MODIFIED POLYACRYLAMIDE BY INCORPORATING SILICA FOR DRILLING FLUID TECHNOLOGY

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DISSERTATION SUBMITTED IN FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF PHILOSOPHY

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MODIFIED POLYACRYLAMIDE BY INCORPORATING SILICA FOR DRILLING FLUID TECHNOLOGY

ABSTRACT

Drilling is a process to remove the cutting in the excavations and offshore industry. Polyacrylamide (PAM) is a commercial additive in the drilling industry nowadays, but PAM has poor thermal, chemical, and pile stability in the geotechnical industry. Therefore, the functionalised material is required to be involved in the PAM-based drilling fluid. This study focuses on the modification of PAM incorporated with silica (SiO_2). The rheological investigation was optimised using various PAM concentrations (500-2000 ppm) for the subsequent testing with the effect of SiO_2, sodium dodecyl sulphate (SDS), temperature, and pH. Meanwhile, the promising formulation of modified PAM was identified via the rheological study with the effect of SiO_2 and SDS. This formulation further studied the effect of temperature and pH. The drilling fluids were characterised by Fourier Transform Infrared Spectroscopy (FTIR), tensiometer, and contact angle. The results showed that 1000 ppm PAM was the critical association concentration as the rheological properties were better below 1000 ppm PAM. Further, 0.5 wt% SiO_2 and 0.2 wt% SDS are promising formulations because both demonstrated better rheological performance than others. All modified PAM had better rheological performance than bare PAM. The rheological performance of PAM and modified PAM were significantly affected by temperature, which showed a better performance after heating to 60 °C and 40 °C, respectively. PAM and modified PAM had a better rheological performance at pH 10. Future studies can demonstrate the modified PAM in the bored pile construction to investigate the frictional resistance.

Keywords: PAM, SiO_2, SDS, rheological, temperature, pH.

PERUBAHSUAIAN POLIAKRIMIDA DENGAN PENAMBAHAN SILIKA UNTUK TEKNOLOGI BENDALIR PENGGERUDIAN

ABSTRAK

Penggerudian adalah satu proses untuk membuang keratan dalam industri penggalian dan luar pesisir. Poliakrilamida (PAM) ialah bahan tambahan komersil dalam industri penggerudian pada masa kini, tetapi PAM mempunyai kelemahan terhadap kestabilan haba, kimia dan cerucuk dalam industri geoteknikal. Oleh itu, bahan berfungsi perlu terlibat dalam cecair penggerudian berasaskan PAM. Kajian ini memfokuskan kepada pengubahsuaian PAM yang ditambah dengan silika (SiO_2). Pengoptimuman kajian reologi telah dijalankan menggunakan pelbagai kepekatan PAM (500-2000 ppm) untuk penyelidikan seterusnya yang dikaitkan kesan SiO_2, natrium dodesil sulfat (SDS), suhu, dan pH. Sementara itu, formulasi yang berpotensi dalam PAM yang diubahsuai dikenalpasti melalui kajian reologi dengan kesan SiO_2 dan SDS. Formulasi ini mengkaji dengan kesan suhu dan pH selanjutnya. Cecair penggerudian dicirikan oleh Fourier Transform Infrared Spectroskopi (FTIR), tensiometer, dan sudut sentuhan. Keputusan menunjukkan bahawa 1000 ppm PAM adalah kepekatan persatuan kritikal kerana sifat rheologi adalah lebih baik di bawah 1000 ppm PAM. Selanjutnya, 0.5 wt% SiO_2 dan 0.2 wt% SDS adalah formulasi yang berpotensi kerana kedua-duanya menunjukkan prestasi reologi yang lebih baik daripada lain. Semua PAM yang diubahsuai mempunyai prestasi rheologi yang lebih baik daripada *bare* PAM. Prestasi reologi PAM dan PAM yang diubahsuai telah terjejas dengan ketara oleh suhu, di mana ia menunjukkan prestasi yang lebih baik selepas pemanasan kepada 60 °C dan 40 °C, masing-masing. PAM dan PAM yang diubahsuai mempunyai prestasi reologi yang lebih baik pada pH 10. Pada masa depan, kajian ini boleh mendedahkan PAM yang diubahsuai dalam pembinaan cerucuk *bored* untuk menyiasat rintangan geseran.

Kata Kunci: PAM, SiO_2, SDS, reologi, suhu, pH

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LIST OF SYMBOLS AND ABBREVIATIONS

AASHTO	the American Association of State Highway and Transportation Officials
AIBN	2,2’-azobis (2-methylpropionamide) dihydrochloride
AM	acrylamide
AMPS	2-acrylamido-2-methylpropanesulphonic acid
API	the American Petroleum Institute
AV	apparent viscosity
Ca^{2+}	calcium ions
C-H	carbon-hydrogen bond
Cl^-	chloride ions
cm^{-1}	reciprocal wavelength
cm^3	cubic centimetres
cm^3/s	cubic centimetres per second
cmc	critical micelles concentration
C-N	carbon-nitrogen bond
CNC	cellulose nanocrystal
CNT	carbon nanotubes
CO_2	carbon dioxide
C=O	carbonyl group
Co.	Corporation
cp	centipoise

DMAA	N, N-dimethyl acrylamide
EDS	energy-dispersive analysis system
EBSD	electron back scatter diffraction
eV	electronvolt
f_b	ultimate base resistance
FESEM	Field Emission Scanning Electron Microscope
FTIR	Fourier Transform Infrared ray
f_s	mobilised Shaft Friction
g	gram
GMA	vinyl-terminated glycidyl methacrylate
GO	graphene oxide
GPTMS	gamma-glycidoxypropyltrimethoxysilane
GPTS	3-glycidoxypropyl-triethoxy silane
h	hour
HMP	hydrophobically modified polyacrylamide
HTHP	High-Temperature-High-Pressure
H_2CO_3	carbonic acid
H_2O	water
H_2S	hydrogen sulphide
IA	itaconic acid
K^+	potassium ions

K_b	empirical factor for base resistance
kg/m^3	kilograms per cubic metre
K_s	empirical factor for shaft friction
LAOS	large amplitude oscillation shear
lb/bbl	pounds per barrel
lb/100 ft^2	pounds per hundred square feet
LTLP	Low-Temperature-Low-Pressure
m	metre
MEA	mono ethanol amine
Mg^{2+}	magnesium ions
mD	milli darcy
min	minutes
ml	millilitres
mm	millimetres
mPa.s	millipascal.second
MPS	3-methacryloxypropyltrimethoxysilane
mN/m	millinewton per metre
mV	millivolts
N	standard penetration tests blow count
N_2	nitrogen gas
Na^+	sodium ions

