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Surface Hydrophobicity of Starch Acetate for Enhanced Bioplastic Properties

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Abstract

Bioplastics describes the beginning of life based on the carbon bonds present in the polymer molecule, while biodegradability, focuses on the end of life of bioplastics that will address environmental clean up by microorganisms. Constructing a carbon backbone in bioplastics is a vital food for taught that will ensure plastic breaks down readily without affecting its performance. Retrodegradation is one of the challenges of starch bioplastic involving gelatinized starch undergoing rearrangement of disaggregated amylose and amylopectin chains into more ordered structures. Therefore surface modification via esterification by substituting the highly reactive hydrophilic hydroxyl group (–OH) on the starch polymer with acetic anhydride as a hydrophobic components has shown a reduction in water absorption, percentage solubility, and stable structure. The FTIR spectra of acetylated starch, showed new bands spectra at 1450-1350 cm^{-1} and 1240 cm^{-1} assigned to CH_3 antisymmetry/symmetry deformation vibration, and carbonyl C-O stretch vibration, respectively. The result further showed no impact in the cyanide concentration with corresponding increase in acetic anhydride concentration. The Degree of Substitution (DS) and percentage acetylation (Ac %) of acetylated starches ranged from 0.062 to 0.116, and 1.62 to 2.98 g/100g respectively. Therefore, blending acetylated starch with synthetic polymer has future prospect for altering the persistent –C-C- bonds, resulting to possible controlled degradation with enhanced surface properties.

1. Introduction

Based on the food sustainability mandate, the need to harness waste into other viable products that is income driven is key to human development and environmental preservation [1, 2]. Plastic products are usually described as bioplastic if their source materials are bio-based (i.e derived from renewable feedstock, e.g. corn, sugarcane and beet, potato, wheat, and cellulose) and are biodegradable (i.e decomposed by microorganisms, under specified conditions) [3, 4]. Cassava peels is one of the promising waste raw materials with high starch content [5, 6]. Biodegradable plastics have been reported from various studies involving cassava starch due to it availability all year round, but focus on the peels has not been fully exploited [7]. The waste management system of plastics was not given much attention as a future concern with respect to their various applications, including widespread use as disposable items [8]. Plastics are lightweight materials, resistant to corrosion [9, 10]. Their inexpensive and electrical insulation properties, makes them a good material that is highly sorted after [11]. Daily human endeavours, involve the use of plastics, ranging from packaging materials, telecommunications, footwear etc [12]. Despite these various applications, continuous research into other sustainable application has been in the rise in recent time in medicine, source of renewable energy and other forms of light packaging materials [12]. Despite the environmental friendliness of starch biodegradable plastics, other factors such as colour, bacteria degradation and low mechanical properties have been major drawback towards its application [13]. Consequently upon the aforementioned, the need for modification geared towards enhanced properties through the addition of additives, plasticizers and other chemical components has been the interest of most researchers. According to Vieira *et. al.,* [14], Glycerol, gelatin and sorbitol are commonly used plasticizer in the production of biodegradable plastics. Bartz *et. al*., [15] describes esterification of starch to involve the introduction of functional groups into the starch molecules via the available hydroxyl (-OH) surfaces with potential to alter certain physicochemical properties. In another study, Ashogbon & Akintayo, [16]; Huang *et al.,* [17] noted that the degree of substitution is dependent on the nature of the substituent. This side chain substitution is commonly expressed as the degree of substitution (DS). Colussi *et. al.,* [18] in a related study, described the influence of DS on water solubility of starch acetate films, (i.e. DS < 1.1 are soluble in water, DS>1.1 are insoluble in water). Studies has also shown that bioplastics have superior advantage compared to conventional plastics with respect to change in shape when an external force is applied without altering their chemical composition, thereby still retaining their basic elemental structure [19]. Most conventional plastic waste, accumulates in landfills, and can remain undegraded over many years, thereby posing a serious course of concern in the ecosystem [20]. Bozena Mrowiec, [21] in another study, stated that the production of 335 million tones of plastics in 2016, has possible projected increase to double this figure in the next 2 decades. The demands for a new approach towards a new future of bioplastics targeted at creating a sustainable plastics economy by improving the economics and uptake of recycling, reuse, and controlled biodegradation with enhanced potential towards a drastic reduction in the leakage of plastics with enhanced surface [22]. Therefore, the use of waste biomaterials opens new doors towards a more sustainable bioplastics production. However, daily human existence needs the synergy between organizational and social awareness, which plays a key role in National economy [23]. Irena *et al.,* [24] in their finding, noted that future economic determinant will leverage on the bioplastics production from waste biomaterials. Bioplastics have two possible representations that are independent; as the beginning of life that will be anchored on the carbon in the polymer molecule while biodegradability addresses the end of life of bioplastics that will address environmental clean up by indigenous microorganisms [4, 25]. The possibility of altering the carbon back-bone as contained in polyethylene without affecting performance, but opens up the possibility of a controlled biodegradation as compost, rather than creating a perceived bioplastics that is non biodegradable, thereby arousing more environmental concern.

