



SYNTHESIS AND CHARACTERIZATION OF GRAFT COPOLYMERS OF NATIVE AND PHTHALATED CASSAVA (*Manihot esculenta*) STARCHES WITH ACRYLONITRILE AS A GRAFTING AGENT

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ABSTRACT

Graft copolymerization is a promising method for properties modification of natural polymers. Cassava starch, a natural polymer was extracted using wet extraction route. Part of the obtained starch was pre-gelatinized at above 70°C and esterified using phthalic anhydride. CaO (catalyst) was prepared by calcining snail shell powder in a muffle furnace at 800°C for 4 h. The native and pregelatinized/phthalated starch solutions were grafted with acrylonitrile at 120°C in the presence of CaO catalyst. The prepared CaO catalyst was characterized using SEM, EDS, TGA, XRD, and FTIR for surface assessment, elemental evaluation, thermal degradation, amorphosity/crystallinity determination, and functional group evaluation, respectively. The SEM-EDS of the prepared CaO catalyst revealed spherical shape and the elemental compositions. The FTIR spectra of the grafted native cassava starch copolymer and grafted phthalated cassava starch copolymer revealed the existence of C≡N- peak at 2364 and 2262 cm⁻¹, respectively which is an evidence of grafting. The surface of the native cassava starch grafted copolymer granules was eroded with cracks, while that of the phthalated cassava starch grafted copolymer showed coagulated and coerced morphology. The XRD result of the native cassava starch grafted copolymer revealed one major sharp peak at angle 2θ=25° while that of the phthalated cassava starch grafted copolymer revealed numerous peaks. The TGA analysis revealed that the phthalated cassava grafted copolymer framework was completely broken at 500°C unlike the native cassava starch grafted copolymer whose complete decomposition was about 420°C. It was observed that the modified samples had improved features over the native sample.

1. Introduction

Plastics as packaging materials perform important roles in the food manufacturing sector because of their lightness, durability, and flexibility unlike ceramics and metals (Kutz, 2012), hence, do not biologically decompose. Incineration and recycling methods had been used to mitigate these problems, however, a few percentage of plastic wastes is recyclable and most of them get migrated into the municipal

landfills. One solution to control this environmental menace is the use of degradable polymers most importantly in the packaging sector to substitute petroleum-based polymers which are undegradable (Ali *et al.*, 2013; Monica *et al.*, 2015). Recently, attention has been drawn to the production of new materials by incorporating natural biopolymers such as cellulose, chitosan, starch, etc. into many stable synthetic polymers (Salmoral *et al.*, 2000; Park

et al., 2001). The widely proposed and considered natural biopolymer for this purpose has been starch: a biodegradable; relatively cheap; non-toxic; renewable; and readily available in several forms (Suvorova *et al.*, 2000; Vroman and Tighzert, 2009). Starch film has some level of permeability making it useful in food packaging system. When it is used as blends with non-biodegradable polymers, it increases the microbial activities at the surface (Koenig and Huang, 1995).

Watanabe *et al.* (2009) reported that, if starch materials are blended with polyolefin matrix, polysaccharide-loving bacteria, enzymes, fungi, etc, will be attracted to them and degradation will be initiated.

Several studies have been successfully conducted on composites of starch and synthetic polymers (Arvanitoyannis *et al.*, 1999; Graaf *et al.*, 2001). Some researcher used starches that were obtained from rice (El-Rahim *et al.*, 2004), potato (Borghai *et al.*, 2010), and sago (Danjaji *et al.* 2001; Danjaji *et al.* 2002; Abdul-Rahman *et al.*, 2006) to produce biodegradable blends.

One major drawback for starch-based composites is that starch and several polymers are immiscible and this generally leads to the poor properties of starch/polymer blends. However, chemical modification of starch is generally embraced to overcome this drawback by the interaction of appropriate moieties with the hydroxyl groups in starch matrix (Bao *et al.*, 2003). The obtained derivatives always have some physico-chemical features which deviate significantly from the parent starches, however, their biodegradability is maintained still. Also, Graft copolymerization is another promising technique to modify some physico-chemical properties of naturally available biopolymers (Lv *et al.*, 2008; Kalia and Kaith, 2008).

