Drug Discovery

Comparative evaluation of the functional properties of natural and modified African Bitter Yam (*Dioscorea dumetorum*) starch as potential excipients in drug formulations

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To Cite:
Makinde M, Adetunji O, Samuel B. Comparative evaluation of the functional properties of natural and modified African Bitter Yam (*Dioscorea dumetorum*) starch as potential excipients in drug formulations. *Drug Discovery* 2025; 19: e22dd3015
doi:

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Peer-Review History
Received: 12 April 2025
Reviewed & Revised: 27/April/2025 to 23/September/2025
Accepted: 05 October 2025
Published: 16 October 2025

Peer-Review Model
External peer-review was done through double-blind method.

Drug Discovery
pISSN 2278–540X; eISSN 2278–5396

DISCOVERY SCIENTIFIC SOCIETY

ABSTRACT

The purpose of modifying native starch is to enhance its role in drug delivery. African Bitter Yam starch (ABY) was modified physically by pregelatinization to yield PABY and chemically using both citric and phosphoric acid to obtain CAMABY and PMABY respectively. Functional properties of the starches as potential excipients were then compared. The four starch samples were categorized using photomicrography, density measurements, flow properties (angle of repose), swelling and pasting properties, and Fourier Transform Infrared (FTIR) spectroscopy as assessment criteria. Results were analysed using mean (n=3), standard deviation and analysis of variance, ANOVA ($p<0.05$). Photomicrography revealed that the starch samples were spherical in shape. ABY starch particles appear more tightly packed with fewer void spaces. PABY, CAMABY and PMABY showed agglomeration of the starch granules and increased pore spaces. Deformation characteristics of the modified starches (measured by Carr's index) were significantly better than the native starch, however, PABY had the highest bulk density (0.59±0.021). The angle of repose ranked ABY(48.18^0)>PMABY(39.61^0)>CAMABY (36.23^0)>PABY(25.97^0), indicating that phosphorylation conferred better flow properties. The swelling properties ranked CAMABY(1.47±0.08)>PMABY>PABY> ABY(0.76±0.02). Significant differences were observed in the pasting properties of the starches, with PMABY and CAMABY having the highest (131.02 cP) and lowest (12.13cP) breakdown viscosity, respectively, implying the highest degree of substitution in PMABY. Characteristic FTIR peaks of ABY at 784.80 cm^{-3} and 1330.40 cm^{-3} were also observed for PABY, CAMABY and PMABY, which showed additional peaks due to the modifications, but maintained the basic structure of the native starch. This study showed that physical and chemical modification showed substantial improvements on the functional properties of the native African Bitter Yam starch. The chemical modification methods adopted in this study can be further

exploited for use in other polymers, with physicochemical parameters tested as well as other parameters predictive of improved desirable excipient properties.

Keywords: Starch, Excipients, African Bitter Yam, Pregelatinization, Chemical modification.

1. INTRODUCTION

Excipients are extremely important in dosage form designs as they contribute to the quality and performance of the dosage form. They are incorporated in drug formulations where they serve as stability enhancers (antioxidants), modify drug release (disintegrants, biodegradable polymers, wetting agents), make manufacturing technology possible (binders, lubricants, glidants), or to improve organoleptic properties such as taste and odour (flavours) thereby improving patient's acceptability or to aid identification (colourants) (Chowhan, 1998).

Starch is a major excipient used in solid dosage forms because of its safety profile and versatility (Mohammed, 2017). The nature, quantity, processing steps and incorporation technique are all factors that determine the various roles that starches play in tablet formulations. Hence, additional sources of starch that will serve as competitive alternatives to official starches are also needed for use as excipients in immediate release and modified release formulations. Tropical roots and tubers are a rich source of edible starch, many of which are neglected and /or under-utilized with little or no industrial application. African Bitter Yam (*Dioscorea dumetorum*, Family: *Dioscoreaceae*) is one such example (sparingly used as food because of its characteristic bitter taste). It is rich in starch and may be potentially used as a starch source by the industry. The Food and Agriculture Organization (FAO) of the United Nations projected the need to increase global food production to 60% by 2050 in order to meet increased demands worldwide due to a rapid population growth and increase in per capita food consumption (Konuma, 2018). The development, characterization and standardization of neglected and under-utilized could also serve as raw materials for the food and pharmaceutical industries, thereby reducing the pressure on the species that are over-utilized as official sources of starch.

Tropical roots and tubers are crops with starchy roots, stems, corns, rhizomes and tubers. They contain 70 – 80% water, 16 – 24% starch, and trace quantities (<4%) of proteins and lipids (Hoover, 2001). These roots, tubers, grains, fruits and seeds have been used as staple foods all over the world for many centuries. Their high starch content (40–80% w/w dry basis), makes them potential starch sources as raw materials for the industry. Some of the plants grow wildly, not requiring much artificial inputs and usually have high moisture content. Moreover, coupled with the effect of the tropical climate, these crops are highly perishable, with an estimated annual loss of 10 to 60% in some cases (Shujun et al., 2006) One way to preserve these crops and minimize losses is by processing them into starches. Some of these crops can be classified as neglected and under-utilized species, and are mainly planted for subsistence and not for commercial purposes (Odeku, 2013).