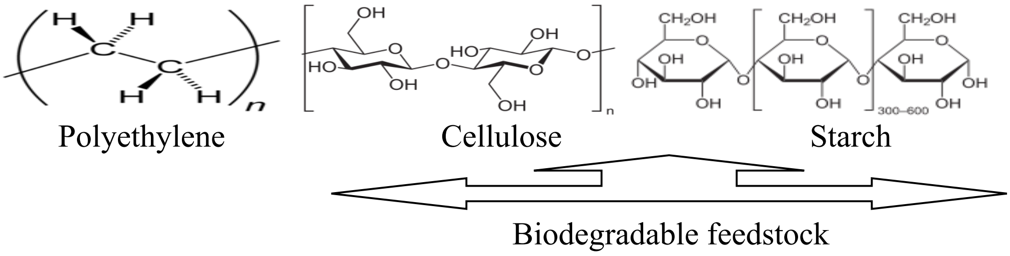

Fig 1. Some polymeric carbon backbone found in biomaterial feedstock

The polyethylene biobased carbon source has been reportedly produced from BioSource such as sugarcane to form biopolethylene [26]. But irrespective of the feedstock obtained from a biomaterial, their biodegradability potential can suffer setback due to the presence of the persistent -C-C- backbone as compared to the other biobased feedstock as shown in Figure 1. This paper unveils the possibilities of using acetylated starch from cassava waste peels as raw materials for bioplastics production with enhanced surface properties. The produced plastic film was tested based on water solubility and water absorption. The focus of this study was, producing starch acetate from esterified waste peels cassava starch with different degrees of acetylation and used it in the preparation of biodegradable plastic. The results from the study were analyzed with respect to the FTIR peaks to ascertain its functional group modification and hydrophobic properties.

2. Experimental Details

2.1 Materials

Sorbitol 99% was obtained from BDH chemical limited Poole England. Analytical grade chemical reagents were used in this study.

2.2 Sample Collection and Starch Extraction

The raw materials were obtained from freshly harvested cassava tubers at Agbarha-Otor market which is located in Ughelli North Local Government Area of Delta State, Nigeria on longitude 6° 2' 54" E /5° 30' 40" N. The tubers were properly peeled and washed. The peels were carefully separated from other layers (cortex and parenchyma) with a clean knife. The separated cassava peels (100 g) were washed again with clean water before blending to small pieces with a blender. The blended cassava peels were then soaked in water (100 ml) for 45 minutes. Subsequently, sediments were separated from the slurry and the residual white starch were pre-dried under the sun to remove all the moisture with further oven drying at temperature of 70 ^{o}C for removal of any residual water with subsequent blending into homogenized sizes [27].

2.3 Acetylation of Starch

Synthesis of starch acetates was carried out in an aqueous medium. The starches were acetylated with some modification in line with proposed method by Phillips *et. al.,* [28]. A suspension of 50 g of cassava peels starch in distilled water (100 ml) was subjected to shaking at 1500 rpm (ZENGJI 800) for 60 min at 25 ^{o}C. Aqueous 3.0 g/100g NaOH solution was added to the suspension to adjust the pH to 8.0. Slow addition of acetic anhydride (5, 10 and 15 g/100g) were added into separate reaction flask, while maintaining the pH between 8.0 and 8.4 with a 3.0 g/100g NaOH solution. The reaction was sustained for 15 min after the complete addition of the respective acetic anhydride concentrations. Adjusting the pH to 4.5 with a 0.5 mol equi/L HCl solution was employed to quench the reaction. The final suspension was centrifuged for 3 min at 1000 x g with subsequent washings with 95 mL/L ethyl alcohol. The residual starches were dried in an oven at 40 ^{o}C.

2.4 Bioplastic Preparation

Method according to Maulida *et al.,* [29] was adopted for this study with some modification as reflected in Figure 2. The ratio of 10 g mixture of 8:2 acetylated starch and sorbitol was prepared. The various concentration of acetylated starch and sorbitol was dissolved in distilled water with starch mixture : distilled water = 1 : 10 (w/v) ratio. The resulting starch solution was heated and stirred on a hotplate between 65^{o}C to 70^{o}C to ensure gelatinization for 10 minutes. Furthermore, the hot film produced from the heating was cooled, poured onto a flat surface and dried in an oven at 60^{o} C for 24 hours. The bioplastic obtained from the process was removed from the surface, placed in a desiccators and ready to be analyzed.

