

## Cross-linked Starch from *Icacina trichantha* Oliv. Tuber as an Additive in Water Based Drilling Mud

Kennedy Ogunwa<sup>1</sup>, Ozioma Achugasim<sup>2</sup>, Leo Osuji<sup>2</sup>, Onyewuchi Akaranta<sup>1,2</sup>

<sup>1</sup> World Bank Africa Centre of Excellence in Oilfield Chemicals Research, University of Port Harcourt, Nigeria

<sup>2</sup> Department of Pure and Industrial Chemistry, University of Port Harcourt, Nigeria

Received July 26, 2021; Accepted January 17, 2022

### Abstract

Starch from *Icacina trichantha*, Oliv. was extracted, characterized and reinforced by cross-linking using Sodium trimetaphosphate (STMP). Starch derivative of two degrees of crosslinking (20.7% and 39.6%) were produced. The new derivatives, the native starch and a commercial drilling starch were used to prepare water based muds. Studies on the rheological and filtration properties of the resulting muds showed that the muds with the cross-linked starches had improved yield stress and gel strength compared to the commercial drilling starch. The flow behavior index of the new muds was less than 1.0, showing non-Newtonian and Pseudoplastic flow behavior. Fluid loss of 9cc, 8cc and 7cc were recorded for mud with the native starch, cross-linked starches and commercial starch respectively. All the muds were found to obey the American Petroleum Institute (API), Power law and Herschel-Bulkley models for static filtration and fluid rheology.

**Keywords:** *Icacina trichantha* Oliv.; Starch; Mud; Rheology; Di-starch phosphate.

## 1. Introduction

The high cost of petroleum products in most cases are attributable to the cost incurred during crude oil drilling. Starch, an important material for crude oil drilling is hitherto largely sourced from edible tubers and cereals. Large tons of starch are required daily in the oil industry. This places a lot of pressure on food security worldwide and raises the cost of crude oil drilling especially in oil producing provinces where the starches are imported. Production of starch from non-edible sources especially tubers can mitigate the global food shortage and help in the development of the value chain for the non-food tubers. Careful and adequate processing is usually needed for new raw materials to achieve the intended purpose of replacing the conventional ones.

Starch from a non-food tuber, can be extracted, modified to obtain starch derivatives as worthy additives and feedstock for different industrial processes. *Icacina trichantha*, Oliv. (ITO) is a non-food plant that belongs to the family of Icacinaceae. It is a prominent shrub with broad leaves and large underground tubers and was first classified by Burkill [1]. The work by Ogunwa and others reported a tuber weight of 3kg and a starch yield of 61% from a single ITO plant [2].

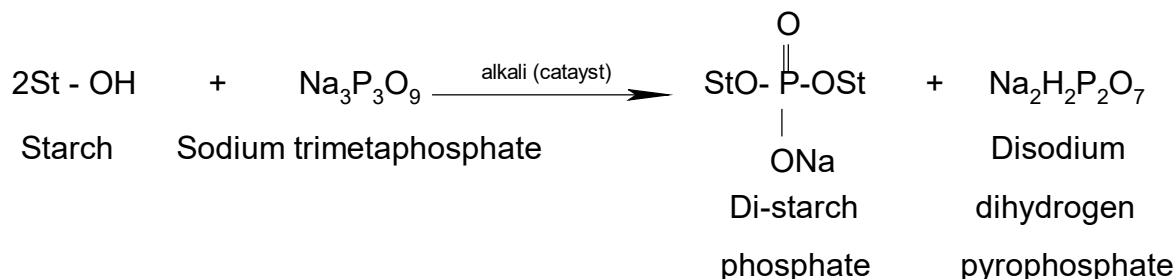
However, native starches irrespective of their source may not possess the functional attributes needed for certain industrial applications, hence the need for starch modifications. Major variations in native starches are basically due to the amylose-amylopectin ratio, presence of minor components of protein, lipids and trace elements [3].

Starches are modified physically, chemically, genetically or any combination of these where the modifications depend largely on the starch native origin.

Physical modification involves heat or mechanical treatment to alter the granular structure of the starch molecules. They include heat-moisture treatment, gelatinization, retrogradation,

pregelatinization. Chemical modifications on the other hand involves the treatment of starch with chemicals to introduce new functional groups, effect molecular scission and rearrangement to significantly alter the physicochemical properties of the starch. The different kinds of chemical modification include substitution with monofunctional compounds, starch crosslinking with polyfunctional reagents, starch conversion and graft copolymerization with starch.

