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Application of Micronized Carboxymethyl Starch as Additive in Water–Based Mud

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Abstract

Biodegradable natural products are increasingly investigated for different industrial applications mostly due to wider range of disposal options with minor health, safety and environmental impacts. In the petroleum industry, research into the products of natural polymeric materials to substitute synthetic chemical products used as additives in drilling fluids is aimed at reducing the overall cost and environmental impact of drilling operations. In this study, micronized carboxymethyl starch (CMS) was investigated and compared with carboxymethyl cellulose (CMC) as additive in water–based mud. Natural starch obtained from yam, potato tubers, and rice was modified by carboxymethylation, micronized to different particle sizes, and analyzed using Fourier Transform InfraRed (FTIR) Spectrometry. The rheological properties of the mud were determined at different micro–sizes (63μm and 75μm) and concentrations (0.5, 1.0, 1.5 grams) of the additives, and temperature ranging between 30ºC to 85ºC following the American Petroleum Institute recommended practice (API RP 13B–1). The major functional groups identified in the starch products are six–membered ring carbonyl group at 1735cm^{-1}, carboxyl group at 1605cm^{-1} and 1650cm^{-1}, and methyl group between 1450cm^{-1} to 1300cm^{-1}. The CMS at 63μm compared favourably with CMC and had approximate average yield point/plastic viscosity ratio of 1.5 above 30ºC. The results further showed that CMS is a suitable alternative viscosifier to CMC for water based mud and recommended for field trials.

Keywords: *Natural products; Carboxymethyl starch; Micronized; Water–based mud; Rheological properties.*

1. Introduction

Drilling muds are complex fluid mixtures containing different additives that are dissolved into a continuous fluid phase to improve its functionalities in well control, rheology, lubrication, and filtration. They are generally classified as Water–Based Mud (WBM), Oil–Based Mud (OBM), and Synthetic–Based Mud (SBM) based on the type of continuous fluid phase it contains [1-3]. Additives are usually required in certain proportions to meet drilling mud specifications, while ensuring strict compliance to health, safety and environment regulations. Although, most drilling operations initially require muds containing less additives for increased penetration rate, but certain subsurface and well conditions are subsequently encountered which can only be managed by muds containing special additives.

The formulation and application of drilling muds are recently faced with several challenges mainly from increasing cost of additives, the use of synthetic chemicals (as additives) which could not meet the toxicity and green level biodegradability required of oilfield chemicals, and environment regulations on the disposal of mud and drilled cuttings. In addition, the cost of importation of these additives has comparatively increased the overall cost of drilling in different oil producing countries. Meanwhile, recent studies applied local materials derived from natural products as substitutes to imported additives [4-6]. Most of the recommended local materials are natural polymeric products such as starch, cellulose, and clay. Udoh and Okoh [7] and Olatunde *et al.* [8] both revealed the potential of gum Arabic, soda ash and sweet potato starch as suitable additives for water–based muds. Ademiluyi *et al.* [9] investigated the effect of cassava starch on the properties of water–based muds, which showed improved performance in fluid loss control than rheology when compared to imported additives.

In this study, natural starch from different sources was chemically modified by carboxymethylation and the products were investigated as additive for the enhancement of the properties of water–based mud. Starch is a commercially available product and the most widely distributed natural polymer. It is a multifunctional organic compound that has found wide application in major industrial processes due to its high compatibility with many materials, easily tailored to form many different derivatives, virtually non–irritating, non–toxic and readily biodegradable. Its versatility is a tribute to the renewable origin and unique combination of physicochemical properties. Its derivatives have been extended to different areas of oilfield production chemical research especially for gas hydrate inhibition, enhanced oil recovery, and drilling fluids [10-12].

Starch is the first natural polymer to be used for formulating bentonite drilling fluids due to its swelling capacity and colloidal nature in solution [9, 13]. It contains a linear chain amylose which enhances the gelling behavior and a branched chain amylopectin which reduces the mobility and orientation in aqueous medium. However, the continous use of natural starch in major industrial processes have been limited due to insolubility in cold water, degradation at high temperature, low paste clarity and stability. Akintola and Isehunwa [4] investigation on the temperature and time dependent behaviour of water–based mud formulated with corn and cassava starch reported the rate of thermal degradation of starch. For improved application, starch is modified by physical, chemical, and enzymatic methods to enhance its water holding capacity, salt and heat resistance, and binding and thickening properties [14-16]. Such chemical modifications have produced carboxymethyl starch, oxidized starch, hydroxyethyl and hydroxypropyl starch, and starch phosphates. Carboxymethylation substitute the hydroxyl group (–OH) in natural starch with a carboxymethyl group ($CH_2COO–$) by alkalization and etherification to produce starch with low gelatinization temperature, high solubility, and high shelf life [17].