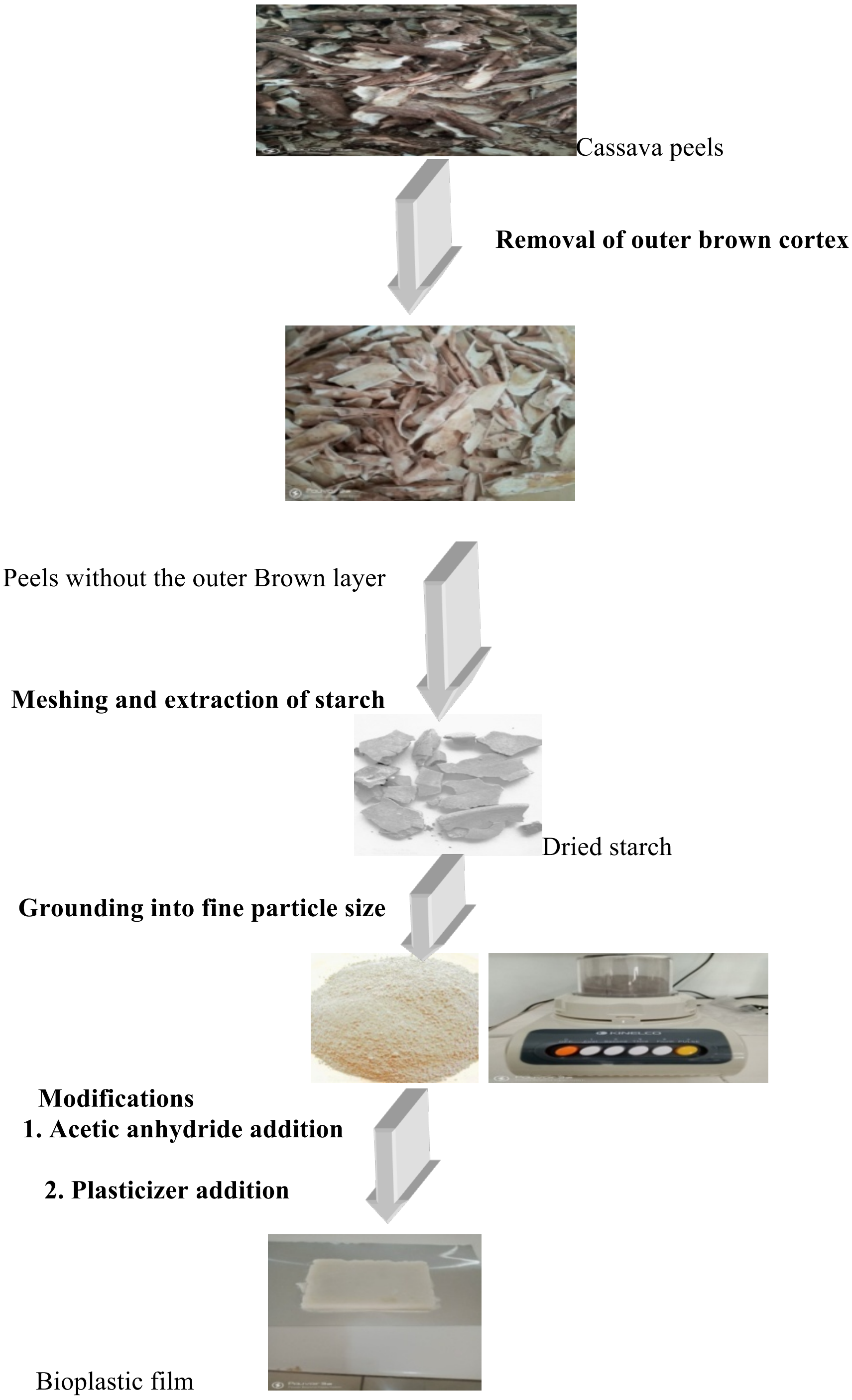

Fig. 2 Chart of starch extraction for bioplastic film production

2.5 Instrumentation

FT-IR spectra of samples as described by Liang *et al.,* [30] was adopted for this study, using SHIMADZU FTIR-8400S equipped with deuterated triglycine sulphate (DTGS) as detector, potassium bromide (KBr) as beam splitter. The measurements were carried out on a HATR surface at room temperature in the IR region of 4000–450 cm^{-1}, by accumulating 40 scans with a resolution of 4 cm^{-1}.

2.6 Water Absorption

Water uptake of samples was investigated by weighing film samples with an area of approximately 1 x 1 cm^2. The samples were then dried at 70 ºC for 3 hours, cooled, and then immediately weighed. The film samples were then submerged in distilled water for 3 hours without agitation. After the immersion period, the samples were then removed from the water and weighed. The percentage water absorption was calculated thus; (Wittaya, 2009; Mukuze, Magut, & Mkandawire 2019) [31,32].

$$(\%) = \frac{[M_2 - M_1]}{M_1} \times 100$$

Where: $M_2 = FinalWeight$, $M_1 = InitialWeight$

2.7 Solubility in Water

Dried samples with an area of approximately 1 x 1 cm^2 were weighed. Each sample was subsequently immersed in 50 mL of distilled water under constant agitation for 3 hours at room temperature. Insoluble portion of the film was air dried for 24 hours and reweighed. The water solubility (%) of the films was calculated thus; [27, 31].