NaCl	sodium chloride
Na_2CO_3	sodium carbonate
Na_2O	sodium oxide
NaOH	sodium hydroxide
NMR	nuclear magnetic resonance
NVP	N-vinyl-2-pyrrolidone
-OH	hydroxyl group
O-Si-O	oxygen-silicon bond
OTES	octyltriethoxysilane
PAM	polyacrylamide
Pa	Pascal
PEI	polyethyleneimine
pH	potential of hydrogen
PHPAs	partially hydrolysed polyacrylamide
ppb	parts per billion
ppm	parts per million
PSS	polystyrene sulphonate
PTP-1	first preliminary test piles
PTP-1A	second preliminary test piles
PV	plastic viscosity
rpm	revolution per minute

RSM	response surface methodology
s	second
SAOS	small amplitude oscillation shear
SDS	sodium dodecyl sulphate
Sdn Bhd	Sendirian Berhad
SiO_2	silica
S=O	sulphoxide bond
SO^{3-}	sulphonate ion
SSS	sodium p-styrene sulphonate
STA	Simultaneous Thermal Analyser
TEOS	tetraethyl orthosilicate
TiO_2	titanium oxide
wt%	weight per cent
w/v	weight per volume
YP	yield point
μD	microdarcy
τ_0	10-second gel strength
τ_f	10-minutes gel strength
°	degree for contact angle
°C	degree Celsius
%	Per cent

Φ	dial reading
~	approximately

LIST OF APPENDICES

CHAPTER 1 INTRODUCTION

The specific behaviour of PAM presents the potential for drilling fluid applications such as bored pile construction. Nevertheless, the usual issues, such as unstable bored piles, the “soft toe” issue, and others, inhibit the usage of PAM in bored pile construction. For this reason, scientific inventions are demanded in bored pile foundations to improve the overall rheological performance of drilling fluids in a cost-effective, green environment manner. This introduction begins by demonstrating the motivation for improving PAM as a potential rheological enhancer material and the reason behind the functionalised material involved in the modification of PAM. The chapters end with a disclosure of the objective, significant and relevant study, the novelty of the research, and the outline.

1.1 Research Background

Drilling is a process of removal of borehole cuttings. Drilling can be applied to the foundation, offshore, and excavation industries. There are various types of drilling fluid. In this study, water-based drilling fluid was focused on drilling fluid technology. Water-based drilling is mostly used in the foundation industry to build the bored pile and diaphragm. Therefore, pavement, transportation, and building construction rely on the stability of drilling fluid operations. Traditionally, bentonite fluid has been utilised in the foundation field for over 60 years due to its excellent performance. Subsequently, due to economic and environmental concerns, a synthetic polymer such as polyacrylamide (PAM) emerged as an alternative in the 1990s.

To date, PAM is a common additive in drilling fluid technology. Generally, PAM is a water-soluble polymer that is a synthetic linear, cross-linked, or a mixture of acrylamide and acrylic acid, normally using N.N’-methylenebisacrylamide (Kanna et al., 2017). Further, it is the most common flocculant in wastewater treatment (Shaikh et al., 2021). With the superabsorbent gel particles in cross-linked PAM, the high losses in the coarse ground can be restrained during drilling operations. Therefore, there is much attention on PAM in deep excavations today due to better-mobilised shaft friction and ultimate base resistance (Ejezie et al., 2021; Lam & Jefferis, 2014).

However, PAM has thermal and chemical stability limitations, affecting the rheological performance of drilling. Besides, the bored pile stability is another concern in the foundation (Lam & Jefferis, 2014). One of the methods to improve the polymer-based drilling fluid is the modification of polymer with various additives, such as monomers, cross-linking agents, and others. But these modifications still had limitations in terms of thermal stability, pH in the saline environment, and rheological performance. Meanwhile, the feasibility of this modification is questionable.

Alternatively, the functionalised material can be used in drilling fluid technology. Various types of functionalised materials are hybridised with polymer drilling fluid, such as carbon nanotubes, zinc oxide, silicon oxide, zeolite, and others. Many modified polymers with various functionalised materials have been reported to date. Therefore, PAM is required to hybridise with the functionalised particles in the drilling system. This study summarises the recent development of engineered polymer and their modification with the functionalised particles.

Significant advances in improving the rheological performance of modified drilling fluid by incorporating functionalised silica (SiO_2) have been developed in the past few years (Al-Yasiri et al., 2019; Inturi et al., 2019; Kumar et al., 2020). Besides, functionalised SiO_2 is an inert material and has low water solubility. Among all these modifiers, the surfactant is the most economical, environment-friendly, and easy experimental set-up in industrial commercialization. Furthermore, a surfactant such as SDS can absorb the oppositely charged ion of silica to create the bonding between the functionalised SiO_2 with PAM. However, there is insufficient information on the bare PAM and modified PAM evaluation regarding rheological performance with thermal heating and pH.

In this study, the rheological performances between the bare PAM and modified PAM were investigated over various parameters, including the effect of PAM concentrations, SiO_2 concentrations, SDS concentrations, temperature, and pH. Additionally, SiO_2 is characterised by Field Emission Scanning Electron Microscope (FESEM) and simultaneous thermal analyser (STA). Fourier Transform Infrared Ray (FTIR) and tensiometer are used to characterise the bare PAM and its modified PAM in terms of chemical properties and surface tension properties, respectively. Indeed, modified PAM drilling fluid has been proven to be of great interest for use in the construction of bored piles and diaphragm walls in recent years.

1.2 Problem Statement

PAM was the alternative in drilling operations over a few decades due to its several advantages. However, a few problems are still faced in its usage in drilling operations, such as unstable excavation on the coarse ground and low particle holding and viscosity. Thus, high-performance drilling systems are challenging to enhance using polymer-based as the source of raw materials. Besides, polymer-based material has concerns in thermal stability, chemical stability, and rheological properties of drilling fluid. Therefore, the enhancement of the polymer-based material is required using functional materials for drilling operations.

Most functionalised materials can further improve the thermal stability, chemical stability, and rheological properties of polymer-based drilling fluid up to its functionalised material concentration as control parameters. Because these functionalised materials must consider cost, toxicity, source availability, environmental impact, and simplicity of use in industrial applications, functionalised SiO_2 becomes a possible dopant in drilling formulation. This study is required to understand the chemical properties of PAM and functionalised SiO_2.