2. Materials and method

The natural starch samples used in this study were produced from yam, potato tubers, and rice grains following the method of Dankwa *et al.* [11]. The organic solvents (isopropanol and methanol) used were analytical grade, and all other chemicals including sodium hydroxide, monochloroacetic acid, distilled water, and bentonite were used as supplied.

2.1. Sample preparation

The natural starch samples were sequentially modified by alkalization using NaOH (equation 1) and carboxymethylation using monochloroacetic acid (equation 2).

$$(C_6H_{12}O_6)_n + NaOH \xrightarrow{Alkalization} [(C_6H_{11}O_5)_n - ONa] + H_2O \tag{1}$$

$$[(C_6H_{11}O_5)_n - ONa] + [Cl - CH_2COONa] \xrightarrow{Carboxymethylation} [(C_6H_{11}O_5)_n - O - CH_2COONa] + NaCl \tag{2}$$

10g of each starch sample was dispersed into a solution containing 100mL of 80% isopropanol and 4mL of 2M NaOH, and stirred at 25°C for 10 minutes using a magnetic stirrer equipped with a stir bar. Afterwards, 10mL of 40% monochloroacetic acid was added to the mixture, stirred and maintained at 70°C for 60 minutes. Equation 3 expresses the overall reaction which combined the two process steps.

$$(C_6H_{12}O_6)_n + [Cl - CH_2COONa] \xrightarrow{NaOH} [(C_6H_{11}O_5)_n - O - CH_2COONa] + NaCl + H_2O \tag{3}$$

The reaction products were filtered under vacuum, washed repeatedly with 80% isopropanol to remove excess reactants and air–dried. The dried products were separately micronized using dry micro–grinding technique, and separated into 63μm and 75μm particle sizes using testing sieve sizes of 240 and 200 B.S.S respectively. All the samples were stored properly at 25°C in air–tight containers and labelled accordingly as provided in Table 1.

Table 1. Micronized carboxymethyl starch samples

Sample	Name
MCMYS	Micronized carboxymethyl yam starch
MCMPS	Micronized carboxymethyl potato starch
MCMRS	Micronized carboxymethyl rice starch

2.2. Qualitative analysis

The quality of the products were determined by identifying the functional groups of organic compounds from the FTIR spectrum generated for each sample. The spectrum was generated between 4000cm^{-1} to 450cm^{-1} using infrared spectrometer. The vibration frequencies of functional groups of organic compounds identified on each spectrum was interpreted according to Coates [18].

2.3. Mud preparation

Water based muds were separately formulated with each CMS samples and CMC at varying concentration. Table 2 provides the type and quantity of additives used for mud formulation. The additives were added accordingly and stirred to form a homogenous mixture using a high–speed spindle type multi–mixer. The muds were kept for 16 hours for hydration before testing.

Table 2. Formulation of the muds

Additives	Unit	Concentration		
Water	mL	350	350	350
Bentonite	g	22.5	22.5	22.5
CMS/CMC	g	0.5	1	1.5

The API recommended practice for field testing water–based drilling fluids (API RP 13B–1, 2019) [19], was used as a guide for the mud test experiments. Baroid mud balance was used to measure the weight of the mud. The rheology of the mud samples was determined at 30°C, 50°C, 70°C, and 85°C using the direct indicating Ofite 8–speed viscometer. The viscometer dial reading at 600RPM and 300RPM were used to determine the plastic viscosity and yield point according to equation 4 and 5 respectively. The gel strength at varying temperature was recorded at 10 seconds and 10 minutes.

$$PV = \theta_{600} - \theta_{300} \qquad (4)$$

$$YP = \theta_{300} - PV \qquad (5)$$

3. Results and discussions

With reference to Coates [18], the functional groups of organic compounds in the starch samples were identified using the frequency of the absorbance bands on the FTIR spectra shown in Figure 1.

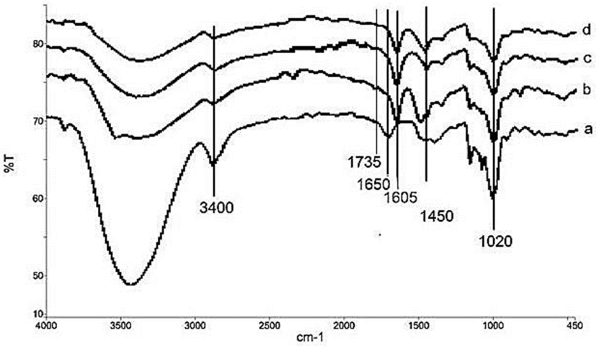

Figure 1. FTIR spectra of starch samples (a) Natural starch (b) MCMYS (b) MCMPS (d) MCMRS