Improved rheological and filtration properties are usually achieved through starch crosslinking. Cross-linking is conducted by treating starch slurry with reagents which can form ether or ester linkages between the hydroxyl groups on the starch molecules. These reagents are called Polyfunctional chemicals. A very good example of this is sodium trimetaphosphate (STMP), see scheme 1.



Scheme 1. Cross-linking of ITO atarch with STMP

Starch cross-linking reactions generally strengthens the structure of the starch upon gelatinization, adds molecular bonds at random locations across the chains and within the granules. Cross-linked starches have enhanced resistance to acid conditions, resistance to viscosity breakdown due to high temperature [4]. The variation in physicochemical properties of a particular starch largely depends on the extent of cross-linking and the botanical source of the starch. Very low levels of cross-linking usually stabilize the starch granules and allow them to attain a higher degree of granule swelling than the native starch during heating [5-6]. However, progressive higher degree of cross-linking does not lead to increased granule swelling stability [7-9]. Several researchers have utilized native starches as additives in water based mud (WBM). Chike-Onyegbula, Ogbobe & Nwanonenyi studied the effect of concentration and temperature variation on a biodegradable polymer drilling mud prepared using Guinea corn starch pre-gelatinized in the absence of a solvent and confirmed its suitability [10]. Studies on rheological and filtration performances of local cassava starch to those of an imported starch has been conducted [11]. Egun & Achadu compared cassava starch to polyanionic cellulose (PAC) as fluid loss agent in WBM, and reported very good fluid loss control [12].

Starches are generally used as Gelling, Fluid loss control and Viscosity enhancing agent in water based muds (WBMs). A mud must exhibit certain amount of gel strength to be able to sustain drill cuttings when mud circulation is suspended, fluid loss control to check rate of water (continuous phase or base fluid) loss into the formation and good viscosity for efficient suspension of drill cuttings during drilling operation. Since gelling is improved with starch cross linking, it is expected that ITO cross-linked starches will enhance the rheological and fluid loss properties of water based muds.

After the formulation of the muds with the modified starches, the shear stress and shear rate of the various muds are obtained using the following expressions.

Shear stress ( $\tau$ ) is given by:  $\tau = 0.01066 \times \theta_i \times N$  (1)

where  $\theta_i$  is the dial reading at  $i^{\text{th}}$  rpm and  $N$  is a spring factor which is 1.

The shear rate ( $\gamma$ ) is given by:  $\gamma = 1.703 \times \text{RPM}$  (2)

where RPM is revolution per minutes of the instrument.

The shear rate of a particular mud directly depends on the amount of the applied force, which determines the flow rate of the fluid through a particular geometrical configuration. The plots of flow pressure versus flow rate or shear stress versus shear rate are termed flow

models. Two flow models, Power law and Herschel -Bulkley are usually used to characterize the rheological properties of various mud formulations.

The Power law model relates shear stress to shear rate in a nonlinear manner [13]. The mathematical expression is given by the following equation:

$$\tau = K\gamma^n \quad (3)$$

Where:  $\tau$  = shear stress,  $\gamma$  = shear rate,  $K$  = consistency index and  $n$  = flow behavior index.

The  $n$  ranges in values from one to zero. At low values of  $n$ , the flow profile is flat and tends towards plug flow while at high values of  $n$ , it is laminar and streamlined. As  $n$  decreases, the mud tends to become more shear-thinning. As  $k$  increases, the pressure loss increases during the circulation.

Taking logarithm of equation 3, we have:

$$\text{Log } \tau = \text{log } k + n \text{ log } \gamma \quad (4)$$

where,  $n$  = slope and  $k$  = intercept.

Herschel- Bulkley model describes the behavior of yield-pseudoplastics fluids [14]. Applications of Herschel- Bulkley law model have important implications for measuring drilling mud hydraulics and assessment of hole cleaning efficiency. The model is as follows:

$$\tau = \tau_y + K\gamma^n \quad (5)$$

where  $\tau$  is the shear stress,  $\tau_y$  is the yield stress,  $k$  is the consistency index,  $\gamma$  is the shear rate, and  $n$  is the flow index.

The Power law and the Herschel-Bulkley models were used for the analysis of the flow behavior of the muds formulated in this study. This current work will synthesize di-starch phosphates of two different degrees of cross-linking using *ITO* tuber starch and compare the rheological and filtration properties of water based muds prepared with the di-starch phosphates to those of a commercial drilling starch.

## 2. Experimental

### 2.1. Materials

Sodium trimetaphosphate, sodium hydroxide, hydrochloric acid, sodium thiosulphate, potassium chloride, acetic anhydride, sodium monochloroacetate, ethanol, methanol, paraffin oil, acetic acid and distilled water.

