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ORIGINAL ARTICLE

Synthesis and characterization of native and modified bitter yam starch grafted with acrylonitrile

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Abstract

This analysis studied the effects modification on the properties of starch-based polymer grafted with acrylonitrile (copolymers). Starch was extracted from bitter yam. The starch was modified by heating the solution above 70 °C and then esterified with phthalic anhydride to produce a pregelatinized phthalated derivative. Acrylonitrile was grafted onto natural and pregelatinized phthalated starch at 120 °C using calcium oxide from snail shell as the initiator. The grafting reaction of starch with poly(acrylonitrile) and the phthalation of the starch were both confirmed by Fourier transform infrared (FTIR). Scanning electron microscopy analysis revealed changes in the morphology of the pregelatinized phthalated grafted copolymers. The X-ray diffractogram showed that native starch grafted copolymer displayed broad diffraction peaks (amorphous), but the phthalated bitter yam starch grafted with acrylonitrile had prominent diffraction peaks (crystalline). Thermogravimetry analysis revealed that the phthalated grafted copolymer has better thermal stability than the native grafted copolymer.

Keywords: *acrylonitrile, biopolymers, bitter yam, copolymers, phthalic anhydride.*

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1. Introduction

Because plastics are flexible, light, resilient, inexpensive, and readily available, they are used in a wide range of industries and everyday materials[1]. These petroleum-based polymers are non-biodegradable, and their use and disposal have major effects on the environment. The use of biopolymers to partially or totally replace petroleum-based polymers may provide a solution to environmental contamination problems[2]. Biopolymers, also known as bio-based polymers, are environmentally benign, biodegradable, and renewable polymers that can be used to replace petroleum-based polymers[3]. Many biodegradable polymers are currently available, including polyester amide (PEA), polybutylene adipate terephthalate (PBAT), polyhydroxy alkanoates (PHAs), polyhydroxy butyrate (PHB), polycaprolactone (PCL), and polylactic acid or polylactide (PLA), but they are uneconomical due to the high cost of production[4]. Even still, the cost of making biodegradable polymers prevents them from being used as a substitute for synthetic polymers in some cases[5]. Natural raw resources such as starch, keratin, lignin, cellulose, gelatin, collagen, and chitosan could be used to make biopolymers instead of petroleum-based polymers[5]. Among the natural polymers, more emphasis is placed on starch. Because of its low cost, renewability, non-toxicity, and availability, as well as complete biodegradability, starch is a high molecular weight naturally occurring substance with extensive applications in food, chemical industry, and as a raw material in industrial processes[6-8]. Despite the fact that starch has always been used as a food ingredient, it has also been shown to be a reliable alternative in a variety of industries, including pharmaceuticals, textiles, papers, adhesives, plastics, and cosmetics[9]. It is utilized as a stabilizer, bulking agent, thickener, and viscosity booster, among other things[10]. Enzymatic or chemical hydrolysis of starch yields compounds such as maltose, glucose, cyclodextrins, and maltodextrins[11].

However, starches in their natural state have drawbacks such as strong hydrophilicity, high water solubility, low miscibility with hydrophobic synthetic polymers, poor heat stability, processability issues, and weak mechanical qualities, which limit their utilization in a variety of fields[12,13]. As a result, there is a need to change these natural starches in order to increase and improve their industrial use for a variety of purposes[14]. A great deal of work has been done on starch modification using chemical, physical, and enzymatic methods[15]. Among all the chemical modification procedures, esterification can simply and effectively enhance the flexibility and hydrophobicity of starch[16]. Although aliphatic anhydrides such as octene succinic anhydride, octene succinic anhydride, and acetic anhydride have been used to alter starch[17-20], aromatic anhydrides such as phthalic anhydride have received less attention in starch esterification than aliphatic anhydrides[21]. When an aromatic group of esters is added to starch, however, it can improve flexibility, hydrophobicity, and diminish hydrogen bonds between starch molecules. Grafting is another important way for changing the characteristics of polymers. Grafting allows synthetic polymer and starch to adhere together after graft copolymerization rather than physically combining them[22]. Multiple studies have shown that chemical initiators such as potassium permanganate/citric acid[23], ceric ammonium nitrate[24], potassium bromate-thiourea, and ammonium persulfate[25,26] can graft several vinyl monomers onto starch. Despite the fact that graft polymerization of starch has several advantages, some chemical initiators pollute the environment and are also expensive to produce, making grafted copolymers competitive with petroleum-based polymers. To replace these chemical initiators, it is critical to develop an environmentally acceptable and low-cost heterogeneous catalyst for copolymer synthesis.

