Evaluation of the effect of silver nanoparticles and biopolymer on modified Nigeria bentonite rheological properties

K. W. Okunoye¹, O. P. Ogundile², K. K. Adeyemo³, F. O. Badmus⁴; T. E. Arijaje⁵, S. O. Ajayi⁶
¹Department of Chemical Engineering, Ladoke Akintola University of Technology, Oyo state, Nigeria  
²Department of Mathematics, Covenant University, Ogun State, Ota, Nigeria  
³Department of Mechanical Engineering, Ladoke Akintola University of Technology, Oyo state, Nigeria  
⁴Department of Mechanical Engineering Ladoke Akintola University of Technology, Oyo state, Nigeria  
⁵Department of Physics, Covenant University, Ogun State, Ota, Nigeria  
⁶Department of Chemistry, Covenant University, Ogun State, Ota, Nigeria

*Corresponding Author: opeyemi.ogundile@covenantuniversity.edu.ng

Abstract. During drilling mud preparation, large quantities of imported Bentonite clay are consumed by activities to develop petroleum and underground natural resources. In this research, locally made Bentonite clay was used, its rheological properties were investigated and compared with the stipulated America petroleum institute (API) standard values. The raw bentonite obtained in Gombe state, Nigeria, was weighed, crushed, and prepared to remove the impurities at room temperature. The cake gotten was sundried and broken into powder. The clay's swelling ability was studied using a design expert software to generate the combined ratio of 3.75g of clay, and 0.3g of sodium carbonate (Na₂CO₃) dispersed in a fixed volume of distilled water in a measuring cylinder for 24 hours. The procedure was then repeated for other runs. The clay beneficiation was done by scaling up the optimal value obtained for both clay and Na₂CO₃. Beneficiated clay was impregnated with silver nanoparticles (Ag/NPs) acquired from the Department of Biology, Ladoke Akintola University of Technology. The food gum obtained from the market was peeled and pounded; the liquor extracted was sundried and reduced to a particle size of 0.12 µm. In determining the rheological properties, a viscometer (OFITE model 900 viscometer) was used. It was observed in this study that the local made Bentonite rheological properties like plastic and apparent viscosity, gel strength, and yield point were significantly improved at various temperatures of 23°C and 100°C when compared with API standard values. Similarly, the impregnation of beneficiated clay with Ag/NPs has no significant effect on the Gombe Bentonite clay's rheological properties.

1. Introduction
Drilling is a complicated and expensive operation compared with other activities in the oil and gas industry's well program. Drilling fluids (water or oil-based) are considered essential components of drilling wells as all drilling operation depends directly on the fluid properties. One such feature is the...
rheological property. Nigerian bentonite clays started in Abia state between the rates of 2500-3000 tons per day and peaked at 5106 tons per day from 1961 to 1963. Beyond this period, few scholarly pieces of research were done on Nigerian bentonic clays, which led to a decline in its use for drilling fluid applications [1]. According to reference [2], Nigerian bentonite clay surfaced in the late 1980s, to improving the clays' properties, the sodium beneficiation technique was considered. However, the low effectiveness of these techniques, coupled with the high demand for bentonite in the Nigerian oil and gas sector, initiated the importation of foreign bentonite clays to meet the sector's requirement.

The earliest characterization study of Nigeria bentonite clays been deposited can be traced to the work of [3], which depicts that these clays possess mostly low-grade calcium montmorillonite. Reference [4] and [5] reported there is always a need for beneficiation since most of Nigeria's bentonite clay samples obtained from deposits contain varieties of impurities in its raw form. By definition, bentonite is used in drilling fluids for cooling and lubricating cutting tools, and also it helps prevent blowouts during the drilling process [6]. Moreover, the usefulness of bentonite in the drilling and geotechnical industries comes from its unique rheological properties. Rheological properties are known as the basis of all analyses in wellbore hydraulics and in assessing the mud system's functionality. According to [7], controlling and maintaining rheological properties is critical as its failure could result in loss of time and finance, and in extreme cases, it could result in the abandonment of the well. With the increased cost of importing sodium bentonite, it becomes imperative to improve the locally produced clay's rheological properties to drive sustainability and accessibility. According to [8], the utilization of Ag/NPs has been widely adopted in many quotidian commercial products like cosmetics, environmental protection, drug delivery, and Nano-medicine. Also, Ag/NPs are utilized in the textile industry in water filtration membranes so as to protect the water from a series of bacteria and other microbes [9-11].

