APPLICATION OF POLYPROPYLENE NANOSILICA AS ADDITIVES IN WATER BASED MUD TO IMPROVE RHEOLOGICAL PROPERTIES AND SHALE STABILITY

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DEDICATION

I would like to dedicate this work of mine to my family especially my parents for always being there for me, supporting me and caring for me from the moment I opened my eyes until now.I also would like to dedicate this work to lecturers and my friends who supported and helped me directly and indirectly.

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ABSTRACT

Drilling in swelling clay formation is rather challenging owing to the delicate formation of the wellbore. This is mostly because of the propensity of clay to swell when in contact with water. The high reactivity of swelling clays with water causes their constituents to swell and these can cause severe drilling problems, such as damage to the production zone. Potassium chloride (KCl) has been the most typical shale swelling control additive used to formulate WBM. However, at higher concentrations of KCl in WBM, the mud separates into two phases, which are liquid and sediments, and the swelling-control activity of the KCl is short-lived in WBM. A better efficient clay swelling-control additive, such as composite of polymer and nanoparticle, might be more effective. Therefore, in this study, the efficiency of synthesized polypropylene based nanosilica composite (PP-SiO2 NC) on clay swelling was carried out and its performance was compared to KCl mud and other types of water based mud. Samples of shale from Simpang Renggam shale formation were selected and tested for swelling behaviour over five different types of WBMs, which are (i) Basic mud (ii) KCl mud (iii) PP-SiO2 NC mud, (iv) Commercial SiO2 NP mud, and (v) Mixture of KCl and PP-SiO2 NC mud. At normal temperature 80°F and elevated temperature 250 °F, PP- SiO2 NC mud gave better results in the rheological properties such as gel strength, plastic viscosity, and yield point compared to other type of WBM. Improved shale swelling inhibition were achieved at a lower concentration (0.3 -1.0 g) of synthesized PP-SiO2 NC compared to 30g conventional KCl mud, which is required to attain its optimum inhibition level. 0.6g of PP-SiO2 NC based mud alone prove to be the best formulation as it only cause shale to swell up to 7.11% compared to KCl mud at 15.3%, mixture of KCl and PP-SiO2 NC mud at 9.2%, and commercial SiO2 NP mud at 10%. Indubitably, the synthesized PP-SiO2 NC mud provide better in rheological properties at normal and elevated temperature and more efficient in minimizing clay swelling behaviour compared to other type of WBM and it has a higher propensity to prevent loss of filtrates into the formation.

ABSTRAK

Penggerudian di syal agak sukar kerana perlu menghadapi isu formasi yang lembut dalam lubang telaga. Ianya disebabkan oleh ciri-ciri pembengkakan syal terutama apabila bersentuhan dengan air. Kereaktifan tinggi pada syal apabila bersentuhan dengan air menyebabkan komponen pada tanah liat membengkak dan ini menyebabkan berlaku banyak masalah seperti kerosakan pada zon pengeluaran. KCl telah menjadi aditif kawalan bengkak yang paling biasa digunakan untuk merumuskan WBM. Walau bagaimanapun, pada kepekatan KCl yang lebih tinggi di WBM, lumpur itu memisahkan dua fasa, iaitu cecair dan sedimen, dan aktiviti pengendalian bengkak KCl mempunyai jangka hayat yang pendek. Aditif pengawalan bengkak tanah liat yang lebih baik, seperti komposit polimer dan nanopartikel, mungkin lebih berkesan. Dalam kajian ini, kecekapan komposit polypropylene nanosilica (PP-SiO2 NC) pada kebengkakan tanah liat dijalankan dan prestasinya dibandingkan dengan lumpur KCl and lumpur WBM yang lain. Sampel syal dari Simpang Renggam telah dipilih dan diuji untuk tingkah laku bengkak ke atas lima jenis WBM yang berbeza, iaitu (i) Lumpur asas (ii) Lumpur KCl (iii) Lumpur PP-SiO2 NC (iv) Lumpur komersial SiO2 NP, dan (v) Lumpur campuran KCl dan PP-SiO2 NC. Pada suhu normal 80 °F dan suhu tinggi 250 °F, lumpur PP-SiO2 NC memberikan hasil yang lebih baik dalam sifat reologi seperti kekuatan gel, kelikatan plastik, dan titik hasil berbanding dengan jenis WBM yang lain. Perencatan bengkak syal yang lebih baik dicapai pada kepekatan yang lebih rendah (0.3 -1.0 g) lumpur PP-SiO2 NC yang disintesis berbanding dengan 30g lumpur KCl, yang diperlukan untuk mencapai tahap perencatan optimumnya. 0.6g lumpur PP-SiO2 NC menjadi formulasi terbaik kerana ia hanya menyebabkan syal membengkak sehingga 7.11% berbanding lumpur KCl pada 15.3%, campuran KCl dan PP-SiO2 NC lumpur pada 9.2%, dan lumpur komersial SiO2 NP pada 10%. Secara tidak langsung, lumpur PP-SiO2 NC yang disintesis memberikan prestasi lebih baik dalam sifat rheologi pada suhu normal dan suhu tinggi dan lebih berkesan dalam mengurangkan pembengkakan tanah liat berbanding dengan jenis WBM yang lain dan ia mempunyai kecenderungan yang lebih tinggi untuk mencegah kehilangan filtrat ke dalam formasi.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