When properly developed, starch obtained from African Bitter Yam (ABY) can serve as excipients with applications in tablet formulations and other dosage forms (Okunlola, 2015). ABY is relatively easy to cultivate, as it grows without needing much artificial inputs; it is less utilized as food because of its characteristic bitter taste. ABY will contribute to food security if it finds industrial use by competitively replacing some official starch sources, such as corn starch, that are important food sources.

Modification of starch consists of the restructuring of starch granules, thereby optimising the starch to improve its properties and enhance the scope of its industrial use. Generally, there are three main methods of modifying starch. These are chemical, physical, enzymatic or crystalline-genetic methods of starch modification (Adetunji, 2019). The use of enzymes such as hydrolases, amylomaltases, cyclomaltodextrinase to modify starch is known as enzymatic modification (Kaur et al., 2012). Substitution involves replacing one or more of the three free hydroxyl groups or each glucose residue with an ester or ether. Esterification can also include cross-linking the glucose chains with an ester (Adetunji, 2019). Citric acid occurs naturally in foods and as such, it is a safe food additive both for the natural environment and human health. It can be also be used as a reagent for esterification and cross-linking of starch (Golachowski et al., 2020). The *D. dumetorium* starch citrate is anticipated to possess enhanced excipient properties. The aim of this study, therefore, is to evaluate the functional properties of native African Bitter Yam starch in comparison with the pregelatinized, citric acid and phosphate modified forms of the starch.

2. MATERIALS AND METHODS

2.1. Materials

The materials used include citric acid powder (Lot 21345; Gift from Bond Chemicals Limited, Aawe, Oyo State, Nigeria), monosodium phosphate 50%v/v (Mitushi BioPharma Ltd, Ahmedalad, India), African Bitter Yam (*Dioscorea dumetorum*, Fam: *Disocoreacea*) starch (extracted from the tubers of African Bitter Yam purchased from a local commercial market in Ibadan, South West, Nigeria) and authenticated at the Forest Herbarium, Ibadan, Nigeria (FHI 10883), sodium hydroxide solution (Mitushi BioPharma Ltd, Ahmedalad, India), ultrapure and distilled water (from the Research Laboratory, Pharmaceutics and Industrial Pharmacy, UI). All the other reagents used were of analytical grade, and their applications were adjusted as described.

2.2. Methods

2.2.1. Collection and Extraction of African Bitter Yam (ABY) Starch

Tubers of African Bitter Yam (*Dioscorea dumetorum* Pax, Family: *Dioscoreacea*) were weighed, peeled, cut into smaller pieces, washed and wet-milled. The resulting slurry was sieved, allowed to stand for 6 h before decanting to leave a wet mass which was dried in the oven at 40 ^{0}C until a constant weight was obtained. The resulting dry mass was dry-milled and sieved to obtain the dried starch powder, which was packed in an airtight container (Adetunji and Ibrahim, 2022).

2.2.2. Citric acid modification of the ABY Starch

100 g of ABY starch was mixed with 200 mL of 30% w/v citric acid. The pH was adjusted to 3.5 with the addition of sodium hydroxide solution and ultrapure water until the volume became 500 mL. The mixture was left to stand for 16 h at 26±2 °C and then heated in the oven at 60 °C for 6 h. The water was emptied out from the solid and the resulting substrate was dried in the oven at 100 °C for 4 h. The dried solid was pulverized to fine powder. The product was washed with ultra-pure water to eliminate any unreacted citric acid. The product was further dried in the oven at 60 °C for 4 h (Utomo *et al*., 2020), and the resulting starch citrate (CAMABY) was stored in an airtight container. CAMABY was also tested for its identity as starch (Sofowora, 1993).

2.2.3. Phosphorylation of the ABY Starch

The method of Adetunji and Kolawole (2018) was implemented for this modification. 100 g of ABY starch was soaked in 1000 mL of ultrapure water containing 50 %v/v monosodium phosphate for 10 minutes. A slurry was thereafter made which was then heated at 85 °C using the water bath and consistently stirred with the glass stirrer for about 20 minutes. The resulting paste was then dried in hot air oven (Gallenkamp BS oven 250 size 1, England) at 60 °C for 48 h. The resulting dried mass was powdered using a laboratory mill (03200 Landers and Ciasa, Corona, USA) before storing the starch phosphate (PMABY) in an airtight container. PMABY was also tested for its identity as starch (Sofowora, 1993).

2.2.4. Pregelatinization of the ABY Starch

Exactly 200 g of ABY starch was dispersed in 200 mL of distilled water and heated with slow mixing until it turned to paste. The paste was spread out on ceramic tiles as a thin film and oven dried at 100 °C for 24 h. It was then milled and sieved through a mesh with size 0.315 mm and the resulting pregelatinized starch (PABY) was stored in an air tight container (Odeniyi et al., 2011).

2.3. Characterization of The Starches

2.3.1. Microscopic analysis

Photomicrograph of ABY, CAMABY, PMABY and PABY starch samples were taken with the aid of a light microscope installed with a calibrated eye piece. Surface morphologies were then determined using a desktop scanning electron microscope (FEI-XL 30SEM, Phenom World, Netherlands).

