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COMPARATIVE STUDIES OF ACETYLATED AND CARBOXYMETHYLATED STARCHES OBTAINED FROM RED COCOYAM (*Colocasia esculenta*) AND WHITE COCOYAM *(Colocasia antiquorum*)

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ABSTRACT

Interest in biopolymer is on the rise due to the non-biodegradability of synthetic polymers. Starches obtained from red cocoyam and white cocoyam were subjected to chemical modifications through acetylation using acetic anhydride and carboxymethylation using monochloroacetic acid in the presence of sodium hydroxide followed by determination of their physicochemical and functional properties. The proximate analysis showed that moisture, protein and fat contents reduced following the modification. Moisture content falls within the permissible limit with white cocoyam starch (WCS) having the least in both native and modified starches. Carboxymethylated starches had higher fat and ash content than acetylated starches while acetylated starches had higher protein content. In addition, swelling power, solubility, oil and water absorption capacities increased following modification. Pasting temperature and peak time reduced following modifications, with carboxymethylation having slight reduction. There was a significant difference in the peak, trough, breakdown, final and setback viscosities of native and modified cocoyam starches. The viscosities increased following acetylation but decreased following carboxymethylation. Viscosities of the acetylated red cocoyam were higher than that of acetylated white cocoyam starches. FTIR studies revealed the introduction of new functional groups in the modified starches, with the bands of the -C=O shifting to a higher and -OH to a lower value. Chemical modification improved the physicochemical properties of the starches studied. The physicochemical properties of the native and modified red cocoyam starch make it a better binder than white cocoyam.

Keywords: Cocoyam starches, Acetylation, Carboxymethylation, Pasting, Biopolymer

INTRODUCTION

The demand for biopolymers and their derivatives has continued to increase due to their diverse applications in recent years. Starch is found abundantly in the seeds (legumes), grains (rice, wheat, maize, sorghum and other grasses), tubers (potatoes, yams) and fruits (banana) (Jyothi *et al.*, 2010;Tharanathan, 2005). It is composed almost entirely of polysaccharides, amylose and amylopectin (Toinga-Vipafuerte *et al.*, 2022). The physical arrangement of amylose and amylopectin and the interaction between starch and other components in food determine the physiocochemical properties of starch. These properties affect the quality of starch-based products and are essential in determining the potential application of starch as well as its enzymatic transformation (Kozich & Wastyn 2012; Mweta, 2008; Wurzburg *et al.*,1986). However, starch by itself could not be satisfactorily applied in industrial processes (Xu *et al.,* 2004). Native starches, irrespective of their sources are undesirable for many applications because of their inability to withstand processing conditions. They have some disadvantages

such as their hydrophilic character, poor mechanical properties and dimensional stability especially in an aqueous environment (Pornsuksomboon, 2016; Lawal, 2009). Chemical modifications can enlarge the range of certain physical properties of the parent starch (Lawal *et al.*, 2008; Rutenberg and Solarek, 1984) and enhances their use in several applications found in industrial processes and food manufacturing (KozichandWastyn, 2012; Olu-owolabi, 2010; Tharanathan, 2005). It is generally achieved through *derivatization* such as etherification, esterification, cross-linking and acid hydrolysis (Santacruz *et al.*, 2002).

Cocoyam (Taro) is a common name for the corms and tubers of several plants in the family *Araceae*. It is a perennial, tropical plant primarily grown as a root vegetable for its edible starchy corm and as a leaf vegetable (Lyongaand Nzietchueng, 1986). Cocoyam is an important source of carbohydrate and is majorly cultivated in tropical and subtropical regions (Nwanekezi*et al.*, 2010). There are many varieties of cocoyam but the most common are the soft variety used mainly as soup thickeners and the yam-like variety that can be boiled in a short time and eaten with pepper sauce. In Nigeria, the corms are usually eaten boiled, mashed or sometimes pounded, frequently mixed with other staples, such as yam or plantain (Fufa, *et al*., 2021; Boakye *et al*., 2018). The high carbohydrate content of cocoyam and its wide availability makes it a good source of starch for both domestic and industrial uses in Nigeria and Tropical Africa (Awokoya*et al.*, 2012). The aim of this study is to compare the physicochemical and functional properties of acetylated and carboxymethylatedred and white cocoyam starches.

