# Preparation of Biodegradable Plastic Films from Tuber and Root Starches

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***Abstract:*** *Starches were isolated from Irish potato, cocoyam and cassava tubers and were modified by chemically treating the native starches with Hydrochloric Acid (HCl). Proximate analysis and functional properties test namely, moisture content, protein content, crude fat content, ash content, crude fiber content, pH value, bulk densities (loose and packed), amylase and amylopectin were carried out on the native and modified starches. X-ray diffraction analysis of both the native and the modified starches were carried out. From the X-ray diffraction, Miller indices, particle size and the degree of crystallinity were calculated. The native and modified starches were then used to prepared plastic film. The mechanical properties, namely, tensile strain, tensile stress, and young modulus were calculated from the mechanical properties data, which were obtained from the Instron 3369 mechanical testing machine.*

*Proximate analysis and functional properties test result show that the three tuber starches isolated have low non-starch component which make them a good raw materials for plastic film. X-ray diffraction of both native potato and cassava starches gives degree of crystallinity of 20.6% whereas X-ray diffraction of modified native and potato has degree of crystallinity of 41.7% and 44.3% crystallinity respectively. The increase in degree of crystallinity of modified starches may due to the breaking down of amylopectin to amylose.The mechanical properties of the films improved when the starches were modified. The results showed that the selected tuber root starches are beneficial and capable of replacing the popular synthetic plastic materials that are not environmental friendly.*

***Keywords:*** *Biodegradable, Crystallinity, Film, Starch, X-ray diffraction.*

## I. Introduction

Increased use of synthetic packaging plastic has led to serious ecological problems due to their total non-biodegradability. Continuous awareness by one and all towards environmental pollution by the latter and as a result the need for a safe, eco-friendly atmosphere has led to a paradigm shift on the use of biodegradable materials, especially from renewable agriculture feedstock and food processing industry [1]. Most widely used polymeric materials for packaging purposes, developed in the past 50–60 years, are durable and inert in the presence of microorganisms, leading to a long-term performance. However, in view of the current emphasis on environmental pollution problems and the shortage of land for solid waste management, the need for environmentally degradable polymers has increased [2]. This development has received widespread government support in developing countries. Several studies have been performed to analyze the properties of starch based biodegradable plastic. Starches from roots and tubers (Irish potato, cocoyam, cassava) were studied in their slurry, powdered, gelatinous and crystalline form. Since starch contains about 30% of amylose, and amylose is responsible for the film forming capacity of starches [3]. Starch will be good raw materials to prepare biodegradable film plastics sinceit is a renewable source, widely available, relatively easy to handle, and inexpensive [4].

Biodegradable plastics are plastics that will decompose in natural aerobic (composting) and anaerobic (landfill) environments. Biodegradation of plastics occurs when microorganismsmetabolize the plastics to either assailable compounds or to humus-like materials that are less harmful to the environment. They may be composed of either bioplastics, which are plastics whose components are derived from renewable raw materials or petroleum-based plastics which contain additives.Polymer additives play a vital role in modern plastics, from overcoming obstacles in processing, to increasing material durability, to helping product designers obtain the trendy looks, feel and performances that their consumers demand for their applications. Additives can also be used to comply with local regulations. Most plastics contain other organic or inorganic compounds blended in. The amount of additives ranges from 0% for polymers used to wrap foods to more than 50% for certain electronic applications. The average content of additives is 20% by weight of the polymer.

Starch as a cost-effective additive to synthetic plastic was developed in the 1970s, but it was also realized at that time that standard starch was unsuitable. This led to the discovery of the benefits of modifying the starch/polymer interface by making the normally hydrophilic starch surface hydrophobic, and the need to reduce the moisture content of starch so that it could be processed in polymer melts above 160°C [5]. Stabilizers

for polymers are used directly or by combinations to prevent the various effects such as oxidation, chain scission and uncontrolled recombination and cross-linking reactions that are caused by photo-oxidation of polymers. Plasticizers are additives that increase the plasticity or fluidity of a material.

Biodegradable Plastics decomposes to environmental friendly composites. Most biodegradable plastics contain no allergens and are safe for atopic consumers. Biodegradable products are non-toxic. They are made from natural elements therefore contain no chemicals to exude toxic and poisonous wastes while breaking down in compost. The natural composition of the biopolymers is fully absorbed by the earth. With national concerns for energy conservation, a great advantage of using biodegradable products is the potential to rely less on oils. A significant amount of the oil used to produce plastics will be conserved. Producing biodegradable products made from local biomass materials can save the country considerable amounts of energy, ultimately leading to a reduced dependency on oil sources. In the long run, adapting to using biodegradables can lead to domestic solutions [6]. Biodegradable plastics are easier to recycle because they are made from materials that are fully biodegradable. Biodegradable plastics can be used and reused more efficiently even as household utensils and in restaurants [7].

