Original Research Article

Comparative Evaluation of the Physico-chemical Characterization of Native and Modified Starches from Jackfruit, Corn and Cassava as Potential Additives in Drilling Fluid.

ABSTRACT

Physicochemical properties of modified starches obtained from jackfruit were analyzed and compared with native jackfruit (JF), corn (MN) and cassava (CN) starches to determine their usability as additives in drilling fluid formulation. Starch from jackfruit pulp was chemically modified with two carboxymethylation methods (JC1 & JC2) and acetylation method (JA). The physicochemical properties were assessed using Scanning Electron Microscopy, Differential Scanning Calorimetry, Fourier transform infrared spectroscopy and Thermogravimetric analysis. The results revealed that at 90 °C, JC2 was found to have the highest swelling power and water holding capacity when compared with other modified and native starches. The result of the thermal properties of the starches showed that JC2 produced better thermal properties with the peak gelatinization temperaturein the decreasing trend JC2>JC1>JF>MN>JA>CN. The SEM result showed that modification reduced the particle size of the starches thereby increasing the surface area of the starches for better reactivity than the native jackfruit, corn and cassava starches. The thermal stability of the starches showed that modification by carboxymethylation (JC1 and JC2) improved the stability of the starches while the reverse was the case for JA. In comparison with corn and cassava, the modified starches JC1 and JC2, performed excellently in all the properties analyzed. The possession of the highest swelling power, highest water holding capacity, highest thermal stability and excellent gelatinization temperature of 90 ℃ (Tp) places JC2 above other modification methods thereby making it a potential replacement for corn and cassava as an additive in drilling fluid formulation.

Keywords: Corn, Cassava, Drilling fluid, Modified starch,Physicochemical properties, Jackfruit.

1. INTRODUCTION

The discovery of petroleum as a non-renewable source of energy has led to the development of diverse skills, techniques, instruments, and materials for effective drilling of this natural resource [1,2]. Drilling can simply be described as a process of making an opening for already discovered hydrocarbon to be produced at the surface through permeation of the earth’s crust to several thousand feet where the hydrocarbons are deposited in a reservoir using rotary drilling process[3].Numerous technological breakthroughs have been achieved as to how drilling operations can be conducted in the most economic and environmentally friendly way possible[3,4]. One of these improved techniques is the use of drilling fluids. Drilling fluids are heterogeneous mixture of chemical, water or oil and clay materials, which circulate through a well in order to remove cuttings from a wellbore[5]. They are vital in successful well drilling as they have common properties that facilitate safe and satisfactory completion of the well such as bottom-hole cleaning while serving as a cooling agent, controlling high pressure zones, minimize formation damages, reduce circulation loss and removal of cuttings to the surface[6,7].The importance of drilling fluid, also known as ‘‘drilling mud’’ cannot be over emphasized as the knowledge of drilling fluid is a requisite in the rotary drilling operation in the petroleum industry[8]. The composition of a drilling fluid differs with the type of drilling fluid[9]. There are many drilling fluids such as water based, synthetic based and oil-based fluid[10,11]. The most commonly used is the water-based fluids which usually comprises of bentonite clay (gel) with additives such as barium sulphate (barite), calcium carbonate (chalk) or hematite. Various thickeners are used to influence the viscosity of the fluid, e.g. xanthan gum, guar gum, glycol, carboxymethylcellulose, polyanionic cellulose (PAC), nanoparticles or starch[12-14].The particular function to be carried out by a drilling fluid in a particular site determines the fluid to be used and hence its composition. Nevertheless, a good drilling fluid should have a stable rheological property which covers wide pressure and temperature range and should be able to prevent loss of water by forming cakes[10,11].

Starch is a natural biopolymer that is biodegradable, renewable, cheap and can be obtained from a large variety of plants[15,16]. Starch is deposited in most parts (stem, roots, fruit) of green plants as photosynthetic products [16].Starch is employed in a diversity of ways to achieve present-day technological desires. In the food industry, it is a useful raw material for gelling, thickening, stabilizing, binding, texture improvement, and as a bulking agent[15].Additionally, it is also utilized in the production of a wide range of goods that are of high industrial value such as paper, textiles, construction materials and alcohol for fuel[15,17]. Starch has also been used as drilling fluid additives in drilling processes. Starch can serve as an additive capable of enhancing and improving the mud viscosity and control the fluid loss[2,17]. It contains two important components: amylose and amylopectin[17]. The starch action is triggered by its capacity to swell and increasing of its volume caused by free water absorption[18]. Many polymers have been used as drilling fluid additives and they tend to help with diverse drilling problems although there is no particular drilling fluid that can provide solution to all drilling problems. Guar gum, xanthan and starch are examples of natural polymers that have been used as drilling fluids additives. Carboxymethylcellulose (CMC) and lignosulfonate are modified natural polymers while some synthetic ones such as polyacrylamides and polyalphaoleins are all used as drilling fluid additives to control the fluid loss and viscosity in oil and gas industry[19-22].

Starch derived from corn are the first and most widely used starch source as drilling fluid additive with bentonite. Corn-starch is used to control filtration characteristics and is effective as colloids, eventually increasing viscosity. Ashaye et al.[23] believed that corn-starch has the potential to serve as an efficient drilling fluid after examining its physiochemical properties. Another study showed that at certain concentration, cassava-starch (although not specified) could be used as additives in drilling[18, 23]. Many other raw high starchy content food crops have been used as drilling fluid including cassava, potato, maize, guar gum and grain crops like millet etc[24].The high cost of the starches obtained from cash crops can also result in increased cost of producing drilling fluids and will have a resultant effect on the cost of drilling in general. It has been reported that drilling fluids accounts for about 20% of the total drilling cost during oil and gas exploration[1].