MATERIALS AND METHODS

Materials

Cocoyam was obtained from Ijebu-Igbo market, Reagents used were HCl, H_2SO_4, NaOH, isopropanol, methanol, acetone, acetic anhydride and silver nitrate. All reagents used were of analytical grade.

Extraction of Cocoyam Starch

The method described by Lawal *et al.* (2007) was used for the extraction of cocoyam starch. The cocoyam tubers were washed to remove soil and dirt from the skin and then peeled using a kitchen knife. The peeled roots(corm) were washed, grated and sieved by washing off in a basin of water. The mixture was filtered through a fine-mesh sieve (Muslin cloth). The filtrate was allowed to settle, after which the supernatant was decanted and sediment was collected to obtain the wet starch. The wet cocoyam starch was air-dried at room temperature for 48 hours and ground to powder form using a blender. The powdery cocoyam starch was stored in a polythene bag until further use.

Acetylation of Starch

The method of Lawal (2004) was adopted for starch acetylation. The starch (70 g) was dispersed in 350 mL distilled water, was stirred magnetically for 20 minutes and maintained at a constant temperature. NaOH (1 M) was added in dropwise to adjust the pH to 8.0, after which 10 mL of acetic anhydride was added slowly to the mixture over a period of 1 hour while maintaining a pH range of 8.0 to 8.5. The reaction was allowed to proceed for 5 minutes after the addition of acetic anhydride. The pH of the slurry was finally adjusted to 4.5 using 0.5 M HCl. It was then filtered, washed three times with distilled water and air-dried at room temperature for 48

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hours. The acetyl content (expressed as a percentage in dry basis) and the degree of substitution were determined according to Lawal (2004). The acetylated starch (5 g) was placed in a 250 mL flask. After the addition of 50 mL distilled water, a few drops of phenolphthalein indicator was added and the suspension was titrated to a permanent pick end-point using 0.1 M NaOH.A 25 mL of 0.45M NaOH solution was then added after which the flask was sealed tightly with a rubber stopper and shaken vigorously for 30 minutes. After shaking, the stopper was carefully removed and washed down together with the wall of the flask with distilled water. The saponified mixture containing excess alkali was then titrated with a standard solution of 0.2 M HCl until the disappearance of the phenolphthalein colour. The native starch was treated in the same manner to obtain a blank value. The percent acetyl and degree of substitution were determined from Eqns 1.0 and 2.0 respectively.

$$\textit{Percent acetyl (dry basis)} = \frac{(\text{Blank titre} - \text{sample titre}) ml \times Acid\ Molarity \times 0.043 \times 100}{sample\ weight\ in\ g\ (dry\ basis)} \quad 1.0$$

$$\textit{Degree of substitution (D.S)} = \frac{162\ A}{4300 - 42\ A} \quad 2.0$$

A = % acetyl dry basis;

Blank titre = Native starch;

Sample titre = Modified starch

Preparation of Carboxymethyl Starch (CMS)