KCl	-	Potassium Chloride
PP-SiO2	-	Polypropylene Nanosilica
PNC	-	Polymer Nanocomposites
PAM	-	Polyacrylamide
LPLT	-	Low Pressure Low Temperature
HPHT	-	High Pressure High Temperature
PPgMA	-	Polypropylene Grafted Maleic Anhydrite
XRD	-	X-ray Diffraction
TEM	-	Transmission Electron Microscopy
XRF	-	X-ray Florescence
FESEM	-	Field Electron Scanning Microscopy
FTIR	-	Fourier Transform Infrared Spectroscopy
LSM	-	Linear Swell Meter
PP	-	Polypropylene
NP	-	Nanoparticles
MA	-	Maleic Anhydride
SiO2	-	Nanosilica
CEC	-	Cation Exchange Capacity
WBDF	-	Water Based Drilling Fluid
OBM	-	Oil Based Mud
CMC	-	Carboxy Methyl Cellulose
PAC	-	Polynomic Cellulose
PHPA	-	Partially Hydrolized Polyacrylamide
XG	-	Xanthan gum
PV	-	Plastic Viscosity
YP	-	Yield Point
GS	-	Gel Strength
MWCNT	-	Multiwall Carbon Nanotubes
TGA	-	Thermal Gravimetric Analysis
EDA-G	-	Ethylenediamine Modified Graphene
API	-	American Petroleum Institute

LIST OF APPENDICES

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Shales are clastic sedimentary rock type of fine-grained constituents, which is a mixture of clay flakes and silt-sized particles (tiny fragments) of other minerals, such as calcite and quartz. Shale has the tendency to absorb water and swell owing to the presence of clay in the shale. This is due to the high sensitivity of clay minerals in water because of their high water absorption capacity. Montmorillonite is a common typical water sensitive clay. Other water sensitive clays are smectite/inter layered montmorillonite and illite. Kaolinite, Chlorite, apalite, feldspar, quartz, gypsum and carbonate are also clay rock minerals with lower swelling affinities (Ismail, 1996).

More than 75% of the drilled formations worldwide are composed of shale (Berry, 2008). The swelling characteristics of different rock types to mud combinations is crucial in predicting different problems of drilling. It will also help to determine the appropriate mud system to make stable the unforgiving shale environment. This rock characteristic is very complex and is dependent on the type of rock and the nature of the mud compositions, and greatly contributes to caving, heaving, sloughing and progressive wellbore expansion problems in the shale section of the wellbore (Chenevert, 1989). As shale encounters water, there is an exchange of which induces the rock to absorb water. Thus, swelling of shale swells and weakened rock formation (Eurock, 1996). Furthermore, shale swelling leads to easy parting of shale particles from both the drilled debris and wall of the borehole seeping into the mud system as another solid material. This leads to substantial changes in the muds rheological properties, causing other wellbore problems, such as induced fracturing and pipe sticking (Chenevert,1989).

It is generally understood that high contents of montmorillonite (smectite clay) in the shale is the major cause for undue shale swelling characteristics. In drilling, it is always very difficult to comprehend the unusual shale swelling characteristics found in some shale rocks with little or no swelling clays. Nevertheless, some rich shale formations, in which montmorillonite is the highest constituent contain less swelling behavior in comparison with shales of low stretchy clay content. This help other factors to control the shale-swelling tendency (Amanullah, 1993). A significant consideration in these drilled formations is on how to safeguard the water-sensitive clays from having contact with water and to lessen problems caused by the adsorption of water by the clay. Numerous investigations have been carried out to analyze the performances of different mud additive for shale swelling reduction. Potassium Chloride (KCl) is still considered as the most efficient additive for shale stabilization via cationic exchange (Boyd, 2012). It is believed to be the most functional shale stabilizer in conventional based mud. However, wells drilled with KCl drilling mud needs high amount of K^+ ions to constrain shale. Brien and Chenevert (1973), Clark et al. (1976), and Chang and Leong (2014) reported that high KCl concentration in WBM can separate KCl into two phases, such as sediment and liquid. High filtration loss volumes have been achieved by using KCl based drilling mud.