The inherent danger with biodegradables is with its improper disposal, this leads to an inefficient breakdown of the plastic, which can release toxins into the environment. These toxins may include methane and carbon dioxide, both of which contribute to the greenhouse effect. The most efficient way to dispose of biodegradable plastic is by composting. Biodegradable plastics are made from organic sources which include Corn and soybeans. The present work is carried out to compare the proximate analysis and functional properties of the native starches isolated from three different tubers which are Irish potato, cocoyam and cassava.

## II.    Experimental
### Sample Collection
The sample starches Irish potato, cocoyam and cassava were bought at Agbekoya market in Apata Ibadan, Nigeria.

### Isolation of Sample Starches
About 3kg of Irish potato tuber was washed, peeled, washed again and sliced for easy blending, this sample was put into the blender bit by bit, after blending, the slurry was sieved. The water was allowed to settle for 10 minutes after which the supernatant was decanted. The residual starch was dried. The sample was then stored. The same method was used to isolate starches from cassava and cocoyam tubers.

### Proximate Analysis of Starches
The proximate analysis of the starches was determined by AOAC, 1990. These are moisture content, ash content, crude fat, protein and carbohydrate.

### Moisture content determination
Moisture content determination was carried out using the air oven method. Crucibles were washed and dried in an oven. They were allowed to cool in the desiccators. 3g of each sample starch was then transferred into the crucibles and dried at temperature between $103\text{-}105^{o}$c. The dry samples were cooled in a desiccators and the weight noted. They were later returned to the oven and the process continued until constant weights were obtained.

% Moisture content= Weight Loss x 100
                     Weight of sample

### Determination of Ash content
3g of each starch of finely grounded sample was weighed into clean; dried previously weighed crucible with lid ($W_1$). The sample was ignited over a low flame to char the organic matter with lid removed. The crucible was then placed in muffle furnace at $600^{o}$C for 6 hours until it ashed completely. It was then transferred directly into desiccators, cooled and weighed immediately ($W_2$).

% Ash= $\underline{W_2\text{-}W_1}$           x       100
        Weight of sample

### Determination of crude fat
The soxhlet extraction method (AOAC, 1996) was used. This method could only give the approximate fat content in a sample because all the substances soluble in chosen solvent (petroleum ether, $40^{o}$C-$60^{o}$c boiling range) were extracted from the sample. About 3g of each starch sample was weighed into a weighed filter paper and folded neatly. This was put inside pre-weighed thimble ($W_1$). The thimble with the sample ($W_2$) was inserted into the soxhlets apparatus and extraction under reflux was carried out with petroleum ether ($40^{o}$C-$60^{o}$c boiling

range) for 6 hours. At the end of extraction, the thimble was dried in the oven for about 30 minute at $100^{o}$C to evaporate off the solvent and thimble was cooled in a desiccator and latter weighed ($W_3$). The fat extracted from a given quantity of sample was then calculated:

%Fat (w/w) = $\dfrac{\text{Loss in Weight of sample}}{\text{Original Weight of sample}}$ x 100
p

= $\dfrac{W_2 - W_3}{W_2 - W_1}$ x 100

## Protein Determination

The crude protein content was determined using microKjeldahl method as described in AOAC(1996); 0.3000g of each starch sample was weighed into a long necked Kjeldahl flask with 25 cm3 of conc. $H_2SO_4$.The flask was swirled gently clamped in an inclined position and heated electrically in a fume cupboard. The heating continue until a clear solution was obtained .The clear solution was cooled ,poured into $100cm^3$ volumetric flask and made up to mark with distilled water 10ml of the resulting mixture was measured into the distillation set through the funnel.5 $cm^3$ of boric acid was pipetted into $100cm^3$ conical flask and placed at the receiving end of the distillatory.

The conical flask was placed such that the delivery tube dipped completely into the boric acid inside the flask.40% NaOH was used to liberate ammonia out of the digest under alkaline condition during the distillation 2 drops of methyl orange were always added to the round bottom flask containing the digested samples before 40% NaOH was added. As soon as the contents became alkaline, the red color changed to yellow showing NaOH to be in excess. Steam was then generated into the distillation set using a steam chest. The liberated ammonia was trapped in the boric acid solution and about 50 $cm^3$ of the solution collected into a conical flask. The solution in the flask was titrated against 0.1M HCl until the first permanent color change was observed. A blank sample was though the sample procedure and the titre value for the blank was used to correct the titre for samples.

%N = $\dfrac{\text{(molarity of HCl x Sample titre-blank titre) x 0.014x DF x100}}{\text{Weight of sample used}}$

%Nitrogen was converted to the percentage crude protein by multiplying by 6.25.

## Crude Fiber

Two hundred (200ml) freshly prepared 1.25% $H_2SO_4$ was added to 1g of the residue each of starch sample obtained from fat extraction and this was brought to quick boil. Boiling was continued for 30 minutes. The mixture was filtered and residue washed until it was free from acid. The residue was transferred quantitatively into a digestion flask, 1.25% NaOH was added and brought to boiling point quickly. Boiling was continued for 30 minutes. The mixture was filtered and residue washed free of alkali. The residue was then washed with methylated spirit, thrice with petroleum ether using small quantities. It was allowed to properly drain and the residue was transferred to a silica dish (previously ignited at $600^{O}$c and cooled).The dish and its content were dried to constant weight at $105^{o}$C.The organic matter of the residue was burnt by igniting for 30 minutes in a muffle furnace at $600^{o}$c. The residue was cooled and weighed. The loss on ignition was reported as crude fiber (AOAC 1996).

