



EFFECTS OF PHOSPHORYLATION AND CROSS-LINKING ON STARCHES
OBTAINED FROM BANANA (*Musa acuminata*) AND PLANTAINS (*Musa paradisiaca*
and *Musa balbisiana*)



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Abstract

Starch isolated from banana (*Musa acuminata*) and plantains species (*Musa paradisiaca* and *Musa balbisiana*) were phosphorylated with sodium tripolyphosphate (STPP) and cross-linked with phosphorous oxychloride (POCl_3). Functional and physicochemical properties of native and modified starches were investigated. Moisture content of the banana (*M. acuminata*) decreases following modification while that of plantains increases. The ash and fat content reduced after modification but crude protein content increased in cross-linked *Musa paradisiaca* starch. Swelling power and solubility increased as temperature increases and more pronounced in phosphorylated starches with highest water absorption. Pasting temperature increases except in phosphorylation plantain starches while breakdown viscosity decreases. Modified starches gels better than native with decrease in their bulk densities. Formation of modified starches was evident in the changes observed in their FTIR absorption. The study showed that modified starches can find application in noodles (cross-linked starches), soups and sauces (phosphorylated starches).

Keywords: Cross-linking, Gelatinization, Phosphorylation, Physicochemical, Pasting properties.

Introduction

Starch is the main polysaccharide stored in various part of plants and next in abundance renewable and biodegradable biopolymer to cellulose and chitin (Tharanathan, 2005; Ziaud-din *et al.*, 2017). It acts as the most important polymeric carbohydrate in terms of its functionality that impacts to products in diverse industries such as pharmaceutical, food and adhesives. It consists of two glucose polymers (amylose and amylopectin) spatially arranged in granules with morphology, chemical composition and relative arrangement of macromolecules in the solid state depending on the botanical source. Amylose is essentially a linear polysaccharide with the D-glucose units linked by α -D-(1-4) glycosidic bonds which give rise to a helical structure (Yoshimoto *et al.*, 2000; Hoover *et al.*, 2010). Amylopectin consists of chains of D-glucopyranose residues linked together mainly by α -D-(1-4) linkages, but with 4-5 percent of α -D-(1-6) bonds at the branch points. The properties of starch such as granule size, shape, specific area, porosity, crystalline or amorphous character is influenced by the different botanical origins, which consequently determines its use in the food and non-food industries (Tharanathan, 2005).

Banana and plantain belong to the *Musa* spp, grown in wide range of environment with diverse applications/usage (Nelson *et al.*, 2006). The annual harvest is approximately 145 million tons worldwide with about 85% grown in small plots and residences (Ortiz & Swennen, 2014). Ghana, Nigeria and cote d'Ivoire are the major producer in West Africa (Olumba & Onunka, 2020). World gross exports of banana were 13,893.7 thousand metric tonnes in 2010 (FAO, 2011). *Musa* species contains approximately 75% water and 25% carbohydrate along with trace amount of protein and fat as well as high levels of calcium, potassium, phosphorus and carbohydrate (Okareh *et al.*, 2015). Starch is the main carbohydrate component of green bananas and their systematic isolation and

characterization can be traced back to the work by Kasiyuc *et al.* (1981).

In recent times, many types of chemically modified starches have been prepared by acid hydrolysis, oxidation and etherification. One common starch modification is phosphorylation, which is the process of introducing a phosphate group $-(\text{PO}_4)_3$ into a starch, usually with the formation of a phosphoric ester, a phosphoric anhydride or a phosphoric amide using STPP, POCl_3 with Na_3SO_4 (Blennow *et al.*, 2002; Passauer *et al.*, 2010; Sanyaolu *et al.*, 2021). Cross-linking is one of the widely used methods for starch modification and the cross-linking agents commonly used are phosphorous oxychloride, adipate and epichlorohydrin (Subroto *et al.*, 2021). When starch is cross linked, its properties vary. The extent of crosslinking can be predicted with the help of properties like viscosity and swelling power (Tharanathan, 2005; Bakouri & Guemra, 2019; Akinterinwa *et al.*, 2020). Modification tends to alter the structure of starches leading to improved properties and consequently their application (Ashogbon & Akintayo, 2014). The aim of this research work is to evaluate the effects of phosphorylation and cross linking on the physicochemical and functional properties of banana and plantain starches.