Polymeric materials in drilling mud were developed to improve rheological properties (Guo *et al.*, 2006) and inhibit shale swelling behaviour (Fritz and Jarrett, 2012; Deville et al., 2011). Polymers contained remarkable hydrophilicity and a well-proportioned hydrodynamic volume successive to hydration, which can make the drilling mud rheological properties to be stable, and subsequently control the filtrates loss properties. As well depth rises, the thermal gradient increases, which leads to harsh downhole environment. Polymer behavior in drilling fluids at high temperature is indicative of the effectiveness of such polymer (Mao et al., 2015). Results from fields indicates that polymeric based drilling fluid are unstable at high temperature, and are always prone to degradation (Amanullah *et al.*, 2011). Thus, drilling personnel's are seeking for novel materials that are physically small, environmental friendly, multi-functional, chemically and thermally stable to be added in drilling fluid for enhanced drilling operation (Amanullah and Al-Tahini, 2009; Hoelscher *et al.*, 2013; Zakaria *et al.*, 2012).

Applications of nanotechnology have been envisaged to usher in new opportunities for exploration phase especially in drilling industry. Drilling fluid rheology and thermal stability can be improved with nanoparticles (NPs) (Abdo and Haneef, 2013). Different applications of NPs in drilling muds have been reported, and they range from viscosity stabilization, prevention of loss circulation at high temperature, enhancing the carrying ability of the mud of drilled cuttings, abating water seepage into the formation, dehydrating clay and minimizing pipe-sticking incidents. Variety of NPs have been examined for viscosity enhancement and shale inhibition characteristics of drilling muds. The most investigated NPs for drilling are nanosilica, multi-walled carbon nanotubes, graphene oxide, copper oxide and zinc oxide and (William *et al.*, 2014).

Micro-nanoparticle composite can be the needed solution for the shale swelling inhibition. Composite materials of organic polymer/inorganic nanoparticle have been widely examined for a long time as reported in literatures. When NP phase in the polymer matrix become nanosized (1-100 nm), they are referred to as polymer nanocomposites (PNCs) (Kickelbick, 2003; Prasad and Geckeler, 2011). PNCs indicates the production and manipulation of polymer or copolymer materials with NPs dispersed in the polymer matrix with at least one of its dimension in the nanometer range of 1-100 nm (Kickelbick, 2003). The tiny size, high area of surface to volume ratio, and high surface energy of NPs empowers it to adsorb over the surface of the clay and seals its pore throats. Commonly used shale inhibitive polymer, such as partially hydrolyzed polyacrylamide (PHPA) have been proven to have the characteristics of coating the shale surface (Hale and Mody, 1993). Thus, shale plugging and coating can be attained with the combination of polymeric material and nanoparticle to form a nanocomposite with enhanced properties more than the properties of the individual constituent. PNC can be produced by directly inserting the nanofiller into the polymer, or by grafting NP into the polymer. It can also be produced through entrapment of the polymer in the NP, such as entrapment of hydrophobic chemically inert polypropylene (PP) at the surface of nanosilica (Zu et al., 2013). This will enhance the properties of the polymer matrix, such as viscoelastic, stronger flame resistant, self-assembly, barrier properties, thermal and chemical stability, and improve the alterations in surface wettability.

Literatures on PNC has showed that the advances made on PNC as an additive of drilling mud is still recent, and its full application in oil and gas industry, more importantly the drilling industry is still in the early stage. Hence, this study was conducted to examine the performance of water-based mud (WBM) formulated with different concentrations of synthesized polypropylene nanosilica (PP-nanosilica) composite as it influences the WBM rheological properties, and its effect on shale swelling inhibition.