The method of Lawal *et al.* (2007) was adopted. Carboxymethylation of cocoyam starch was carried out in aqueous-organic liquid media. The organic solvent used in this experiment was isopropanol. Sodium hydroxide (8 g) was added to 100 mL distilled water in a flask and the mixture was stirred magnetically at 250 rpm until complete dissolution of sodium hydroxide. Isopropanol (250 mL) was added to the solution and allowed to homogenize. Cocoyam starch (40 g) was added to the mixture and it was stirred at 400 rpm for 30 min. Monochloroacetic acid (10 g) was added to the mixture and stirred for another 30 minutes. At the end of the reaction, the starch slurry was filtered, suspended in methanol and neutralized. After filtration, the slurry was dispersed in 80 % methanol and washed several times with 80 % methanol until the silver nitrate test for chloride of the filtrate was negative. The slurry obtained was suspended in acetone, stirred for 20 minutes, filtered and air dried for 48 hour. The DS for the carboxymethylated starch was determined using the titrimetric method as described by Lawal *et al.* (2007).Sample of CMS (2 g) was dissolved in 1 % aqueous NaCl solution and titrated with 1 M NaOH solution using phenolphthalein indicator until a colourless solution was observed. The D.S was then determined using Eqn. 3.0

$$DS = \frac{nNaOH \times M_0}{m_c - nNaOH \times M_R} \quad 3.0$$

$$m_c = m_p - \frac{(m_p \times F)}{100} \quad 4.0$$

M_o =molar mass of the anhydroglucose unit=162g/mol;

nNaOH = quantity of sodium hydroxide used [mol];

M_R=molar mass of carboxymethyl residue=58g/mol;

m_p = weight of modified starch taken [g];

m_c = corrected weight of weight of modified starch [g];

F= moisture content [%]

Proximate Analysis

Standard Association of Official Analytical Chemistry (AOAC, 2005) methods were used to determine moisture content, total ashcontent (AOAC, 1990), crude protein and crude fat content (AOAC, 2000).

Physicochemical Properties

Water and Oil Absorption Capacities

The method described by Adebowale *et al.* (2005) was used to determine the oil and water absorption capacities of the starch. Distilled water and oil (10 mL) respectively were added to 1 g each of starch samples. The mixture was thoroughly mixed for 30 seconds and allowed to stand for 30 minutes. Then the volume of the supernatant was recorded. The mass of oil or water absorbed was expressed as g/g starch on a dry weight basis.

Free Swelling Capacity and Solubility

Swelling power and solubility were determined in the temperature range of 50 – 90 °C, using the method of described by Lawal (2004). Starch sample (1 g) was accurately weighed and quantitatively transferred into a clear-dry test tube and weighed (w_1). Distilled water (10 mL) was added to the test tube and the mixture was mixed thoroughly for 30 seconds. The resultant slurries were heated at desired temperatures, between 50 – 90 °C for 30 minutes in a temperature-regulated water bath. The mixture was cooled to room temperature and centrifuged at 5000 rpm for 15 minutes. The residue obtained from the above experiment after centrifugation with the water it retained and the test tube was weighed (w_2). The swelling power was determined using Eqn. 5.0.

$$Swelling\ power\ \frac{g}{g} = \frac{W_2 - W_1}{weight\ of\ starch} \qquad 5.0$$

Aliquots (5 ml) of the supernatant obtained after centrifugation were dried to a constant weight at 110 °C. The residue obtained after drying the supernatant represents the amount of starch solubilised in water. The solubility was then determined in percentage from Eqn. 6.0.

$$Solubility\ (\%) = \frac{weight\ of\ solid\ after\ drying}{weight\ of\ sample} \times 100 \qquad 6.0$$

Pasting Properties of Starch

Starch pasting properties were evaluated using Rapid Viscosity Analyser (New port Scientific RVA super 4, Central Laboratory, Ibadan, Oyo state). A 3.5 g sample was weighed and 25 mL of distilled water was dispensed into a canister. Paddle was placed inside the canister. This was placed centrally onto the paddle coupling and then inserted into the RVA machine. The measurement cycle was initiated by pressing the motor tower of the instrument. The profile can be seen as it is running on the computer monitor connected to the instrument. The 13 minutes profile and time-temperature regime were used. Idle temperature of 50 °C for 1 min, heated from 50 °C to 95 °C in 3 min 45 sec and then held at 95°C for 2 min 30 sec.The sample was subsequently cooled to 50 °C over a period of 3 min 45 sec, followed by a period of 2 min where the temperature was controlled at 50 °C. The initial viscosity, peak viscosity (PV), peak viscosity time (Pt), trough, breakdown viscosity (BV), final viscosity (FV) and setback viscosity (SV) were recorded by rapid viscosity analyser.