### 2.2. Methodology

#### 2.2.1. Sample collection/starch extraction

*Icacina trichantha*, (Oliv.) tubers (Figure 1) were harvested from Agulu in Anambra State, Nigeria and the starch was extracted by the wet milling method.



Figure1. *Icacina trihcantha*, (Oliv.) tubers

### 2.2.2. Synthesis of ITO Di-starch phosphate

The method of Woo & Seib was used with slight modification [15]. 100g of starch sample was suspended in 250mL distilled water and 3% sodium trimetaphosphate (STMP) cross-linking agent was added into the suspension. The mixture was adjusted to pH of 10.5 using 5%NaOH while maintaining a gradual continuous stirring and was heated at 45°C for 2hours. The reaction was terminated with 1M HCl by adjusting the pH to 5.5. The slurry was then mixed with large volume of distilled water and the acid neutralized with 1M NaOH. This process was repeated with 4% STMP. The precipitate (ITO starch diphosphate) was recovered from the slurry with Buchner funnel equipped with vacuum pump. The precipitate which was white was washed thoroughly with distilled water and dried in an oven at 50°C for 24hours.

### 2.2.3. Degree of cross-linking

The degree of cross-linking was determined from the viscosity value using combined methods [16-17]. The viscosity was measured with rapid visco-analyzer. 2.5g of the cross-linked starch was suspended in 25mL distilled water and heated to 95°C. The slurry was held at this temperature for 3mins, then cooled down to 50°C and was again held at this temperature for 6mins. The pasting parameters were automatically computed by the analyzer and recorded. The degree of cross-linking was calculated by the equation below:

$$\text{Degree of cross-linking} = \{(A-B)/A\} \times 100 \quad (6)$$

where: A – peak viscosity of native ITO starch; B – peak viscosity of cross-linked ITO starch.

Two different degrees of substitution were achieved for this study; ITO cross-linked starch 1 (ITO-CrLiS1) and ITO cross-linked starch 2 (ITO-CrLiS2).

### 2.2.4. Proximate/physicochemical analysis

The determination of the proximate and physicochemical parameters like the moisture, ash, protein, carbohydrate and fat contents, pH, and starch yield of the ITO tuber and its native starch (ITON) is as described by [2]. The following parameters were determined for both the starch and its cross-linked derivatives: gelatinization temperature GT (°C) water absorption capacity WAC (%) by the methods of [18-19]. Swelling power SP (%) was by [20] while amylose content (%) was determined following the methods of Radley [21] and Austin [22]. The results are presented in Tables 1 and 2. FTIR spectroscopic analysis was conducted on the native starch and the derivatives to confirm modifications.

### 2.2.5. Mud formulation

WBM samples were prepared based on pound per barrel (lb./bbl.) units in the industry. The formulation technique of Hamilton [23] was used as listed below: water (base fluid-316.4mL), caustic soda (alkalinity control-0.2g), soda ash (calcium ion removal-0.2g), native ito starch/cross-linked ITO starch/commercial starch (filtration control and viscosifier-2.0g), xanthium gum (viscosifier-2.8g), potassium chloride (inhibition control-18g) and barite (weighting agent-76.8g)

The mud samples were prepared using Egun & Achadu [12] method with little modification. 316.4mL of water was taken in a Hamilton beach mixer, and appropriate quantities of additives were measured into water (base fluid) at a controlled mixing time of 2mins between each addition in the order listed above. Continuous stirring was maintained. Four different mud samples were prepared and coded as Mud-ITON (Mud with native starch), Mud-ITO-CrLiS1 (Mud with lower percent cross-linked starch), Mud-ITO-CrLiS2 (Mud with higher percent cross-linked starch, and Mud-C-STARCH (Mud with commercial starch).

### 2.2.6. Rheological tests

Fann viscometer (model 35) fitted with spring and bob was used for the rheology test [24]. The dial readings at 3, 6, 100, 200, and 600rpm were recorded for the four different muds and tabulated in Table 3. The plastic viscosity(PV) and yield point (YP) were calculated using the following equations:

$$PV = 600\text{rpm Reading} - 300\text{rpm Reading} \quad (7)$$

$$YP = 300\text{rpm reading} - PV \quad (8)$$

### 2.2.6.1. Determination of gel strength

Fann viscometer (model 35) fitted with standard spring and bob was used. The prepared mud samples were poured into the viscometer cup at room temperature. The rotor sleeve of the Fann 35 viscometer was then immersed to the scribed line. The fluid was agitated for 10s at 600rpm and turned off. After 10s the motor gently turned on at 3rpm and maximum reading attained was noted as the initial gels at 10s. The fluid was stirred again for 10s at 600 rpm and after which the motor was switched off. The motor was gently turned on at 3rpm and the maximum reading attained was noted as the gel strength for 10 minutes. Values at 10secs and 10mins were recorded in Table 6.