Materials and Methods

Unripe commercial plantains fruits (*Musa paradisiaca* and *Musa balbisiana*) and banana (*Musa acuminata*) was obtained at Oluyole local government secretariat, Idi Ayunre Ibadan, Oyo state Nigeria. The plantain fruits were identified at International Institute for Tropical Agriculture, Ibadan, Nigeria. Analytical grade Sodium tripolyphosphate [$\text{STPP}(\text{Na}_3\text{P}_3\text{O}_{10})$], Phosphorus Oxychloride (POCl_3), potassium hydroxide (KOH) and anhydrous sodium sulphate (Na_2SO_4) were used.

Isolation of Starch

The unripe banana and plantain fruits were peeled and divided into two equal halves to remove the black pods inside. It was cut into smaller pieces, rinsed thoroughly with water and macerated with blender (Saisho blender). The slurry was mixed with large volume of water, sieved with double muslin cloth and was left to settle for 3 hours after which the supernatant was decanted off. The starch slurry was rinsed severally and the process was repeated until highly clean charf was obtained. The starch obtained was air-dried for 72 hours and blended to fine particles.

Preparation of Phosphorylated Starch

Phosphorylated starch was prepared using the method of Lim and Seib (1993). 70 g of starch was dispersed in distilled water and mixed thoroughly. 5 g of STPP in the presence of 5 g of Na₂SO₄ was also mixed with distilled water. The starch slurry and the solution of STPP and Na₂SO₄ were mixed thoroughly using magnetic stirrer for 1 hour while adjusting the pH to 6 with 1 M HCl. The mixture was dried to 10-15% moisture at 40 °C. The dried sample cake was heated for 2 hours at 60 °C in an oven and then cooled to 27 °C. It was dispersed in distilled water (350 ml) and the starch phosphate was recovered by filtration. The filtrate was dispersed in another 600 ml of distilled water and the pH adjusted back to 6.5 with 1 M KOH. This then was washed with distilled water severally and dried at 40 °C. The dried phosphorylated starch was ground to more fine particles.

Preparation of Cross-linked Starch

Cross-linked starch was prepared using the method of Singh & Nath (2012) and Garcia-Alonzo *et al.* (2009) with little modification. 100 g of starch dispersed in distilled water (350 ml) to form a slurry was mixed with 7.5 g Na₂SO₄ solution prepared at pH 9 with 1.0 ml of POCl₃ added in dropwise over 20 mins. The mixture was stirred vigorously on magnetic stirrer at 25 °C for 1 hour, while maintaining the pH at 6 with 1.0 M KOH. The mixture was left for 6 hours at room temperature for the reaction to complete. The pH was then adjusted to 6.5 with 1.0 M HCl. The modified starch was recovered by filtration. It was washed severally with distilled water and dried at 40 °C in an oven.

Proximate analysis

Standard Association of Official Analytical Chemistry Methods (AOAC) were used for estimating moisture content, total ash, crude protein and crude fat (Yussuf *et al.*, 2018).

Determination of Swelling Power and Solubility

The Swelling power and solubility were determined using the method of Takashi and Sieb (1988). About 1 g of sample was added to 20 ml of distilled water in a centrifuge tube and mixed gently. The slurry was heated in a water bath at 50, 60 & 80 °C respectively for 15 min. During heating, the slurry was stirred gently to prevent clusters of the starch. After 15 min, the tubes containing the paste were centrifuged at 4000 rpm for 10 minute using Merlin 503 (SPECTRA U.K) centrifuge. The supernatant was decanted instantly after centrifuging and the sediment weight was recorded. The moisture content of the gel was thereafter determined to get the dry matter content of the gel from equation 1. The process was repeated for phosphorylated and cross-linked starches. The supernatant obtained was dried in an oven at 130 °C to have a dry starch and weighed. The residue obtained after drying the supernatant represents the amount of starch solubilized in water. The solubility is expressed in percentage (%) according to equation 2.