2.3.2. Bulk and Tapped Density Determinations

Thirty grams each of ABY, CAMABY, PMABY and PABY starch samples was measured into a graded measuring cylinder (50mL) of a known diameter at an angle of 45^0 through a funnel. The height the powder reached was measured and the volume and the bulk density were determined. The bulk density was determined by calculating the ratio of the sample's mass to its volume within the cylinder. The determinations were done in triplicate for each of the samples (Alebiowu and Itiola, 2002). For the tapped density, 100 taps were applied to each sample in the cylinder (Reus-Medina et al., 2004). The height reached by the powder was measured and the tapped density was calculated as the ratio of the mass of the sample to the volume occupied. The determinations were done in triplicate for the samples (Alebiowu and Itiola, 2002).

2.3.3. Determination of Hausner's Ratio and Carr's Index (Compressibility Index)

The Hausner's ratio was determined as the ratio of the bulk volume to the tapped volume for each of the starch samples (Hao, 2015) as seen in equation (1), while Carr's Index was determined using equation (2)

$$\text{Hausner's Ratio} = \frac{\text{Bulk Density}}{\text{Tapped Density}} \qquad (1)$$

$$\text{Carr's Index (\%)} = \frac{\text{Tapped density} - \text{Bulk density}}{\text{Tapped density}} \times 100 \qquad (2)$$

2.3.4. Determination of Angle of Repose

Angle of repose was determined using an open-ended cylinder of fixed diameter placed on a base with similar diameter. Twenty grams of each of the samples was separately measured and allowed to flow freely through the orifice of the funnel to form a heap. The height and the diameter of the heap were measured and the angle of repose was calculated according to the equation below (Reus-Medina et al., 2004). Each determination was done in triplicate.

$$\tan \theta = h / r \qquad (4)$$

Where:

Θ = angle of repose, h = height of the powder, r = radius of the circular heap.

2.3.5. Swelling Index

The method of Iwuagwu and Onyekweli (2002) was employed to determine the swelling capacity of the starches. Ten grams of each starch sample (ABY, CAMABY, PMABY and PABY) was transferred to a 100 mL measuring cylinder. The volume occupied was noted (Vs). Sufficient UPW was added into the cylinder to make a suspension. The set-up was allowed to stand for 24 h and the final volume (Vt) was noted. The swelling capacity was calculated in triplicate using the formula:

$$\text{Swelling capacity} = Vt - Vs \qquad (5)$$

2.3.6. Determination of pasting properties

The pasting properties were determined using a differential scanning calorimeter (DSC; Model DSC 204 F1; Netzsch, Selb, Germany). Exactly 5 g of each of ABY, CAMABY, PMABY and PABY were placed in the aluminium pans of the equipment and scanned between 60 °C and 300 °C at a heating rate of 10°C/min under constant nitrogen flow.

2.3.7. Fourier Transformed Infrared (FTIR) Spectroscopy

The FTIR spectra of the ABY, CAMABY, PMABY and PABY starch samples were obtained on an IR spectrophotometer using potassium bromide (KBr) disk (approximately 2 mg samples in 200 mg KBr). The scanning was done in the range 400 – 4000cm^{-1}. Plots of percentage transmittance (%T) versus wavenumber (cm^{-1}) were created on the computer monitor. The plots were analysed for characteristic functional groups present in each sample.

2.3.8. Statistical Analysis

One-way ANOVA and Turkey's multiple comparison post-hoc test ($p<0.05$) were used to analyse the statistical difference between the different starch samples.

3. RESULTS

Photomicrographs: The photomicrographs of the starch samples (ABY, PABY, CAMABY and PMABY) are presented in Figures 1. All the starch samples were spherical in shape; however, ABY starch appears more tightly packed, with fewer void spaces between the particles. PABY, CAMABY and PMABY all showed agglomeration of the starch granules and increased pore spaces within the powder bed, with CAMABY showing the highest pore spaces.

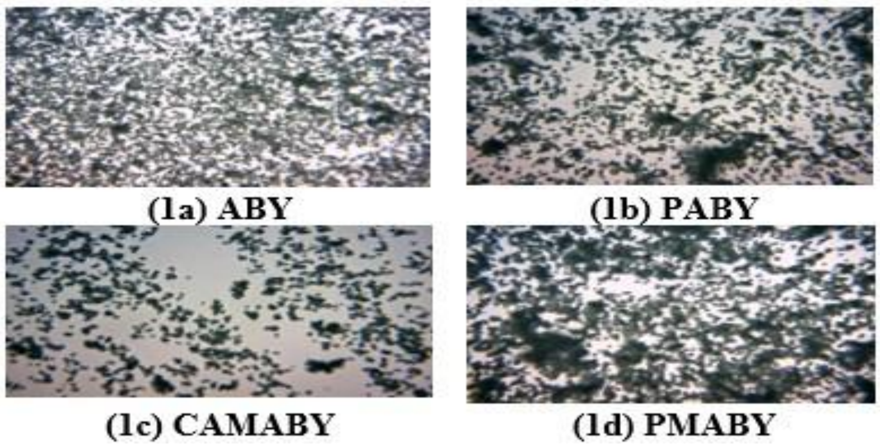

Figure 1: Photomicrograph of starches showing the surface morphology (X 40 magnification)

Physicochemical Properties: The physicochemical properties of the starches showing the bulk and tapped densities, Hausner's ratio, compressibility index and angles of repose are presented in Table 1.