Hence, this paper discusses how to modify Nigeria bentonite using sodium carbonate (Na$_2$CO$_3$), and evaluate silver nanoparticles (Ag/NPs) synthesized from rice husk on the clay rheological behavior in the presence of bio-polymers and its hydraulic characterization.

2. Materials and methods
This paper uses clay, food gum, polyanionic cellulose (PAC), and ionized water as materials needed for the study. Raw bentonite sample obtained from the Gombe state was weighed and crushed down from lumps to powder form. The coarse powder was soaked with water, and the mixture was stirred at room temperature. The stirred mixture was allowed to settle for some minutes for the coarse quartz impurities to sediment. The clay obtained was allowed to settle and thicken. The resulting cake was then sun-dried to constant weight, broken down to powder, and stored in a large plastic container.

The swelling ability was studied by placing 7 grams (g) of the clay in a measuring cylinder. An equal amount of distilled water was added. The number of clay samples was constant in all the cylinders, and the design expert software was used to generate a combined ratio. The optimal value obtained from the swelling index test was scaled up for both clay and Na$_2$CO$_3$. In a 500mili beaker, 100g of clay was placed with 100ml of distilled water and stirred until homogeneity was obtained, after which it was preheated for 5 minutes. After heating, 8g of salts were added, stirred, and placed on the heating mantle for 70 minutes at a constant temperature of 90°C. This procedure was repeated until the required quantity of modified clay was obtained. 17g of modified clay, raw clay, and impregnated clay was added to 350ml of distilled water in a separate stainless cup. The mixture was then mixed for 5 minutes in a multi-mixer running at 1100rpm to achieve homogeneity. In other to thoroughly hydrate the homogenous mixture, the mixture was left covered for 16 hours at room temperature. The sample was stirred for 5 minutes before the rheological measurements, and PAC and food gum solution was prepared similarly. After hydration, the rheological measurements, PAC and food gum solution was prepared similarly, the bentonite dispersion and the polymer solutions were mixed for 10 minutes to ensure thorough mixing.

The viscometric data was acquired with Office rotary viscometer. The samples were poured into the
cup and appropriately placed under the viscometer. The cup was adjusted until the spindle was immersed exactly to the scribed line. The lock screw of the sample was tightened at the position. The top knob was turned to 600 rpm and dial reading was noted when it comes to a stable value through the eyepiece on top of the viscometer. This process was repeated for 300 and 60 rpm, starting from high to low shear rates. However, all measurements were obtained at an average temperature ranging between 23°C and 100°C. Also, the gel strength of each sample was obtained. The viscometer samples were analyzed using the formula below where the unit of the Apparent Viscosity and Plastic Viscosity (PV) is centipoise (cp) while that of yield point is lb/100 sqft:

\[
\text{Apparent Viscosity} = \frac{600}{2} \tag{3.1}
\]

\[
\text{Yield Point} = \frac{300 - PV}{2} \tag{3.2}
\]

\[
\text{Plastic Viscosity} = \frac{600 - 300}{300} \tag{3.3}
\]

3. Results

The result obtained from the clay sample's swelling index test shows that the best swell was achieved at a combined ratio of 3.75g and salt of 0.3g with an initial height of 2.00 ml and a final height of 22.50 ml. It is illustrated in the table 1 and 2 below, where IC represents the impregnated clay, MC represents the modified clay, and RC represents the raw clay.