$$\text{Swelling power} = \frac{w_3 - w_2}{w_1} \quad (1)$$

$$\text{Solubility \%} = \frac{w_4}{w_1} \times 100 \quad (2)$$

w₃=weight of the sediment; w₂=weight of centrifuge and starch; w₁=weight of starch sample; w₄=weight of the supernatant

Determination of Oil and Water 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 s and allowed to stand for 30 min. 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.

Bulk Density

Starch sample (50 g) was placed inside a measuring cylinder and the level of the starch was noted. The cylinder with starch was tapped for 100 times and the level of the starch was noted (Emeje, 2012). The bulk density was evaluated using equation (3)

$$\text{Bulk density (g/mL)} = \frac{\text{weight of sample}}{\text{volume of sample after tapping}} \quad (3)$$

Determination of pH

Starch (5 g) was weighed inside a beaker and mixed with 20 ml distilled water. The mixture was stirred vigorously for 5 min and left to settle for 10 min before the supernatant pH was check using calibrated pH meter (AOAC, 1990).

Determination on Gelation Capacity

This was determined by the method of Sathe and Salunkhe (1981). Starch (5 g) suspensions were prepared in test tubes with 10 ml of distilled water. The starch suspensions were mixed with a magnetic stirrer for 5 min. The test tubes containing the suspensions were heated to 30, 50 & 80 °C in water bath followed by cooling under running cold tap water. The tubes were further cooled at 40 °C for 30 min. The least gelation concentration is the concentration at which the sample from the test tube did not fall.

FTIR

The FTIR spectra of starches were run as KBr pellets on FTIR spectrophotometer (Spectrum BX Perkin Elmer, England). 2 mg of the sample was ground and mixed uniformly with 200 mg pure KBr powder. This mixture was next 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 500 cm⁻¹.

Determination of Pasting Properties

Starch pasting properties were evaluated using Rapid Viscosity Analyser (New port Scientific RVA Super 4). 3.5 g of 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.

Results and Discussion

Proximate composition

The ash, crude protein, crude fat and moisture contents of native, phosphorylated and cross-linked starches are shown in Table 1. The results shows that cross-linked *M. balbisiانا* has the highest moisture content and the native *M. paradisiaca* has the least. The moisture content of the banana (*M. acuminata*) decreases following modification while that of plantains increases. Similar report of increase in moisture was reported by Lawal and Adebowale (2005). Low moisture content indicates a longer shelf-life of starch containing product such as excipient which impact stability on a drug (Gope *et al.*, 2016). Ash content of the starches decreases

upon modification for phosphorylated and cross-linked *M. balbisiانا* and ranges between 0.0010-0.0025%. However, cross-linking has no effect on the on the ash content of both Banana (*Musa acuminata*), plantain (*Musa paradisiaca*), while significantly reducing that of *Musa balbisiانا* (0.0025-0.0010%) The fat content of the both the native and modified starches which range between 0.090-0.135% are relatively low. The fat content did not change significantly following modification with slight decrease. The low values indicate that *Musa species* starch and other products from it are not susceptible to quick rancidity due to its low-fat content (Yussuf *et al.*, 2018). Protein content of the starch was between the range of 0.35 -0.42 percent with all the native samples having similar value. The crude protein decreases after modification except for cross-linked *Musa paradisiaca* which increased slightly. These reductions may be due to the various degradation that took place during the modification processes (Ibikunle *et al.*, 2019)

Table 1: The Proximate Analysis of Native, Phosphorylated and Cross-linked Starches