Swelling Capacities: The swelling capacities of the starches are presented in Table 2. The swelling properties ranked CAMABY > PMABY > PABY > ABY.

Table 1: Physicochemical properties of the starches (n=3±S.D)

Sample Properties	ABY	PABY	CAMABY	PMABY
Bulk Density (g/cm^3)	0.27±0.01	0.59±0.021 ^{a}	0.55±0.13	0.54±0.19
Tapped Density (g/cm^3)	0.43±0.15	0.77±0.18	0.78±0.08	0.70±0.26
Hausner's Ratio	1.61±0.15	1.31±0 .11	1.44±0.02	1.30±0.14^{a}
Carr's Index (%)	38.02±0.05	23.53±0.18^{a,c,d}	30.38±0.15 ^{a,b,d}	22.87±0.04 ^{a,b,c}
Angle of Repose (^{0})	48.18±2.35	25.97±0.75^{a,c,d}	36.23±0.28 ^{a,b}	39.61±0.87 ^{a,b}

ABY = Native African Bitter Yam, PABY= Pregelatinized African Bitter Yam, CAMABY = Citric acid modified African Bitter Yam, PMABY = PMABY = Phosphoric acid modified African Bitter Yam; a: statistically significant compared to ABY ($p<0.05$), b: statistically significant compared to PABY ($p<0.05$), c: statistically significant compared to CAMABY ($p<0.05$), d: statistically significant compared to PMABY ($p<0.05$).

Table 2: Swelling capacities of the starches (n=3±S.D)

Sample	Swelling Capacity
ABY	0.76±0.02
PABY	0.83±0.12 ^{c,d}
CAMABY	1.47±0.08 ^{a,b,d}
PMABY	1.06±0.06 ^{a,b,c}

ABY = Native African Bitter Yam, PABY= Pregelatinized African Bitter Yam, CAMABY = Citric acid modified African Bitter Yam, PMABY = PMABY = Phosphoric acid modified African Bitter Yam; a: statistically significant compared to ABY ($p<0.05$), b: statistically significant compared to PABY ($p<0.05$), c: statistically significant compared to CAMABY ($p<0.05$), d: statistically significant compared to PMABY ($p<0.05$).

Pasting Properties: The values obtained from the pasting properties of the starches are presented in Table 3. Substantial differences were observed in the pasting properties of the starches, with PMABY and CAMABY having the highest and lowest breakdown viscosity respectively, implying the highest degree of substitution in PMABY.

Table 3: Pasting properties of the starches

Sample	Peak Viscosity (cP)	Trough Viscosity (cP)	Breakdown Viscosity (cP)	Final Viscosity (cP)	Setback Viscosity (cP)	Peak Time (min)	Pasting Temperature (^{0}C)
ABY	163.45	39.18	67.27	74.15	53.13	4.18	92.33
PABY	266.00	225.00	41.05	318.10	93.27	4.61	86.35
PMABY	161.00	30.00	131.02	44.13	14.03	5.42	66.81
CAMABY	207.00	81.00	12.13	149.28	68.03	5.27	72.62

ABY = Native African Bitter Yam, PABY= Pregelatinized African Bitter Yam, CAMABY = Citric acid modified African Bitter Yam, PMABY = Phosphoric acid modified African Bitter Yam

Fourier Transformed Infrared (FTIR) Spectroscopy: The occurrence of FTIR peaks in the different starch samples are presented in Table 4, and the FTIR spectra for the starch samples (ABY, PABY, CAMABY and PMABY) are presented in Figures 2a to 2d, respectively.

Table 4. Table showing the occurrence of FTIR peaks in the different starch samples

Starch Code	Peak (cm^{-3})	Starch Code	Peak (cm^{-3})	Starch Code	Peak (cm^{-3})	Starch Code	Peak (cm^{-3})
	784.80		760.00		784.00		756.80
	1330.40		1226.40		1172.80		1173.60
	1699.20		1697.60		1622.40		1620.80
ABY	2370.40	PABY	2368.80	CAMABY	2368.00	PMABY	2368.00
	2923.20		2922.40		3044.00		3047.20
	3448.00		3448.80		3877.60		3876.80
	3931.20		3938.40				

ABY = Native African Bitter Yam, PABY= Pregelatinized African Bitter Yam, CAMABY = Citric acid modified African Bitter Yam, PMABY = Phosphoric acid modified African Bitter Yam