Using functionalised SiO_2 to modify PAM, there is a concern regarding the chemical wettability profile of functionalised SiO_2 before being incorporated with PAM. It is a fact that functionalised SiO_2 is poor in water solubility. Thus, the surface of functionalised SiO_2 is modified with sodium dodecyl sulphate (SDS) before incorporating into the PAM-based drilling fluid in this study. During PAM modification, SDS can be acted as a surface modifier of SiO_2 due to SDS being cross-linked with SiO_2 using the hydrophilic head and hydrophobic tail in the chemical nature of SDS.

As reviewed, synthesising modified functionalised SiO_2 using SDS in PAM-based drilling fluid remains less unexplored in bored pile foundations. This drilling model is mostly focused on enhanced oil recovery. Another important reason for using functionalised SiO_2/PAM in drilling fluid systems is because of rheological enhancement. Thus, this study mainly aims to achieve and enhance the rheological properties of PAM in drilling operations through this modification with this study.

1.3 Research Objectives

The research aims to investigate the surface chemistry and the formation mechanism of modified polymer in drilling fluid technology. Below are the objectives of this study:

i. To synthesise PAM and modified PAM using an in-situ polymerisation approach with their characterisation to impart and compare their chemical and physical properties of drilling fluid.

ii. To study the effect of PAM concentrations, functionalised SiO_2 concentrations, and SDS concentrations with the rheological study of PAM to improve the rheological performance of modified PAM than that of the unmodified PAM.

iii. To study the effect of temperature and pH with the rheological study of PAM and modified PAM to compare the rheological performance between PAM and modified PAM.

1.4 Significant and relevant Study

This project is embarks based on the following scopes:

i. To explore and understand the surface chemistry and the formation mechanism of the modified polymer through a literature review, as well as the cross-linking agent study between functionalised SiO_2 and PAM.

ii. To characterise the chemical structure of PAM and its modified PAM via a Fourier transform infrared (FTIR) and tensiometer.

iii. To study the surface properties and contact angle of PAM and modified PAM via a tensiometer.

iv. To characterise the surface imaging of functionalised SiO_2 via a field emission scanning electron microscope (FESEM).

v. To characterise the thermal stability of functionalised SiO_2 via a simultaneous thermal analyser (STA).

vi. To study the rheological properties of PAM and its modified PAM with various parameters, such as PAM concentrations, SiO_2 concentrations, SDS concentrations, temperature, and pH, via a 6-speed rotational viscometer.

1.5 Novelty of the study

The main aim of this study is to investigate the water-based drilling fluid using modified PAM. Although several researchers reported on the modified PAM using several functionalised materials, as well as using functionalised SiO_2, there is insufficient information regarding the plastic viscosity, apparent viscosity, yield point and gel strength in rheological studies of modified PAM using functionalised SiO_2. The rheological studies are the primary criteria for designing the drilling fluid operations. Thus, the present study investigates the rheological properties of modified PAM using SiO_2 via a 6-speed rotational viscometer to obtain plastic viscosity, apparent viscosity, yield point, and gel strength. For functionalised SiO_2 in PAM-based drilling fluid, several researchers reported that functionalised SiO_2 modification using SDS was primarily performed in the oil-recovery application, but the present study uses this drilling model for bored pile foundation in the future. Hence, the effect of SDS with SiO_2 in the modification of PAM is required to be further investigated in the present study.

1.6 Outline of Dissertation

The findings of this master's degree project are outlined as follows. In Chapter 2, a summary of the overview of drilling with its application is presented, highlighting the potential area of research interest. This section also focuses on the fundamentals and directions from the literature review, which transforms into the experimental design process in order to target the aims of the master's degree study. This dissertation is organised following an article-based format. Chapter 3 presents the influence of PAM concentration in rheological studies. Chapter 4 studies the fabrication of modified PAM with the effect of functionalised SiO_2 and SDS. Then, a comparative study of pH and temperature between bare PAM and modified PAM were investigated in Chapter 5. Lastly, the dissertation summarises conclusions, limitations, recommendations, and commercialisation in Chapter 6.

CHAPTER 2 LITERATURE REVIEW

2.1 Introduction

This chapter studies the overview of drilling fluid technology (Section 2.2) and the history and development of water-based drilling fluid technology (Section 2.3). Further, there is a brief description and discussion about the constituents of water-based drilling fluid with their limitations (Section 2.4) and the drilling fluid with piling foundation (Section 2.5). Numerous pieces of literature are discussed with regard to the various polymers (Section 2.6), as well as polyacrylamide (Section 2.7), followed by nanomaterials in drilling fluid technology (Section 2.8). Besides, the surface modification of functionalised material is presented (Section 2.9). Lastly, the factors that affect the physicomechanical properties of polymer nanocomposite in drilling are also discussed (Section 2.10).

2.2 Overview of drilling fluid technology

Drilling fluid is a critical component in exploration and excavation. In Malaysia, a support fluid or a full-length casing is used in the stabilisation of the excavation site, which is then followed by the formation of concrete casting, known as a bored pile. Fluid design is an important part of the operations of drilling fluid technology, which is related to drilling operations efficiency (Moghaddam & Saadatabadi, 2020; Lam & Jefferis, 2016b). Usually, drilling fluids consist of a mixture of chemicals, solids, and liquids that support the drilling process (Mahmoud et al., 2018). Fluid design is an important part of the operations of drilling fluid technology, which is related to drilling operations efficiency (Moghaddam & Saadatabadi, 2020; Lam & Jefferis, 2016b). Usually, drilling fluids consist of a mixture of chemicals, solids, and liquids that support the drilling process (Mahmoud et al., 2018). They can be classified into 4 major types according to their principal constituents, which are water-based, oil-based, synthetic-based, and gas-based drilling fluids (Gudarzifar et al., 2020; Karakosta et al., 2021;

Paulauskiene, 2018; Saboori et al., 2019). The drilling fluid can also be classified according to fluid base, which is gas or liquid, as shown in Figure 2.1 (Karakosta et al., 2021; Paulauskiene, 2018). However, detailed classification according to principal constituents is shown in Figure 2.2. The detailed advantages and disadvantages of oil-based, water-based, synthetic-based, and pneumatic-based drilling fluids are illustrated in Table 2.1.