The use of a waste heterogeneous catalyst has the potential to lower the grafted copolymer's current high cost of production, making it competitive with petroleum-based copolymer. $Ca(NO_3)_2$, $CaCO_3$, or $Ca(OH)_2$ are the most common basic materials used to make CaO catalysts[27]. CaO catalyst can be made from a variety of natural calcium sources, including mollusk shell, eggshell, and bone waste. In fact, using waste-derived CaO catalyst could reduce catalyst costs and make the copolymer environmentally friendly.

The purpose of this study is to extract starch from bitter yam and use phthalic anhydride to make pregelatinized starch phthalate bitter yam starch. Using CaO from the snail shell as an initiator, the native and pregelatinized starch phthalates were grafted onto acrylonitrile. The thermal stability, structural qualities, and morphological aspects of natural and modified composites were studied.

2. Materials and Method

2.1 Materials

Bitter yam *(Dioscorea dumetorum*) tubers were purchased in the Ago Aduloju market in Ado–Ekiti, Ekiti State, Nigeria in 2019. CaO was produced using the Hadiyanto approach as described in 2.5. All other reagents were of analytical grade and purchased from Sigma Aldrich.

2.2 Sample preparation

In preparation for starch extraction, the tuber yams were peeled, washed with distilled water, and cut into smaller pieces (about 1 - 2 cm^2) with a sharp knife.

2.3 Starch isolation

Wet extraction method was used to extract the starch[28]. The cut tubers were blended in a blender for five minutes. The slurry was collected using a muslin cloth and putdown into a bucket filled with distilled water. The starch was ejected into the bucket of water by continually squeezing the contents. The starch was allowed to settle overnight, and the supernatant was decanted, the product was being rinsed regularly to remove soluble contaminants until the supernatant was clear. The completed product was spread on a flat substrate and air-dried.

2.4 Preparation of pregelatinized starch phthalate

Gelatinization and esterification were involved in this process[29]. The gel was gelatinized by heating the starch solution to 70 °C, then oven-dried, grinded and sieved. The esterification reaction was carried out by mixing 10% pregelatinized starch with 16.7% solution phthalic anhydride in 96 percent ethanol in distilled water. Throughout the reaction, 10 M NaOH was continuously injected to keep the pH between 8 and 10. To absorb surplus moisture, anhydrous sodium sulphate was applied. Stirring was carried out at a speed of 1000 rpm for 30 minutes before being left alone for 24 hours. HCl solution was used to modify the pH of the mixture to 6.5-7.0. To wash the unreacted phthalate, 50 percent ethanol was added to the neutralized solution. To make pregelatinized *Dioscorea dumetorum* starch phthalate powder, the final precipitate was dried, crushed, and sieved.

2.5 Preparation of calcined snail shell powder

The Hadiyanto approach was applied to prepare the CaO catalyst[30]. Snail shell was bought from a restaurant in Ado-Ekiti and cleansed carefully with tap water until dust and filth were removed. The clean samples were then dried for 24 hours in a hot air oven at 105 degrees Celsius. It was calcined for 4 hours at 800 °C in a muffle furnace. Calcined snail shell ash (CSSA) was crushed to a fine powder (CaO) and filtered through a stainless steel sieve of 60 mesh before being stored in a covered utensil to prevent air reaction.

2.6 Preparation of native and phthalated starches grafted with acrylonitrile

The method reported by Pourjavadi et al.[31] for graft copolymerization of acrylonitrile onto starch was used. In 300 ml of distilled water, 20 g of starch was dispersed, and 1 g of calcined snail shell powder was added. For 15 minutes, the calcined snail shell was allowed to interact with the starch while being constantly agitated. The combination was then given a dose of acrylonitrile (20 ml). A graft copolymerization of acrylonitrile on starch was performed at 120 °C for 6 hours with constant agitation. The pH of the reactant was adjusted to 7, and the solution was rinsed to precipitate the polymer. The precipitate was centrifuged at 6000 rpm for 15 minutes, and the supernatant was decanted.