| Table 1: Rheology Properties at 23°C |
| RUN | PAC | FOOD GUM | GEL 10sec | GEL 10min | 600RPM | 300RPM | 60RPM |
|-----|-----|---------|--------|--------|-------|-------|-------|
| 1   | 0.2 | 1       | 2      | 2      | 8     | 6     | 6     |
| 2   | 0.4 | 2       | 2      | 2      | 8     | 7     | 8     |
| 3   | 0.6 | 3       | 2      | 2      | 8     | 8     | 8     |
| 4   | 0.8 | 4       | 2      | 2      | 9     | 10    | 10    |
| 5   | 1   | 5       | 2      | 2      | 10    | 12    | 10    |
| CONTROL | 8 | 6 | 8 | 4 | 4 | 6 | 2 |

| Table 2: Rheology Properties at 100°C |
| RUN | PAC | FOOD GUM | GEL 10sec | GEL 10min | 600RPM | 300RPM | 60RPM |
|-----|-----|---------|--------|--------|-------|-------|-------|
| 1   | 0.2 | 1       | 2      | 2      | 6     | 4     | 4     |
| 2   | 0.4 | 2       | 2      | 2      | 6     | 6     | 6     |
| 3   | 0.6 | 3       | 2      | 2      | 6     | 6     | 7     |
| 4   | 0.8 | 4       | 2      | 2      | 7     | 7     | 8     |
| 5   | 1   | 5       | 2      | 2      | 8     | 9     | 8     |
| CONTROL | 4 | 5 | 5 | 2 | 3 | 3 | 2 |

Figure 1: shows the result of the effect of polymer concentration on the viscosity of the mud at 600 rpm for different samples of clay at different temperatures. The impregnated clay has higher viscosity at a low PAC (0.2g) than beneficiated clay and raw clay with a threshold of 0.6g of PAC concentration. This implies that an increase in the clay's viscosity is directly proportional to an increase in the concentration of polymers beyond 0.6g.

Also, for the beneficiated clay at low and high temperatures, as the viscosity increases, the polymer concentration increases. For the raw clay, as the polymer concentration increases, the
viscosity also increases and attains a constant viscosity value when the concentration of the polymer is at 0.8g for PAC and 1g for food gum at high temperature. At low temperature, the polymer concentration increases as viscosity increases and later attains a constant viscosity at a concentration of 0.4g and 0.6g for PAC before their concentration later increased to maintain constant viscosity. Generally, for the three clay samples, the viscosity decreases as the temperature increases.

![Figure 1: Effect of concentration of PAC on viscosity at 600 rpm for different clays at 23°C and 100°C](image)

Figure 1: Effect of concentration of PAC on viscosity at 600 rpm for different clays at 23°C and 100°C

Figure 2 shows the result of the behavior of different clays on viscosity at different polymer concentrations. As shown in the figure, the impregnated clay has constant viscosity value between the concentration 0.2g and 0.6g. From the threshold concentration of 0.6 g upward, the curve shows Bingham plastic fluid's behavior. For impregnated clay, an increment in the temperature, led to a decrement in viscosity. Also, for the beneficiated clay, as the temperature increases, the viscosity decreases, and the curve shows the behavior of Bingham plastic fluid. For the raw clay, an increment in the temperature, led to a decrement in viscosity, and the curve shows the behavior of Bingham Pseudo-plastic fluid.

![Figure 2: Behavior of different clays on viscosity at different PAC concentration and temperature.](image)
Figure 3 shows the result of the three clay samples' plastic viscosity at different polymer concentrations and temperatures. Plastic viscosity (PV) is referred to as the resistance to the flow of fluid, and according to the Bingham plastic model, the plastic viscosity is the slope of shear stress to shear strain. As shown in figure 3, the modified clay's plastic viscosity increases as the concentration of the polymer increases and maintain a constant trend between conc. 2 to 3 g before starting to increase to 5cp at low temperature. Also, at high temperature, PV of the clay sample rise between the concentration of 1 to 2g high equivalent to 2 to 3cp and PV drop as the concentration increase further to 2 cp.

Plastic viscosity of the impregnated clay is constant at 4cp as the concentration of the polymer increases as shown in figure 3, at low temperature and at high temperature the PV rises to 3cp at concentration 1g and later drop to 2cp as the concentration increase between 2 to 3g after this point, PV increase as the concentration increases. PV of the raw clay is maximum at 4cp and drop sharply to 2cp as the concentration increase further but increase gradually from this point as the concentration increase further at low temperature. At high-temperature, PV is constant at 2cp as the polymer concentration increase from 1 to 2g and increases to 3cp as the concentration increase to 3g and later constant at 2cp as the concentration increase further. Generally, it can be observed that modified clay gives the highest plastic viscosity of 5cp at a polymer concentration of 5g at low temperature, and impregnated clay gives the highest PV of 4cp at a polymer concentration of 5g at high temperature.