## Carbohydrate

The carbohydrate content was calculated by difference.
%CHO = 100- (Sum of the percentage of moisture, ash, fat, protein and crude fiber)

## Functional Properties

Functional properties have been defined as the characteristics that govern the behavior of nutrients food during processing, storage and preparation as they affect food quality and acceptability. Some important functional properties that influence the utility of certain foods are water absorption capacity, oil absorption capacity, emulsion capacity, whippability, foam stability, viscosity, swelling capacity e.t.c. The practical determination of some of these functional properties shall be considered (Muntungi et al., 2010).

## Bulk Density (BD)

10ml capacity graduated measuring cylinder was weighed. The cylinder was gently filled with the sample of each starch. The bottom of the cylinder on the laboratory bench was gently tapped several times until there is no further diminution of the sample level after filling to the 10ml mark.

The bulk density (g/ml) = $\dfrac{\text{Weight of sample (g)}}{\text{Volume of sample (ml)}}$

**Water/Oil Absorption capacity** (WAC/FAC)

1 g sample of each sample starch was weighed into a conical graduated centrifuge tube using a warning whirl mixer, the sample was mixed thoroughly and 10ml distilled water or oil was added for 30 seconds. The sample was allowed to stand for 30 minutes at room temperature and then centrifuged at 5000 g for 30 minutes. The volume of free water or oil (the supernatant) was read directly from the graduated centrifuge tube. Absorption capacity is expressed as grams of water or oil absorbed (or retained) per gram of sample. The amount of oil or water absorbed (total minus free) was multiplied by its density for conversion to grams. Density of water is 1g/ml that of oil will vary depending on the type of oil (which can be determined). Bleached palm oil for example has a density of 0.88g/ml.

**Foam Capacity (FC) and Foam stability**

2g of each starch sample was blended with 100ml distilled water in a warring blender (the suspension was whipped at 1600 rpm for 5 minutes). The mixture was poured into a 250ml measuring cylinder and the volume was recorded after 30 seconds. Foam capacity is expressed as percentage increase in volume using the formula of Abbey and Elssandra da Roza, (2011).
**Foam Capacity** (% Volume increase or % whippability) =
Volume after whipping –Volume before whipping x 100
Volume before whipping

The foam volume was recorded at 15, 30, 60 and 120seconds after whipping to determine the foam stability (FS) according to Ahmed and Schmidt (1979).
Foam stability =Foam volume after time't' x 10
Initial foam volume

**Gelation Capacity**

2-10% (W/V) in 10ml distilled water suspensions of each starch sample was prepared in test tubes. The sample was heated for 1 hour in a boiling water bath, followed by rapid cooling under running cold tap water. The sample was cooled further for 2hr at $4^{O}$c. The gelation capacity is least gelation concentration when the sample from the inverted test tube will not fall or slip.

**pH Measurement**

10% (W/V) in 10ml distilled water suspensions of each starch sample was prepared in test tubes. The suspension was mixed thoroughly in a warring micro-blender; the pH was measured using the pH meter.

**Amylose Content Determination**

Amylose content of the samples was determined by the procedure described by Fabiano et al., (2004), which involves the use of spectrophotometer for estimating the amylase content of the samples.100ml of the sample was weighed into 100ml volumetric flask, 1 ml of 95% ethanol and 9ml of 1M NaOH was added carefully. The sample was heated for 10 minutes in a boiling water to gelatinize the starch. The starch gel was cooled and diluted to the mark with distilled water; also 5 ml portion of the starch solution was pipetted into a 100ml volumetric flask followed by adding 10ml of 0.1M acetic acid and 2ml of iodine solution. The solution was finally diluted to mark with distilled water and shaken and allowed to stay for 2 minutes before the absorbance was taken at 620nm.The amylose content was calculated by 3.06 x Abs. x20%. 3.06 is the conversion factor calculated as:  mg amylose in unit absorbance.

**Modification of starches**

0.1 M of HCL was used to wash the starch granules and the mixture was filtered then dried.The sample modified by washing is thinned when heated to gelatinize.

**X-Ray Diffractometer analysis**

X-ray diffraction analysis of native and modified starch nanoparticles was done using Mini diffractometer (MD10), Cu-k α,X-rays of wavelength (λ)=1.5406nm within 20mins of exposure and data was taken for the 2θ range of $16^{o}$-$72^{o}$. It is governed by Bragg's law as follows:
$2d\sin\theta = \lambda n$ -------------------- (1)
Where;
**n**= No of sample introduced in the machine per time (usally1)
**λ** =wavelength
**D**= Interplanar spacing or D-spacing and
**θ**= angle of reflection

The full-range diffraction has detection limit from $3^o$-$120^o$ on 2θ angle
This full range comprise of 2 substance
The first sub-range:$3^o$-$65^o$
The second sub-range:$65^o$-$120^o$

**Preparation of the plastic film**

25 $cm^3$ of distilled water was added to the beaker containing 2.5g of each starch sample. After this, 3 $cm^3$ of 0.1M of hydrochloric acid and 2 $cm^3$ of propane-1, 2, 3-triol was added to the starch slurry. Watch glass was put on the beaker. The mixture was heated using the bunsen burner. The mixture was brought carefully to boil, and then boil gently for 15 minutes without allowing it to dry.