1.2 Problem Statement

Recently, one of the most serious issues confronting drillers in the oil and gas industry is on how to develop a smart, cost effective and environmentally friendly WBM which can ensure stability of the mud's rheological properties at high pressure high temperature (HPHT) conditions and enhance shale inhibition properties of the mud (Chu *et al*., 2013; Mao *et al.*, 2015). Instability in muds rheology and shale may cause different serious wellbore problems that will hinder effective hydrocarbons productions. These problems can occur in the form of high loss of filtrates into the producing formation, spud losses, reduce drilled cutting and other solids particles transportation efficiency, reduce drilling rate, shale collapse and sloughing, and increase differential stuck pipe (DeNinno *et a*l., 2016; Mohiuddin *et al.*, 2007). These problems can be resolved if the mud rheological properties, such as plastic viscosity (PV), yield point (YP) filtrates loss control volumes, lubricity are improved and shale swelling behavior are inhibited by the drilling mud. While KCl have been mostly employed to dehydrate clay and inhibit shale swelling behaviour, its limitation of forming two phases in drilling mud have been a serious concern to drilling personnels. High KCl concentration in WBM can cause KCl to develop into two phases, such as liquid and sediments. These sediments in drilling mud can lower the drilling rate, thus prompting higher pump power requirements. Besides, it is not eco-friendly when high concentrations are required to minimize shale high swelling rate. Therefore, low concentrations of KCl are preferred in the drilling mud, but the usage of low concentrations of KCl alone is somewhat ineffective in reducing shale instability (Deville, Halliburton, 2011). It is thought that PHPA-KCl polymer mud system can achieve the desired shale swelling inhibition, but this combination also has proven to be inactive in unforgiving formations, such as shale, HPHT, deep-water and ultra – deep water (Berry, 2005). Therefore, to address these problems, the combination of hydrophobic chemically inert PP with the ability to repel water molecules in the mud owing to its hydrophobicity and nanosilica proven to be effective in plugging the shale nano-void space were used to inhibit shale-swelling characteristics and drill-in effectively in the unforgiving formations. The synthesized PP-nanosilica composite based drilling mud were used in this study on account of their attractive properties and functionalities, such as enhanced shale plugging characteristics, rheological properties, thermal and chemical stability.

1.3 Objectives

The main aim of this study was to enhance the rheological properties and shale inhibition characteristics of conventional WBM using synthesized PP-SiO2 composite. This study was conducted to achieve the outlined objectives:

i. To synthesize and characterize PP-SiO2 NC material.
ii. To investigate the rheological properties of synthesized PP-SiO2 NC in WBM at different concentrations and compared with typical rheological properties of drilling fluids employed for drilling in shale formation at low pressure-low temperature (LPLT) and high pressure-high temperature (HPHT) conditions.
iii. To identify the types of minerals of different shale samples in order to determine the most suitable shale to be used for easier facilitation of shale swelling data interpretation.
iv. To analyze the clay hydration and shale swelling behavior of synthesized PP-SiO2 NC in WBM on the selected shale sample.

1.4 Scope of Study

The scopes of this study are as follows:

i. Synthesizing, and characterizing PP-SiO2 NC material.
ii. Formulating five muds system: basic mud, KCl mud, PP-SiO2 NC mud, SiO2 NP mud, and a mixture between KCl and PP-SiO2 NC mud systems.
iii. Different weight amounts of synthesized PP-SiO_2 NC of 0.3g, 0.6g, and 1.0g was added to the prepared WBM.
iv. Mineral components and clay compositions were identified using x-ray diffraction for different types of shale samples.
v. The rheological properties of synthesized PP-SiO2 NC based drilling mud, such as plastic viscosity, yield point, gel strength, API filtrate loss volumes compared with those of based mud and KCl mud employed for drilling shale under LPLT and elevated temperature.
vi. Shale swelling behavior of synthesized PP-SiO2 NC drilling fluids are examined at 3 different concentrations from 0.3 g, 0.6 g, and 1.0 g and compared with other type of water based mud using Linear Swell Meter equipment.

1.5 Significance of the Study

It is expected that this study will offer the following contributions;

1. The findings of this study could lead to a new approach and prospects in improving drilling operations especially clay dehydration, shale swelling inhibition and environmental consideration under elevated temperature.
2. The outcomes of this study could also provide optimum rheological properties needed to effectively drill shale formation under both LPLT and elevated temperature conditions.

3. Application in the real field could benefit the oil and gas industry in terms of making the drilling of sensitive reactive water formation more efficient and economic.
4. The polymer and nanoparticle product can be used in other areas of oil and gas industry, such as EOR, workover, and completion jobs.

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