The present study is aimed at modifying native starch obtained from cassava tubers with acrylonitrile using CaO obtained from snail shells as catalyst, and compare the properties of both the native and modified starches through instrumental analysis.

2. Materials and methods

2.1. Materials

Cassava tubers, all the reagents such as acrylonitrile, phthalic anhydride, etc. were of analytical grade.

2.2.1. Samples

Cassava tubers were obtained from a local market in Ado-Ekiti, Nigeria. The starch was isolated by wet extraction method as described by Wang *et al.* (2006). The fresh tubers were thoroughly washed with water, cut into small pieces, blended for homogeneity, the resultant slurry was packed into a muslin cloth and immersed into a bucket filled with distilled water to expel the starch. The starch was allowed to settle for 24 h and the supernatant was decanted. Further washing of the obtained starch was done using distilled water, this process was repeated till the supernatant was clear, and the wet starch was thereafter air-dried.

2.2.1. Preparation of Pregelatinized Starch Phthalate

Pre-gelatinized Starch Phthalate was prepared using the method of Surini *et al.* (2014). This method involves two major steps: gelatinization and esterification. Gelatinization was carried out as the starch solution was heated at 70°C, the resulting gel was oven-dried, ground, and sieved to obtain uniform particle size. The esterification process was carried out by contacting 10% pre-gelatinized starch in distilled water with 16.7% phthalic anhydride solution in 96% ethanol. NaOH (10 M) was continuously added during the reaction to keep the pH between 8 and 10, anhydrous sodium sulphate was added to absorb excess moisture with constant stirring at 1000 rpm for 30 more min. The resulting mixture was allowed to stay for 24 h, the mixture pH was adjusted to 6.5 – 7.0 using HCl solution. 50% Ethanol was added to the neutralized solution to wash off the unreacted phthalate, the final precipitate was dried, ground, and sieved to obtain pre-gelatinized cassava starch phthalate (PCSP).

2.2.2. Preparation of Calcined Snail Shell Powder

A catalyst (CaO) was prepared according to Nurhayati *et al.* (2016). Snail shells were

thoroughly washed with tap water until they were free from dirt, the clean shells were oven-dried at 105°C, calcined in a muffle furnace at 800°C for 4 h. The calcined snail shell ash (CSSA) was pulverised to fine powder as CaO, sieved, and stored in a closed container to avoid exposure to air.

2.2.3. Preparation of Native and Phthalated Starches Reinforced with Acrylonitrile

Graft copolymerization of acrylonitrile and starch was carried out using the method described by Pourjavadi *et al.* (2007) with slight modification. 20 g of starch was dispersed in 300 mL of distilled water, 1 g of the prepared CaO was added to the mixture and allowed to interact with the starch solution for 15 min as 20 mL of acrylonitrile was later added to the mixture with constant agitation. Graft copolymerization of acrylonitrile onto starch was done at 120°C with constant agitation for 6 h, the pH of the product was adjusted to 7, the solution was washed to precipitate the polymer, the precipitate was centrifuged for 15 min at 6000 rpm and the supernatant was decanted. The residue was washed again with water to remove any remaining acrylonitrile, the final product was air-dried to obtain phthalated starch grafted with acrylonitrile.

$$\% \text{ Yield} = \frac{\text{weight of copolymer obtained}}{\text{weight of starch} + \text{weight of acrylonitrile}} \times 100 \quad (1)$$

Table 1. Yield of grafted copolymer

Sample	Percentage yield (%)
NCSS	23.75 ± 0.02
PCSS	30.43 ± 0.01

NCSS - native cassava starch; PCSS - phthalated cassava starch

3.3. FTIR Analysis of Grafted Copolymer

The FTIR spectra of the grafted native and phthalated starches are presented in Figure 1a and Figure 1b. In the spectrum of native cassava starch grafted copolymer (Figure 1a), the peak at 3454 and 2923 cm⁻¹ correspond to O-H and C-H stretches, respectively, while the peaks at 2364, 1447, and 1022 cm⁻¹ correspond to C≡N stretch, C-H bend, and C-O stretch, respectively. Similar

2.2.4. Statistical analysis

All the analyses were done in triplicate and the data were subjected to Analysis of Variance (ANOVA) using SPSS (IBM Statistics 21). The results are presented as means of replicates (determined on a dry weight basis) ± standard deviation. The significant difference was at $p < 0.05$.