To eliminate any leftover acrylonitrile, the residue was rinsed again with water. The residue was air dried and weighed after the product was filtered. The degree of percentage grafting (%Gr) was calculated as described in Equation 1, and the yield (% Y) was calculated by dividing the weight of the grafted polymer by the weight of the monomer and multiplying by 100 (Equation 1).

$$\%Gr = \left(\frac{Wgp - Ws}{Ws}\right)*100 \tag{1}$$

$$\%Y = \left(\frac{Wgp - Ws}{Wm}\right)*100 \tag{2}$$

Where Gr, Y, Wgp, Ws and Wm represent grafting, yield, weight of bitter yam starch grafted with acrylonitrile, weight of bitter yam starch and weight of monomer (acrylonitrile), respectively.

2.7 Statistical analysis

All analyses were carried out in triplicate, and the results were statistically analyzed using SPSS for Analysis of Variance (ANOVA) (IBM Statistics 21). The results are the standard deviations of the means of replicates (calculated on a dry weight basis), which are substantially different at $p < 0.05$.

2.8 The native and modified composite characterization

Thermo Nicolet FT-IR spectrophotometer (Model JASCO FT-IR-5300) was used to determine the IR spectra of native and phthalated grafted copolymers in solid state utilizing the KBr pellet method. The IR spectra were measured in the 4000-400 cm^{-1} range.

Energy-dispersive X-ray spectroscopy (EDX) with a 6742A/Thermo-Scientific equipment linked to a JSM6510/JEOL scanning electron microscope was used to qualitatively analyze the chemical composition of the grafted copolymers.

X-ray diffraction (XRD) was used to characterize the physical structure of the grafted copolymers (crystalline and/or amorphous) using a Shimadzu XRD6000 diffractometer (Shimadzu, Kyoto, Japan) with CuKa radiation, from 10° to 80°, at 2θ min^{-1}.

The grafted copolymers' thermal analysis (TGA) was performed in a TA Q500 thermal analyser (TA Instruments, New Castle, DE) using a synthetic air atmosphere and a 60 ml/cm flow rate. The samples were heated at a rate of 10 °C/min from ambient temperature to 600 °C.

Scanning electron microscopy (SEM) was used to examine the morphology of the native and phthalated copolymers using a JSM6510/JEOL model microscope (JEOL instrument, Austin, EUA). Using a SCD 0050/LEICA metallizer, the samples were mounted on SEM stubs with double-sided adhesive tape and coated with a 20 nm gold layer (LEICA instrument, California, EUA).

3. Results and Discussion

Table 1 shows the percentage yield (%Y) and grafting (%Gr) of native and phthalated grafted copolymer. The percentage yield (38.00%) and percentage grafting (54.23%) of phthalated grafted copolymer were found to be higher than the native grafted copolymer's percentage yield (35.95%) and percentage grafting (50.62%). The increase observed in percentage grafting of phthlated bitter yam grafted with acrylonitrile (PBGC) when compared with the native bitter yam grafted with acrylonitrile could be due to the addition of phthalic anhydride to the hydroxyl groups of the starch[32].

Results are expressed as means ± standard deviations (n = 3). NBGC = native bitter yam grafted copolymer; PBGC phthalated bitter yam grafted copolymer.

Table 1. Percentage yield and degree of percentage grafting of grafted copolymers.

Samples	Percentage yield (%)	Percentage grafting (%)
NBGC	35.95 ± 0.05	50.62± 0.03
PBGC	38.00± 0.02	54.23 ± 0.02