The glass rod was dipped into the mixture and dotted on the indicator paper to measure the pH. Sufficient sodium hydroxide solution was added to neutralize the mixture. Indicator paper was used to ascertain the pH.value of the film after each addition of NaOH. The amount of NaOH added was almost the same as hydrochloric acid used. A drop of coloring was added and the mixture was mixed thoroughly and poured into a labeled Petri dish .Glass rod was used to spread the film on the dish to ensure even distribution. The process of plastic film making was repeated without adding hydrochloric acid and sodium hydroxide. The mixture was left to dry for two days at room temperature.

**Mechanical properties**

Computerized Mechanical Testing Machine (INSTRON 3369) of capacity 50kn with speed 5mm/second was used to test the mechanical properties of the plastics produced from native and modified starches. Sample was cut to Tensile strength dimension, packed with tissue paper and placed in the machine which is connected to signal decoder where the tensile stress and tensile strain are read.

## III. Result And Discussion

**Chemical Composition and Amylose Content of Native Starches**

The purity of starch is related to its chemicals composition in which low ash, protein and lipid contents are required (Table 1). As expected for root and tuber starches, all samplesdisplayed low content of thoseconstituents. According to Goni et al., (2008), root and tuber starches are characterized by low lipid content (<1%)) which does not have a pronounced effect on the functional properties compared to those from cereal starch. Proteins and Ashes that are in low quantities in starches do not have pronounced influence on their functional properties yet (Wioletta, 2012). Among the selected root and tubers for this research work, only cassava has crude fiber of 0.1%, Irish potato and cocoyam do not have crude fibers.Protein contents of cassava, Irish potato and cocoyam were found to be 0.2, 0.1 and 0.1 respectively.

These protein contents values and the one reported byWioletta et al., 2007. Cassava (0.2), sweet potato (0.15) and Yam (0.09) were almost the same. The only remarkable difference was found in potato due to differences in variety. Lipid or Fat (%) of cassava, Irish potato and cocoyam were found to be 0.1, 0.2 and 0.1 respectively. These values compared to Wioletta et al., 2007  cassava 0.15, sweet potato 0.17 and Yam 0.1. The values found for cassava and Irish Potato was lower than Wioletta et al., 2007 findings.

Ash contents were found to be 0.45, 0.7 and 0.55 for cassava, Irish potato and cocoyam respectively. These values were higher compared to the values stated by Wioletta et al., in 2007. Carbohydrate content was found to be 89.7%, 89.30% and 88.95% for cassava, Irish potato and cocoyam respectively. Moisture content was found to be 9.45, 9.7 and 10.25 for cassava, Irish potato and cocoyam respectively. Cocoyam has the highest moisture content while cassava has the lowest. Low moisture content plays a vital role in long storage. However, higher moisture level can be deleterious because it will favor microbial growth and cause the starch to be discolored, especially if the moisture content exceeds 18% [14].

Among the starches Irish potato and cocoyam has the same protein content (0.1%) while cassava has 0.2%. the highest fat content was observed in Irish potato (0.7%), cassava and cocoyam has 0.45% and 0.55% respectively. The low non- starch component of the sample starches make them useful for some industrial applications. In low fat content is vital in the long storage when such is necessary.

The amylose content (Table 2) affects gelatinization and retrogradation properties, swelling power and enzymatic susceptibility of Cassava, Irish potato and cocoyam are 20.6, 20.2, and 21.0 respectively which agrees with the result of Wioletta et al, 2012 that Most starches contained 20-30% amylose depending on botanical source.

**Table 1.** Proximate analysis of cassava, Irish potato and cocoyam starches

| SN | PARAMETERS( %) | CASSAVA | IRISH POTATO | COCOYAM |
|---|---|---|---|---|
| 1` | Moisture Content | 9.45 ± 0.05 | 9.70 ± 0.10 | 10.25 ± 0.05 |
| 2 | Protein | 0.2 | 0.1 | 0.1 ± 0.05 |
| 3 | Ether Extract (Fat) | 0.1 | 0.2 | 0.1 |
| 4 | Ash | 0.45 ± 0.05 | 0.7 | 0.0 |

| 5 | Crude Fibre | 0.1 | 0.0 | 0.0 |
| 6 | Carbohydrates(By Difference) | 89.7 | 89.3 9 ± 0.01 | 89.0 ± 0.05 |

**Table 2:** Amylose and Amylopectine constituent of starch.

| SN | PARAMETERS (%) | CASSAVA | POTATO | COCOYAM |
|----|----------------|---------|--------|---------|
| 1 | Amylose content | 20.6 | 20.2 | 21.0 |
| 2 | Amylopectine | 79.4 | 79.8 | 79.0 |