Sample	Moisture Content %	Ash content %	Fat Content %	Crude Protein %
A1	15.30	0.0025	0.135	0.410
A2	10.24	0.0025	0.140	0.410
A3	11.25	0.0025	0.120	0.410
B1	11.21	0.0015	0.150	0.250
B2	14.70	0.0020	0.100	0.385
B3	15.32	0.0015	0.130	0.340
C1	11.72	0.0025	0.120	0.370
C2	12.01	0.0025	0.115	0.720
C3	15.73	0.0010	0.090	0.355

A1-A3, B1-B3, C1-C3 represents Native, phosphorylated and cross-linked starch samples from Banana (*Musa acuminata*), plantain (*Musa paradisiaca*) and plantain (*Musa balbisiانا*) respectively

Swelling Power and Solubility

The swelling power and solubility of the native and modified starches increases with increase in temperature as shown in Table 2. It was also observed that plantain have lower swelling power than the banana starch. When an aqueous suspension of starch is heated, the temperature increases and exceeds gelatinization temperature, the starch granules become weakened and the intermolecular bonds of the starch molecule become distorted. This enables water molecules to become more attached to the starch molecules and the granules continue to swell as they absorb more water (Gunaratne and Corke, 2007). Table 2 also shows a decrease in the swelling and solubility of all cross-linked starches compared to the native starches. Cross-linking has been reported to decrease the swelling power and solubility of starches from various sources (Hoover and Sosulski, 1986).

Singh *et al.* (2007) reported a reduction in solubility and swelling of various cross-linked starch systems. Wang and Wang (2003) also indicated that the cross-linkages may reduce the movement of starch molecules, causing reduction in water solubility and water absorption of cross-linked starch. The results obtained from the table also shows that phosphorylation increases the swelling power and solubility compared to the native starches as temperature increases. Starch becomes more thermodynamically activated which leads to increase in granular mobility and enhance water penetration and swelling ability due to increase in temperature (Rincon *et al.*, 2004). High swelling power results into high digestibility and ability to use starch in improved dietary properties and in a range of dietary applications. The swelling power and solubility have been related to the associative binding within the starch granules and apparently produces high swelling power (Wootton *et al.*, 1984).

Table 2: Swelling Power, Solubility and Absorption capacities (Water & Oil) of Starch Samples

Temp(°C)	50		60		80		Absorption Capacity (gg ⁻¹)	
Sample	SWP	SOL	SWP	SOL	SWP	SOL	Water	Oil
A1	0.9	40	1.2	60	3.0	80	1.1	1.0
A2	0.8	50	0.8	70	5.3	90	1.0	0.7
A3	0.7	50	0.9	60	5.5	80	0.5	0.2
B1	0.8	60	0.9	80	3.4	90	1.5	1.1
B2	0.7	50	0.9	70	4.6	90	2.0	1.0
B3	0.7	50	1.2	70	4.9	90	2.0	1.0
C1	0.8	40	1.0	70	2.1	90	1.3	1.0
C2	0.6	40	0.7	60	2.5	80	1.0	0.9
C3	0.5	30	0.6	50	4.0	90	1.5	1.3

*SWP = Swelling Power; *SOL = Solubility

Oil and Water Absorption

The results of oil and water absorption of native, phosphorylated and cross-linked starches are shown in Table 2. Oil and water-absorption capacity of native and modified starches presented in Table 2 shows that hydrophilic tendency of the starch increases after phosphorylation. Likewise, the oil absorption increased in phosphorylated starch than the native starch which is in accordance with Lawal and Adebowale (2005). The results indicated that all the starches had more water absorption capacities than oil absorption capacities. This result also indicates that starch phosphorylation and crosslinking improved water absorption capacity. The introduction of bulky functional groups and their electrostatic repulsion facilitate percolation and absorption of water within the starch matrices (Sharma *et al.*, 2016; Sanyaolu *et al.*, 2021). Increase in water absorption capacities following esterification reaction has also been reported by Awokoya *et al.* (2011) for red cocoyam.