### 2.2.6.2. Filtrate (fluid loss) measurement

Fann's low temperature low pressure (LTLP) filter press was used and the cell parts were put together following the specifications in the equipment operations manual. The prepared drilling mud samples were poured in turns into the cell to within 1cm to 1.5cm of the top of the cell. A dry graduated cylinder was placed under the drain tube to collect the filtrate. The relief valve was closed and a pressure of 100psi applied through the regulator using carbon (IV) oxide cartridge. The timer was started simultaneously as the pressure was applied. The volume of filtrate collected at time intervals of 5min from zero time to 30mins were measured and recorded (table7), the flow was stopped through the pressure regulator and then trap pressure bled turned off through the relief valve.

## 3. Results and discussions

### 3.1. Proximate/physicochemical properties of the tuber/starch

The fat, protein, carbohydrate and moisture content of the ITO tuber is as presented in Table 1. Their values are more similar to those of tubers than cereals [7]. The pH of 4.3 is quite low, requiring a long washing time to obtain starch of higher pH for derivatization. The starch from the tuber is off-white in colour. Starch yield of 50% from the tuber is very pleasing, pointing to the potential of the tuber as a veritable source of starch in the future.

Table 1. Proximate analysis of the ITO tuber

Parameters	Values	Parameters	Values
Moisture content (%)	62.48	Ash (%)	2.96
Protein (%)	0.75	Starch yield (%)	61.00
Carbohydrate (%)	71.13	Crude fiber (%)	6.86
pH	4.13	Fat (%)	0.87

Physicochemical properties (Table 2) like starch granule size of 4-15 $\mu$  and the low amylose content (10%) points to the crystalline nature of the starch and explains the ease of starch extraction from the tuber.

Table 2. The physicochemical properties of the ITO native starch (ITON)

Parameters	Values
Starch granule size ( $\mu$ m)	4-15
Water absorption capacity (%)	108.93
Swelling power at 50oC	11.71
Moisture content (%)	10.5
Gelatinization temperature (oC)	78
Amylose content (%)	10
Ash (%)	0.26
pH	6.01



The FTIR spectra of ITO native starch and its derivatives (Figure 2) presented a special pattern that is similar to that of the native starch except the variations that occurred at 900-1200 $\text{cm}^{-1}$  region. This was due to the P-O-C, P=O and  $\text{PO}_4^{3-}$  bond stretching/bending which have absorptions at this region. This confirmed that extra bonds involving phosphorus were introduced between the starch chain molecules. The similarity may be due to the fact that this modification only introduced linkages between starch chains hence may not have alteration along each of the starch chains. Similar absorption was reported for cross-linked sweet potato starch [25].