FTIR Analysis

The FTIR spectra of starches were run as KBR pellets on FTIR spectrophotometer (Spectrum BX Perkin Elmer, England). A 2 mg sample was ground and mixed uniformly with 200 mg pure KBr powder. This mixture was next

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placed in pellet forming-die and then pressed in a hydraulic press to form a KBr pellet. The sample pellet was placed in a cell holder and then inserted into the FTIR equipment and scanned at a range of 4000 to 350 cm^{-1}.

RESULTS AND DISCUSSION

Proximate Composition

Table1 show the results of proximate composition of native and modified starches. The values obtained for the ash, protein and fat contents are all below 1%. This result establishes high level of purity of the starch samples and the efficiency of the isolation method used (Yussuf*et al*., 2018). Reduction in the fat and crude protein contents of the native starches was observed following modification. The replacement of hydrogen atom(s) with carboxymethyl group(s) and acetyl groups reduces carbohydrate functionality. This also minimized hydrogen bonding which reduced the starch interaction with other constituents such as protein, fat and crude fiber leading to their easy removal during processes such as filtration and washing (Akinterinwa *et al.,* 2014; Oderinde *et al.,* 2020). The fat content of the starches was between 0.05 and 0.16%in the order RCS > WCS in both native and modified starches. It was also observed that carboxymethylated starches had higher fat content than acetylated starches. Protein content ranged from 0.24 - 0.51% with red cocoyam having higher value in both native and modified starches while acetylated samples content is higher than carboxymethylated ones. Ash content increased after modification and ranged from 0.003 - 0.013% in the order RCS >WCS. Carboxymethylated starches had higher ash content than acetylated starches. This result is in accordance with the results obtained by Olu-Owolabi *et al.* (2014) on *acha* starch and Adebowale and Lawal (2005) on jack bean for protein and fat content, while Akinterinwa *et al.* (2014)reported ash content of carboxymethylated scarlet runner bean starch and Sanyaolu *et al*.(2021)on modified cassava/red cocoyam starches. The moisture content of the starches ranged from 8.28 - 9.91%, which falls within the maximum allowable limit (≈ 14%) for moisture in starch flour, as higher values will promote the growth of organisms which causes odour and off-flavour(Moreno *et al.*, 2018). Moisture content reduced following modifications, with red cocoyam samples having the highest value. It was also observed that acetylated starches had higher moisture content than carboxymethylated starches. This reduction in moisture content after modification will improve the shelf duration of the modified starches (Olu-Owolabi *et al.,* 2014; Olayinka *et al.,* 2013).

Table 1: Proximate Compositions of Native and Modified Starches

Samples	Moisture content (%)	Ash content (%)	Fat content (%)	Crude Protein (%)
RCS	9.910	0.005	0.160	0.480
WCS	9.860	0.004	0.140	0.450
ARC	9.140	0.008	0.100	0.330
AWC	8.510	0.007	0.080	0.270
CRC	9.120	0.012	0.130	0.270
CWC	8.280	0.008	0.100	0.240

*RCS= Native red cocoyam starch, *WCS= Native white cocoyam starch, *AWC= Acetylated white cocoyam starch, *ARC= Acetylated red cocoyam starch, *CRC= Carboxymethylated red cocoyam starch, CWC= *Carboxymethylated white cocoyam starch.

Degree of substitution (DS)

The degree of substitution of modified starches are presented in Table2. The result shows that white cocoyam starch have the highest DS for acetylated starch while the red cocoyam starch has the highest DS for white cocoyam carboxymethylated starch. This variation may be due to origin of the parent starch, the species and to the fact that starch composition differs depending on their sources. This is similar to the results obtained by Tijani *et al. (*2016) Karmakar*et al.* (2014) and Sodhi and Singh (2005).