**Functional properties of starch**

The results of the various functional properties under study are in Table 3. Potato has a pH value of 6.3; cassava has pH value of 6.1 and cocoyam with pH value of 5.7. Potato had the highest bulk densities (loose and packed) 0.2825 and 0.5272, cassava had the next 0.2160 and 0.44435 and cocoyam had the least 0.1945 and 0.4089 respectively. These indicate their particle sizes. Cocoyam had the highest oil absorption capacity (200%), Irish potato and cassava has 120% oil absorption capacities each. The absorption capacity of cocoyam and cassava were the same (100%), while potato had 60% water absorption capacity. Irish potato and cassava has the same swelling capacities while cocoyam has 1.1. All the sample starches had 0.0 foaming and stability capacities. Potato had the least gelation concentration of 10%, followed by cocoyam 8.0% and cassava 6.0%. These parameters are indicators to the particle sizes of the tubers.

**Table 3.** Functional Analysis of cassava, Irish potato and cocoyam starches.

| SN | PARAMETERS | CASSAVA | IRISH POTATO | COCOYAM |
|----|------------|---------|--------------|---------|
| SN | pH | 6.1 | 6.3. | 5.7 |
| 1 | Bulk Density (Loose) | 0.2160 ±0.03 | 0.28 ± 0.0015 | 0.1945±0.0055 |
| 2 | Bulk Density (Packed) | 0.4435± 0.0044 | 50.5272±0.0016 | 0.4088±0.00025 |
| 3 | Oil Absorption Capacity % | 120 | 120 | 200 |
| 4 | Water Absorption Capacity % | 100 | 60 | 100 |
| 5 | Swelling Capacity | 1.3 | 1.3 | 1.1 |
| 6 | Foaming Capacity | 0.0 | 0.0 | 0.0 |
| 7 | Foam Stability % | 0.0 | 0.0 | 0.0 |

**X-ray diffraction**

The X-ray diffraction pattern can be used to calculate the size of a particle, the degree of crystallization and the specific surface area. The Miller Indices (h k l) to each peak s assigned in first step. The details are in Table 4, 5, 6 and 7 for native cassava, modified cassava, native potato and modified potato respectively.

**Table 4:** Miller indices (hkl) of native cassava starch.

| 2θ of peak (deg) | D value (A) | $1000/d^2$ | $(1000/d^2)6.9$ | hkl |
|------------------|-------------|------------|------------------|-----|
| 16.44 | 5.39242 | 34.39 | 5 | 210 |
| 18.02 | 4.92277 | 41.26 | 6 | 211 |
| 35.19 | 2.55031 | 153.75 | 22 | 332 |
| 35.22 | 2.29625 | 189.65 | 27 | 333 |
| 41.51 | 2.23550 | 200.10 | 29 | 432 |

**Table 5:** Miller indices (hkl) of modified cassava starch.

| 2θ of peak (deg) | D value (A) | $1000/d^2$ | $(1000/d^2)3.58$ | hkl |
|------------------|-------------|------------|------------------|-----|
| 16.27 | 5.44717 | 33.70 | 10 | 310 |
| 17.11 | 5.18185 | 37.24 | 11 | 311 |
| 29.30 | 3.23457 | 95.58 | 27 | 333 |
| 30.88 | 2.89596 | 119.22 | 34 | 433 |
| 34.24 | 2.61860 | 145.83 | 41 | 540 |

**Table 6:** Miller indices (hkl) of native potato starch.

| 2θ of peak (deg) | D value(A) | $1000/d^2$ | $(1000/d^2)6.61$ | hkl |
|------------------|------------|------------|------------------|-----|
| 32.12 | 2.78675 | 128.767 | 19 | 331 |
| 32.95 | 2.71786 | 135.377 | 20 | 420 |
| 33.36 | 2.68588 | 138.620 | 21 | 421 |
| 35.53 | 2.52632 | 156.684 | 24 | 422 |
| 36.60 | 2.45529 | 165.880 | 25 | 430 |
| 37.01 | 2.42863 | 169.542 | 26 | 431 |

**Table7:** Miller indices (hkl) of modified potato starch

| 2θ of peak (deg) | d value(Å) | $1000/d^2$ | $(1000/d^2)/5.58$ | hkl |
|------------------|------------|------------|-------------------|-----|
| 16.40 | 5.40331 | 34.25 | 6 | 211 |
| 28.58 | 3.12351 | 102.50 | 17 | 322 |
| 29.40 | 3.03760 | 108.38 | 18 | 330 |

| 30.16 | 2.96295 | 113.91 | 19 | 331 |
|-------|---------|--------|----|-----|
| 31.12 | 2.87362 | 121.10 | 21 | 421 |
| 33.75 | 2.65591 | 141.77 | 24 | 422 |

**X-ray Particle Size Calculation**

From this study, considering the peak at degrees, average particle size has been estimated by using Debye- Scherrer formula.