The FT-IR spectra of native bitter yam starch grafted with acrylonitrile and phthalated starch grafted with acrylonitrile are shown in Figures 1-2. For the native starch grafted with acrylonitrile (Figure 1), peaks at 3436 cm^{-1} and 2937 cm^{-1} corresponded to O-H stretch and C-H stretching, respectively, whereas the peaks at 2375 cm^{-1}, 1442 cm^{-1}, and 1007 cm^{-1} corresponded to CN stretch, C-H bend, and C-O stretch, respectively. For phthalated starch grafted with acrylonitrile (Figure 2), peaks at 3415 cm^{-1}, 2923 cm^{-1}, and 2324 cm^{-1} were assigned to O-H stretch, C-H stretch, and C-N stretch respectively, whereas peaks at 1646 cm^{-1}, 1421 cm^{-1}, and 1022 cm^{-1} were assigned to C=O, C-H bend, and C-O stretch, respectively. There was a decrease in vibrational frequency from 3436 cm^{-1} in the native starch to 3415 cm^{-1} in the phthalated starch and this decrease could be due to weakening effects on the O-H bond from the hydrogen bond in the glycosidic ring thereby causing a shift in the absorption band[33]. Also, an increase was observed in vibrational frequency of the carbonyl group from 1582 cm^{-1} in the native starch to 1646 cm^{-1}in the phthalated starch grafted with acrylonitrile. Evidence of acrylonitrile grafting on both native and phthalated bitter yam starch was revealed by the presence of CN- peak at 2375 cm^{-1} and 2324 cm^{-1}, respectively. The FTIR report of ungrafted native and phthalated starch of bitter yam was reported earlier[34].

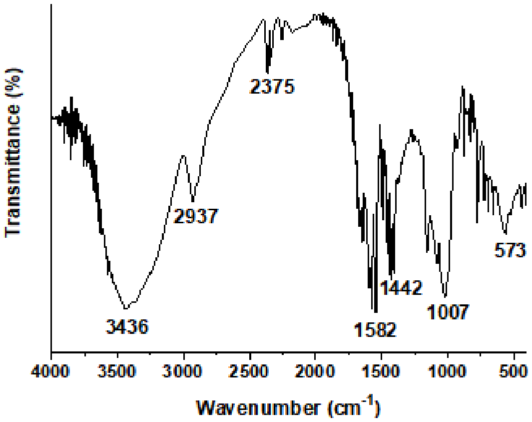

Figure 1. FTIR of native bitter yam starch grafted with acrylonitrile.

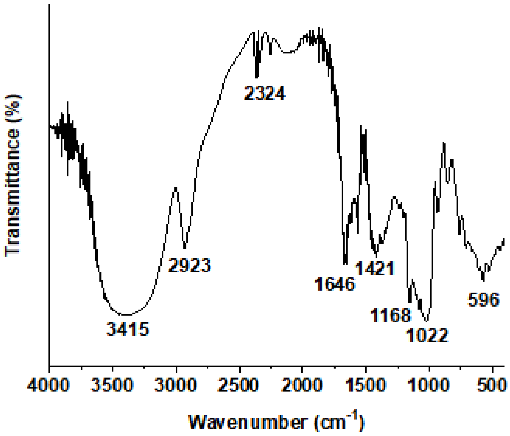

Figure 2. FTIR of phthalated bitter yam starch grafted with acrylonitrile.

A micrograph of the native bitter yam starch grafted with acrylonitrile is shown in Figure 3. The native starch grafted with acrylonitrile had a smooth, fractured surface and a continuous matrix that was homogenous. Figure 4 shows a micrograph of phthalated bitter yam grafted with acrylonitrile with a rough, nonuniform surface and a gel-like bulk. The observed changes in morphological structure could be due to the phthalation process in the grafted phthalated copolymer. Starch grafted with acrylonitrile was shown to have a similar loss of uniformity[35]. By displaying a good adhesion characteristic, phthalation improved the incorporating behavior of acrylonitrile in bitter yam starch, also, the mechanical properties of phthalated bitter yam starch grafted with acrylonitrile are expected to improve.

The native bitter yam starch grafted with acrylonitrile XRD pattern (Figure 5) showed a broad diffraction peak at 21°(2θ)), indicating its amorphous character. For native cassava starch grafted with acrylonitrile, similar observations of only one large broad peak were reported[35]. The phthalated bitter yam starch grafted with acrylonitrile (Figure 6) exhibited prominent peaks at 8°, 19°, 20°, 23°, 27°, 32°, and 45°(2θ). The higher crystallinity in the phthalated bitter yam grafted with acrylonitrile could be due to additional alterations that occurred during the grafting process.