Table2: Degree of Substitution of Red and White Cocoyam Starches.

Sample	Degree Of Substitution (DS)
ARC	0.077
AWC	0.079
CRC	0.086
CWC	0.083

Swelling Power and Solubility

Table 3 shows that swelling and solubility of native and the modified starches are temperature dependent (Sun*et al*., 2015; Mweta, 2008; Lawal, *et al.*, 2005). Swelling power and solubility increases as temperature increases in both native and modified starches. Modified starches had higher swelling power and solubility than the native starches with the carboxymethylated starches been the highest. The result also showed that red cocoyam starch had higher swelling and solubility power than the white starch samples. The observed increase in the swelling power on chemical modification might be due to the weakening of the intra-granular binding forces within the starch granule, which offered less restriction to swelling of the modified starches as the molecules get distorted (Sanyaolu *et al*., 2021; Oderinde *et al*., 2020; Adebowale and Lawal, 2003). High swelling power implies suitable application in water containing medium (Akanbi *et al.*, 2009). Solubility increases as temperature increases due to improved solvent capacity of starch molecules soluble fraction (Lawal and Adebowale, 2005). The variation in the cocoyam starch species reveals that each type of starch swells differently, indicating differences in the molecular organization within the granules. The degree of swelling and the amount soluble depend on the starch species (Mandala, 2004). This observation is similar to the result obtained by Awokoya *et al.* (2012) on white and red cocoyam starches, Adebowale and Lawal (2003) on mucuna bean starch and Akinterinwa *et al.* (2014) on carboxymethylated scarlet runner bean.

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Table 3: Swelling Power, Solubility and Absorption capacities (Water & Oil) of Starch Samples

Temp (°C)	50		60		70		80		90		Absorption Capacity (gg^{-1})	
Sample	**SWP**	**SOL**	**SWP**	**SOL**	**SWP**	**SOL**	**SWP**	**SOL**	**SWP**	**SOL**	**Water**	**Oil**
RCS	1.69	0.89	1.72	0.91	2.73	1.12	3.98	1.50	4.86	1.80	1.52	1.02
WCS	1.60	0.89	1.63	0.90	2.65	1.10	3.83	1.46	4.40	1.78	1.43	0.98
ARC	2.01	1.42	2.12	1.68	3.97	1.87	4.89	2.27	5.96	3.39	1.67	1.29
AWC	1.97	1.42	2.11	1.64	3.86	1.83	4.76	2.23	5.84	3.38	1.65	1.25
CRC	2.08	1.75	3.15	1.75	4.23	1.98	5.31	2.38	6.53	3.43	1.76	1.38
CWC	1.99	1.70	3.09	1.70	2.11	1.95	5.17	2.32	6.09	3.40	1.69	1.30

***SWP =** Sowelling Power; ***SOL** = Solubiity

Water and Oil Absorption Capacities

The results of oil and water absorption capacities in Table 3, shows that the starch samples absorb more water than oil. Both water and oil absorption capacities improved following modifications, with carboxymethylation having the having the highest absorption and RCS absorbing most. Introduction of bulky groups caused electrostatic repulsion among starch molecules, thereby facilitating access of water and oil into the starch matrices (Sharma *et al*., 2016; Sanyaolu *et al*., 2021). This result agrees with observations reported on the water and oil absorption capacities of modified bambarra ground nut starch (Adebowale *et al.,* 2002) and also that of cocoyam starch (Lawal, 2004) but contrary to results obtained by Yusuf *et al.* (2007) on mucuna starch and Akintayo *et al.* (2000) on lima bean starch where it was reported that modification reduced oil and water absorption capacity and that of Sathe and Salunkhe (1981) which showed that modification did not affect both oil and water absorption capacities of the Great Northern bean starch.