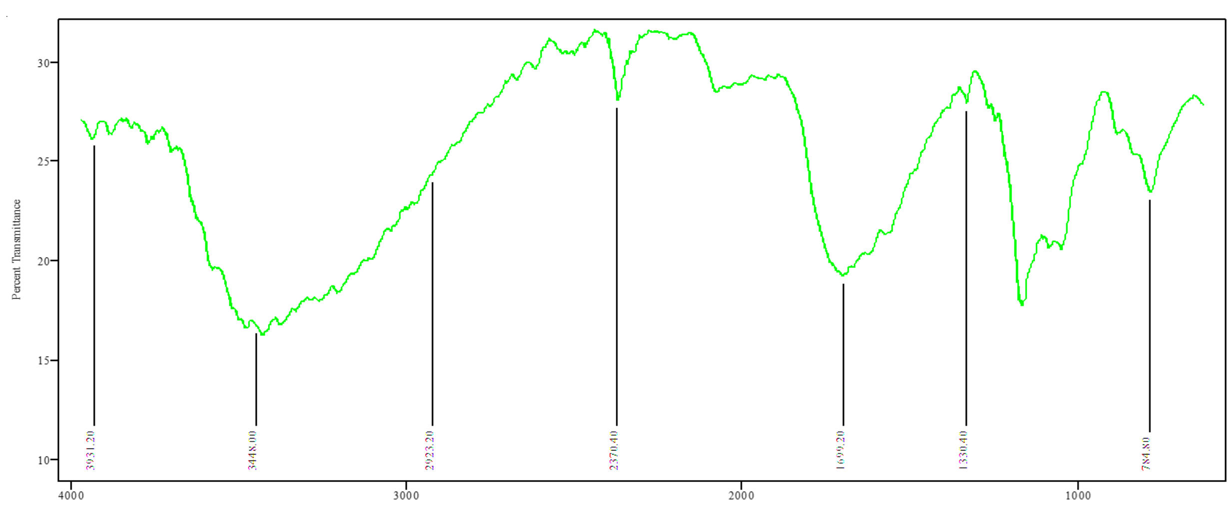

Figure 2(a): FTIR spectrum of African Bitter Yam starch

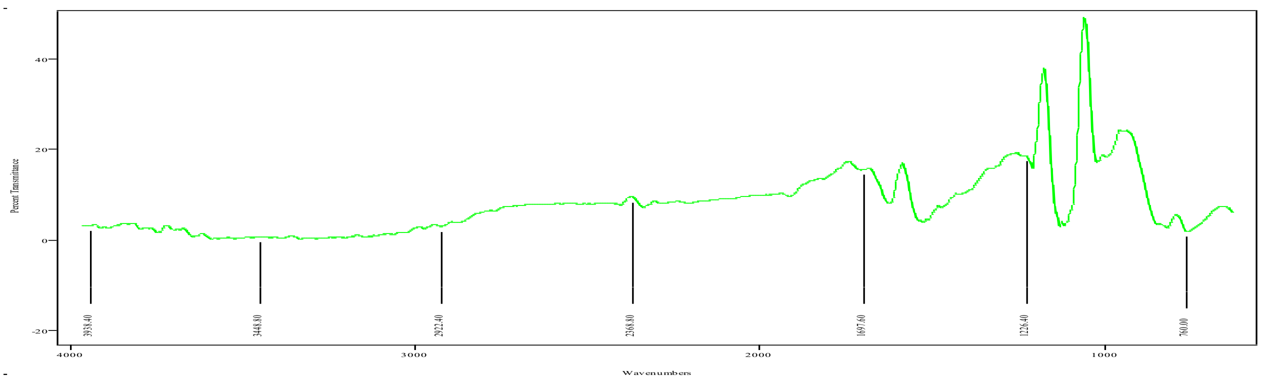

Figure 2(b): FTIR spectrum of Pregelatinized African Bitter Yam starch

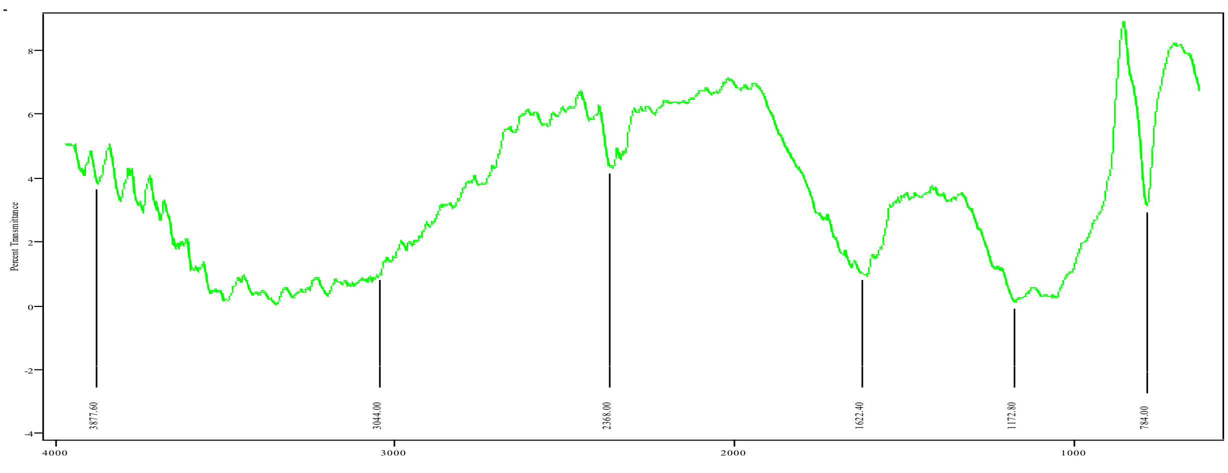

Figure 2(c): FTIR spectrum of citric acid modified African Bitter Yam starch

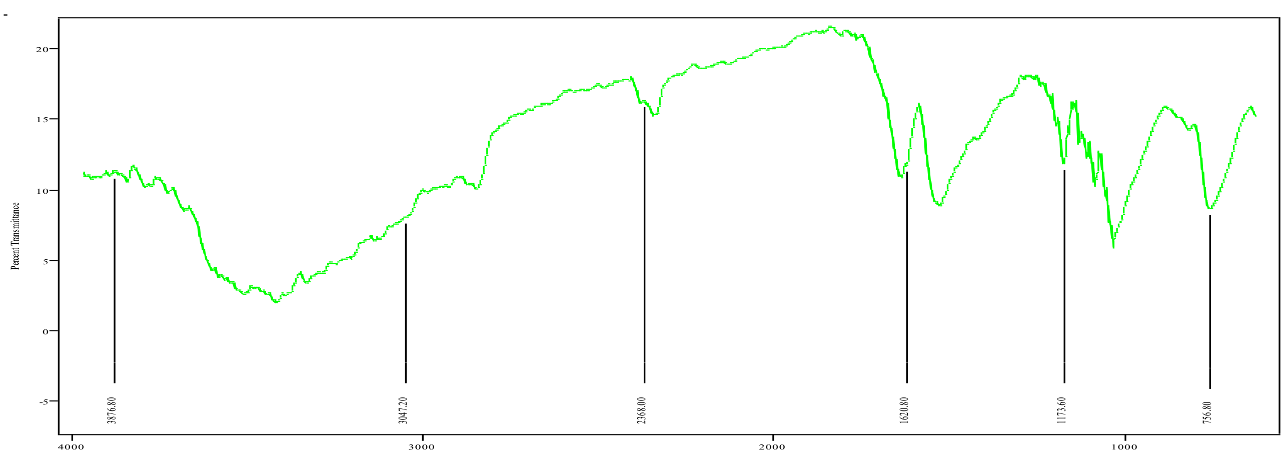

Figure 2(d): FTIR spectrum of phosphate modified African Bitter Yam starch

4. DISCUSSION

The flow properties of powders are dependent on their particle shape, particle size and size distribution. Several processing operations in the manufacture of tablets and capsules, such as feeding and discharge from hoppers, die and capsule filling, pneumatic conveying are all affected by the shape, size and size distribution of powders (Adetunji et al., 2021). Adequate flow is essential in the filling of die cavities in high-speed tabletting/encapsulating machines in order to ensure weight and content uniformity of the resultant tablets/capsules (Olayemi et al., 2021). Spherically-shaped particles are more desired for use in solid formulations because they have better flow rates than irregularly-shaped particles (Alebiowu & Itiola, 2002). The spherical shapes of all the starch samples suggests their applicability as excipients in solid dosage forms. Physical (pregelatinization) and chemical (esterification) modifications of the native starch caused disruption of the starch granules and consequent agglomeration, thereby producing voids within the powder bed. In 2024, Olayemi and other authors reported that this disruption reduces the inter-particulate friction and improves flowability, thereby influencing the packing behaviour of the modified starches. Consequently, this implies that the modified starches will have better flowability compared to the native ABY starch.

The density of powders is very critical in pharmaceutical processing as it affects the homogeneity of the drug-excipient mixture. A homogenous mix is essential for the dosage form to have dose uniformity in each unit tablet or capsule. Density of a powder significantly affects its flow and the uniformity of mixing with other powders. Generally, achieving a uniform mix requires that the powders are of similar densities (Pharmacy180, 2023). Bulk density is the ratio between the combined mass of loosely packed particles of a powder sample and its total volume. This total volume is the interparticulate (also known as the void volume) and intraparticulate (also known as the porosity of the particle) volume occupied by air. This is in addition to the volume occupied by the solid component(s) of the particle. This parameter plays a significant role in powder processing as it directly