Bulk Density & pH

The results of bulk density of native, phosphorylated and cross-linked starches are shown in Table 3. Bulk density is a measure of the degree of coarseness of the starch sample. The bulk density of starches is in the range of 0.77 to 0.93. A decrease in bulk density was observed for the phosphorylated and crosslinked starches except crosslinked *Musa balbistiana*. Decrease in bulk density might be attributed to increase in crystallinity following chemical modification. This decrease in bulk density is contrary to Emeje *et al.* (2012) and Akanbi *et al.* (2008) which reported increase in the value of bulk density following modification. The pH values for native and modified starches are also shown in Table 3. The results show an increase in the pH of native starch following modification, but the pH for all the starches are slightly alkaline. This observation is in the agreement with reports by Ibikunle *et al.*

(2019) for African star apple and Akanbi *et al.* (2008) for Breadfruit starches, while Sanyaolu *et al.* (2021) reported a decrease in pH of phosphorylated cassava and red cocoyam starches.

Table 3: Bulk Density & pH of Native and modified starches

Sample	Bulk density (g/mL)	pH
A1	0.83	7.39
A2	0.96	7.32
A3	0.83	7.05
B1	0.77	7.59
B2	0.93	8.02
B3	0.77	8.08
C1	0.83	7.60
C2	0.83	7.80
C3	0.91	8.00

Gelation Properties of Native Starch and Modified Starches

The results of the gelation properties of native, phosphorylated and cross-linked starches are shown in Table 4. From the results it was observed that as the temperature increases, the gelation increases in phosphorylated starch and cross-linked starches gels than in native starch except in *Musa balbistiana* starch at higher temperature. Tie *et al.* (2008), reported that native starch from Sago palms gels at lower temperature and phosphorylated starch gels at higher temperature. Also, Lawal (2004), reported a reduction in gelation properties of native starch following acetylation. The results from this study indicated that starches from *Musa spp.*, especially phosphorylated starch will be very useful in food and other chemical industries for binding.

Table 4: Gelation Properties of Native and Modified Starches

Sample	30 °C	50 °C	80 °C
A1	Viscous	Viscous	Gel
A2	Viscous	Viscous	Gel
A3	Viscous	Gel	Firm gel
B1	Gel	Gel	Firm gel
B2	Gel	Firm gel	Firm gel
B3	Gel	Firm gel	Firm gel
C1	Gel	Firm gel	Firm gel
C2	Gel	Firm gel	Firm gel
C3	Gel	Firm gel	Firm gel

Pasting Properties of Native and Modified Starches

Pasting is a result of a combination of processes that follow gelatinization from granule rupture to subsequent alignment due to mechanical shear during the heating and cooling of starches. The results of the pasting properties of native, phosphorylated and cross-linked starches are shown in Table 5. The modified starch, had higher values for peak viscosity and trough viscosity, except for the modified banana starches. The breakdown viscosity reduced following modification but increased in the phosphorylated plantain starches. The lower breakdown of modified starches compared to native starches shows lower paste stability during the hold period. The lower breakdown may suggest a weak cross-linking among its starch granules and higher breakdown indicates that there was less granule rupture in the starch, hence better paste stability and resistant to breakdown similar to report by Zhang *et al.* (2005). The final viscosity of cross-linked starches increased and decreased in phosphorylated starches with cross-linked *Musa balbisiaca* having the highest final value. The increase in final viscosity is a result of re-association between starch molecules, especially amylose, to a greater or lesser degree, when it occurs to a greater degree it leads to formation of a gel which is usually indicated by a rise in viscosity (Ai and Jane, 2015; Shah *et al.*, 2016). The pasting temperature (temperature at

