, however hydrogen is not shown on the spectrum, the reason is that hydrogen does not have a core electron that the machine can pick up. Fig. 3b shows the EDS chart of phthalated cassava starch, the following elements, C, O, Na, and Cl are shown. Na and Cl appear in the spectrum, this was because NaOH and HCl were used to adjust the pH during modification.

The XRD measurements were performed to check if chemical modification altered the crystallinity of the native starch. The XRD pattern of the native and phthalated starches are presented in Fig. 4a and 4b, respectively. The XRD pattern of native starch (Fig. 4a) showed strong peak at 17.5° , 20° , 21° and 27.5° (2θ). The XRD pattern of the phthalated starch (Fig. 4b) showed the collapse of crystallinity observed for native starch in Fig. 4a, and this change brought about the amorphous nature observed in the phthalated starch (Fig. 4b). This may be because of the hydroxyl group that has been replaced by phthalate group; also, it might be that the phthalation took place in the crystalline region of the starch. Zhang *et al.* (2009) reported that acetyl groups replaced some hydroxyl groups of yellow ginger acetate starch, which reduced the formation of inter and intra-molecular hydrogen bonds and resulted in a partial destruction of the original ordered crystalline structure [23].

Thermogravimetry analysis (TGA) curves were employed to examine the change of thermal stability caused by phthalation. Fig. 5a shows TGA curves of native cassava starch. The initial weight loss of native cassava starch was observed at a temperature range of $1\text{--}100^\circ\text{C}$, indicating the loss of water in the starch sample, another weight loss was observed at 280°C , this resulted from the decomposition of organic matters in the starch sample. At 350°C , it was observed that the structural matrix has completely collapsed, leaving the residues. Presented in Fig. 5b is the TGA curve for phthalated cassava starch. The initial weight loss began at temperature below 100°C , signaling the removal of water content in the granules. The second weight loss was observed at 220°C , largely due to the decomposition of organic matters present in the starch derivative. In the third stage, there was further reduction in the weight of the phthalated starch at a temperature around 360°C , further enlongation of the temperature until 800°C revealed a gradual weight loss of the sample. Therefore, phthalation had a beneficial effect on the thermal stability of starch product. Zhang *et al.* (2009) reported similar result [23].

5. CONCLUSION

The result showed that phthalation of the native starch converted its crystallinity to amorphous structure in modified starch. Thermal stability of phthalated starch increased because of the modification. The smooth surface of the native starch granules was disrupted after modification, birthing a film-like pattern and an irregular structure.

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