3. Results and discussions

3.1. Calcined Shells as Copolymerisation Catalyst

The percentage yield of calcined snail shell (also known as CaO) as obtained at 800°C using a muffle furnace was 35.50%. The obtained CaO was used as catalyst in the co-polymerisation reaction.

3.2. Grafted Copolymers

The grafted copolymer yield of the native and phthalated starches is shown in Table 1.2. The acrylonitrile grafted percentage yield of native cassava starch copolymer (23.75%) was increased after treatment with phthalic anhydride (30.43%). This increase in percentage yield of phthalated starch acrylonitrile grafted copolymer may be that during the course of grafting, phthalated starch was modified and the modification was not done in native starches

report was submitted by Mano *et al.* (2003). Phthalated cassava starch grafted copolymer (Figure 1b) showed various peaks at 3428, 2976, and 2262 cm⁻¹ which are credited to O-H stretch, C-H stretch, and C≡N stretch, respectively, while the peaks at 1659, 1400, and 1181 cm⁻¹ correspond to C=O, C-H bend, and C-O stretch, respectively. The spectra of the grafted native cassava starch copolymer and grafted phthalated

cassava starch copolymer which showed the presence of $C\equiv N-$ at 2364 and 2262 cm^{-1}

respectively was an indication of grafting with acrylonitrile.

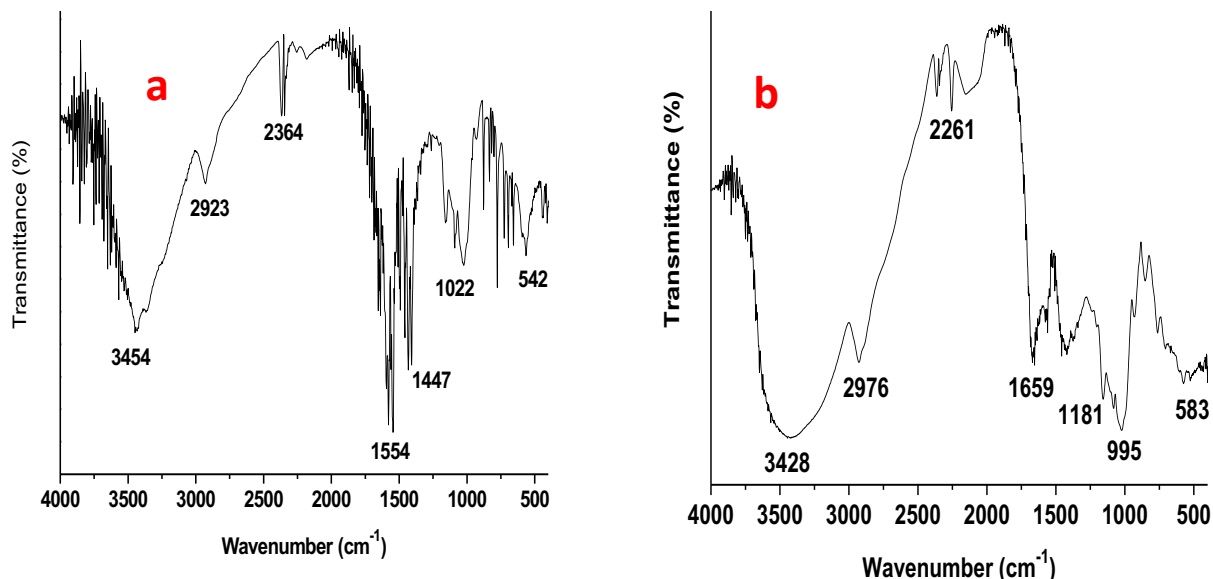


Figure 1. FTIR spectra of native cassava starch (a) and phthalated cassava starch grafted with acrylonitrile (b)