Starch is rarely consumed in its natural or native form and it is cannot be used for any industrial process like drilling fluid formulation in the aforementioned form. Most native starches are limited in their direct application because they are unstable with respect to changes in temperature, pH and shear stress[25]. Native starches show a strong propensity for disintegration and retrogradation. Moreover, some starch granules are inactive, non-miscible in water at ambient temperature, vastly resistant to enzymatic hydrolysis and are subsequentlylacking in some functional properties. Hence, native starches are frequently modified to advancedefinite properties such as solubility, texture, adhesion and tolerance to heat temperatures in industrial processes[26].Quite a lot of techniques have been employed to alter or modify starches with a wide range of physical characteristicsfor diverse applications. All of these techniques alter the starch polymer structure, making it highly flexible and changing its physicochemical properties and structural attributes to increase its value for food and non-food industries[27]. Modifications of starch can be achieved through physical, chemical and enzymatic methods[28].

The continued use of cash (edible) crops for production of starch used in drilling fluid formulation poses great challenges to food security, thus leading to the search for alternative sources of starch in most of the wild edible/non-edible species of fruits and other naturally occurring plants. A perfect example of one of such fruit is *Artocarpus heterophyllus lam* (commonly known as Jackfruit)[29].Jackfruitis considered to be the largest tree-borne fruit in the world and have been found useful in many industrial applications[30,31]. Jackfruit contains many classes of compounds such as carotenoids, flavonoids, volatile acids, sterols, and tannins contributing to its many health benefits and their concentration vary with the variety/type and parts of the fruit.[30] Jackfruit is a known source of food, used in nutrition especially for high carbohydrate, starchy purposes and fiber (which help in constipation). They are usually found in wild in Nigeria and are not cultivated intentionally for commercial purposes even though it is edible.

This study aims to extract starch from matured but unripe jackfruit. Thereafter, the starch obtained was modified and their physicochemical characteristics evaluated with starch from corn (*zea mays*) and cassava (*Manihot esculenta*) which are currently utilized as drilling fluid additives.

2. MATERIALS AND METHODS

2.1. Materials

Artocarpus heterophyllus Lam (Jackfruit) was harvested from an *Artocarpus heterophyllus Lam* tree in Port Harcourt, Rivers State, Nigeria. Corn (*Zea mays*)and cassava(*manihot esculenta*) crops used were obtained from Bwari Area council, Abuja, Nigeria.

All chemicals and reagents used were of analytical grade and were obtained from Chemistry Laboratory, Department of Pure & Applied Chemistry, Veritas University Abuja, Nigeria.

2.2. Starch Extraction

The relatively unripe fruit pulp of Artocarpus heterophyllies (Jackfruit) was weighed and washed, the bulb peeled and the seeds carefully removed and the bulb was cut into irregular smaller sizes; the starch was extracted using the procedures of Omojola et al.[32] The extraction of starch from cassava was achieved using the wet method as described by Noorfarahzilahet al.[33].

2.3. Starch Modification

The specific type of modification used in this study was the chemical method.

2.4. Starch acetylation

Starch acetylation was attained through the methods developed by Bolade and Oni.[34] Starch (100 g) was dispersed in 500 ml and the mixture was continuously stirred for one (1) hour at 30 °C. Thereafter, 3 % Sodium Hydroxide was added dropwise to the suspension to achieve a pH of 8.0; instantaneously, 12g of acetic anhydride was added to the mixture at the same time sustaining the pH value within the range of 8.0–8.4. The mixture was stirred continuously for 10 minutes and the pH adjustment to 4.5 was done by the addition of 0.5 M Hydrochloric acid. The starch was allowed to settle, the precipitate formed was rinsed trice with water after which 95 % ethanol was used once to neutralize the acid.

2.5. Starch carboxymethylation (SCMProcedure 1)

The SCM procedure 1 was obtained using the wet methods of Nwokocha and Ogunmola.[35] with slight modification. Starch (100 g) was dispersed in an isopropanol/water mixture in a ratio of 80:20, while adjusting the pH with a 2 M solution of NaOH. Subsequently, 40 % (wt/vol) monochloroacetic acid was added and consecutively, the solution was incubated at 30 °C while stirring continuously. Washing and filtering was carried out numerously until little or no chloride was detected in the filtrate using silver nitrate test. The cake obtained was washed thoroughly with absolute ethanol and dried to constant weight at 313 K in an oven for 48 hours.

2.6. Starch carboxymethylation (SCM Procedure 2)

The SCM procedure 2 was done in an electric blender as described by Li et al.[36] Solid NaOH and the starch were blended together in a blender to form a powdery mixture of uniform size. Little quantity of absolute ethanol (2 wt%) was added and further stirred for 1 hour. Thereafter, powdered sodium monochloroacetate (SMCA) was added and the reaction proceeded at 28 ℃ for an hour. As soon as the reaction was concluded, the modified product was carefully rinsed with 85 % ethanol solution and sieved to eliminate any salt formed in the course of the reaction. Washing and filtering was carried out numerously until little or no chloride was detected in the filtrate using silver nitrate test. The cake obtained was washed thoroughly with absolute ethanol and dried to constant weight at 313 K in an oven for 48 hours.