![Figure 3](image)

**Figure 3:** Plastic viscosity of the clay samples at different food gum concentration and temperature

Figure 4 shows the result of the apparent viscosity of the three clay samples at different polymer concentrations and temperatures. As shown in the figure, the three clay samples' apparent viscosity increases as the polymer concentration increased, but apparent viscosity decreases as the temperature increases. It can also be observed that modified clay gives the highest apparent viscosity of 6cp at a polymer concentration of 5g (food gum) and 1g of (PAC).
Figure 4: Apparent viscosity of the clay samples at different concentrations of polymer and temperature.

Figure 5 shows the result of the yield point (YP) of the three clay samples at different polymer concentrations and temperatures. The yield point is a rheological parameter for drilling fluids, and it shows the resistance of stress required to initiate fluid movement. Figure 5 depicts the YP of three clay samples with different polymer concentrations and different temperatures. The YP goes up for modified clay as polymer concentration increases at high temperature but decline at low temperature. Also, for the impregnated clay the YP increases at high temperature up to 2 lbf/100ft³ at a polymer concentration of 3g (food gum) and 0.6g of (PAC) but decline as the concentration increase further, at low temperature impregnated clay gives zero YP up to a concentration of 3g (food gum) and 0.6g of (PAC) and the YP later increase to 2 lbf/100ft³.
Figure 5: Yield point of the clay samples at different concentrations of polymer and temperature.

4. Conclusion
The presented study allowed the authors to conclude that the modified clay gives the highest plastic viscosity, which is a vital property when determining clay's suitability as a drilling fluid. Also, the impregnation of the clay with silver nanoparticles does not have much effect on the rheological property of the clay sample. The yield point of the sample is positively affected as the concentration of food gum and PAC increases. For future research, since sodium carbonate was used for the clay beneficiation, it is recommended that other sodium base salt be used for beneficiation while other natural biopolymers could also be investigated with food gum.

Acknowledgment
The authors sincerely appreciate the financial support of the management towards the publishing of this paper.

Reference
[1] Agwu O O, 2015 A review of Nigerian bentonitic clays as drilling mud. Presented at the Nigeria Annual International Conference, Paper SPE-178264-MS 1-18.
[2] Omole O, Adeleye J O, Falode O, Malomo S, and Oyedeji O A, 2013 Investigation into the rheological and filtration properties of drilling mud formulated with clays from Northern Nigeria. Journal of Petroleum and Gas Engineering, 4(1), 1-7.
[3] Oyawoye M O, and Hirst D M, 1964 Occurrence of a montmorillonite mineral in the Nigerian younger granites at Ropp, Plateau Province, northern Nigeria. Clay Minerals Bulletin, 5(32), 427-433.
[4] James O O, Mesubi M A, Adekola F A, Odebunmi E O, and Adekeye, J I, 2008 Beneficiation and characterization of a bentonite from North-Eastern Nigeria. J. N. C. Acad. Sci. 124 (4),
154-158.

[5] Obaje, S O 2013 Suitability of borno bentonites as drilling mud Int. J. Sci. Technol. 3 (2),151–152.

[6] Hosterman J A 1992 Bentonite and fuller’s earth resources of the United State. U.S Geological survey, paper 1522.

[7] Darly H C H and Gray G R 1988 Composition and Properties of Drilling and Completion, published by Gulf publishing Company, Houston.

[8] Murawala P T A 2014 In situ synthesized BSA capped gold nanoparticles: effective carrier of anticancer drug methotrexate to MCF-7 breast cancer cells. 158-167.

[9] Ahamed M A M 2010 Silver nanoparticle applications and human health. 411: 1841-1848.

[10] Adekoya J A, et al, 2015 Tandem synthesis of some low and high indexed monometallic nanoparticles in polyols, poly (vinylpyrrolidone), trisodium citrate and dodecanethiol matrices. Digest Journal of Nanomaterials and Biostructures, 10(4), 1311-1327.

[11] Akinsiku A A et al, 2018 Modeling and synthesis of ag and ag/Ni allied bimetallic nanoparticles by green method: Optical and biological properties International Journal of Biomaterials 9658080