Pasting Properties

Pasting temperature and peak time reduced following modification which was more pronounced in acetylation (Table 4). This reduction indicates granule fragility. This will economise the cooking energy and may also be utilized in products that are susceptible to high temperature (Akinterinwa *et al.*, 2014). Native cocoyam starches had the highest pasting temperature which indicates that the starch from the native cocoyam is highly resistant to swelling during cooking (Tijani *et al.,* 2016). The results in Table 4 also showed the order of the pasting temperature is in the order WCS >CWC >RCS > CRC > AWC > ARC. There was significant difference in the peak, trough, breakdown, final and setback viscosities of native and modified cocoyam starches. These viscosities increased following acetylation but reduced following carboxymethylation. Peak viscosity is the maximum viscosity developed by a starch-water suspension during heating (Adebowale and Lawal, 2005). High peak viscosity of acetylated cocoyam starch obtained in this study might be linked to the weakened granule integrity caused by the acetyl groups replacing hydroxyl group in starch polymer (Sindhu, *et al*., 2021; Sudheesh *et al*., 2019; Perez *et al.*, 1997). The lower peak viscosity of carboxymethylated cocoyam starches can also be due to a partial degradation in the structural network and granule fragility. The higher trough viscosity in acetylated starches indicates the greater ability of the paste to withstand breakdown during cooling. It also indicates the ability to form paste or gel after. The lower final

viscosity in carboxymethylated starch can be attributed to the restriction in the tendency of the molecule to realign after cooling which will facilitate a lower setback (Akinterinwa *et al.,* 2014). The order of the final viscosities is ARC >AWC >WCS> RCS > CWC > CRC. The result is in accordance with those obtained by Tijani *et al.* (2016) for cocoyam starch and Akinterinwa *et al. (*2014) for scarlet runner bean but contrary to those reported by Adebowale and Lawal (2005) on jack bean. Peak time ranged from 3.52 to 4.40 minutes; WCS had the highest and CRC had the lowest values. Acetylated red cocoyam starch had the highest setback indicating a greater degree of retrogradation (Ding *et al.,* 2020) and the lowest breakdown viscosity of carboxymethylated starch is indicative of higher resistance to heat and stress during processing (Wang et al., 2020).

Table 4: Pasting properties of native and modified starches

Sample	Parameters						
	Peak Viscosity (cP)	Trough Viscosity (cP)	Breakdown Viscosity (cP)	Final Viscosity (cP)	Setback Viscosity (cP)	Peak Time (min)	Pasting Temp (°C)
RCS	174.333	91.417	65.833	183.250	45.417	4.200	84.10
WCS	183.167	105.333	77.750	197.917	65.415	4.400	84.50
ARC	260.167	151.083	109.083	250.833	99.000	4.000	81.50
AWC	200.083	123.750	98.250	201.669	70.917	4.200	83.25
CRC	115.250	76.1670	49.917	130.583	50.917	3.520	84.05
CWC	145.667	85.9170	56.917	140.000	55.500	4.000	84.20

FTIR spectra of Native and Modified Starches

Figures 1, 2, and 3 show the FTIR spectra of native, acetylated and carboxymethylated cocoyam starches. The broad band around 3300 cm^{-1} is assigned to O-H stretching, which decreases slightly following modification (Oderinde *et al.,* 2020).The peakaround~~at~~ 2930 cm^{-1}can be attributed to methyl group (-CH_2stretching vibrations), carbonyl group (C=O stretching) at 1646 cm^{-1}, - CH_2scissoring at 1427 $cm^{-1}$and -OH bending vibration at 1348 cm^{-1}. In the modified starches, the bands of the carbonyl group (C=O) and methyl group (-CH_2) concurrently increased, but the band of the hydroxyl group (-OH) decreased. This result confirms that modification took place on the starch molecules. Similar observations were reported by Rahim et al. (2019) on Arenga starch, Dao *et al*. (2017) on maize starch, Rachtanapun *et al.* (2012) on rice starch, for carboxymethylated mungbean starch (Kittipongpatana *et al*., 2006) and yam starch (Lawal *et al*., 2008).