The operations mechanism of pneumatic-based, synthetic-based, and oil-based drilling fluids are more complex in their drilling operations (Apaleke et al., 2012; Paulauskiene, 2018; Gautam & Guria, 2020; Karakosta et al., 2021). Correspondingly, water-based drilling fluid requires simple preparation with an easy-access source such as water, polymeric additive, and others. Further, the rheological performance of oil-based drilling fluid is better than that of water-based drilling fluid because oil-based drilling fluid can create low reactivity to shale formation (Aramendiz & Imqam, 2019). Additionally, oil-based and synthetic-based drilling fluid creates lower friction and torque values than water-based drilling fluid (Ma et al., 2021; Smith et al., 2018). Besides, the cost of water-based drilling is lower than that of oil-based, synthetic-based, and pneumatic-based due to drilling operations requirements. Water-based and synthetic-based drilling fluids are more eco-friendly than oil-based and pneumatic-based drilling fluids (Aramendiz & Imqam, 2019; Gudarzifar et al., 2020; Karakosta et al., 2021; Li et al., 2020; Ma et al., 2021; Mahmoud et al., 2018; Saboori et al., 2018, 2019). To sum up all of the considerations detailed as shown in Table 2.1, the water-based drilling fluid is the most promising option in drilling fluid technology.

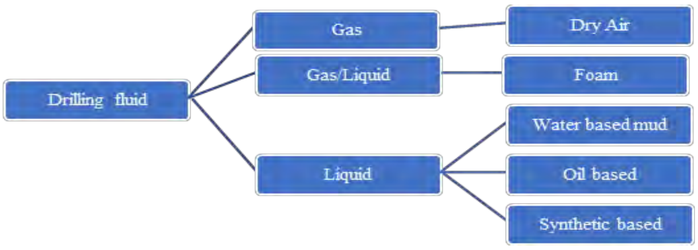

Figure 2.1: Drilling fluid classified according to the fluid base (Karakosta et al., 2021; Paulauskiene, 2018).

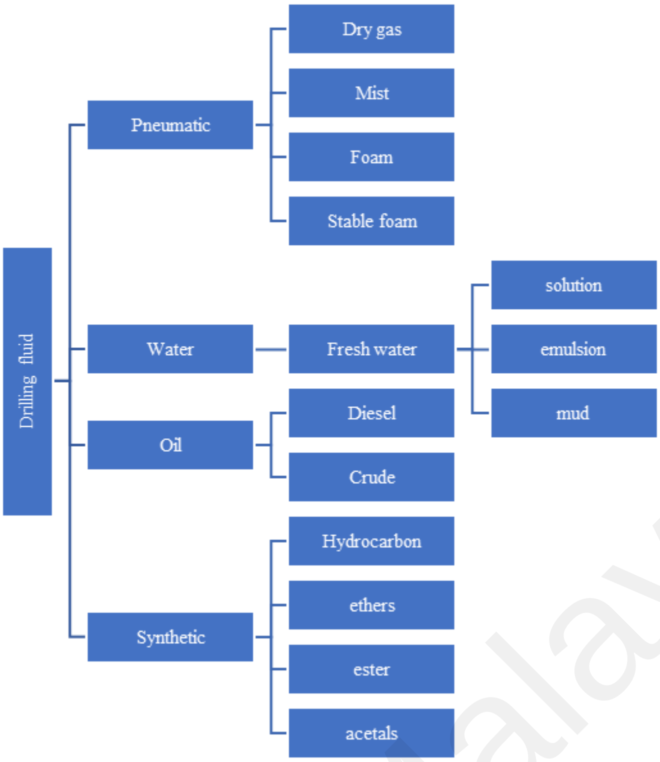

Figure 2.2: Drilling fluid classification according to principal constituents (Karakosta et al., 2021).

Table 2.1: Advantages and disadvantages of each drilling fluid.

Types of drilling fluid	**Advantages**	**Disadvantages**
Oil-based drilling fluid	- Is traditionally used in HPHT due to better viscosity, fluid-loss control ability, thermal stability, lubrication behaviour, and clay stabilisation (Gautam & Guria, 2020; Karakosta et al., 2021) - Superior performance, especially in ultra-deep drilling operations (Smith et al., 2018) - Better drilling performance and low reactivity to shale formation while maintaining downhole stability (Aramendiz & Imqam, 2019) - Improve rheology and reduced friction factor, which result in less wear on the drill string and a lesser chance of stuck pipe (Smith et al., 2018)	- Drilling requires several complex operations that lead to operations problems (Kasiralvalad, 2014) - Need to ensure that the operator regulates drilling operations by adhering to the protocols and approved activities (Aghdam et al., 2020) - High cost (Smith et al., 2018) - Environmental concerns such as waste management challenges (Aghdam et al., 2020; Kasiralvalad, 2014; Smith et al., 2018) and damages to the subsurface layers of fresh water (Parizad & Shahbazi, 2016)

Table 2.1, continued.

Water-based drilling fluid	- Simple preparation (Gudarzifar et al., 2020; Ma et al., 2021) - Source of material is widely available (Li et al., 2020) - Better cooling, cutting removal ability, rapid formation, and breakdown rate (Balding et al., 2020) - Lower operations efficiency and shale inhibition capacity, as well as remarkable rheological properties (Gudarzifar et al., 2020) - Environmentally friendly and low cost (Aramendiz & Imqam, 2019; Gudarzifar et al., 2020; Karakosta et al., 2021; Li et al., 2020; Ma et al., 2021; Mahmoud et al., 2018; Saboori et al., 2018, 2019)	- Shale instability problem with thick cake issue (Saboori et al., 2018) - Suspension behaviour and filtration/fluid loss behaviour issues (Davoodi et al., 2019; Saboori et al., 2018) - Large amount of water content causes water intrusion, which contributes to shale hydration, swelling, and formation collapse. Thick cake on borehole wall leading to borehole damage and stucked drill (Ma et al., 2021) - Limited to HPHT due to temperature-induced flocculation and gelation under static and dynamic conditions (Gautam & Guria, 2020)
Synthetic-based drilling fluid	- Good borehole stability (Paulauskiene, 2018) - High penetration rate (Paulauskiene, 2018) - Good control of drilling fluid properties and wellbore stability (Paulauskiene, 2018) - Good filtration properties and cutting transport efficiency (Paulauskiene, 2018) - Suitable for offshore drilling due to exceptional performance - Environmental friendly (Karakosta et al., 2021)	- Complex system with high solid content (Paulauskiene, 2018) - High initial cost (Karakosta et al., 2021) - Geoscientific investigation difficulties (Paulauskiene, 2018)
Pneumatic-based drilling fluid	- Low damage on reservoir (Apaleke et al., 2012; Paulauskiene, 2018) - High penetration rate (Paulauskiene, 2018) - Good performance of drill bit (Paulauskiene, 2018) - Low water uptake, drilling fluid loss, air quality requirement, and hydrostatic pressure for foam drilling (Paulauskiene, 2018) - Easy cleaning of the borehole (Paulauskiene, 2018)	- Restriction on the possible lithological structure (Paulauskiene, 2018) - Drilling length is limited to a horizontal section of the well (Paulauskiene, 2018) - Additional cost to rent equipment (Paulauskiene, 2018) and gas cost. - Utilisation of gas and foam issues (Paulauskiene, 2018), such as corrosive gas (Apaleke et al., 2012) - High risk of fire (Paulauskiene, 2018) and explosion (Apaleke et al., 2012)