measures the volume a specific mass of powder occupied under standard conditions (Pharmacy180, 2023).Tapped density, however, is the packed volume of a given mass of particles after it has been subjected to a well-defined rate and extent of agitation'. It is the ratio of the mass of the consolidated sample to the total volume it occupies. It helps to determine the extent of powder consolidation to expect during manufacturing processing and it is used in conjunction with the bulk density to determine the compressibility index (or Carr's index, CI) and the Hausner's ratio of the powder. These ratios help compare the relative degree of consolidation and estimated flow characteristics of different powders (Byrn et al., 2017). Pregelatinized starch had the highest bulk density value of 0.59g/cm^3, followed by the acid modified CAMABY and PMABY, having comparable densities of 0.55g/cm^3 and 0.54g/cm^3 respectively. The native ABY starch had the lowest bulk density of 0.27g/cm^3. Only the pregelatinized starch showed a statistically significant difference in bulk density, compared to the native starch, ABY. This suggests that the pregelatinized variant, PABY, has a greater ability to promote even packing when confined in a die cavity during a tabletting operation, compared to the acid-modified variants with lower densities and much less the native ABY starch, whose bulk density is only about half the value obtained for the acid-modified starches. Acid modification improved the bulk density significantly, but pregelatinization did better. Carr's index (CI) gives a measure of the ability of a material to deform under pressure. Materials with a CI ≤ 10% are considered to have excellent flow, those between 11% and 15% − good flow, between 16% and 20% − fair, and those >25% − poor flow. Conversely, Hausner's Ratio (HR) gives the measure of material cohesiveness, which depicts the degree of densification. Values ≤1.11 show that the material is cohesive, and it is less cohesive when HR values are between 1.12 and 1.20. (Lefnaoui & Moulai-Mostefa, 2015). Based on Carr's index, the results showed that pregelatinized (PABY) and phosphate modified (PMABY) starches had fair deformation properties of 23.53% and 22.87% respectively, whereas the native ABY and CAMABY starches fell into the poor range. This suggests that PMABY and PABY will promote more uniform packings when confined into tabletting dies for compaction (Eraga et al., 2017) The Hausner's ratios obtained ranged between 1.30 to 1.61, depicting poor cohesiveness of the starches, with PMABY and PABY having the lower values of the set, approximately 1.30. All the starch samples showed statistically significant differences in the values obtained for the Carr's indices.