$$Solubility\ (\%) = \frac{[W_0 - W_1]}{W_0} \times 100$$

where: W_0 = Weight before submersion, W_1 = Weight after submersion

2.8 Hydrogen Cyanide Determination

The cyanide concentration in acetylated waste peels cassava starch was determined using ninhydrin based spectrometer of trace cyanide at 485 nm [32, 33]. Concentrations of 0.02, 0.04, 0.08, 0.1 and 0.2 µg/ mL was used to generate a calibration graph within linear range by adding appropriate volumes of cyanide solutions at concentration of 20 µg CN^-/mL to 1 mL of 2% Na_2CO_3. Ninhydrin solution (0.5 mL) containing 5 mg/mL in 2% NaOH was added to each standard cyanide solution. Homogenization and incubation of the mixure for 15 minutes for colour development was performed. In the same vein, the blank containing 1 mL of 2% Na_2CO_3 without CN^- was added. Different concentrations of cyanide was measured using UV/Vis Spectrophotometer (UV 2100C) at 485 nm. Thereafter, 0.1 g of the ground sample was added in a standard volumetric flask (5 mL) and made up to mark with 0.1% $NaHCO_3$. Sonicated of the sample for 20 minutes in a water bath was followed up with centrifugation at 10,000 rpm for 10 minutes. An automatic pipette was used to obtain a clear supernatant. The aliquots (2 mL) was added to 0.5 mL ninhydrin in NaOH, allowed for 15 min for colour development and absorbance measured at 485 nm.

2.9 Determination of the acetyl percentage (Ac%) and degree of substitution (DS)

The percentage of acetyl groups (Ac%) and the degree of substitution (DS) of the acetylated starches were determined using method described by Wurzburg [34]. Ethanol (50 mL) containing 75 mL/L ethanol in distilled water was used to dissolve the acetylated starch (1 g). An aluminium foil was used to cover the 250 mL flask containing the slurry and placed in a water bath at 50 °C for 30 min. To the cool sample, 40 mL of 0.5 mol equi/L KOH were added, and the slurry was kept under constant stirring at 200 rpm for 72 h. Thereafter, the alkali excess was titrated with 0.05 mol equi/L HCl, using phenolphthalein as an indicator. The solution was left to stand for 2 h and then any additional alkali, which may have leached from the sample, was titrated. A blank, using the unmodified starch, was also used. The Ac % and the DS were calculated according to Equations (1) and (2) respectively.

$$Ac\ \% = \frac{([V_{blank} - V_{sample}] \text{ x Molarity of HCl} + 0.043 \text{ x } 100)}{\text{Sample weight}} \qquad (1)$$

Where: V_{blank} = titration volume used for the blank sample.

V_{sample} = titration volume used for each sample.

Both titration volumes were expressed in mL; the sample weight was expressed in g. DS is defined as the average number of sites per glucose unit that is possessed by a substituent unit

$$DS = \frac{(162 \times \text{Acetyl }\%)}{(4300 - [42 \times \text{Acetyl }\%])} \quad (2)$$

3. Results and Discussion

3.1 FTIR Analysis

The changes in the chemical conformation of the treated starch were analyzed using FTIR. The results from the FTIR spectra in Figure 3, 4, 5 and 6 show two main regions of absorbance within the range of 500-1750 cm^{-1} at lowwavenumbers and 2000-3500 cm^{-1} at higher wavelengths. This observation was in line with the studies done by Nordin *et al*., [35] on starch films reinforced with microcellulose fibres**.** Also in another study by Moràn *et al.,* [36] and Lani *et al*., [37], showed that their results are in agreement with the results from this study. The broadband atregions between 3373.61 $cm^{-1}$to 3414.12 cm^{-1} for all plastic is attributed to the hydroxyl group -OH stretching vibrations [38].