the onset of rise in viscosity) of the starches was between 82.50 – 86.60 °C with phosphorylated banana starch having the highest. The pasting temperature indicates that starches have high gelatinization temperature. The high gelatinization temperature implies that the granules resisted swelling. Phosphorylated *Musa paradisiaca* has lowest pasting temperature implying that the starch has lower gelatinization temperature hence a shorter cooking time compared to plantain starch. The pasting temperature of starches investigated in this study is very similar to that of starches from *Dioscorea rotundata* and *D. alata* (Otegbayo *et al.*, 2006) and African breadfruit kernel (Oderinde *et al.*, 2020), but higher than that of chickpea starch (Kaur and Singh, 2005). Higher setback viscosity was observed for cross-linked starches which implies that it will form a more cohesive paste and has higher retrogradation tendency than phosphorylated and native starches (Kim *et al.*, 1995; Oduro *et al.*, 2000; Lawal, 2004; Otegbayo *et al.*, 2006). Therefore, cross-linked starches will be more appropriately utilized in products such as noodles where retrogradation of starch is desired. Phosphorylated starches with a low setback viscosity can be used in soups and sauces, which undergo loss of viscosity and precipitation as a result of retrogradation (Adebowale and Lawal, 2003).

Table 5: Pasting Properties of the Native and Modified Starches

Samples	Parameters						
	Peak Viscosity (cP)	Trough Viscosity (cP)	Breakdown Viscosity (cP)	Final Viscosity (cP)	Setback Viscosity (cP)	Peak Time (min)	Pasting Temp (°C)
A1	464.50	372.30	92.30	560.60	188.33	5.10	83.30
A2	410.50	327.60	82.90	566.90	239.00	5.10	84.90
A3	471.70	337.60	134.10	484.20	146.60	4.80	84.20
BA	390.80	323.80	67.60	540.30	217.20	5.40	86.60
B2	523.00	386.10	130.90	503.90	115.90	5.00	82.50
B3	543.20	353.60	189.60	485.80	132.30	4.70	83.60
C1	398.40	367.80	25.80	650.50	282.80	5.60	84.80
C2	464.60	420.60	44.00	720.10	299.50	5.30	85.10
C3	566.80	505.30	61.70	1026.50	521.30	5.20	84.90

FTIR

The FTIR spectra of the representative of the *Musa spp* starches are presented in Figure 1 to confirm the modification of the native starches.