The differences identified on the spectra clearly indicate the effect of carboxymethylation on natural starch. For example, the absorption bands at 3400cm^{-1} for polymeric hydroxyl (–OH) stretch is broad for natural starch but short in the modified starch products due to the substitution of –OH in the reaction. The sharp peak at 1735cm^{-1} correspond to the six–membered ring carbonyl (C=O) compound, and the carboxyl (COO–) functional group in the modified starch products and natural starch is registered at 1605cm^{-1} and 1650cm^{-1} respectively. Other vibrational frequency of bonds found in the samples are; methyne (C–H) stretch of alkane at 2900cm^{-1}, cyclohexane ring vibrations at 1020cm^{-1}, methyl (–CH_3) bend and carboxyl group absorptions between 1450cm^{-1} to 1300cm^{-1}, and the short absorption bands between 720cm^{-1} to 550 cm^{-1} corresponding to out–of–plane vibrations of –OH group.

3.1. Mud properties

The properties of water-based muds formulated with the modified starch samples and CMC were compared, and the effects of concentration and particle size of starch samples on rheological properties of the muds at increasing temperature was determined. It was observed that the concentration of starch samples and temperature have no significant effect on the mud weight which ranges between 8.43 and 8.45 ppg.

3.1.1. Plastic viscosity

The plastic viscosity of drilling fluids is a measure of the resistance to flow due to internal friction between liquid–liquid and solid–liquid layers. It mostly depends on the viscosity of the fluid phase, and the quantity, type, and size of solids in the mud. This property improves the rate of penetration of drilling bit and enhances lifting and suspension of drilled cuttings during mud circulation. At constant temperature, the plastic viscosity increases with increasing concentration and decreasing particle size of the starch samples as shown in Figure 2. Similarly, the plastic viscosity increases with increasing temperature and stabilizes at higher temperature. The plastic viscosity also varies with the type of starch where MCMYS had the highest value and compared favourably with CMC.

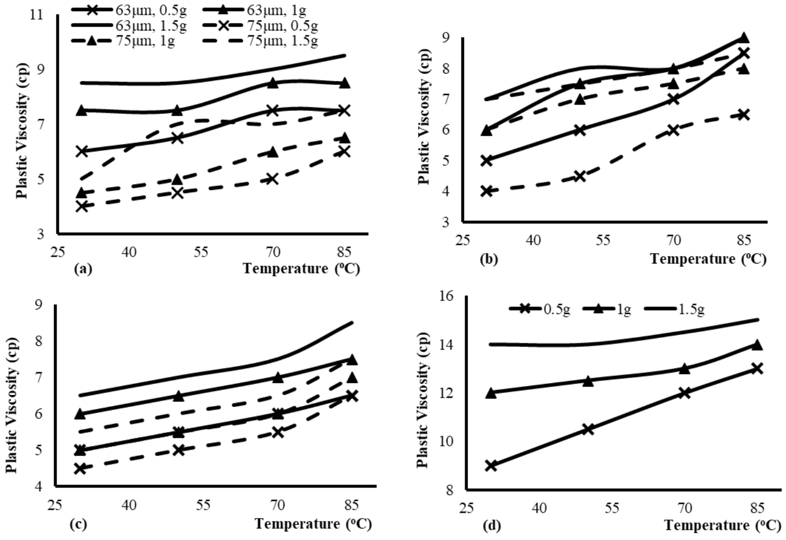

Figure 2. Influence of temperature on plastic viscosity at increasing concentration and particle size of (a) MCMYS, (b) MCMPS, (c) MCMRS, and (d) CMC

3.1.2. Yield point

The yield point of drilling fluids measures the internal resistance to initial flow and the attractive forces under flow condition. It depends mostly on the solid–solid attractive forces in the mud caused by electrical charges on the surface of the solid particles. Therefore, an effective control of drilled cuttings improves the yield point of the mud while drilling. The yield point of drilling fluids indicates the ability to carry drilled cuttings to the surface and to prevent differential sticking while drilling. Figure 3 shows the variation of yield point of mud with concentration and particle size of the starch products. At constant temperature, the yield point of the mud samples increases with increasing concentration and decreasing particle size of the starch samples. The yield point also increases with temperature, and it is higher in mud sample containing 63µm starch particles than 75µm. This is due to increased surface area of the particles leading to greater solid–solid attraction in the mud. The MCMYS product comparatively increases the yield point of the mud than other starch products and CMC.