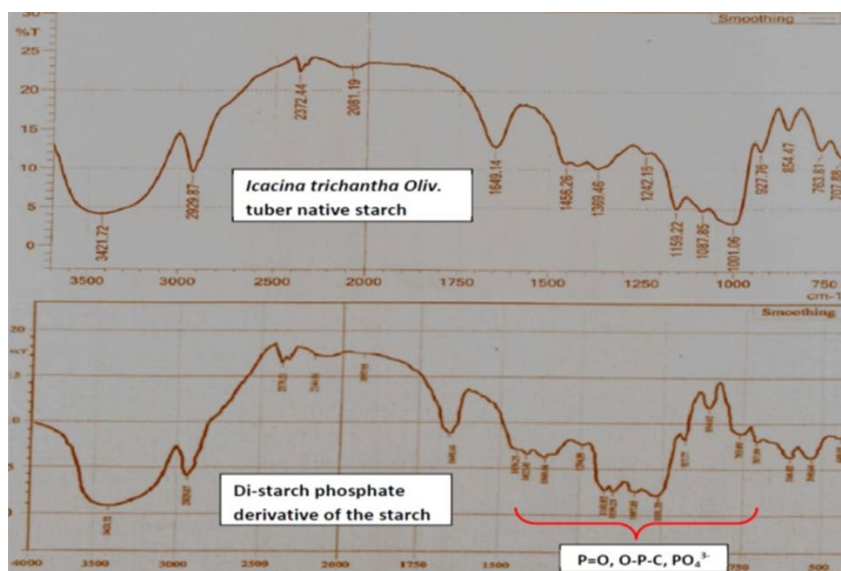


Figure 2. FT-IR Spectra of ITO native starch and its Di-starch phosphate

The swelling profile of the native starch and its cross-linked derivatives increased with increase in temperature from 60-90°C and increase in the percentage cross-linking. It was observed that at the swelling onset temperature (50°C) in Table 3, the cross-linked starches ITO-CrLiS1 and ITO-CrLiS2 experienced delay in swelling, but latter exceeded that of ITON as the temperature increased beyond 60°C. This agreed with David & Williams [26] that cross-linked starches exhibits low swelling than the ordinary starch but gets higher as heating progresses. The extent of cross-linking was below 50% for both cross-linked products obtained (Table 3). From tables 3 and 4, ITO-CrLiS1 with lower %C-L recorded higher swelling power than ITO-CrLiS2 from 60°C and above, this agrees with another report that reduced swelling power of cross-linked Oak starch with increasing degree of cross-linking [27]. This decrease in swelling power is owed to the formation of internal inter-molecular bridges within the starch chains by the cross-linking agent [28-29]. This effect becomes more pronounced with starches that have greater degree of cross-linking [4].

Table 3. Effect of temperature on the swelling power of the native ITO starch and its derivatives

Samples	Swelling power (SP)				
	50°C	60°C	70°C	80°C	90°C
ITON	11.71	11.95	12.73	23.72	30.77
ITO-CrLiS1	7.77	12.74	13.14	26.64	33.74
ITO-CrLiS2	8.58	12.16	10.99	26.08	33.20

The cross-linked starches recorded the lower water absorptive capacity (WAC) than the native starch (Table 4). It was also reported that cross-linking reduces the water binding capacity of starches and that this effect becomes more pronounced with increased degree of cross-linking [30]. The WAC trend as seen in table 4 shows that the WAC reduced with higher degree of cross-linking.

Table 4. Some physicochemical Properties of ITO native starch and its Di-starch phosphate derivatives

Samples/products	WAC (%)	Gelatinization temperature, (°C)	pH	%C-L
ITON	108.93	77	5.01	0
ITO-CrLiS1	83.53	83	5.19	20.7
ITO-CrLiS2	80.37	81	5.70	39.6

From Table 4, it is clear that cross-linking increased the gelatinization temperature (GT) of the starches. This was observed to be the reverse for WAC where ITON had higher WAC than the modified starches. The pH of the samples got higher with modification. This may be due to the extent of work- up procedures e.g. washing.

### 3.2. Rheological tests

Rheology describes drilling mud's behavior when in motion and is necessary for removal of cuttings while drilling. The results obtained for the four mud samples; mud-ITON, mud-ITO-CrLiS1, mud-ITO-CrLiS2 and mud-C-STARCH are presented in Table 5.

Table 5. The rheological parameters from the various starch samples

Samples	ITON	ITO-CrLiS1	ITO-CrLiS2	C-STARCH
Speed (rpm)	Viscometer dial reading			
600	63	61	62	62
300	54	54	55	55
200	50	50	49	50
100	42	42	41	43
6	24	24	24	22
3	15	19	20	19
PV	9	7	7	7
YP	45	47	48	48

Cross-linking lowered the Plastic viscosity (PV) of the muds with ITO-CrLiS but increased the yield point (YP) as can be seen in Table 5. Mud-ITON had the best PV followed by Mud-C-Starch and mud-ITO-CrLiS2 whereas mud-ITO-CrLiS2 had higher YP than that with the native starch ITON. Increase in percentage cross-linking increased the YP of the muds.

Power law and Herschel- Bulkley models were applied to the data sets generated for shear rate-shear stress in Table 6. New sets of predicted data that would give the best fit curve were generated based on these models (equations 4 and 5). The predicted data for Power law model and Herschel-Bulkley model showed little variation with those of the experimental data. The non-linear relationship between shear stress and shear rate indicates that the muds obeyed the power law model and Herschel- Bulkley model for non-Newtonian fluids.

Table 6. Shear stress-shear rate values of the various mud formulations

Speed (rpm)	Shear rate (1/s)	ITON	ITO-CrLiS1	ITO-CrLiS2	C-STARCH
Shear stress (Ibf/100ft <sup>2</sup> )					
600	1022	0.693	0.65	0.661	0.661
300	511	0.576	0.576	0.586	0.586
200	341	0.533	0.533	0.522	0.533
100	170	0.448	0.448	0.437	0.458
6	10.22	0.256	0.256	0.256	0.235
3	5.11	0.16	0.203	0.213	0.203

The regression analysis of the experimental data using the two models (equation 4 and 5) gave coefficients of determination ( $R^2$ ) whose values tends towards 1, and low values of standard error SE were recorded for each of the muds (Table 7). This is an indication that the rheological data from the actual measurements had very good fit with those generated from the test models. These shows that the muds prepared from the cross-linked starches have very good rheological and fluid loss properties.