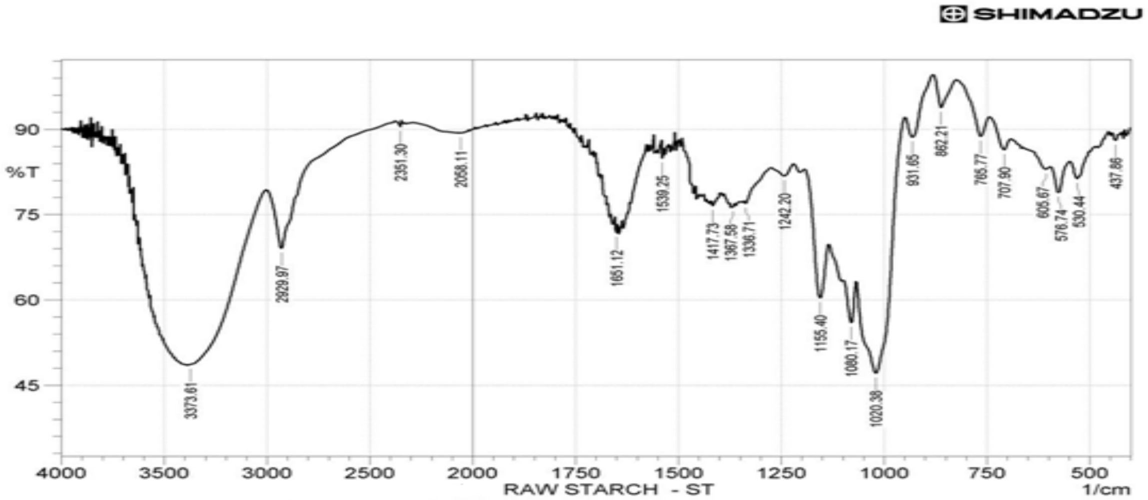

Fig. 3 FTIR chart of raw starch plastic film

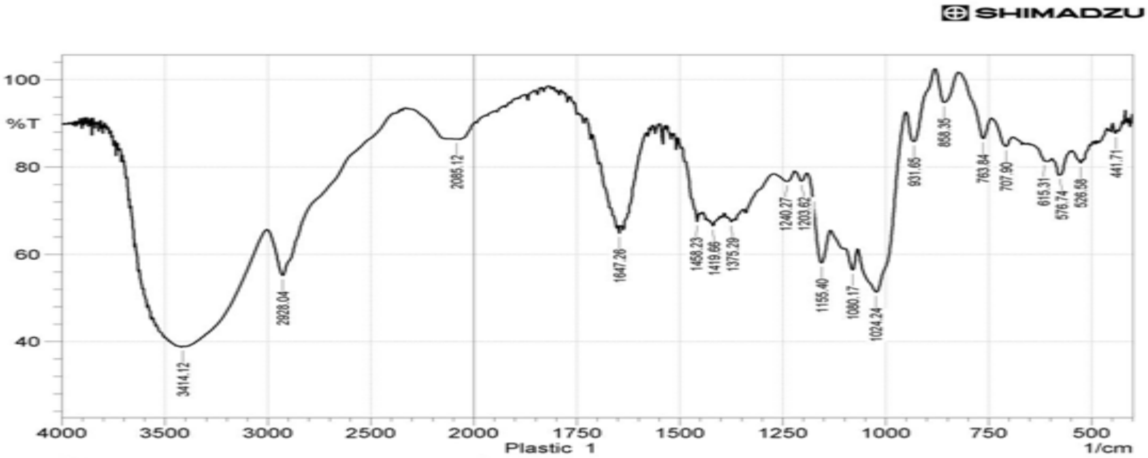

Fig. 4 FTIR chart of 5 % acetylated starch plastic film

The slightly projected peak between 2928.04 cm^{-1} to 2935.76 cm^{-1} corresponded to aliphatic saturated -CH stretching vibrations. Bands at 1732.13 cm^{-1} is commonly associated with the ester carbonyl group

C=O, as a result of acetylation reaction [39, 40]. Further confirmatory peak between 1637.62 cm^{-1} to 1651.10 cm^{-1}is related to C-O bending associated with OH group. Peaks at 1450 cm^{-1} to 1370 cm^{-1} are related to C-C stretch in the various plastics. Also the results showed a C-O stretched peak between 1000 cm^{-1} to 1250 cm^{-1}, reflecting the possible formation of esters, alcohols and ethers. The absorbance bands around 894 cm^{-1} and 1020 cm^{-1} are associated with the C-H rocking vibrations and C-O stretching respectively [40].