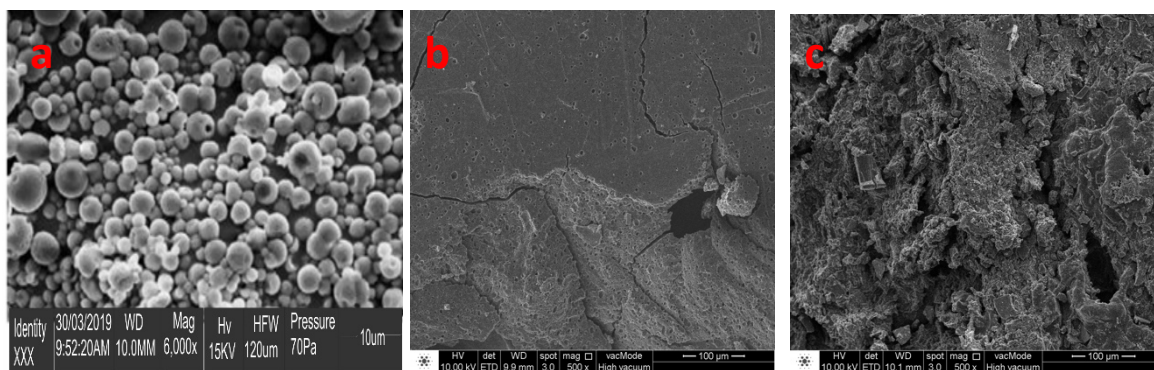


Figure 2. SEM of CaO (a), native (b) and phthalated (c) cassava starch grafted copolymers

3.4. SEM of CaO (Catalyst) and Grafted Copolymers

SEM analysis was conducted to examine the nature of the surface of the synthesized CaO and the result is presented in Figure 2a. The particles on the surface were spherical in shape, porous, and unevenly distributed probably. The uneven distribution could be due to the high calcination temperature in making the catalyst while liberating CO_2 (Ngamcharussrivichai *et al.*, 2010). The shape is similar to that of calcined limestone as reported by Sun *et al.* (2008) whereby the shapes are almost spherical. The surface morphology of native and modified

starch grafted copolymers were also verified using Scanning Electron Microscopy (SEM) (Hitachi SU8030 FE-SEM Tokyo, Japan). The micrograph of the native cassava starch grafted copolymer is presented in Figure 2b. The surface was porous and eroded with cracks, similar morphology has been reported by Xu *et al.* (2004). The surface of phthalated cassava starch grafted copolymer (Figure 2c) showed coagulated and aggregated morphology. Exposure to heat during gelatinization process might have caused the granules of the surface of the grafted copolymer to adhere and stick together to form aggregates of coarse particles.

Also, surface roughness observed on the SEM of the grafted copolymer could be linked to the milling process carried out after drying (Casas *et al.*, 2009). However, rough nature of the surface of the grafted copolymer is expected to be favourable for adhesion improvement because increase in the roughness of the surface will lead to enhancement of surface area in bonding as well as mechanical interlocking (Kaith *et al.*, 2009).

3.5. X-Ray Diffraction Pattern of Grafted Copolymers

The XRD analysis was performed to know the effects of grafting on the crystallinity or amorphousness levels of native and phthalated starch grafted copolymers. The XRD patterns of

the grafted copolymer of both native and phthalated starches are presented in Figure 3. The XRD pattern of native cassava starch (Figure 3a) had one major and broad diffraction peak at 21° (2θ) and another peak at 45° of angle 2θ , other regions of the spectrum were in the amorphous region. This is in line with the work of Kumar *et al.* (2014) which reported that graft reaction leads to amorphousness of structure. The phthalated cassava starch grafted copolymer (Figure 3b) showed various peaks at 7° , 18° , 23° , 28° , 29° , 32° , 33° and 45° of angle 2θ . The sharp peaks observed are actually a function of crystallinity in the copolymer. The incorporation of acrylonitrile into the framework of the phthalated cassava starch could have improved the crystalline nature of the copolymer.