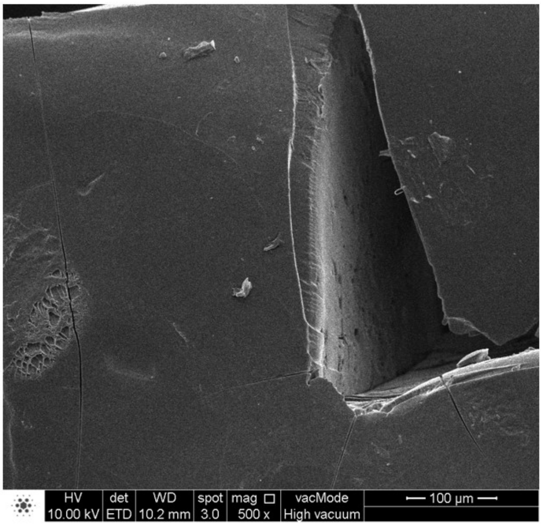

Figure 3. Scanning electron micrograph of native bitter yam starch grafted with acrylonitrile.

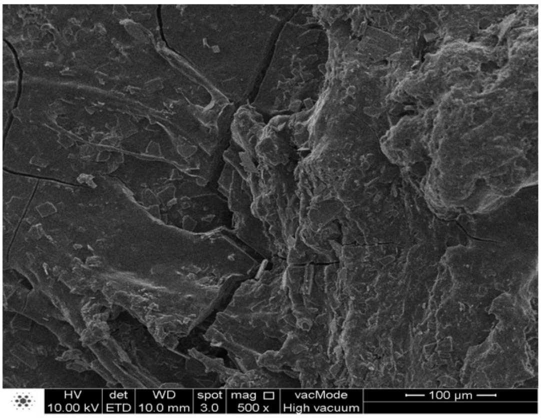

Figure 4. Scanning electron micrograph of phthalated bitter yam starch grafted with acrylonitrile.

Figures 7-8 showed the thermogram curves of the grafted copolymer of native and phthalated starches. At temperatures below 100 °C, native biter yam copolymer began to lose weight, which could be related to the reduction of moisture content in the granules. At 310 °C, the second weight loss was

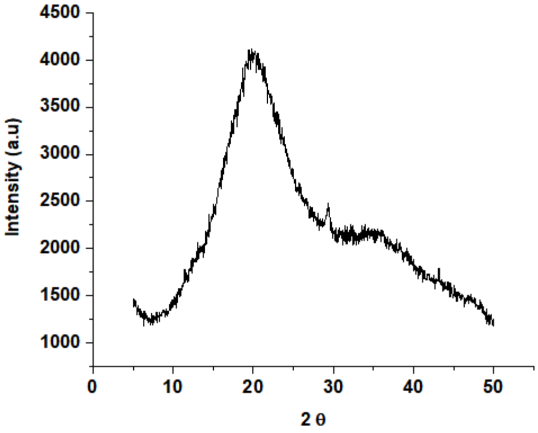

Figure 5. XRD of native bitter yam starch grafted with acrylonitrile.

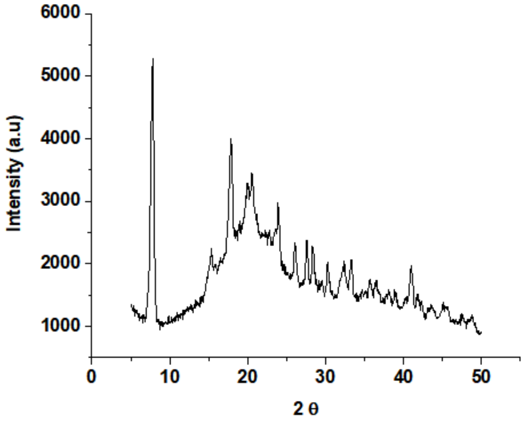

Figure 6. XRD of phthalated bitter yam starch grafted with acrylonitrile.

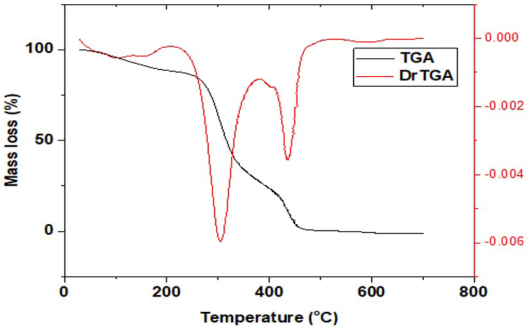

Figure 7. TGA of native bitter yam starch grafted with acrylonitrile.