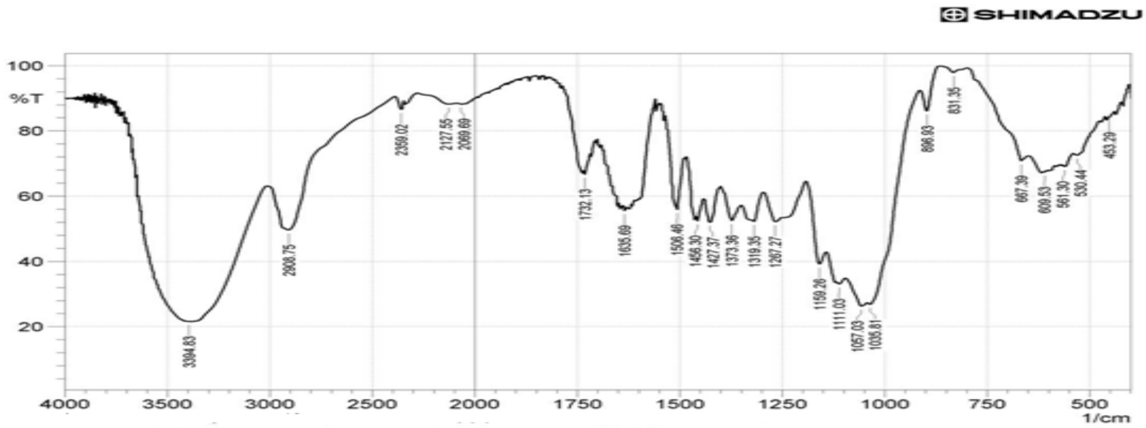

Fig. 5 FTIR chart of 10 % acetylated starch plastic film

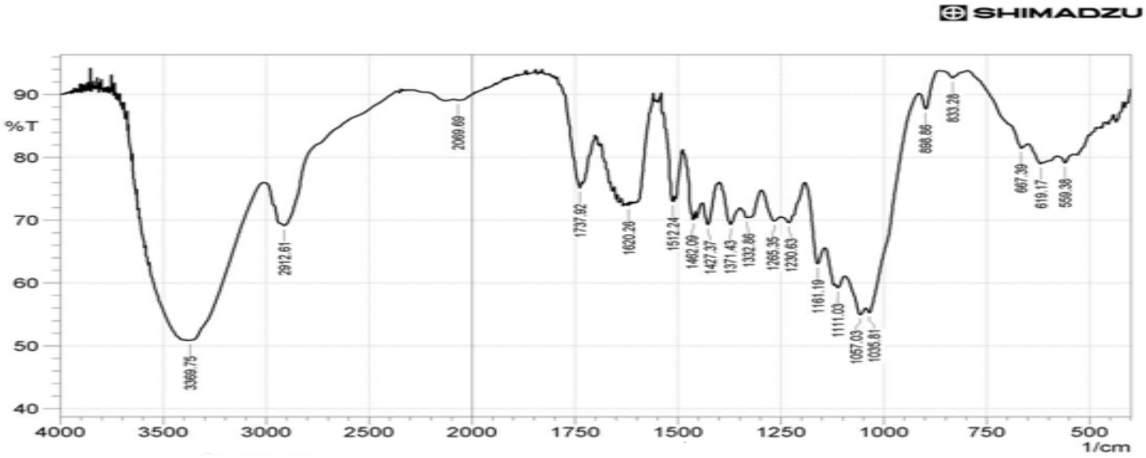

Fig. 6 FTIR chart of 15 % acetylated starch plastic film

3.2 Surface Modification

Subsequently via acetylation reaction upon the addition of acetic anhydride in various proportion as depicted in Figure 7, the FTIR analysis of the acetylated plastic film in Figure 4, 5 & 6, indicate acetyl groups addition to the starch molecule was only reflected in the 10 % and 15 % acetylated bioplastic film. This incorporation of acetyl group in the starch molecule may be visualized by an increase in the peak intensity with 5 % acetic anhydride at a wave number of 1651.12 cm^{-1} for carbonyl C=O corresponding to possible amide, but bands commonly associated with ester carbonyl group C=O, was not detected. Reaction with 10 % and 15 % acetic anhydride, shows new peaks commonly associated with ester carbonyl group C=O at 1732.13 cm^{-1} and 1737.92 cm^{-1} respectively. Other spectra of the acetylated starch, showed some new absorption bands that increases in peak intensity with increase acetic anhydride concentration between 1450 cm^{-1} to 1350 cm^{-1} and 1240 cm^{-1} assigned to CH_3 anti-symmetry/symmetry deformation vibration, and carbonyl C-O stretch vibration, respectively [41]. The result from this study is in agreement with assertion by Chi *et al*., [40], describing these new absorptions as possible acetylated starch products formed during the esterification process. The absence of absorption peak in the region 1950 cm^{-1} to 1750 cm^{-1} implied that the product was free of unreacted acetic anhydride, and the absence of absorption in the area of 1700 cm^{-1} for the carboxylic group indicated that the product was also free of acetic acid byproduct. This claim was also made by Diop, Li, Xie, and Shi [42]. Salaberria *et al.,* [43], noted that variation in the bands as observed in all spectra, is possible even if a pure sample is used.

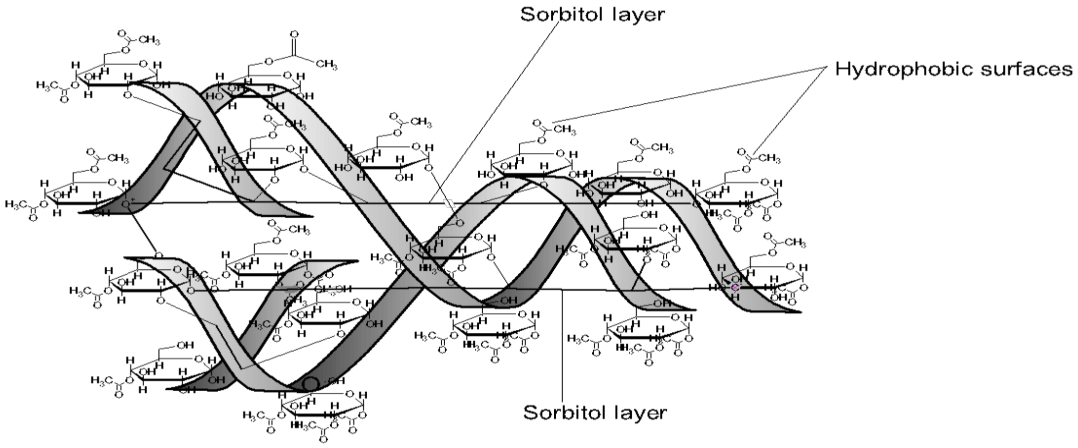

Fig. 7 Proposed surface modification of bioplastic film from cassava peels

Table 1 Acetyl percentage (Ac %) and degree of substitution (DS) of the acetylated starch

Sample	% Ac	DS
Ac$_{5}$	**1.62±1.023**	**0.062**
Ac$_{7.5}$	**2.37±0.001**	**0.091**
Ac$_{10}$	**2.98±0.010**	**0.116**