2.7. Determination of the Swelling Powers of the starch molecules

The swelling power of the starch samples were evaluated according to Sreeletha et al [37] with slight modifications. 0.5 g of starch was spread in 25 ml distilled water in a test tube and heated at temperatures range of 50-90 °C for 30 minutes in a water bath. The mixture was stirred continuously all through the analysis after which it was allowed to cool. At room temperature, the filtrate was filtered off and the residue dried at (105 °C) for at least 5 hours to obtain a constant weight of the starch. The calculation of the swelling power was obtained from equation 1.

$$\text{Swelling power (g/g)} = \frac{\text{weight of wet residue}}{\text{weight of dry residue}} \qquad (1)$$

2.8. Determination of Water binding capacity (WBC)

The WBC of the starch samples was determined according to Rodriguez-Ambriz et al.[38] method with little modifications. 0.5 g sample of each starch was dispersed in 25 ml distilled water and in a centrifuge tube and heated between 50-90 °C temperatures for 30 minutes in a water bath with constant stirring. The samples were cooled to room temperature and the tube was further centrifuged at 3000 rpm for 20 minutes. The supernatant obtained was thereafter discarded and the starch was weighed and dried and the water holding capacity was determined using equation 2.

$$\text{WHC (g/g)} = \frac{\text{weight of wet residue - weight of dry residue}}{\text{weight of dry residue}} \qquad (2)$$

2.9. Starch Characterization

The thermal characteristics of the starch samples were carried out by Differential Scanning Calorimetry (DSC) analysis using Shimadzu DSC-60 (Shimadzu, Japan). The thermal stability was determined using thermogravimetric analysis (TGA) WW. MCE TA instrument TGA Q50. The surface structure was carried out with Scanning Electron Microscopy (SEM) (S-3400N; Hitachi, Tokyo, Japan). The Fourier transform infrared spectroscopy (FTIR) analysis was carried out using Perkin Elmer 3000 MX spectrometer.

3.0. RESULTS AND DISCUSSIONS

3.1. Swelling power (SP) of Native and Modified starches

The swelling power profile of native and modified jackfruit, native cassava and corn starches are presented on Figure 1. Studies carried out by Rondán-Sanabria et al. [39]have shown that starch swelling capacities are directly related with temperature. The polymer structure disruption encountered upon heating a starch-water mixture is as a result of hydrogen bonds cleavage. Lee et al.[40]observed that exposed hydroxyl groups of amylose and amylopectin are joined by hydrogen bonding with the water molecules which results in increasing granule swelling.

The results of the swelling capacity of native and modified starches are shown on figure 1. The result showed a general increasing trend in swelling power capacity of all the starches, but modified starches performed better in terms of swelling power with JC2 having the highest swelling power at 90°C and performed better than MN and CN. The increasing trend of the starches at 90°C are as follows JC2>CN>JC1>JF>JA>MN. The steady rise observed in the modified starchescan be related to the addition of acetyl or carboxy-methyl groups that led to an alteration of the granular structure of glucose molecules that makes up the starch and this allowed water to permeate easily. This result agrees with the work of Carmona-Garcia et al.[41] recently reported that crosslinking of starches had pronounced swelling power at higher temperature than their native starch counterparts. Chatakanonda et al.[42] also revealed that cross-linkingtransformedbanana granule structure and eased the rate at which water permeates.

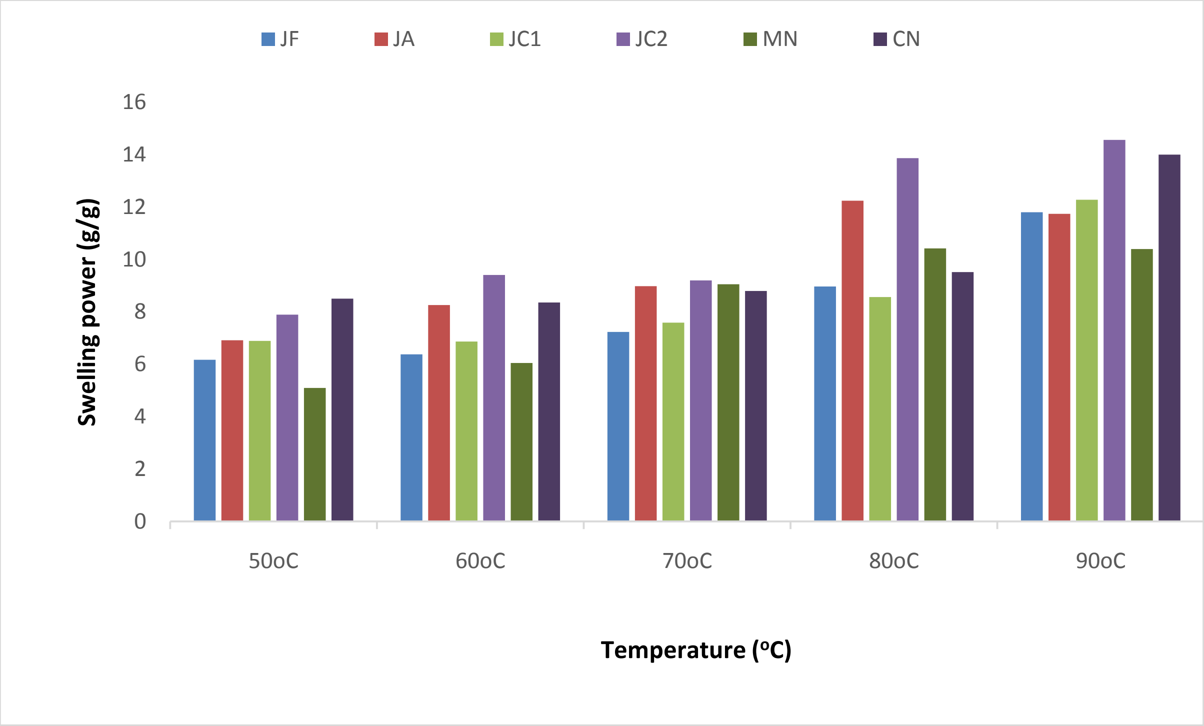

Fig. 1: Swelling power profile of Native and Modified starches

The introduction of starch in drilling fluid formulation has helped in reducing fluid loss and improving mud cake properties of the drilling fluids[24]. However, normal starch has some drawbacks such as low shear stress resistance, thermal decomposition, high retrogradation, and syneresis[40].Hereafter, starch modification, performed via acetylation and carboxymethylation, procedures has been used to conquer these restrictions. In this work, modified starches from JC1 and JC2 have shown to be better alternative starch sources in relation to swelling power at high temperature to MN and CN native starches respectively. Thus, they possess the potential to enhance the viscosity property of water-based fluid.