D = $\underline{0.9\lambda}$
βcos θ …………………………………………2

Where 'λ' is wave length of X-ray (0.1541 nm), 'β' is FWHMM (full width at half maximum), 'θ' is the diffraction angle and 'D' is particle diameter size. The calculated particle size details are in Table 8, 9, 10 and 11. There is a slight increase in size of particle (D nm) of native cassava (50.05) with increase in 2θ of peak (16.44 – 39.23°) and corresponding increase in hkl, (210-333). Conversely d- spacing nm decreases with increase in 2θ of peak (degree) (0.539242 – 0.229625).

**Table 8:** The particle size of native cassava starch

| 2θ of peak (deg) | hkl | FWHM of peak (β) radians | Size of the particle (D) nm | d- spacing nm |
|------------------|-----|--------------------------|------------------------------|---------------|
| 16.44 | 210 | 0.00280 | 50.05 | 0.539242 |
| 18.02 | 211 | 0.00280 | 50.15 | 0.492277 |
| 35.19 | 332 | 0.00288 | 50.52 | 0.255031 |
| 39.23 | 333 | 0.00285 | 50.66 | 0.229625 |
| 41.51 | 432 | 0.00284 | 50.22 | 0.223550 |

There was slight increase in the size of the particle of modified cassava (D) nm when 2θ peak (deg) increases from 16.27 – 17.11, hkl increase from 310 – 311; FWHM of peak is constant 0.00280. When 2θ peak increased to 29.30 and 30.88, there was a decrease in size of the particle (D) nm and d- spacing FWHM ofthe peak increased to 0.00280. At 2θ peak (deg) of 34.24, FWHM of peak (β) decreased to 0.00288, size of particle (D) nm and d- spacing nm increased to 50.39 and 0.61860 respectively (Table 9).

**Table 9:** Particle size of modified cassava

| 2θ of peak (deg) | hkl | FWHM of peak (β) (radian) | Size of the particle (D) nm | d- spacing nm |
|------------------|-----|---------------------------|------------------------------|---------------|
| 16.27 | 310 | 0.00280 | 50.04 | 0.54717 |
| 17.11 | 311 | 0.00280 | 50.09 | 0.418185 |
| 29.30 | 333 | 0.00289 | 49.60 | 0.323457 |
| 30.88 | 433 | 0.00289 | 49.63 | 0.289596 |
| 34.24 | 540 | 0.00288 | 50.39 | 0.61860 |

The particle size of native potato and the modified specie varies drastically, the native potato has the highest particle size to be 29.13 (Table 10) while the modified species has a value of 50.32 (Table 11). When particles size is less than 100nm, appreciable broadening in x-ray diffraction lines will occur. Diffraction pattern will show broadening because of particle size and strain. The observed line broadening will be used to estimate the average size of the particles. The total broadening of the diffraction peak is due to the sample and the instrument. The sample broadening is described by;

FW (S) x cos θ = $\underline{k \times \lambda}$ + 4 x Strain x sin θ
Size …………………………………………….3

The total broadening βt is given by the equation

$\beta^2 t \approx \underline{0.9 \lambda^2}$ + 4Єtan$^{02}$ + β$^2$ ……………………………….4
D cos θ

Є is strain and βo instrument broadening. The average particle size D and the strain Є of experimentally observed broadening of several peaks will be computed simultaneously using least squares method.

**Table 10:** The particle size of native potato starch

| 2θ of peak (deg) | hkl | FWHM of peak (β) radians | Size of the particle (D) nm | d- spacing (nm) |
|------------------|-----|--------------------------|------------------------------|------------------|
| 32.12 | 331 | 0.00505 | 28.58 | 0.278675 |
| 32.95 | 420 | 0.00505 | 28.64 | 0.271786 |
| 33.36 | 421 | 0.00505 | 28.67 | 0.268588 |
| 35.53 | 422 | 0.00503 | 28.95 | 0.252632 |
| 36.60 | 430 | 0.00503 | 29.04 | 0.245529 |
| 37.01 | 431 | 0.00502 | 29.13 | 0.242863 |

**Table 11:** The particle size of Modified potato starch

| 2θ of peak (deg) | D value A (nm) | FWHM of peak (β) radians | Size of the particle (D) nm | hkl |
|---|---|---|---|---|
| 16.40 | 0.540331 | 0.00280 | 50.04 | 211 |
| 28.58 | 0.312351 | 0.00289 | 49.52 | 322 |
| 29.40 | 0.303760 | 0.00289 | 49.61 | 330 |
| 30.16 | 0.296295 | 0.00289 | 49.70 | 331 |
| 31.12 | 0.287362 | 0.00289 | 49.82 | 421 |
| 33.75 | 2.65591 | 0.00288 | 50.32 | 422 |

**X-ray- Degree of Crystallinity**

A starch granule is biosynthesized semi- crystalline granules containing densely packed polysaccharides and a small amount of water, being comprised of crystalline and amorphous domains. It is a semi- crystalline polymer in which amylose forms the crystalline region and amyl pectin forms the amorphous region. The inner structure of starch is that it is formed from two regions – crystalline and amorphous lamellae, which together form the crystalline and amorphous growth rings. When heated in excess water, starch granules undergo an ordered- disorder transition knows as gelatinization. The phenomenon is associated with loss of crystallinity indicated by the disappearance of birefringence.