The DS and Ac % of acetylated starches ranged from 0.042 to 0.116, and 1.11 to 2.98 g/100g, respectively. The acetylated starches with the highest concentrations of acetic anhydride (10 g/100g) presented higher DS and Ac% as compared with other concentration of acetylated starch (Table 1). According to the United State Food and Drug Administration (FDA), 2.5 g/100g, is the safe limit for acetyl group maximum for foods uses [44]. Therefore, results from this study revealed that acetylated starches (5, 10 and 15 g/100g) showed lower Ac %, but slightly above the safe limit at 10g/100g. Results from this study were within range for 5 and 10 g/100g acetic anhydride as reported by Rosana *et al.,* [45]; Vasanthan, Sosulski, & Hoover [46]. In another study involving acetylated maize starch (10g/100g of acetic anhydride in starch slurry of 31 g/100g), Liu, Ramsden, and Corke [47] reported a higher Ac% between 2.71 and 4.22 g/100g and a DS of 0.105-0.165. Similarly in another finding using Corn starch, Luis, Silvia,Antonio & Octavio [48] reported values are in agreement with results from this study. Therefore it could be stated that this variations in DS and Ac% could be as a result of some key factors such as concentration, presence of catalyst, reaction time, type of reagent, structure of starch granules as well as other growth conditions.

3.3 Water Absorption

Decrease in the water absorption was observed with subsequent increase in acetic anhydride concentration as reflected in Figure 8. This trend is in line with the assertion that describes the hydrophilic property starch and cellulose, thereby influencing their water reactivity according to

Dufresne & Vignon, [49]. In another study, Maulida, Siagian, & Tarigan, [29], stated that starch has a low hydrogen bonding capacity as compared to cellulose, thereby making it more easily prone to hydrolysis. This trend was accounted for by Abdullah, Putri, Fikriyyah, Nissa & Intadiana, [50], based on the high hydrophilic property of the solid sugar alcohol. Therefore, it can be concluded that the higher the acetic anhydride concentration, the more the degree of substitution, evident in lower water absorption potential.

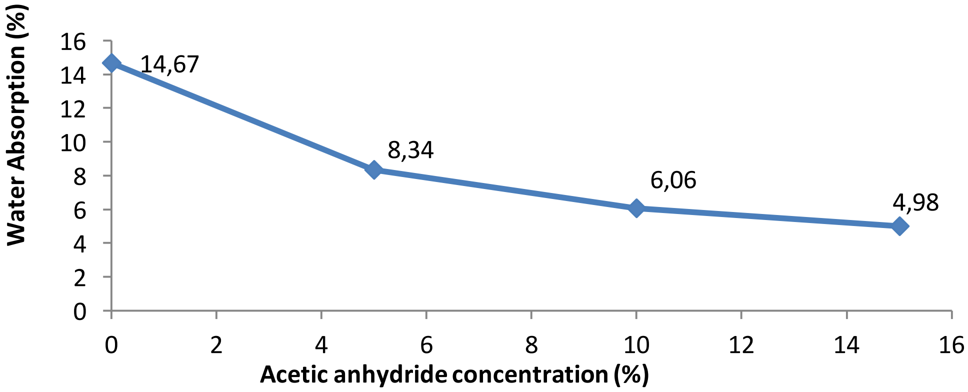

Fig. 8 Percentage Water Absorptivity of Acetylated Starch and Sorbitol Bioplastic film

3.4 Solubility in Water

Hydrogen bonding has been reported to play a vital role in limiting the effective bonding of starch with water [51]. Therefore, the results as captured in Figure 9 revealed a decreasing solubility with increase acetic anhydride concentration. This observed reduction could be caused by the substitution of the OH-groups in the starch molecule by acetyl groups. This assertion is in agreement with report from other studies [52, 53, 54]. Thus, the result from this study has further strengthen the claim by Schmidt, Blanco-PascuaL, Tribuzi, & Laurindo, [54], that acetylation of starch is an interesting method for the development of starch films with improved properties.

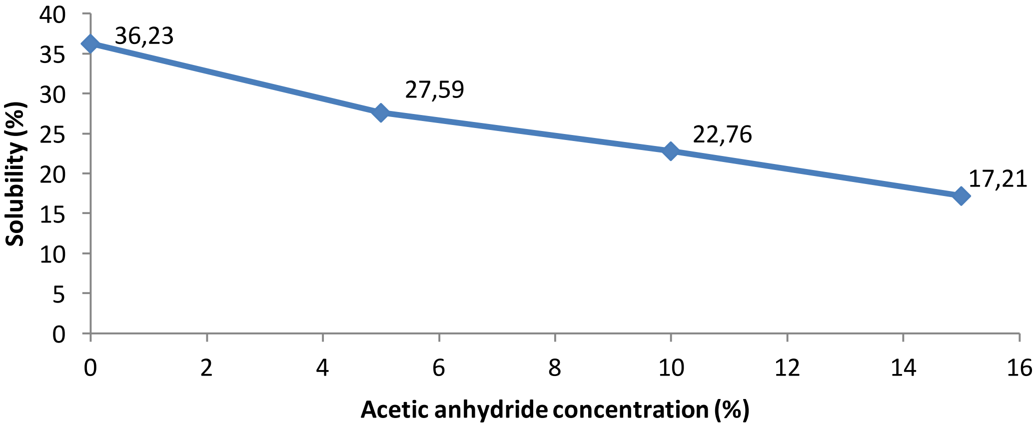

Fig. 9 Percentage Water Solubility of Acetylated Starchand Sorbitol Bioplastic film