3.2. Water Holding Capacity

The Water holding capacity of native and modified jackfruit, native cassava and corn starches are presented on Figure 2.

The result showed a general increasing trend in water holding capacity of all the starches, but modified starches performed better in terms of water holding capacity with JC2 having the highest water holding capacity at 90 ^{o}C and performed better than the standard MN and CN. The increasing trend at 90^{o}C is JC2>CN>JF>MN>JA>JC1. The improvement in water holding capacity by one of the modified starch (JC2) can be linked to the modification procedure carried out on it, resulting in a stronger degree of expansion. The native starches were found to be immiscible in water and their water holding capacity was weak. The water holding capacity of JC2 was higher than those of the native starches (MN, CN and JF) and even other modified starches (JA and JC1) which can be attributed to the amylose content, side-chain length[40]. After modification, the amylose content present increased, resulting in an increase in the double helix content. Better water holding capacity was achieved due to linear short glucan chains[43]. Therefore, JC2 will be a useful additive in drilling fluid formulation.

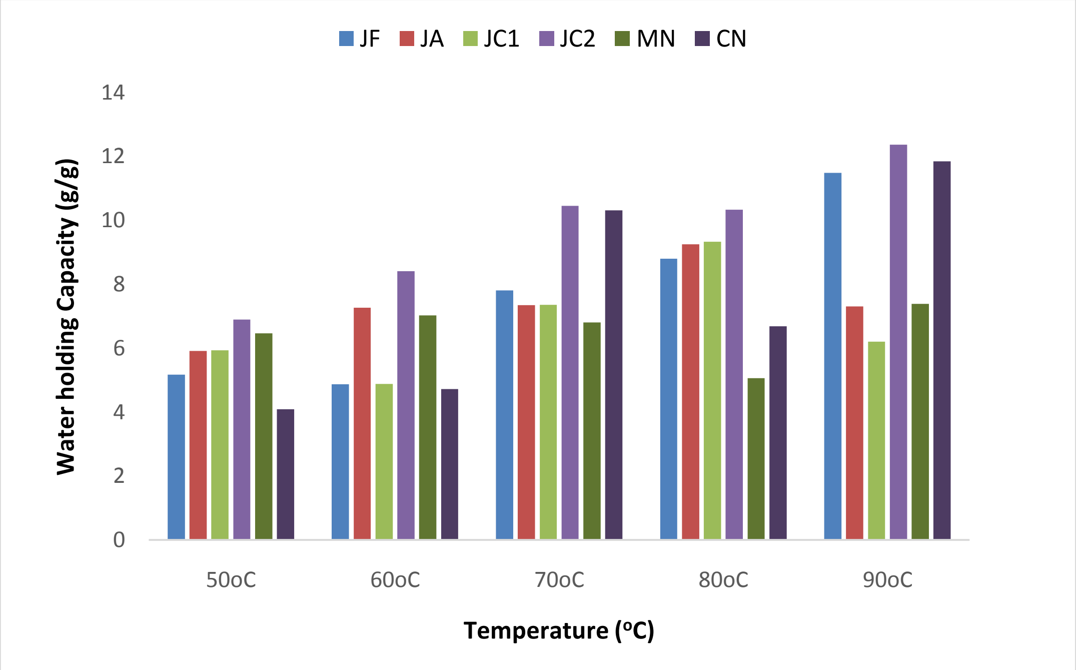

Fig. 2: Water Holding Capacity Profile of Native and Modified Starches

3.3. Morphology determination of modified and native starches at different magnification

The Figures (3-4) shows the morphological images for native and modified starch for Jackfruit, Cassava and Corn starch at 8000x and 9000x magnifications.

At 8000x (Fig. 3), it can be observed that JF has larger starch particle size that were not so clustered together compared to its modified counterparts that displayed smaller starch particle

size which were closely clustered and will result to an increased surface area for better drilling fluid formulation. The starch particle size for CN and MN showed highly unpattern structures with
relatively large spaces between the particles which is indicative of a low surface area to allow for water penetration.