2.3 Historical development of conventional water-based drilling fluid

Around the 1850s, drilling fluid was utilised for cable tool (percussion) drilling. In the 1890s, clay became the additive in drilling. Subsequently, Spindletop was introduced in borehole drilling to suspend the clay particles in 1901 (American Association of Drilling Engineers, 1999; Bridges & Robinson, 2020). With the advent of the pioneering work of Veder in 1953, the typical additive in conventional water-based drilling fluid technology is bentonite clay, which has been employed in construction and geotechnical projects around the world for over 60 years (Lam et al., 2018). It is known as montmorillonite clay. Foundation engineers had studied various polymers such as guar gum and xanthan in the past 40 years. From the 1960s to 1970s, the hydrolysed PAM and its derivatives were launched to enhance drilling operations (Jiang et al., 2021). In the late 1970s, there were concerns regarding the good-quality Wyoming bentonite and the liquid waste management cost. Subsequently, the engineers started to find alternatives, such as a patented natural polymer product called Telmarch in Japan (Lam & Jefferis, 2016a, 2017). However, the application of this material was short-lived; hence many trials on different types of natural biodegradable polymers had been tested from the 1970s until the early 1990s. Nonetheless, none of these managed to impact the industry practice and is thought to face problems such as incompatibility with concrete, high fluid loss, and cleaning difficulties. This situation is perhaps due to insufficient information on natural polymer fluid in civil engineering because of the limited market and the fewer available publications regarding the development of natural polymer fluid in the early phase (Lam & Jefferis, 2017).

In the 1990s, a synthetic polymer such as partially hydrolysed PAM emerged because synthetic polymer offers several advantages in drilling fluid technology, such as filtration reduction, wellbore reduction, drilled solids flocculation, and carrying capacity enhancement (Moghaddam & Saadatabadi, 2020). For example, PAM has a high viscosity, has good water-sensitive performance, and is non-gelling. Besides, it is eco-friendly, has low construction costs, and has better foundation performance (Lam & Jefferis, 2014, 2016b). Thereupon, synthetic polymer became common in drilling model design, and it has evolved with a blended design of different types of polymer products. For this reason, the distinction between synthetic polymer and natural polymer packages is unclear, as some polymer packages have been modified with the utilisation of synthetic polymer or natural polymer, and their properties depend on their design and on-site use (Lam & Jefferis, 2017). Thus, the innovative polymer should be further explored in the market or in publications to provide a better understanding of its system package for drilling sites. Nevertheless, PAM has a few drawbacks, such as low strength and poor shear force. Its viscosity has been affected by the pH, temperature, and hardness, which can drag its performance (de Vasconcelos et al., 2022). These drawbacks cannot be overcome by only optimising the polymer fluid.

So, the functionalised material is required for hybridisation in the drilling fluid technology of this era nowadays. Various functionalised materials can be incorporated with the synthetic polymer drilling fluid, such as carbon nanotubes, zinc oxide, silicon oxide, zeolite, and others. The functionalised material garners attention with regard to the drilling performance due to its unique properties of the functionalised material. Such as plastic viscosity improvement by incorporating an optimum amount of carbon nanotubes (Anoop et al., 2019; Ismail et al., 2018). Likewise, AlBajalan & Haias (2021) studied plastic viscosity, and the yield point were decreased when zinc oxide concentration increased in the drilling. The decline in the plastic viscosity and the decline in the yield point are analyzed due to the functionalised particle distribution and the increased distances among the functionalised particles, respectively. The fluid showed better wellbore stability and filtration loss than the conventional water-based drilling fluid. Moreover, Minakov et al. (2019) reported that 1 wt% silicon oxide had induced a reduction of filtration loss. Similarly, Ozkan & Ozkan (2019) also investigated the rheological performance of drilling fluid in terms of filtration volume reduction by using zeolite that was incorporated in the drilling fluid. The filtration volume reduction can lead to thin cake formation. Ammar et al. (2016) concluded that the use of graphene oxide resulted in good mechanical properties of polymer composite due to its good dispersion and interaction with a variety of polymer matrices, which can enhance the strength of the drilling fluid. Nonetheless, there are negative effects in terms of modulus, tensile strength, and surface wettability when graphene oxide dispersion loading reaches a certain threshold. Its poor dispersion is due to the graphene oxide agglomeration in the matrix polymer (Ammar et al., 2016).

2.4 Constituent of water-based drilling fluid with their limitations

Generally, the water-based drilling fluid comprises water and clay. Bentonite is the basic clay in the drilling fluid. Several studies reported the deficiency of bentonite in drilling when loading with a high concentration of drilling fluid, such as an excessive torque and drag, an incline of differential pipe sticking chance, a reduced penetration rate, a damage formation, a thick filter cake, a poor wellbore cleaning, and others (Ahmad et al., 2018; Saboori et al., 2019; Temraz & Hassanien, 2016; Xie et al., 2018). Additionally, bentonite has detrimental effects when its drilling is performed at high-temperature and high-pressure (HPHT) and in ultra-deep wells, such as flocculation and degradation (Song et al., 2016; Xie et al., 2018). Oppositely, a low concentration of bentonite in drilling fails to achieve the desired rheological properties (Ahmad et al., 2018).

With the simplest formulation in the water-based drilling fluid, several additives can be applied to enhance its drilling performance in challenging conditions of ultradeep and HPHT (Kuma et al., 2020; Maiti et al., 2021). Such as rheology modifiers, fluid loss controllers, weighting agents, pH controllers, lubricants, hydrogen sulphide (H_2S)

scavengers, and others. Each of the additives has its role and limitations in drilling operations, which are described in the following section.