It is generally agreed that the peak breadth of a specific phase of a material is directly proportional to the mean crystallite size of that material. Quantitatively speaking, sharper XRD peaks are typically indicative of high Nano crystalline nature and larger crystallite materials. From our XRD data, a peak broadening of the nanoparticles is noticed.

Using smadchrom software, the degree of crystallinity can be calculated as follows.

$$X_c = A_c / (A_c + A_a) \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots 5$$

Where $X_c$ = refers to the degree of crystallinity, $A_c$ = refers to the crystallized area,
$A_a$ = refers to the amorphous area.
An empirical method of segal for degree of crystallinity calculation is below.

$$Crl = 100 \left\{ \frac{I_{max} - I_{Amorph}}{I_{max}} \right\} \dots\dots\dots\dots\dots\dots\dots 6$$

Where crl is the degree of crystallinity, I max = the maximum intensity of the lattice diffraction and I Amorph = the intensity diffraction. Table 12 belowgives the intensity of XRD peaks.

**Table 12:** Intensity of XRD peak of Native cassava starch

| hkl | 210 | 211 | 332 | 333 | 432 |
|---|---|---|---|---|---|
| 2θ of peak (deg) | 16.44 | 18.02 | 35.19 | 39.23 | 41.51 |
| Relative intensity (%) | 100.0 | 61.9 | 79.4 | 14.3 | 13.2 |

$$Crl = 100 \left\{ \frac{100-79.4}{100} \right\}$$

$$= 20.6\%$$

**Table 13:** Intensity of XRD peak of modified cassava starch

| hkl | 310 | 311 | 33 | 433 | 540 |
|---|---|---|---|---|---|
| 2θ of peak (deg) | 16.27 | 17.11 | 29.30 | 30.88 | 34.24 |
| Relative intensity (%) | 100.00 | 55.7 | 3.7 | 14.9 | 0.4 |

$$Crl = 100 \left\{ \frac{100 - 55.7}{100} \right\}$$

$$= 44.3\%$$

**Table 14:** Intensity of XRD peak of native potato starch

| hkl | 331 | 420 | 421 | 422 | 430 | 431 | 521 | 522 |
|---|---|---|---|---|---|---|---|---|
| 2θ of peak (deg) | 32.12 | 32.95 | 33.36 | 35.33 | 36.60 | 37.01 | 40.39 | 42.34 |
| Relative intensity | 21.2 | 15.1 | 19.0 | 74.0 | 74.2 | 70.5 | 79.4 | 100.00 |

$$Crl = 100 \left\{ \frac{100 - 79.4}{100} \right\}$$

$$= 20.6\%$$

**Table 15:** Intensity of XRD peak of modified potato starch

| hkl | 211 | 322 | 330 | 331 | 421 | 422 |
|---|---|---|---|---|---|---|
| 2θ of peak (deg) | 16.40 | 28.58 | 29.40 | 30.16 | 31.12 | 33.75 |
| Relative intensity (%) | 100.0 | 7.1 | 22.5 | 11.8 | 23.0 | 58.3 |

Crl= 100 $\underline{100 - 58.}$
100

= 41.7 %

Degree of crystallinity of native cassava and Irish potato starches are the same ($20.6^0$). The degree of crystallinity of cassava (44.3%) is slightly higher than degree of crystallinity of modified potato (41.7%) (Tables 13-15). This may be due to breaking down of branched amylopectin to linear amylose which aid in film formation of biodegradable plastic from starches of tubers roots.

**XRD- Specific surface Area**

Specific surface area (SSA) is a material property (Tables 16-19) . It is a derived scientific value that can be used to determine the type and properties of a material. It has a particular importance in case of absorption, heterogeneous catalysis and reactions on surfaces. SSA is the SA perunit mass. Figures 1 and 2 give the various XRD peaks.

SSA = $\underline{SA\ part}$ ……………………………………………7
V part * density

Here SSA is a specific surface area, SA part is surface area of particle, V part is particle volume and density is starch powder density.

S = $6 *10^3 / Dp\rho$…………………………………………..8

**Table 16:** Specific surface area of native cassava starch

| FWHM β radian | Particle size D (nm) | Specific surface ($m^2$/g) |
|---|---|---|
| 0.00280 | 50.05 | 149.85 |
| 0.00280 | 50.15 | 149.55 |
| 0.00288 | 50.52 | 148.46 |
| 0.00285 | 50.66 | 148.05 |
| 0.00284 | 50.22 | 149.34 |

**Table 17:** Specific surface area of modified cassava starch

| FWHM β radian | Particle size D (nm) | Specific surface ($m^2$/g) |
|---|---|---|
| 0.00280 | 50.04 | 149.88 |
| 0.00280 | 50.09 | 149.73 |
| 0.00289 | 49.60 | 151.21 |
| 0.00289 | 49.63 | 151.12 |
| 0.00288 | 50.39 | 148.84 |