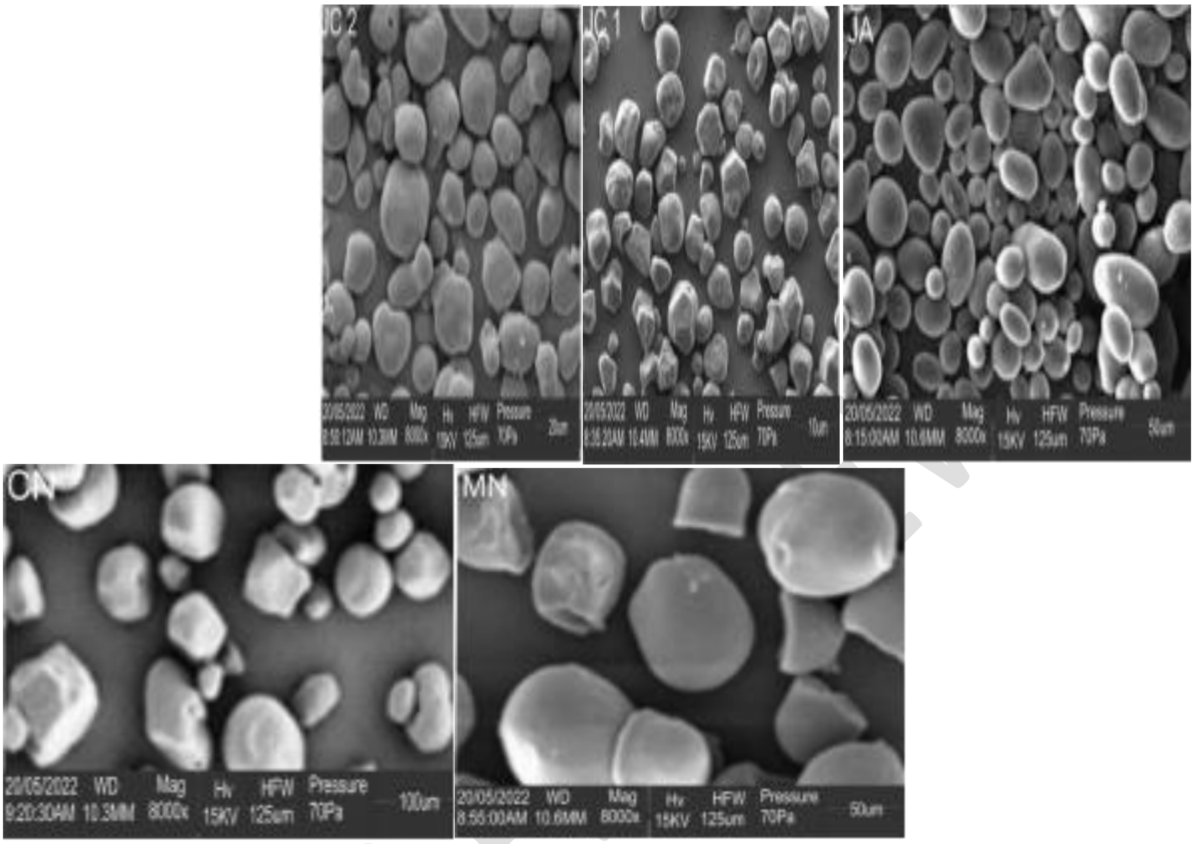

Fig. 3:SEM Image of the starch samples at 8000x magnifications

At 9000x (Fig. 4), it can be observed that JF has larger starch particle size that are not evenly patterned and not clustered together compared to its modified counterparts that displayed smaller starch particle size which were closely clustered. Among the modified starches, JC1 had the smallest starch particle size with fine texture. JA displayed large bean-like structures with relatively low surface area. The starch particle size for CN and MN showed highly unpattern structures with MN displaying more closely clustered particles.

In accordance to the results presented above, it is evident that modification reduces the particle size and increases the surface area (number of particles). There are reduced interstitial spaces thereby forming more clusters in JC1, JC2 and JA than their native counterparts. The morphological structure of native Jackfruit starch is large, spaced, rough and irregular in shape while that of the modified Jackfruit starches are smaller, clustered, smooth and relatively spherical in shape.

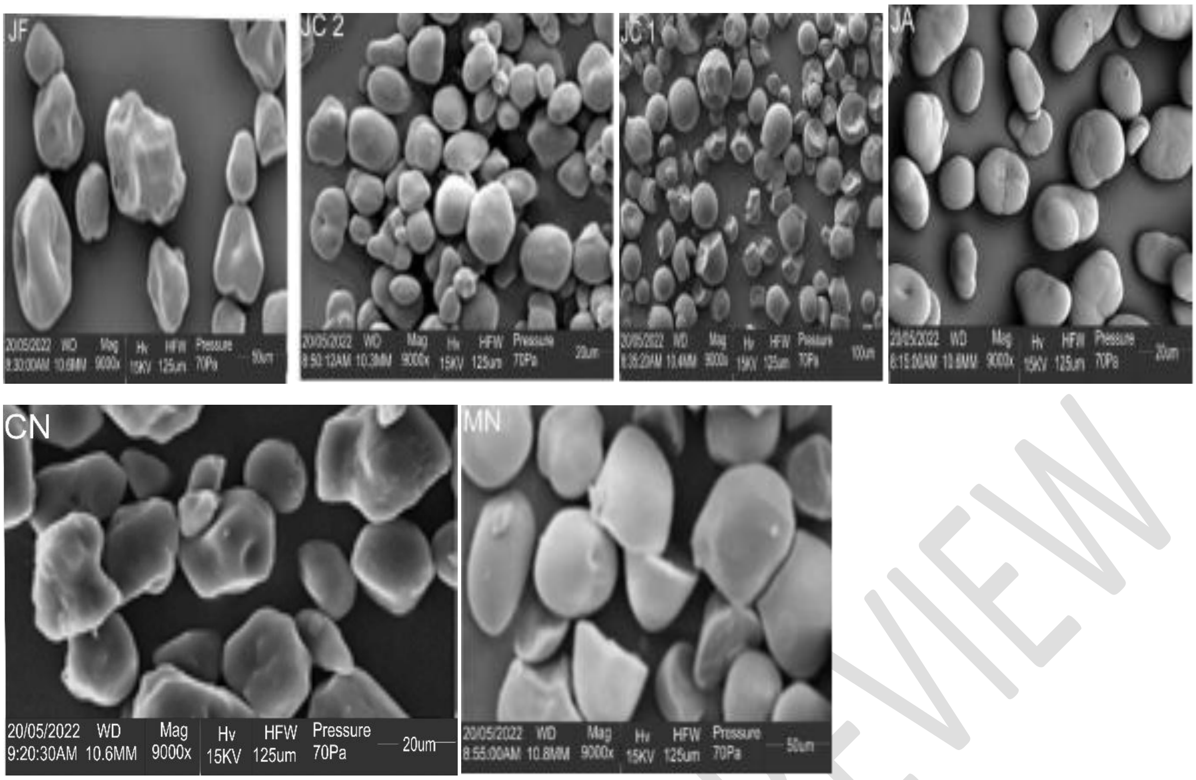

Fig. 4:SEM Image of the starch samples at 9000x magnifications

Afolayan et al. [44] reported that small starch is more reactive than their larger counterparts and are found useful in many industrial applications. Starch granule shape plays a vitalrole in characteristics of starches which determines their area of applications. Starch granule shape plays a crucial part in starch swelling, gelatinization and thickening ratio. Tsakama*et al.*[45] reported on the presence of strong atomic holding in small granules that plays a vital role in its swelling.