Table 7. Flow behavior index ( $n$ ), consistency index ( $k$ ), yield stress ( $\tau_y$ ) of the mud samples in relation to the coefficient of determination ( $r^2$ ) and standard error (se) of the models

Samples	ITON	C-STARCH	ITO-CrLiS1	ITO-CrLiS2
K	0.1284	0.1440	0.1522	0.1509
n	0.2429	0.2226	0.2117	0.2137
$\tau_y$	0	0	0.0400	0.0435
$R^2$	0.9952	0.9990	0.9987	0.9985
SE	0.0255	0.0110	0.0105	0.0112

From Table 7, the flow index values were found to be lower than 1 ( $n < 1$ ) for all the muds. According to Mewis [14] a fluid for which  $n$  value is lower than 1 ( $n < 1$ ) is said to have pseudoplastic flow behavior. Further examination of the table reveals that the consistency index,  $k$  for the muds with modified starches increased. This may be due to the fact that the chemical modification of the starch at various levels caused increase in the viscosity of the mud samples. The resistance of the fluid to the applied rate of shear or force, (shear stress), increased with increase in the consistency index ( $K$ ). There is little variation in the flow index values ( $n$ ). This may be due to low extent of chemical modifications. High degree of substitution above one (1) and percentage cross-linking above 60% gives better reinforcement of starches [3,28]. The low  $K$  index indicates high pumpability, improved mud circulation and down hole cleaning. The reinforcing impact of cross-linking on the native starch is seen on the higher yield stress ( $\tau_y$ ) recorded by the muds from the cross-linked starches (Table 7). This yield stress ( $\tau_y$ ) was also found to increase further with increased degree of cross-linking.

Gel strength is the rheological property of a drilling fluid at rest. It is mainly due to the attraction between the particles and the friction between the solids in suspension or solids and the liquids around them. The highest gel strength (GS) value was obtained with mud-ITO-CrLiS showing that among the muds, it has the highest capability of suspending drill cuttings or particles when circulation is interrupted (stopped). This points to the positive impact of crosslinking on the starch. Generally, muds with high gel strength require high pump pressure in order to break the mud after being static for a long time.

### 3.3. Filtration test

The amount of filtrate collected for each mud sample at the different period of time is shown in Table 8. A suitable drilling mud must be able to give filtrate loss volume less than 15mL over a period of 30 minutes, and any fluid loss additive which could not achieve this is unacceptable [31]. All the mud samples met this criterion.

Table 8. Filtration characteristics of the mud samples

Samples	ITON	ITO-CrLiS1	ITO-CrLiS2	C-STARCH
Time (mins)	$t^{1/2}$	Amount of filtrate (cc)		
0	0	0	0	0
5	2.2361	4	3	4
10	3.1622	5	5	5
15	3.8729	6	6	6
20	4.4721	7	7	7
25	5.0000	8	8	8
30	5.4772	9	8	7
Sorptivity(mL/min <sup>2</sup> )	1.5877	1.5503	1.4925	1.3293



It could also be observed from Table 8 that the fluid loss increased with increase in square root of time. This is consistent with the API model for static filtration, which states that fluid loss of a given mud is proportional to square root of time.

$$V = St^{1/2} \quad (9)$$

where  $V$  is total fluid loss volume,  $S$  is sorptivity of the fluid and  $t$  is time of filtration.

Mud-C-STARCH performed better than the others with filtrate loss of 7cc and the lowest sorptivity value followed by Mud-ITO-CrLiS<sub>2</sub> and then the mud with the native starch (Mud-ITON). Considering the filtrate loss fitness modeling and linear regression, the new model equation becomes:

$$V = xT + y \quad (10)$$

where  $V$  is the quantity of filtrate,  $x$  corresponds to the sorptivity value which is different for each mud sample,  $T$  is square root of time and  $y$  is the spurt-loss (abnormal initial filtrate loss) before filtration settles down to steady rate. A plot of  $T$  against  $V$  gives the graphs shown in Figures 3-4.