Acetylation, shows no impact on the residual cyanide potential of the bioplastic film as reflected in Figure 10. The reduced cyanide concentration could be attributed to other starch processing techniques such as mashing, filtering, drying and subsequent heating above the reported boiling temperature of 26 ^{o}C [55, 56]. The average cyanide concentration of 2.19 mg/kg as reported in this study is below the acceptable values by WHO and hence suitable for use as bioplastic for industrial application [19, 57]. Considering the importance of evaluating the cyanide content, water absorption and solubility of the bioplastic film, a correlation study of these parameters was analyzed on a 3-D plot as shown in Figure 11. The highlight from the graph shows a clear trend of increase in concentration of acetylation as it impacts on these surface parameters with exception to the cyanide content.

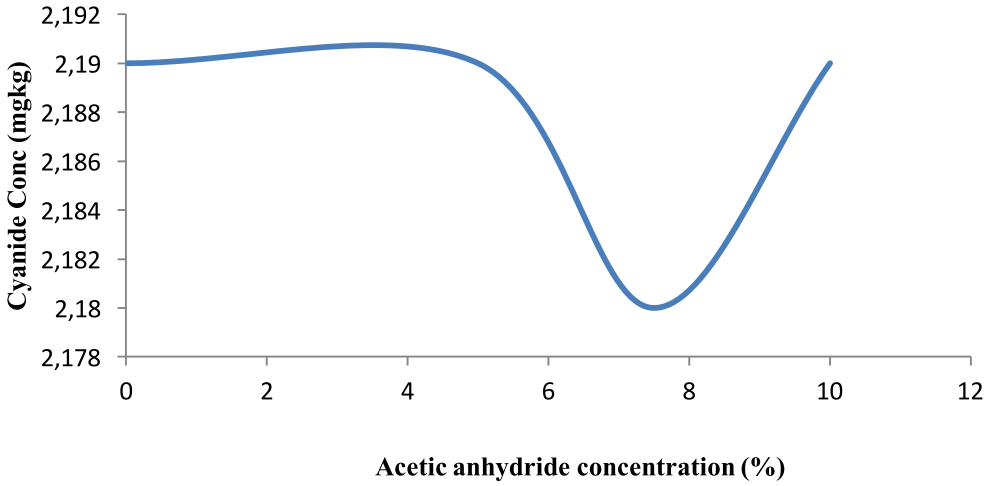

Fig. 10 Residual Cyanide Content in Acetylated Starch

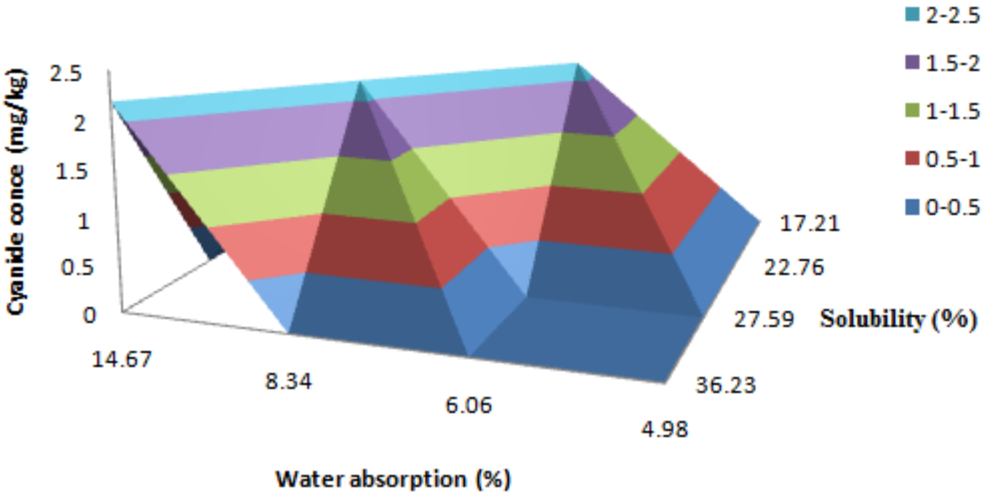

Fig. 11 A 3-D chart on the effect of acetylation on cyanide content, solubility and water absorption of cassava starch bioplastic film

4. Conclusions

Replacing synthetic polymers in packaging application is very essential, but for customer the cost of packaging material weighs over environmental concerns. Therefore, in other to balance the need for environmental sustainability and the demand to turn waste into wealth, the use of cassava waste peels has shown prospect as a potential source for bioplastic production that can address the major limitation in the various applications of bioplastics based on its sensitivity to moisture and retrogradation processes. The result from this finding has shown that surface modification of starch via esterification using acetic anhydride has shown a reduction in water absorption, solubility and no impact on the cyanide concentration. Sequel to the aforementioned, more research is required on possible nanoparticles with a focus on further enhancing its surface against possible hydrolysis resulting to retrogradation, thereby sustaining its mechanical strength during storage that can further be implemented and commercialized as an eco-friendly packaging materials.

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