**Table 18:** Specific surface area of native potato starch

| FWHM β radian | Particle size D (nm) | Specific surface ($m^2$/g) |
|---|---|---|
| 0.00505 | 28.58 | 262.42 |
| 0.00505 | 28.64 | 261.87 |
| 0.00505 | 28.67 | 261.60 |
| 0.00503 | 28.95 | 259.07 |
| 0.00503 | 29.04 | 258.26 |
| 0.00502 | 29.13 | 257.47 |

**Table 19:** Specific surface area of modified potato starch

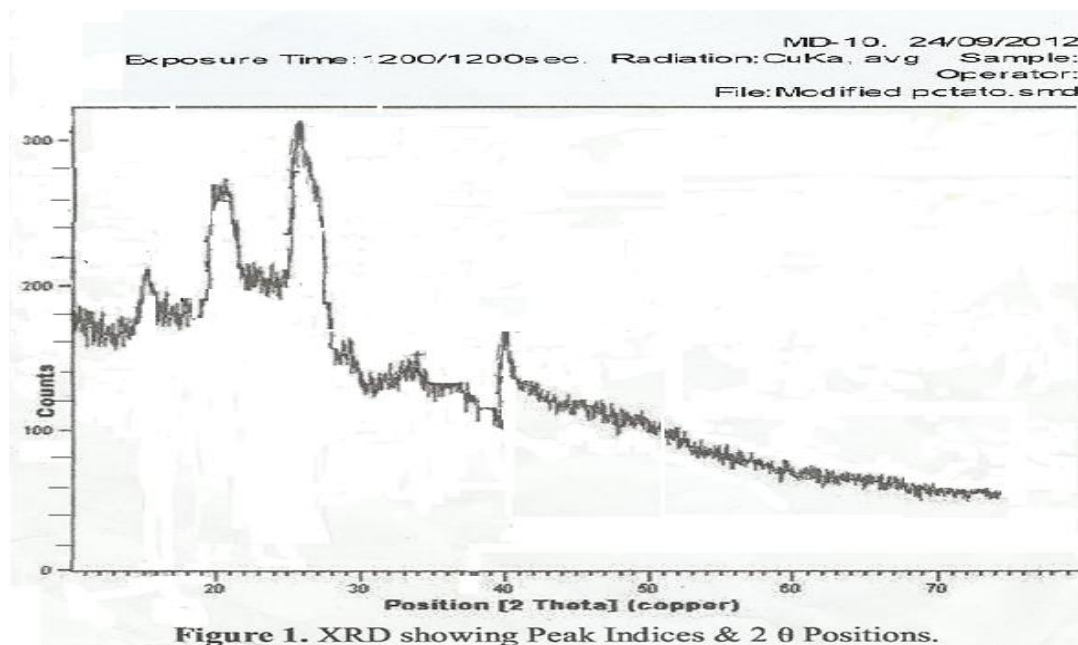| FWHM of peak (β) radians | Size of the particle (D) nm | Specific surface ($m^2$/g) |
|---|---|---|
| 0.00280 | 50.04 | 149.88 |
| 0.00289 | 49.52 | 151.45 |
| 0.00289 | 49.61 | 151.18 |
| 0.00289 | 49.70 | 150.91 |
| 0.00289 | 49.82 | 150.54 |
| 0.00288 | 50.32 | 149.05 |

**Figure 1.** XRD showing Peak Indices & 2 θ Positions.

**Mechanical Properties of Biodegradable Plastic**

From Table 20, the strength of the plastics increases when the starches are modified. This is found in the various FTIR values that follows Table 20. Modifications of starch increase the mechanical properties and make it suitable for biodegradable plastic. From the graphs there is sharp breaking in the line plotted on the graph. This indicate that plastic starch will not be flexible and cannot withstand elongation

**Table 20:** Mechanical Properties of Biodegradable Plastic

| Plastics films | Length (nm) | Maximum load (N) | Tensile stress at max. load (mpa) | Tensile strain at max. load (mm/mm) | Modulus (mpa) |
|---|---|---|---|---|---|
| Modified potato starch | 36.00 | 1.27625 | 0.63837 | 0.15278 | 4.1784 |
| Native potato starch | 36.00 | 1.25337 | 0.62669 | 0.43056 | 1.4462 |
| Modified cocoyam starch | 36.00 | 5.55822 | 2.7791 | 0.15278 | 18.1902 |
| Native cocoyam starch | 36.00 | 2.29923 | 1.14962 | 0.23611 | 4.8690 |
| Modified cassava starch | 36.00 | 2.44317 | 1.22189 | 0.20833 | 5.8652 |
| Native cassava starch | 36.00 | 0.61668 | 0.30834 | 0.93056 | 0.3313 |

Starch can be used as substitute to produce plastics that are biodegradable. On examining the proximate properties of the starches, it was discovered that the three samples selected had low non-starch components. The low starch components of the starches make them valuable in some industrial applications, preparation of biodegradable plastics inclusive.

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