Therefore, the morphological image of the native starches was observed to be large but not clustered when compared with the modified ones. The morphological changes that occurred in the modified starch helped to improve the physical and chemical properties such as high gelatinization temperature as well as swelling and water absorption characteristics.

These improved properties make the modified starches more useful in industrial applications especially in drilling fluid formulation where starches with stronger gels, high stability at high temperature and pressure are utilized in oil wells during drilling.

3.4. Fourier Transform Infrared Spectroscopy Analysis (FTIR)

The FTIR results of the native and modified starches are shown in figures 5. The results from Figures 5 (a, c, d and e), demonstrated strong peaks at 3434-3432 cm^{-1} which were indicative of the presence of O-H stretching vibrations. The peaks came as a result of higher density of strong hydroxyl bonding interaction (O-H) present in the glucose unit of the samples, the result exclusively comparable to that of Rivas, [46] on native starch results. The stretching vibration at 1641-1631 cm^{-1} for all the native starches and modified starches could be attributed to strong vibrational bonds between water (H_2O) and the granules of the starch. The absorption band of all starches at 1195.35-1047.95 cm^{-1} indicates the presence of C-O group. The broad peak at 1070.00 cm^{-1} for cassava indicates that the functional group (C-O) present is in abundance due to the large presence of amylose. There is generally a weak peak around 2900-3000 cm^{-1} which arises as a result of the asymmetric C-H (stretching) vibration of the monomeric glucose ring in the starch structure. The low intensity peaks obtained in this work is in line with those of starch obtained in literature[47].