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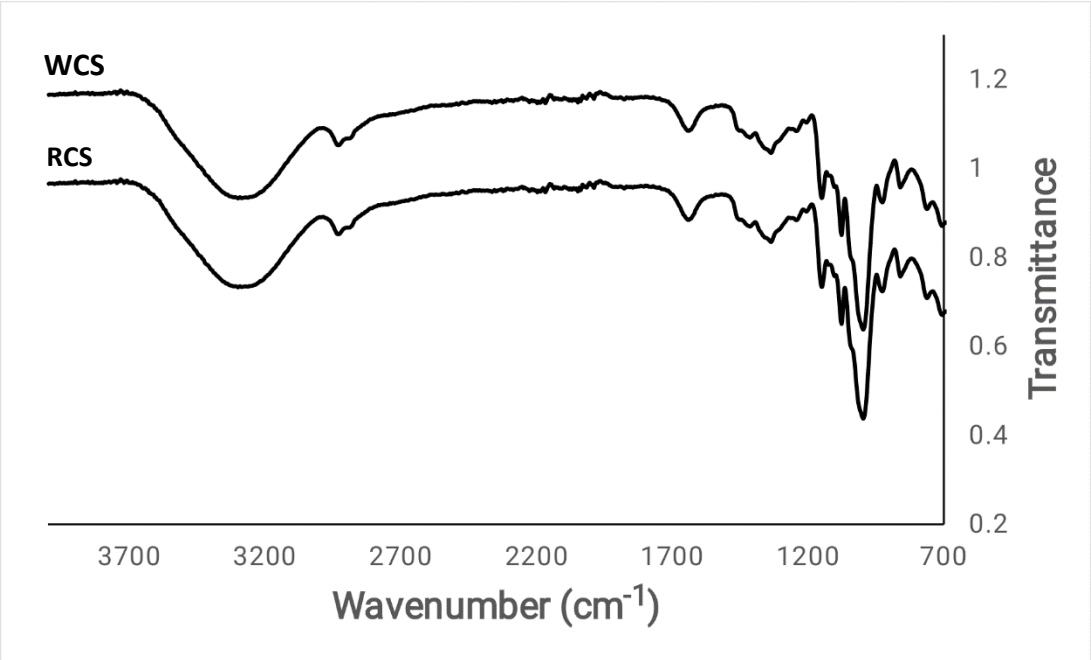

Figure 1: FTIR spectra of white (WCS) and red (RCS) cocoyam starches.