During manufacturing operations, it is sometimes necessary to change a powder's bulk or tapped density in other to achieve the desired flow. Though the true density and porosity of particles are determined by the intrinsic nature of a material, they can be modified by varying manufacturing processes during the preparation of raw materials. The quantity of water and shear applied in wet granulation, as well as granulation techniques involving the use of roller compaction, all help to facilitate particle consolidation, binding and agglomeration of fine particles (Pharmacy180, 2023). Consequently, this will improve powder flow by reducing the compressibility index and Hausner's ratio. The intrinsic flow problems and compressibility limitations identified with African bitter yam starches can therefore be overcome by modifying the processing steps during granulation. The modified starches will be preferable to the native ABY starch since they showed better physicochemical properties in the parameters tested, with the pregelatinized, PABY having a hedge in the physicochemical properties.

The angle of repose reflects the flowability of a powder; values less than 30^0 indicate excellent flow, 31^0 to 35^0 indicate good flow, 36^0 to 40^0 indicate that the flow is fair and values >40° signify poor flow (Mohammadi & Harnby, 1997). The angles of repose measured for the starch samples were in this order: ABY (48.18^0) > PMABY (39.61^0) > CAMABY (36.23^0) > PABY (25.97^0). Only the pregelatinized starch, PABY, displayed good flow with an angle of repose <30^0. The chemically modified variants, CAMABY fell within the range for fair flow, while PMABY displayed fair to poor flow properties. Notably, all the modified starches had lower angles of repose than the native ABY starch, which ranged between 46^0 to 51^0. Therefore, all the modifications improved the flowability of the native starch with the physical modification through pregelatinization having a marked improvement over the chemical modifications.

Swelling discloses the water-absorbing capacity of starch granules. Structural changes due to cross-linking degree and the drug release behaviour of different materials can be evidenced by their swelling behaviours (Lin et al, 2005). The presence of branched polymers in the crystal structure of starches could significantly affect the swelling ability of the starches (Kang et al, 1997). Esterification of native starches were reported to have reduced swelling power compared to native starches from various sources due to a reduction in the water affinity of the modified starches (Golachowski et al., 2020). However different researchers reported differences in swelling power based on botanical source of raw materials and conditions of esterification, which are affected by amylose/amylopectin content and the degree and pattern of crystallinity of the modified starch. Remya et al. (2018) reported an increase in swelling power with citrates of starches obtained from tubers such as potato and cassava, while Lee et al. (2018) showed a correlation between swelling power and pH value of the esterification reaction. In another study, Kapelco-Zeberska et al (2016) correlated water affinity of starches with pasting temperature. Other researchers discovered that the differences in affinity for water of the starch citrates correlated with the degree of substitution. According to Mei et al (2015) and Kim et al (2017), a decrease in solubility and swelling power of starch citrates indicated a higher degree of substitution of the free hydroxyl groups on the glucose residue with an ester. Conversely, Hong et al in 2020 reported that the affinity of starch citrates for water depended on the technology process of modification. In this study, the starch esters had higher swelling capacities of 1.47 and 1.06 for CAMABY and PMABY, respectively compared to the ABY (0.76). This is consistent with the findings of Remya et al (2018), whereby starches obtained from tubers, esterified to form citrates had increased swelling properties, compared to their respective native starch. There was no statistically substantial difference in the swelling capacity of the pregelatinized starch (PABY) compared to the native starch (ABY). Transformation of the granular structures of starches occurs when heat is applied to a bed of starch powder. This transformation involves an initial ordered state to a randomized, but disordered state, which is a result of the swelling of the granules (Jane et al., 1999). The swelling which occurs in the starch granules is due to trapped water, which eventually enhances the melting of the crystal lattice of starch. Therefore, it is expected that starch particles with lower swelling capacities will undergo lower rate of distortion due to the lower number of water molecules trapped in the crystal lattice (Olayemi et al, 2021).