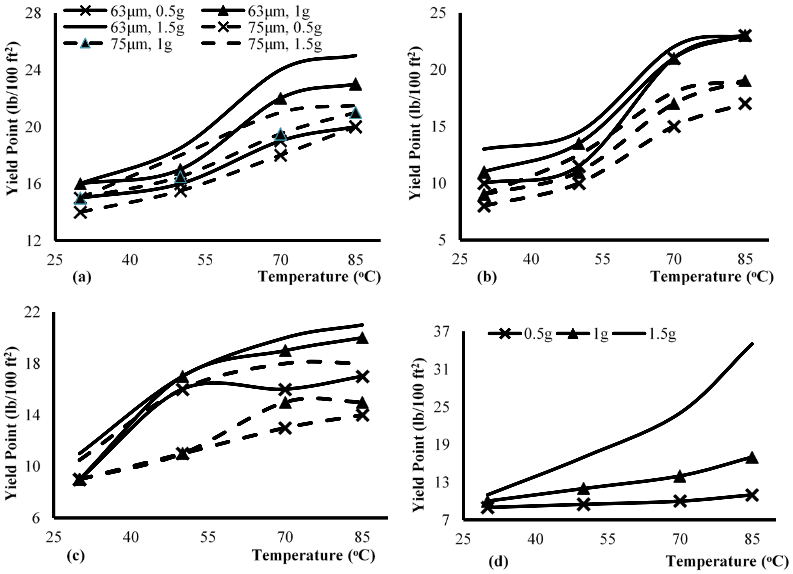

Figure 3. Effect of temperature on yield point at increasing concentration and particle size of (a) MCMYS, (b) MCMPS, (c) MCMRS, and (d) CMC

3.1.3. Gel strength

The gel strength of drilling fluids determines the ability to form gel at static conditions. It is required of a mud to exhibit gelling tendencies so as to suspend solids during stripping and when mud circulation stops. A flat rheology where the gel strength changes slightly with time is mostly desired for drilling fluids. This ensures that lower pump pressure is maintained to overcome mud gel and to start mud circulation at static conditions [20].

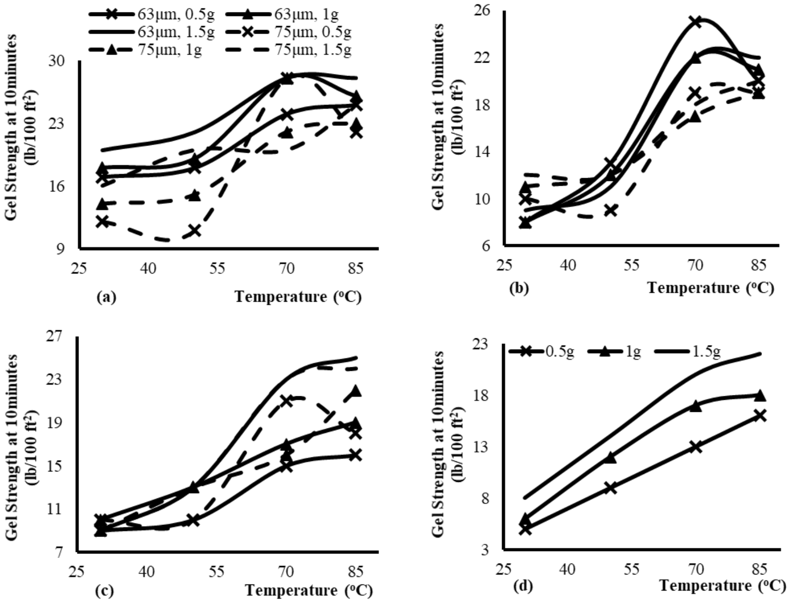

Figure 4 Variation of gel strength with temperature at increasing concentration and particle size of (a) MCMYS, (b) MCMPS, (c) MCMRS, and (d) CMC

Figure 4 shows that the gel strength at 10 minutes for all mud samples increases with increasing concentration and decreasing particle size of the starch samples. Both MCMPS and MCMRS at 63μm exhibits similar gelling behaviour as CMC, while MCMYS had higher gel strength at the same concentration and particle size.

4. Conclusion

Chemical modification of natural starch by carboxymethylation and micronization are cheaper and effective methods of improving the properties of starch for alternative application as viscosifier in drilling fluid formulation. The modified starch enhanced the rheology of water-based mud and had properties that favourably compared with the commercial viscosifier (CMC). The performance of the starch products also depends on the particle size where muds containing 63μm CMS had average yield point/plastic viscosity ratio of 1.5 above 30°C which is higher than the muds containing 75μm CMS. However, both MCMPS and MCMRS exhibit similar gelling characteristics as CMC at 63μm, while MCMYS performed equally as CMC in rheological properties. Therefore, blending the starch products and further reduction of the particle size below 63μm is recommended to enhance the properties of the products for improved drilling fluid applications.

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