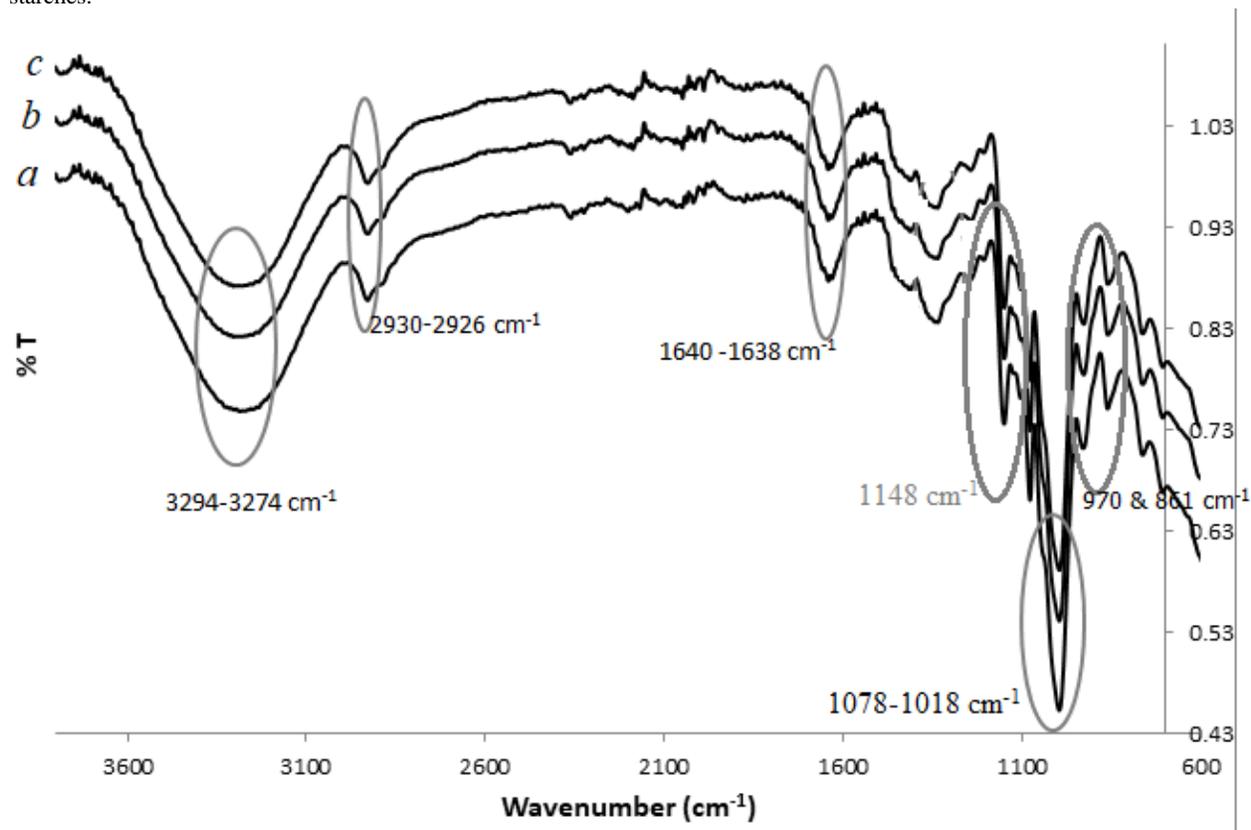


Figure 1: FTIR Spectra of native (a), a representative of phosphorylated (b) and cross-linked (c) *Musa spp* starches.

The broad absorption band in the range 3297-3274 cm^{-1} indicated the existence of characteristic of hydrogen bonded -OH stretching vibration. The band of absorption however decreased following modification of the carboxyl groups (Park *et al.* 2005; Sanyaolu *et al.*, 2021). The O-H absorption of the cross-linked starches is lower than that of the phosphate and native starches. The C-H absorption of the cross-linked starch (2928 cm^{-1}) is higher compared to that of the phosphorylated (2927 cm^{-1}) and native starches (2926 cm^{-1}). A medium strength absorption peak at 1148 cm^{-1} was assigned to the symmetrical stretching of a carboxylic acid while the peaks in the region between 1640-1638 cm^{-1} & 1078-1018 cm^{-1} shows strong absorption peaks assigned to C-C and C-O stretching. The absorption bands for the carbonyl group are within 1640 -1638 cm^{-1} . The C=O absorption band of the cross-linked starch (1640 cm^{-1}) is higher compared to that of the native starch (1638 cm^{-1}) and phosphate starch (1639 cm^{-1}). The region between 1078 cm^{-1} and 1018 cm^{-1} shows the absorption peaks for C-O stretch. The absorption peaks at 970 and 861 cm^{-1} are both assigned to C-H bending (Rahim *et al.*, 2019). The absorption peak of cross-liked starch is highest followed by phosphorylated and native starch is lowest. Thus, the FTIR spectra support the modification of the starches by STPP and POCl_3 .

Conclusion

There were variations in the physicochemical and functional properties of *Musa spp* starches following their modifications by cross-linking and phosphorylation. Noticeably, modified banana starches will have a longer shelf life as a result of their low moisture content compared to their plantain counterpart. Phosphorylation leads to an improved water absorption capacity, swelling power and solubility of starches under study compared to cross-linking. However, pasting temperature of phosphorylated plantain starches reduced while modification generally reduced breakdown viscosity. This study showed that banana and plantain starches have an array of functional, pasting and proximate properties that make them suitable for use in areas where other starches are not. High swelling power of phosphorylated starches impacts higher digestibility and ability to use in improving dietary properties in a range of dietary applications. Cross-linked starches from plantain and banana can be very useful in the formation of food component parts and as a stabilizer, tablet binders in pharmaceutical companies because of the high value of final viscosity.

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