Peak viscosity is a measure of the rate at which granule swelling equals granule breakdown (Olayemi et al, 2021). The peak viscosity (Cp) ranked PABY > CAMABY> ABY>PMABY. Olayemi *et al* (2021) also reported that degradation of starch granules due to pregelatinization could lead to reduced viscosity against shear stress, however, the opposite was the case for this study where pregelatinization led to an increase in peak viscosity. Lovedeep et al (2007) stated that high peak viscosity has a direct relationship with both bulk density and amylose content of starches, and therefore, this could account for the reason why PABY with the highest bulk density had the highest peak viscosity. The breakdown viscosity (measure of degree of disintegration of starch granules during heating) was highest for PMABY and lowest for CAMABY. The inference of these results shows that modification of ABY by cross-linking with phosphates (PMABY) led to a total substitution of the granules available for further disintegration, which may impact more mechanical stability on uncoated tablets if PMABY was incorporated as a disintegrant. The pregelatinized starch (PABY) had a low breakdown viscosity value of 41.05 Cp, indicating that more starch granules are still available for disintegration to occur. Final viscosity is an indication of the resistance of a material to flow on application of heat, while setback viscosity is the measure of the gelling ability or retrogradation ability of starches (Hung and Morita, 2005). The final and setback viscosities ranked PABY > CAMABY > ABY > PMABY. The implication of this is that PABY had the highest resistance to flow on application of heat, though the reverse is the case without application of heat as shown in the results obtained for the angle of repose. The temperature at which the viscosity of the starch material begins to increase during the heating process is known as the pasting temperature (Salman et al, 2008). A high degree of crystallinity, especially when a material is in its unaltered form, will lead to a high pasting temperature (Hung and Morita, 2005), which in this case could be linked to the unmodified starch (ABY) having the highest pasting temperature. Esterification was also reported to cause changes in pasting temperatures. Falade and Ayetigbo (2015) reported that the pasting temperature of starch esters were lower than the native starches, as confirmed in this current study with PMABY and CAMABY. Higher degree of substitution as expected with PMABY (cross-linking with phosphate) may be responsible for its lower pasting temperature compared to starch citrate, CAMABY.

The FTIR spectrum of the native (unmodified) African Bitter Yam (ABY) starch contains characteristic peaks at 784.80 cm^{-3} and 1330.40 cm^{-3}, which are due to strong C-H bonds present in aromatic rings and strong C-N stretch due to aromatic amines respectively (Fan et al, 2012). The same set of peaks were observed in the FTIR plot for the pregelatinized ABY (PABY), but now occurring at 760.00 cm^{-3} and 1226.40 cm^{-3} respectively, while for the citric acid modified ABY (CAMABY) and phosphorylation modified ABY (PMABY), the peaks occurred at 784.00 cm^{-3} and 1172.80 cm^{-3} and 756.80 cm^{-3} and 1173.60 cm^{-3}, respectively. Other characteristic peaks identified in the FTIR spectrum for ABY include 1699.20 cm^{-3} attributable to C=O stretching, 2370.40 cm^{-3} (C≡N stretching) and 2923.20 cm^{-3} due to strong C-H stretch of aldehydes (Nandiyanto et al, 2017). It was observed that no substantial interaction that changed the fundamental integrity of the ABY starch occurred as a result of the physical modification by pregelatinization (PABY) and chemical modifications by citric acid and phosphorylation (CAMABY and PMABY).

5. CONCLUSION

In this study, the functional properties of native African bitter yam starch were evaluated in comparison with a physically modified variant obtained through pregelatinization and two chemically modified variants which were obtained through esterification by substituting with citric acid and cross-linking with monosodium phosphate. The modifications showed significant improvements on the functional properties of the native starch. The physicochemical parameters that predict better desirable excipient properties can be used to further exploit the chemical modification techniques used in this study for use in other polymers.

Acknowledgements

The Technologists in the Research Laboratories of the Departments of Pharmaceutics & Pharmaceutical Technology, Pharmacognosy and Pharmaceutical Chemistry, Faculty of Pharmaceutical Sciences, University of Ibadan, Nigeria are acknowledged for their role in providing technical support during the study.

Authors' Contributions

This work is a result of collaborations between all authors. The conceptualization and study design was by Author Adetunji OA, Authors Makinde M, Adetunji OA and Samuel BB carried out work on methodology, resources and literature search. The laboratory work/statistical analysis was carried out by Author Makinde, while Authors Adetunji and Makinde wrote the manuscript. Supervision was Authors Adetunji OA and Samuel BB. All the authors approved the final manuscript.

Ethical Approval

Not applicable. This article does not contain any studies with human participants or animals performed by any of the authors.

Informed Consent

Not applicable.

Conflicts of interests

The authors declare that they have no conflicts of interests, competing financial interests or personal relationships that could have influenced the work reported in this paper.

Funding

This research did not receive any external funding like specific grant from funding agencies in the public, commercial, or nonprofit sectors.

Data and materials availability

All data associated with this study will be available based on the reasonable request to corresponding author.

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