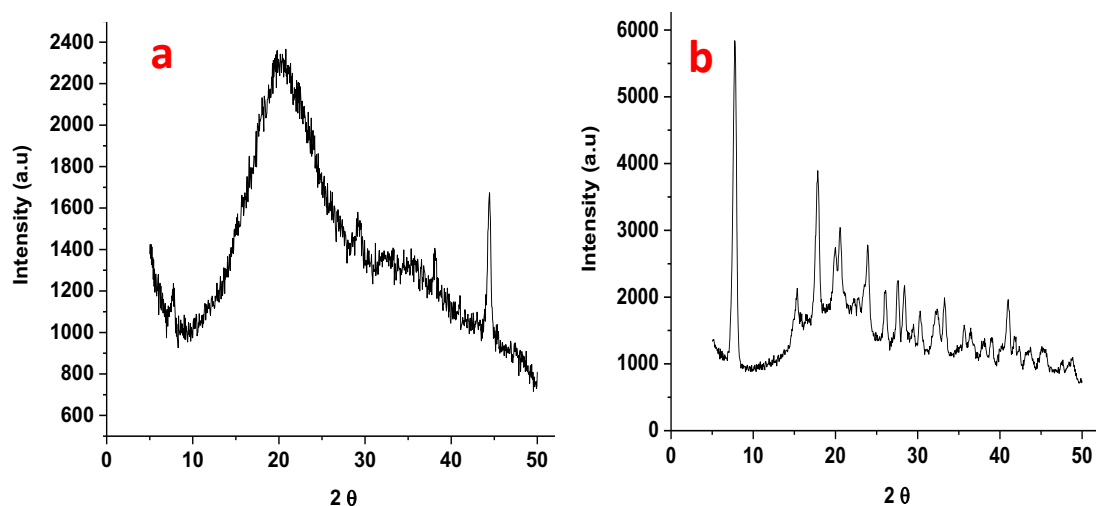


Figure 3. XRD of native (a) and phthalated (b) cassava starch grafted copolymers

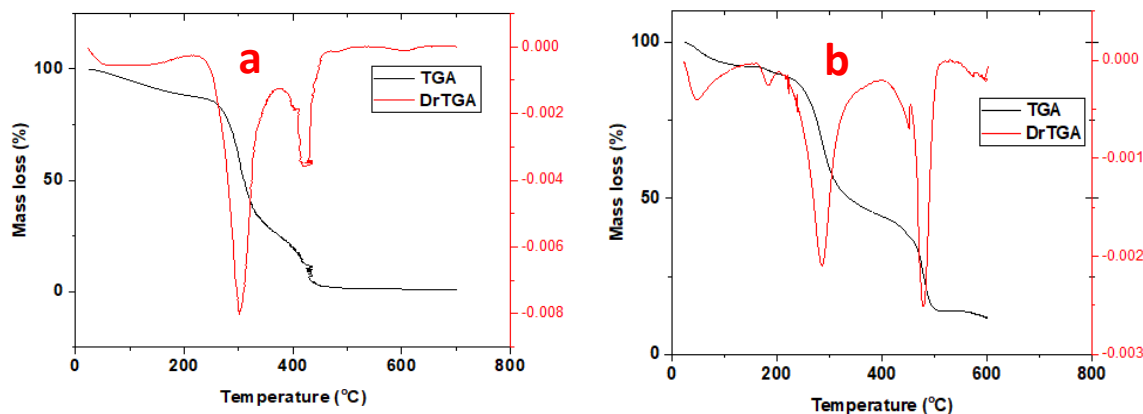


Figure 4. TGA of native (a) and phthalated (b) cassava starch grafted copolymers

3.6. Thermogravimetric Analysis of Grafted Copolymers

The Thermogravimetry analysis (TGA) curves of the of native and phthalated starch grafted copolymers are presented in Figure 4. The initial weight loss of native cassava starch grafted copolymer (Figure 4a) was observed at a temperature between 50 and 100°C indicating the loss of moisture in the copolymer, another weight reduction was observed at 350°C, this could be attributed to the decomposition of organic matters in the starch sample, further reduction in the weight of the native cassava starch copolymer was observed at 400°C. At 420°C, it was observed that the structural matrix has completely collapsed, leaving the residues as ash. For phthalated cassava starch grafted copolymer (Figure 4b), the initial weight loss began at temperature range of 50 to 200°C, indicating the removal of water content in the granules. The second weight loss was observed at 300°C which was largely due to the decomposition of organic matters that are present in the starch derivative. As the temperature increased, there was further reduction in the weight of the phthalated cassava starch grafted copolymer at 480°C. At 600°C, the sample has been reduced to ash which is the inorganic part.

4. Conclusions

Modification of starches often time is aimed at improving the physical and chemical characteristics of the natural polymers. In this present study, it was observed that the modified sample by Graft copolymerization had its both chemical and physical features improved in comparison to the native sample.

5. References

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