2.4.1 Rheology modifier with its limitation

Viscosifier (viscosity enhancer) and viscosity reducer are the rheology modifiers in drilling fluid technology. Various viscosifiers are used in drilling fluid technology, such as asbestos, attapulgite, bentonite, and polymer. Viscosity reducers, such as phosphates, lignites, and tannates, are commonly used to decrease gel strength and viscosity and provide some fluid loss control (Temraz & Hassanien, 2016). In drilling fluid technology, most works focus viscosifier in the water-based drilling fluid, while the viscosity reducer is less explored and commonly utilised in the oil-based drilling fluid, which is interrelated with the nature and density of drilling mud.

To date, the polymer has become a promising viscosifier in water-based drilling fluid because polymer has a better performance as a rheological modifier, shale inhibitor, and fluid loss enhancer (Ahmad et al., 2018; Belayneh & Aadnøy, 2016; Saboori et al., 2019). Polymer utilisation in drilling mainly depends on its molecular weight and the charge of its molecules. For example, natural polymers (such as polyanionic cellulose, carboxymethyl cellulose xanthan gum, and guar gum) are used in the water-based drilling fluid. It can lead to a decrease in fluid loss and an increase in viscosity (Saboori et al., 2019). Likewise, researchers have paid more attention to a hydrophobically modified polymer in recent years because of its improved rheological properties such as temperature, salinity resistances, shear rate, and fluid loss (Moghaddam & Saadatabadi, 2020). At HPHT, a synthetic polymer can work well in terms of fluid loss control, deflocculation, viscosity enhancement, adsorbent, and gel inhibition (Mao et al., 2015).

Previous studies have shown the effectiveness of rheology modifier in drilling fluid. For instance, Balding et al. (2020) studied the water-based drilling fluid formulation with various formulations via free radical grafting and physical blending with chemical additives, such as polystyrene sulphonate (PSS), polyacrylamide (PAM), cellulose nanocrystal (CNC), and modified CNC with vinyl-terminated glycidyl methacrylate (CNC-GMA), which are shown in Table 2.2. The fluid loss and filter cake properties of modified CNC (CNC-GMA) via free radical grafting had poorer performance than that of physical blending and normal CNC free radical grafting. The main reason can be attributed to the GMA particles that were cross-linked with CNC, where they contributed to the restriction of their clay platelets through the formation of a thin and dense filter cake. For grafted or physical mixed modification, PSS had more potential than PAM as a rheology modifier with the hybridisation of CNC (Balding et al., 2020).

Table 2.2: Various formulations of water-based drilling fluid with their rheology performance by Balding et al. (2020). Adapted with permission from Ref. Balding et al. (2020). © 2020 American Chemical Society.

Drilling fluid formulation	Formation method of drilling fluid	Fluid loss, mL	Cake thickness, cm	Permeability, µD
Bare fluid	Not applicable	116.4	0.51	52.8
CNC	Not applicable	86.2	0.62	55.1
CNC-PSS	Free radical grafting	71.7	0.5	32.0
CNC-PAM	Free radical grafting	123.2	1.2	134.4
CNC-PSS-PAM	Free radical grafting	58.9	0.55	29.4
CNC/PSS	Physical blending	68.9	0.5	31.9
CNC/PAM	Physical blending	116.0	1.2	127.1
CNC/PSS/PAM	Physical blending	72.4	0.6	38.5
CNC-GMA-PSS	Free radical grafting	84.1	0.71	52.7
CNC-GMA-PAM	Free radical grafting	121.9	1.21	131.5
CNC-GMA-PSS-PAM	Free radical grafting	93.1	0.72	59.5

Likewise, Shettigar et al. (2018) designed a cationic-surfactant polyacrylamide as viscosifier in drilling fluid, which showed the improvement of rheology and cutting effect due to the hydrophobic and electrostatic interaction between the surfactant (cetyltrimethyl ammonium bromide) and polymer. However, this type of modified polyacrylamide-based drilling fluid can withstand up to 160 °C, which showed better thermal stability than the bare polyacrylamide-based drilling fluid.

Nevertheless, there is a limitation in the performance of the drilling system when a polymer is used, which is the requirement of high temperature and high pressure. HPHT can cause the degradation of the polymer, poor rheological properties, and high fluid loss (Ahmad et al., 2018). Huo et al. (2018) also stated that the traditional synthetic polymer has poor thermal stability and salinity. Hence, there is a need to improve the rheological, thermal, and chemical properties of synthetic polymers in drilling fluid technology (Huo et al., 2018). Therefore, water-based drilling fluid should be formulated with a suitable rheology modifier, as well as with the hybridisation with nanomaterials, for better rheological performance.

2.4.2 Weighting agent with its limitation

The weighting agent is the additive that can contribute to the high density, typically applied to HPHT and ultradeep drilling. Various weighting agents are used in drillings fluid technology, such as hematite, Micromax, manganese tetroxide, ilmenite, barite, calcium carbonate, and others (Bageri et al., 2021; Basfar et al., 2020). Roodbari & Sabbaghi (2021) studied the effect of barite/polyacrylamide nanocomposite in the water-based drilling fluid, which showed the incline of its fluid viscosity and the reduction of fluid loss and filter cake thickness. Besides, Kuma et al. (2020) optimised the polyacrylamide-based drilling fluid with the inclusion of hematite. It demonstrated a small incline of density and specify gravity of mud, a significant decline of the apparent viscosity with a slight increment of filtrate loss and mud cake thickness compared to bare polyacrylamide-based drilling fluid. Similarly, Bageri et al. (2021) investigated the effect of different weighting agents in the water-based drilling fluid. The result showed barite could achieve better rheological performance than that of others in terms of filtration volume (5.3 cm^3), cake thickness (3.0 mm) with its porosity (2.5 %), and permeability (0.0006 mD). This is because of the weighting agent's large fine particle size ratio, which revealed the bridging between the weighting agents in the drilling fluid.

However, a technical conflict exists between the rheological properties and sagging effect in a drilling fluid, especially in a high-density drilling fluid applied in operations. With the high solid content of weighting agents applied in drilling fluid, there is poor rheological performance and sagging issues due to the viscosity reduction that deteriorates the rock carrying and suspension capacity. Besides, there are a few limitations of rheology modifiers in ultra-HTHP, such as clay content, the polymer concentration with its relative molecular mass, and temperature resistance. A traditional rheology modifier is usually non-ideal behaviour in HTHP and ultra-deep drilling. Thereupon, many researchers explored and improved the novel tailored made of chemical additives in the formulation of HTHP and ultra-deep drilling in the past.