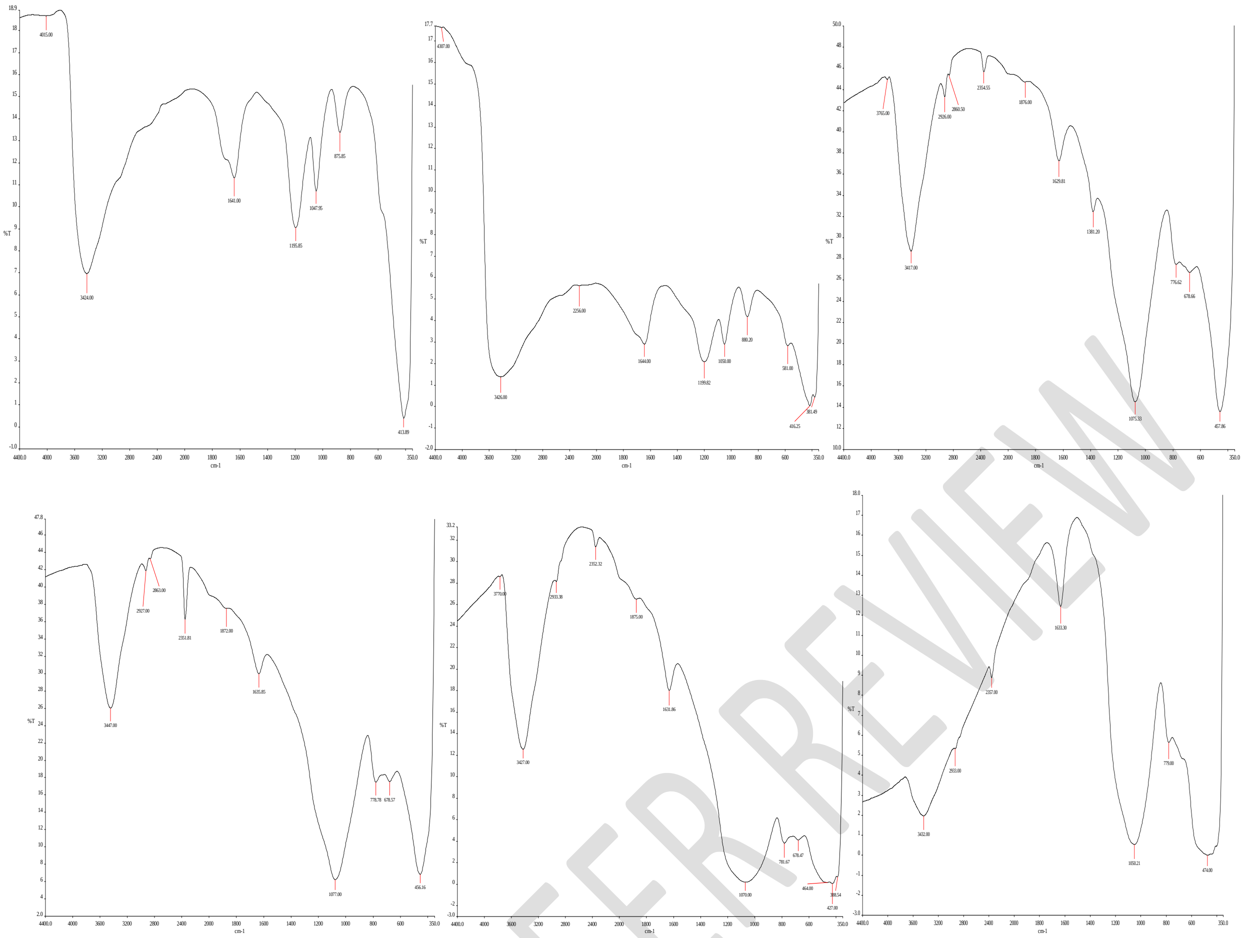

Fig. 5:The FTIR Spectrum of (a) JF (b) JA (c) JCI (d) JC2 (e) MN (f) CN

3.4.1. Effect of Modification on the starch structure

From the results obtained from the FTIR spectra of both the native and modified starches of Jackfruit (JF, JA, JC1 and JC2), it was observed that modification had a pronounced effect on the both the peak strength and size of the modified starches when compared to that of native JF. Modification with carboxymethylation 1 and 2 was found to have a very sharp but lower intensity peaks when compared to the slightly broad and higher intensity peak around 3447-3417 cm^{-1} of the characteristic O-H stretching vibration. JA was also observed to have lower intensity peak but maintain the broad peak. The lower intensity observed in the O-H peak can be attributed to the substitution of the O-H groups in native starches by the alkoxy or acyl groups in the modified starches. conversely, there was an increase in the strength and intensity of the absorption peaks of the modified starch around 1199-1050 cm^{-1} corresponding to the stretching vibration of the C-O group with JCI and JC2 having strong peaks than native JF. The substitution of the O-H by carboxymethylation introduces more C-O functional group during glycosidic bond formation thus increasing the strength of the peaks. Where the reverse is the case for JA modified starch where the introduction of the acyl group (RC=O) decreased the strength of the C-O bond at the same range when compared to JF.

Modification by carboxymethylation has been reported to create interstitial holes due to the addition of large alkyl groups which replace OH functional groups of the starch.[2] As a result of this factor, it was observed that modification caused a shift in the wave numbers of the characteristic functional groups of O-H and C-O stretching vibrations in the modified starches, with JC1, JC2 and JA having a wave number (λmax) of 3417 cm^{-1}, 3447 cm^{-1} and 3426 cm^{-1}

respectively from that of native JF for O-H stretching vibrations. The same trend was observed in the C-O stretching vibration where there was a shift in wave number from 1195 cm^{-1} of JF to 1199 cm^{-1}, 1075 cm^{-1} and 1077 cm^{-1} for JA, JC1 and JC2 respectively.

3.5. Thermogravimetric Analysis (TGA) of the native and modified starches

The native and modified starches of jackfruit were evaluated to determine their thermal stability and decomposition characteristics in comparison to those of corn and cassava and the results are presented on Table 1. Thermogravimetric analysis is utilized to investigate the stability of bio-based materials especially starch-based materials utilized for industrial purposes. The TGA graph of both modified and native jackfruit starches shows related trend, signifyingmass loss through thermal breakdown of the starches occurring at dissimilar phase representing precise event during heating.

Table 1: TGA Result of native and modified Jackfruit, Cassava and Corn

SAMPLES	**MASS LOSS % (TEMPERATURE ^{O}C)**				
	1ST	2ND	3RD	4TH	% RESIDUE
JF	10 (99)	4 (179)	50 (297)	85 (345)	12.60
JA	10 (99)	6 (194)	50 (290)	85 (340)	13.80
JC1	10 (99)	5 (186)	44 (308)	88 (350)	15.20
JC2	10 (99)	3 (194)	45 (320)	85 (358)	13.80
MN	10 (99)	8 (194)	50 (290)	85 (350)	13.80
CN	10 (99)	8 (194)	45 (294)	83 (344)	13.92

KEY: (JF)-Native jackfruit starch, (JA)-acetylated jackfruit starch, (JC1)-jackfruit starch obtained by carboxymethylation method I, (JC2)- jackfruit starch obtained carboxymethylation method II, (MN)-corn starch, (CN)-cassava starch

The first degradation of all the starches occurred at 99 °C with a 10 % weight loss which resulted in mass loss owing to water fragments removal by evaporation. In this phase, the greater the moisture loss,consistently leads to more mass loss. The second degradation of the starches, which is indicative of the initial degradation of the carbon chain of the polymer structure shows that the native JF starch degrade at 179 °C with a 4 % weight loss, and that of corn and cassava starches degrade both at 194 °C with 8 % weight loss. This implies that Jackfruit starch degradation occurs at a lower temperature with less degradation than that that of corn and cassava. The third degradation shows that JF had a 50 % weight loss at 297 °C which occurred at higher temperature than that of corn with 50 % weight loss, and cassava with 45% weight loss at 290 °C and 294 °C respectively. In this stage, weight reduction is correlated to degradation and depolymerization of carbon chain length in the starch structur. The last degradation of the native starches occurred at 350 °C with 85 % weight loss for corn, 344 °C with 83 % weight loss for cassava and 345 °C with 85 % weight loss for JF. This indicated that native corn had the best stability while cassava produced the least stability. The residue after temperature of maximum decomposition of jackfruit starch is 12.60 % which was less than that of corn starch (13.80 %) and cassava starch (13.92 %). The results showed that the native Jackfruit starch was found to be less thermally stable than native corn starches but more stable than cassava.

3.5.1. Effect of different modification on native jackfruit thermal stability

Modification of native JF was found to have an improved impact on its thermal stability. The first degradation which is as a result of mass loss due to moisture content did not have an effect on both the native and modified JF with all occurring at 99 ^{o}C with 10 % weight loss. It was observed that modification improves the stability of the starches when compared to the native jackfruit starch at second degradation which is attributed to initial decomposition of the starch chain structure with the following decreasing trend; JC2 (194 ^{o}C with 3% wt loss) > JA (194 ^{o}C, 8% wt loss) > JC1 (186 ^{o}C, 5% wt loss) > native starch (179 ^{o}C, 4% wt loss).

The third degradation which occurs as a result of depolymerization of the carbon chain (i.e formation of monomers from polymers), it was observed that modification by carboxymethylation (JC1 & JC2) improves the stability whereas modification by acetylation (JA) reduces the stability when compared to that of native JF starch. Thus, the result is in the decreasing trend. JC2 (320 ^{o}C, 45% wt loss) > JC1 (308 ^{o}C, 46% wt loss) > native starch (297 ^{o}C, 50% wt loss) > JA (290 ^{o}C, 50% wt loss). The same trend was observed at the last degradation of the starches. JC2 (358 ^{o}C, 85% wt loss and 13.80% residue) > JC1 (350 ^{o}C, 88% wt loss and 12.60% residue) > JA (340 ^{o}C, 85% wt loss and 13.80% residue). This therefore implies that modification by carboxymethyl 2 method improved the stability of the native JF starch most, with acetylation decreasing the stability of the jackfruit starch. In addition, JC2 produced the best thermal stability than corn and cassava which are currently used starch additives for drilling fluid formulation. Thus, the use of carboxymethyl 2 (JC2) for drilling fluid formulation will improve the stability of drilling fluids at high temperature, high pressure (HTHP) wells.