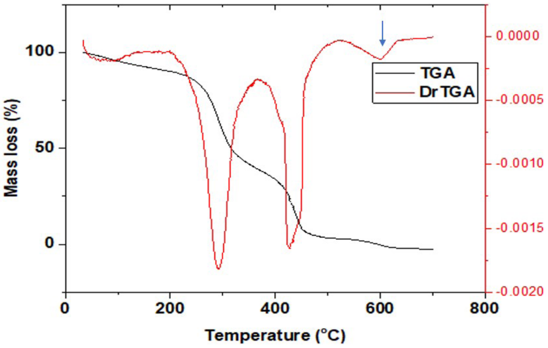

Figure 8. TGA of phthalated bitter yam starch grafted with acrylonitrile.

detected, which could be attributed to C-O-C[36] glycosidic bond breakage. At 420 °C, the weight of the native bitter yam starch copolymer was further reduced in the third stage. The native bitter yam starch grafted with acrylonitrile structural matrix broke completely at 480 °C, leaving only the residues. Figure 8 shows the TGA curve of phthalated bitter yam starch grafted with acrylonitrile. The initial weight loss occurred at temperatures below 100 °C, indicating that water content in the starch was being removed. At 320 °C, the second weight drop was seen. At 550 °C, the weight of the phthalated bitter yam starch grafted with acrylonitrile was further reduced in the third stage. The phthalated bitter yam starch grafted with acrylonitrile structural matrix broke completely at 650 °C, leaving the residues. The thermal stability of phthalated grafted with acrylonitrile was significantly higher than that of native grafted copolymer.

The thermal stability of the grafted copolymers was improved by phthalation because the phthalated starch copolymer's structural matrix broke completely at 650 °C as compared to the native starch which broke completely at 480 °C (indicated by blue arrow in Figure 8). The improved thermal stability of the phthalated starch grafted with acrylonitrile could be related to the copolymer's crystallinity, which requires a greater temperature to destroy the ordered arrangement in crystalline materials. Heat exchanger parts, vehicle polymer parts (bumpers, dashboards, stirring cases, etc.), wire insulators, pump casing, curing containers, and sterilizable containers in medical applications are all examples of polymers that demand higher temperatures.

4. Conclusion

Starch was considered in the development of biodegradable polymers to solve the solid waste problems caused by petroleum-derived plastics (synthetic polymer) which are not readily biodegradable because of their resistance to microbial degradation. In this study, bitter yam starch modification was carried out using phthalic anhydride before grafting with acrylonitrile to produce grafted copolymers. The surface morphology of the graft copolymers studied by SEM revealed that phthalated starch grafted with acrylonitrile displayed a good adhesion characteristic. Thermal stability of phthalated grafted sample was higher in comparism to native starch. X-ray diffractogram showed that there was increase in crystallinity of phthalated starch grafted with acrylonitrile. Grafting of phthalated starch resulted in the creation of novel materials with improved characteristics compared to grafted native starch. The properties of the phthalated starch grafted with acrylonitrile may make it a more promising material for reducing petroleum-based polymers and hence it could be considered as bio- films for packaging industries.

5. Author's Contribution

- **Conceptualization** – Funmilayo Deborah Adewumi; Labunmi Lajide; Ezekiel Adewole.
- **Data curation** – Funmilayo Deborah Adewumi; Labunmi Lajide; Jonanthan Abidemi Johnson.
- **Formal analysis** – Funmilayo Deborah Adewumi.
- **Funding acquisition** – Funmilayo Deborah Adewumi; Labunmi Lajide.
- **Investigation** – Funmilayo Deborah Adewumi; Labunmi Lajide; Ezekiel Adewole.
- **Methodology** – Funmilayo Deborah Adewumi.
- **Project administration** – Labunmi Lajide.
- **Resources** – Funmilayo Deborah Adewumi; Labunmi Lajide; Jonanthan Abidemi Johnson.
- **Software** – Jonanthan Abidemi Johnson.
- **Supervision** – Labunmi Lajide.
- **Validation** – Labunmi Lajide.
- **Visualization** – Funmilayo Deborah Adewumi.
- **Writing – original draft** – Funmilayo Deborah Adewumi; Labunmi Lajide.
- **Writing – review & editing** – Funmilayo Deborah Adewumi; Labunmi Lajide; Ezekiel Adewole.

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