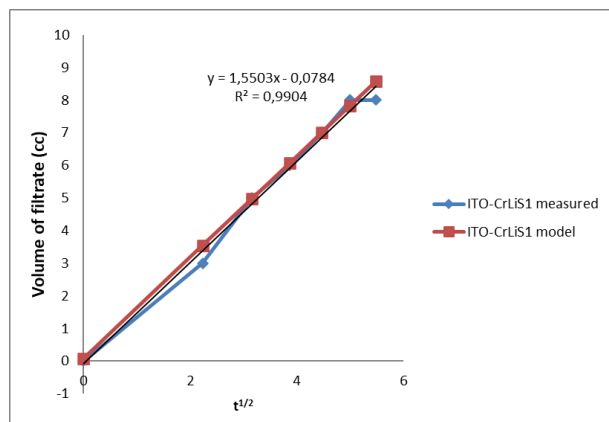


Figure 3. Regression plot of the volume of filtrate loss against the square root of time for mud-ITO-CrLiS1

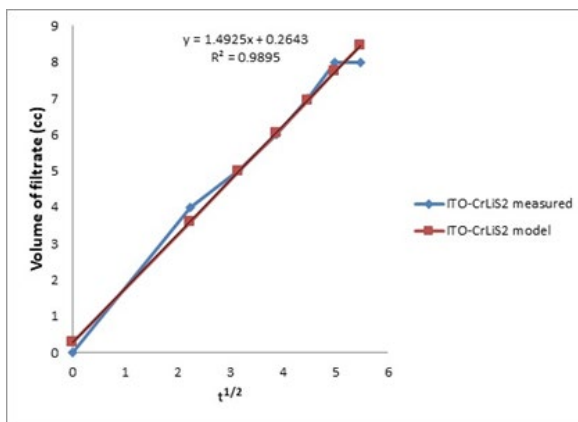


Figure 4. Regression plot of the volume of filtrate loss against the square root of time for mud-ITO-CrLiS2

The coefficient of determination ( $R^2$ ) a measure of goodness of fit for the mud samples with the cross-linked starches approaches one as depicted in the graphs. The percentage error for the entire mud samples were below 10%, which also indicates minimal deviations of the experimental data to predicted data

#### 4. Conclusion

This work has shown that ITO tubers can act as a non-edible source of starch for industrial applications. Starches from ITO tubers can be modified into di-starch phosphates of different degrees of substitution. The research has also confirmed that starch from ITO tuber and its modified form (di-starch phosphate) can be used as fluid loss control agents and viscosifiers in water based drilling muds. Modification especially crosslinking improved the rheological and filtration properties of starches as additives in water based drilling muds.

#### Acknowledgements

The authors are grateful to Halliburton Fluids Laboratory and DUFIL Prima Food Plc. Laboratory, Port-Harcourt for their assistance in carrying out some of the analysis in this work.

#### Symbols

ITO	<i>Icacina Trichanta Oliv.</i>
ITON	<i>Icancina trichanta Oliv. native starch</i>
Mud-ITON	Mud with native starch
Mud-ITO-CrLiS1	Mud with lower percent cross-linked starch
Mud-ITO-CrLiS2	Mud with higher percent cross-linked starch
Mud-C-STARCH	Mud with commercial starch