3.6. Differential Scanning Calorimetry (DSC) Analysis of Native and Modified Starches

DSC is a technique that quantify the variance in quantity of heat essential to increase the temperature of a sample and reference material, such that the temperature difference between them is calculated as a function of temperature. The thermal properties of the modified and native starches were analyzed using the DSC procedure and the thermograms are presented in Table 2.

Table 2: Thermal Analysis of gelatinization temperature of Native and modified starches

S/N	SAMPLE	T_o (°C)	T_p (°C)	T_c (°C)	ΔH (J/g)
1	JF	59.50	65.25	70.55	12.5
2	JA	55.95	61.70	67.30	10.2
3	JC1	65.50	70.00	85.00	16.7
4	JC2	65.00	72.50	88.00	17.4
5	MN	52.00	58.50	66.50	11.8
6	CN	45.90	51.00	55.80	7.9

KEY: $\mathbf{T_o}$ **-** onset temperature, $\mathbf{T_p}$- peak temperature, $\mathbf{T_c}$- conclusion temperature ΔH- Enthalpy change

This method is used to determine the thermal properties of the native and modified starches. Gelatinization endotherm obtained by DSC is an overall measure of the progressive loss of long, medium, and short-range order in starch granules as they are heated in excess water[48].

The DSC of native starch showed their peak gelatinization temperatures (T_p) of 65.25 ^{o}C (JF), 58.50 ^{o}C and 78.00 ^{o}C (MN) and 51.00 ^{o}C (CN). Corn (MN) exhibited two endothermic peaks which is indicative of the presence of two distinct polymers in the corn starch. This may be ascribed to the presence of amylose and amylopectin polymers of the corn starch. Amylopectin is known to be crystalline while amylose is known to be amorphous and form gel at higher temperatures[25,49].Thisexplains the second peak at 78 °C which reveals that corn (MN) contains more amylose that other native starches and thus, form gel at higher temperature than others. This thus predicts that JF (Jackfruit) and CN (Cassava) may contain higher amylopectin than amylose and requires less heat to form gel. Amylose has a very high tendency to retrograde and also produce tough gels and strong films while amylopectin when dispersed in water, is more stable and produces soft gels and weak films[25]. The values observed from Jackfruit starch are similar to those obtained by Tran et al.[50] and Zhang et al.[51] for Jackfruit seed starches. And the corn starch was similar to that obtained by Adewumi et al.[2]and Sandhu and Singh[52].

3.6.1. Effect of modification on Native Jackfruit

The results obtained from DSC analysis shows that modification with (JC1 and JC2) have positive impact whereas, modification with JA had a negative impact on the thermal properties when compared to that of native JF. The peak gelatinisation temperature (Tp) are as follows; 61.70 ^{o}C for JA, 65.25 ^{o}C for JF, 70.00 ^{o}C for JC1 and 72.50 ^{o}C for JC2. From this data the Tp of JC1 and JC2 increased greatly and this may be as a result of the introduction of the carboxymethylated groups into the starch structure. Similar results were reported by Li et al.[53] for the Tp value of treated starches followed by acetylation treatment. Hence, carboxymethylation 1 and 2 was found to have a positive correlation with temperature of native starch while acetylation was found to have a negative correlation with temperature as observed from the DSC thermogram of jackfruit.

Nevertheless, the modified starches JC1 and JC2 were found to have their Tc (which is the conclusion temperature) at 85 ^{o}C and 88 ^{o}C respectively, which imply that the modified starches can be gelatinous up to this high temperature before degrading which is an excellent property when compared to that of corn and cassava. Thus their use as drilling fluid additives for drilling operations will help reduce the impending food insecurity that is associated with the continued use of corn and cassava which are two major cash crops for drilling fluid formulation and will also reduce the cost of drilling.

CONCLUSION

The intensive use of corn and cassava starch sources for industrial applications have great effect on food availability as well as the overall cost of production. However, the use of alternative starch sources especially non-food or less staple starches such as jackfruit that have the potential in industrial or commercial purposes is essential in mitigating the aforementioned effects. The current research demonstrates that starch obtained from modified jackfruit products possess good physicochemical properties such as swelling capacity, gelatinization temperature, thermal stability and morphological properties which were achieved after modification compared to their native starch counterparts with relatively lower physicochemical properties. This makes it highly useful as an alternative source of starch for the formulation of drilling fluids. Scanning electron micrographs of native and modified starch samples were indicative of the fact that chemical modification had significant effect on the morphological properties of starch granules by reducing their particle sizes and thus increases their reactivity. Modification by carboxymethylation of jackfruit starch was found to have an overall positive correlation to swelling power, water holding capacity, thermal stability and gelatinization temperature of the starches when compared to those of the native counterpart of corn, cassava and even jackfruit itself. Modification by acetylation however was found to have a negative correlation especially in thermal stability and gelatinization temperature when compared to their native counterparts. Carboxymethylated jackfruit 2 (JC2) from the analysis carried out exhibited the highest swelling power, highest water holding capacity, highest thermal stability and excellent peak gelatinization temperature of 72.50 ^{o}C (Tp) placing it above other modification methods and shows great potential of replacing corn and cassava (native starches) as an additive in drilling fluid formulation. This will in turn reduce the high cost associated with the use of edible cash crops as additives for drilling fluid formation thereby improving food availability so as to eliminate hunger which is one of the key sustainable development goals (SDG’s).

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