Alternatively, the suspension package can be formulated with proper weighting agent dosage with the dense packing of particles concept to enhance the rheology performance and sagging issue in drilling. This approach focuses on the weighting agent particle size, distribution, and packing of the particles to understand the density limit of drilling. Technically, all means and methods are applied to ensure the dispersion state of the solid weighting agent particles, which subsequently tend to be a more discrete state in drilling operations. According to Mao et al. (2020b), the result found that the rheology and sagging properties are improved by three or even different weighting agents (ferroferic oxide, barite, and ultrafine barite) with using this approach in ultra-HTHP drilling. Thus, the micronised weighting agents with lower viscosity are suggested due to the smaller size of particles with their settling rate in a viscous medium mitigating the sagging issue. Similarly, Ma et al. (2019) compared the weighting agents between micro-manganese and barite, which showed that micro-manganese has better rheological performance and sagging resistance than that barite. This is due to the specific surface area with a strong adsorption of manganese particles with drilling fluid.

However, the micronised weighting material usually is more expensive than traditional weighting agents, like barite. In short, the formulation of weighting agents with a dense packing concept can be considered, rather than the enhancement of chemical additives that can develop a complex physiochemical reaction in ultra-HTHP drilling (Mao et al., 2020b). But this approach is costly, and less published work regarding the modification of polyacrylamide with the weighting agents.

2.4.3 Fluid loss controller with its limitation

The mud filter cake thickness is the indicator of filtration fluid loss. To achieve the low permeable wall filter cake, the fluid loss controller can provide reactive shale formation and wellbore stability. The most common fluid loss additive in water-based drilling fluids are bentonite and polymer. However, conventional fluid loss additives are limited in their performance; hence synthetic fluid loss additives have become more attention recently. Likewise, Aghdam et al. (2020) designed the acrylamide-based drilling fluid using the terpolymer (acrylamide, 2-acrylamide-2-methylpropane sulphonic acid, and 1-vinylimidazole) as a fluid loss controller. As a result, the terpolymer is a potential fluid loss controller in the water-based drilling fluid, performed at a high salt concentration and a high temperature.

Similarly, Ma et al. (2017) developed a zwitterionic copolymer as a fluid loss additive in a water-based drilling fluid, consisting of acrylamide, 2-acrylamide-2-methylpropane sulphonic acid, diallyl dimethyl ammonium chloride, and betaine-type monomer. This work also proved that the filtration loss properties of the zwitterionic copolymer are better than that of the commercial fluid loss additives (sulphonated bitumen, sulphonated phenolic resin, sulphonated lignite, sodium carboxymethyl cellulose, and compound ammonium salt). Due to the more cationic groups in zwitterionic copolymers, its copolymer dispersed in clay particles by absorption led to the formation of a dense filter cake with its lower permeability in the rheological performance of drilling. Davoodi et al. (2019) also compared the fluid loss additives with their performance between the acrylamide copolymer and the starch. As a result, the copolymer can become an alternative to conventional fluid loss additives since it can form a thin filter cake with its low permeability in the rheological properties of drilling.

Furthermore, nanomaterials also can produce denser filter cakes than conventional additives such as bentonite or polymer. Besides, commercial fluid loss additives, such as synthetic polymer, have poor rheological performance in high thermal, salinity, and hardness of fluid (Okon et al., 2020). Thus, the nanomaterials can be considered in drilling to be a competent fluid loss additive. For instance, Ma et al. (2021) developed a nanocomposite-based by using acrylamide, 2-acrylamide-2-methyl-1-propane sulphonic acid, N-vinylpyrrolidone, and graphene oxide, which showed the thinner and denser filter cake due to the increase of particle size of the nanocomposite.

2.4.4 pH controller with its limitation

In drilling fluid, the pH shall be controlled to avoid corrosion and bacterial growth that can prompt the degradation of certain additives (such as viscosifiers) and the synthesis of hydrogen sulphide. Conventionally, the drilling fluid must be maintained in the range of 8 to 10.5. The acidic condition fluid can cause material deterioration and corrosion of equipment. So, the standard pH range of drilling operations shall be followed as defined (Otitigbe, 2021). The basic condition of fluid can be controlled by using a pH controller, such as a basic compound consisting of carbonate and hydroxide ions (Elkatatny et al., 2018).

Soda ash is the most common carbonate-based pH controller in drilling. For instance, Medhi et al. (2019b) used soda ash as a pH controller in a salt polymer nanocomposite (which consisted of partially hydrolysed polyacrylamide, polyamine, and aluminium nanoparticles). This study showed that the rheological performance of salt polymer nanocomposite is better than bare polymer. Besides, Tchameni et al. (2021) designed an acrylamide-based tetrapolymer in drilling fluid using sodium carbonate, which is soda ash.

The most common hydroxide-based pH controller is sodium hydroxide. For instance, Hamad et al. (2020) used sodium hydroxide to adjust the pH of the drilling fluid consisting of multiple polymers (polyanionic cellulose, polyacrylamide, and amphoteric polymer). Furthermore, Tan et al. (2021) designed a zwitterionic copolymer in acrylamide-based drilling fluid by using sodium hydroxide as a pH controller. Similarly, An et al. (2016) used sodium hydroxide as a pH controller to synthesise the acrylamide-based copolymer. Their works also adjusted their pH to 7 – 8. However, Ahmad et al. (2020) developed a novel copolymer (N-vinyl caprolactam and acrylamide monomers) with a pH adjustment of up to 10. Besides, Shettigar et al. (2018) also developed a modified grafted polyacrylamide by maintaining the pH value of 9 using sodium hydroxide in a drilling fluid model. In short, the modified polyacrylamide drilling fluid must be maintained at a pH range of 7 – 10 to avoid an acidic environment that is harmful to the environment and society.

After the pH adjustment of the drilling fluid by the pH controller, the formation of by-products, such as hydrogen sulphide, oxygen, and carbon dioxide, can affect the rheological performance of the drilling fluid. However, it is still considered safe in water-based drilling, according to Aremu et al. (2017). As contained in drilling operations, this issue can be mitigated by hydrogen sulphide scavengers.