## References

- [1] Burkill HM. The useful plants of West Africa. White Friars Press Limited, Britain. (1985); 2, 534.
- [2] Ogunwa KI, Akaranta O, Achugasim O, Osuji LC. Comparative Evaluation of the Physico-Chemical Properties of *Icacina trichantha* Oliv. Tuber Starch with those of some Indigenous Staple Crops. *J. Chem. Soc. Nigeria*, 2016; 41 (1): 27-32.
- [3] Huber KC, BeMiller JN. Modified Starch, Chemistry and Properties. In: A. C. Bertolini (Eds) *Starches; Characterization, Properties and Applications*, New York: Taylor & Francis. 2010, 147-166
- [4] Singh J, Kaur L, McCarthy OJ. Factors influencing the physico-chemical, morphological, thermal and rheological properties of some chemically modified starches for food applications- A review. *Food Hydrocoll.*, 2007 21, 1-22.
- [5] Wurzburg OB, Szymanski CD. Modified starches in the food industry. *J. Agric. Food Chem.* 1970; 18: 997-1001.
- [6] Howling D. The influence of the structure of starch on its rheological properties. *Food Chem.* 1980; 6:51-61.
- [7] Hoover R, Sosulski F. Effect of cross-linking on functional properties of legume starches. *Starch/Stärke*, 1986; 38:149-155.
- [8] Colas B. Flow behavior of cross-linked corn starches. *Lebensm. Wiss. Technol.*, 1986; 19: 308-311.
- [9] Ziegler GR, Thompson DB, Casasnovas J. Dynamic measurement of starch granule swelling during gelatinization. *Cereal Chem.* 1993; 70: 247-251.
- [10] Chike-Onyegbula CO, Ogbobe O, Nwanonenyi SC. Biodegradable polymer drilling mud prepared from guinea corn. *J. Brew. Distill.*, 2012; 3(1): 6-14,
- [11] Ademiluyi T, Joel OF Amuda AK. Investigation of Local Polymer (Cassava Starches) as a Substitute for Imported Sample in Viscosity and Fluid Loss Control of Water Based Drilling Mud. *ARNP J. Eng. Appl. Sci.*, 2011; 6 (12): 43-48
- [12] Egun IL, Abah AM. Comparative Performance of Cassava Starch to PAC as Fluid Loss Control Agent in Water Based Drilling Mud. *Discovery*, 2013; 3(9): 36-39.
- [13] Alderman NJ, Babu DR, Hughes TL, Maitland GC. Rheological Properties of water-based drilling muds, In 4th international Congress on Rheology, Sydney. 1988
- [14] Mewis J., Willaim JF, Trevor AS, Russel WB. Rheology of suspensions containing polymerically stabilized particles, *J. Chem. Eng. Res. Dev.*, 1989; 19: 415.
- [15] Woo KS, Seib PA. Cross-linked Resistant Starch: Preparation and Properties. *Cereal Chem.* 2002; 79: 819-825.
- [16] Kaur L, Singh J, Singh N. Effects of Cross-linking on some properties of Potato Starches. *J. Sci. Food Agric.*, 2006; 86: 1945-1954.
- [17] Koo SH, Lee KY, Lee HG. Effect of cross-linking on the physicochemical and Physiological properties of Corn Starch. *Food Hydroeco.*, 2010; 24: 619-625.
- [18] Attama AA, Nnamani PO, Mbonu IK, Adiku MU. Effect of hypochlorite oxidation on the physicochemical properties of gladiolus starch; *J. Pharm. Allied Sci.*, 2003; 1 (1): 28-35.
- [19] Abbey BW, Ibeh GO. Functional properties of raw and heat processed cowpea (*Vigna unguiculata*) flour. *J. Food Sci.*, 1988; 53: 1775-1777.
- [20] Surendra BA, Parimalavalli R. Functional and Chemical Properties of Starch isolated from Tubers. *Int. J. Agric. Food Sci.*, 2012; 2(3): 77-80.
- [21] Radley JA. Commercial Separation of Amylose and Amylopectin from Starch. In J. A. Radley (Eds) *Starch Production Technology*, London: Academic Press. 1976; 189--479
- [22] Austin HY. Fractionation of Starch. *Starch: Chemistry and Technology* In R.L. Whistler (Eds.) *Starch: Chemistry and Technology*. Academic Press, Inc., 1984; 249-252, 269-283.
- [23] Hamilton Technology Limited. Laboratory Manual, Port Harcourt. 2001.
- [24] Baroid. Fundamental Characteristics of Drilling Fluids. Manual of Drilling fluids Technology, NL Baroid/NL industries, Inc. 1979.
- [25] Guanglei L, Benguo L, Guocong Z, Jie Z, Junliang S, Hanjun M. Characterization of Digestion Resistance Sweet Potato Starch Phosphodiester. *Trop. J. Pharm. Res.*, 2014; 13 (9): 1393-1400.
- [26] David JT, William AA. Starch Modifications; In *Starches*. Grain science Lib. of American Association of Cereal Chemists. AACC International Press, Minnesota. 1998; Pp. 31-48.
- [27] Mirmoghtadale L, Kadivar M, Shahedi M. Effects of Cross-linking and Acetylation on Oat Starch Properties. *Food Chem.* 2009; 116: 709-713.

- [28] Chung HJ, Woo KS, Lim ST. Glass Transition and Entropy Relaxation of Cross-linked Corn Starches. *Carbohydr. Polym.*, 2004; 55: 5-15.
- [29] Wurzburg, O. B. (1986). *Introduction in Modified Starches: Properties and Uses*. Boca Raton: CRC Press, 1986; Chapter 2-4.
- [30] Sudhakara JR, Parimalavalli R, Jagannadham K. Impact of Cross-Linking on Physico-Chemical and Functional Properties of Cassava Starch. *Int. J. Adv. Res.*, 2014; 2(5): 284-289.
- [31] American Petroleum Institute(API). *Recommended Practice for Field Testing Water Based Drill. Fluids*, 1993; 13A.

---

*To whom correspondence should be addressed: Dr. Ozioma Achugasim, Department of Pure and Industrial Chemistry, University of Port Harcourt, Nigeria, E-mail: [ozoma.achugasim@uniport.edu.ng](mailto:ozoma.achugasim@uniport.edu.ng)*