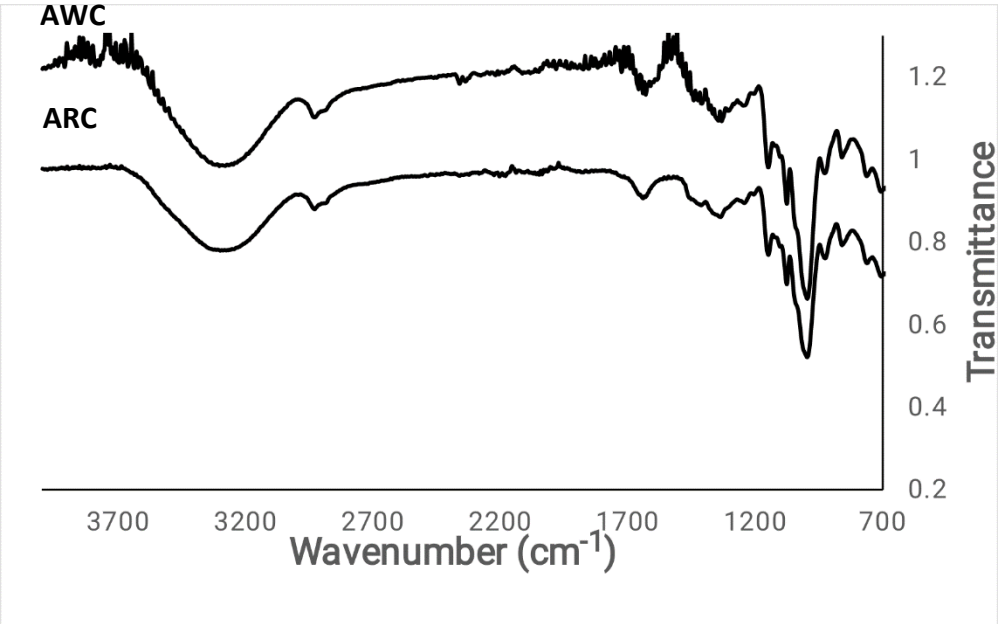

Figure2: FTIR spectra of acetylated white (AWC) and red (ARC) cocoyam starches.

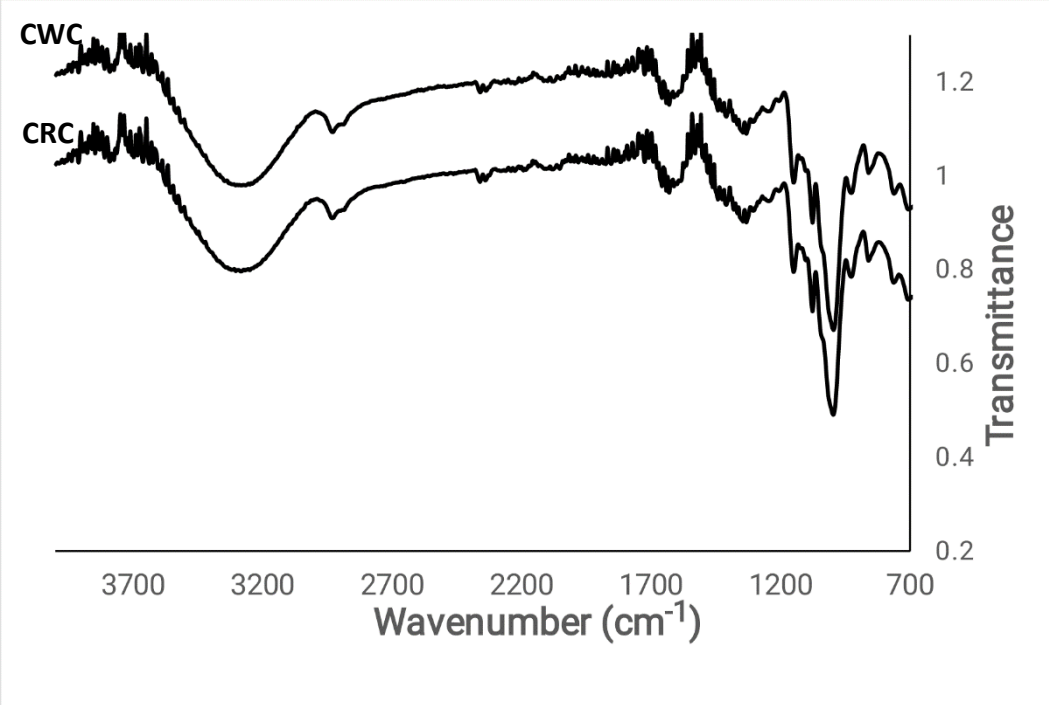

Figure 3: FTIR spectra of carboxymethylated white (CWC) and red (CRC) cocoyam starches**.**

CONCLUSION

Chemical modification brings about structural alterations and introduction of new groups thus affecting the physiochemical properties of starch and making it suitable for various industrial application. Structural changes in the modified starch was evident with shifting in bands of the C=O and -OH to higher and lower values respectively. The influence of modification was more pronounced in red cocoyam starch which makes it more suitable as a binder than white cocoyam starch. Its modification led to higher peak and trough viscosities and can withstand tough processing condition. In addition, the acetylated starches showed improved properties namely viscosity, solubility and stability than the native and carboxymethylated starches and as such will find application in stabilizer and thickeners.

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