2.4.5 Lubricant with its limitation

The lubricant is used to control the drag, friction, and torque in a drilling design. The previous study showed that the lubricity of drilling fluid had been improved by 25 % with the modification of polyacrylamide using zinc oxide, which was studied by Aftab et al. (2016). Ismail et al. (2016) investigated the nanomaterials such as multiwall carbon nanotube, nano silica, and glass beads as lubricant additives in the polymeric-based drilling fluid that consist of polyanionic cellulose and partial hydrolytic polyacrylamide. It is revealed that the modified polymeric-based drilling fluid with those lubricants showed higher lubricity than the bare drilling fluid. Meanwhile, multiwall carbon nanotubes showed the highest reduction of coefficient of friction (44 %).

Furthermore, graphene oxide has been used as a lubricant in polyacrylamide fluid, which showed 46-55 % of friction coefficient reduction. This type of nanocomposite has formed with the lubricating nanolayers between two frictional surfaces (Kumar et al., 2015). Besides, the modified hydrophobic associated polyacrylamide with silica nanoparticles can enhance the reduction of lubrication coefficient (93.4 %) because the synergistic effect of silica nanoparticles and the distinctive properties of this polymer can promote the good drilling, cutting carrying capacity with lubricity function (Mao et al., 2015).

There is less explored on the reason influencing lubrication reduction coefficient, such as the polymer density, contaminant, temperature, and others, which are required to interrelate with the current modification polyacrylamide in drilling. Besides, the lubricity measurement results between the laboratory and site are inconsistent and different with the use of a standard lubricity tester. Thus, this is a limitation in identifying the lubricity of a drilling fluid (Aremu et al., 2017).

2.4.6 Hydrogen sulphide Scavengers with its limitation

Hydrogen sulphide (H_2S) diffusion is a problem in drilling operations that can harm human health and the environment. Additionally, a significant risk occurs when the drilling fluid has an uncontrolled pH environment. Besides, it also corrodes the subsurface of facilities in drilling. Thereupon, an H_2S scavenger is required to remove the toxic gas of H_2S when increasing pH (Ghayedi & Khosravi, 2020; Onaizi et al., 2020; Morgani et al., 2017). The common H_2S scavenger in water-based drilling fluid is zinc oxide due to the highly basic condition of water-based drilling fluid. Additionally, zincate ions can form in drilling fluid when its fluid pH is higher than a value of 11, which is effective in scavenging H_2S. However, an excess amount of zinc-based scavengers can also negatively impact the drilling performance, according to Onaizi et al. (2020).

Alternatively, the oxidising agent can be used to remove the H_2S in drilling fluid, which can form harmless sulphur compounds. Such as potassium manganate, hydrogen peroxide, potassium thiosulphate, and calcium hypochlorite. This approach has been used by several researchers nowadays. For instance, Onaizi et al. (2020) studied the comparison of H_2S scavengers between zinc oxide, copper nitrate, and potassium manganate in water-based drilling. Compared to the other H_2S scavengers applied to the bare mud, results revealed that potassium manganate is most conducive to scavenging H_2S and is more favourable to the rheological properties of water-based drilling fluid

Besides, the nanomaterials are the potential H_2S scavengers that can be utilised with their nanoscale's active surface to enhance the scavenging process. Morgani et al. (2017) investigated the effect of zinc oxide, titanium oxide nanoparticles, and zinc oxide/titanium oxide nanocomposite in H_2S removal for drilling operations. Compared to zinc oxide and titanium oxide nanoparticles engaged in drilling, zinc oxide/titanium oxide nanocomposite is the highest H_2S scavenging rate, with 99 % of its removal from 800 ppm to less than 5 ppm. Similarly, Sarno & Ponticorvo (2018) also designed 3 g of molybdenum disulphide/zinc oxide nanocomposite to remove H_2S (800 ppm) completely within 10 minutes. The result also showed that the time removal of H_2S by zinc oxide nanoparticles alone is completed within 60 minutes. According to the higher surface of this composite, the nanosheet structure of molybdenum disulphide and quasispherical nanoparticles of zinc oxide can promote higher absorption than those single nanomaterial surfaces. Hence, the involvement of nanomaterial in the H_2S removal is suggested with multiple nanomaterials to promote higher surface absorption.

In short, the conventional zinc-based H_2S scavenger is required to control due to its dosage in a formulation. Oxidising agents and nanomaterials can be used as H_2S scavengers in drilling formulation.

2.5 Drilling fluid with piling foundation

The pile formation depends on the foundation of construction that is used. The foundation is the medium via which building loads are carried from the superstructure to the ground in geotechnical and construction fields. The foundations can be divided into two categories: shallow foundations, and deep foundations (Srijaroen et al., 2021; Toprak et al., 2018). The foundation system leans on several factors such as location, type of structure, ground condition, construction equipment accessibility, installation effect on adjacent foundations, local construction practice, and the construction materials' availability and relative cost (Srijaroen et al., 2021). Shallow foundations can be built on soils with a strong bearing capacity and the ability to absorb the superstructure loads with a minimal settlement. However, a shallow foundation is unfeasible on the certain ground condition, where it will be weak when the bearing capacity is exceeded (Toprak et al., 2018). Consequently, the shallow foundation is inadequate to bear a heavy-load construction with imposed vertical and lateral loadings in the ground. As a result, a deep foundation is typically built with a piled foundation to overcome the low shear strength and high compressibility (Srijaroen et al., 2021). In summary, a shallow foundation can support a construction design with minimal load. However, a construction design with a heavy load can only be supported by a deep foundation.

The type of pile can be identified according to the construction method, where it can be divided into a driven pile and a bored pile, as summarised in Table 2.3. A driven pile is a displacement pile that can be used in a deep foundation system for a transportation project and installation in a group using an impact pile driving hammer (Hannigan et al., 2016). Boring is not required in its pile. Its structural capacity is high. The structural construction can be easily adjusted and spliced by using this kind of pile to overcome fluctuations in subsurface conditions in the foundation field. Besides, this pile has more vibration and is noisier during pile driving. Additionally, it is possible for corrosion to occur, which can cause poor piling performance. In brief, driven pile operations may be costly as the structural capacity in the foundation is high and easily corroded.

A bored pile is known as a drift shaft. It is commonly used in the foundation of high-rise buildings, offshore drilling platforms, transmission towers, and other structures (Zhang et al., 2019). For instance, Kuala Lumpur Twin Tower in Malaysia is one of the buildings examples that used the bored pile as its foundation. This kind of pile in the foundation field uses a casing or a circulating and stabilising material like bentonite slurry to construct the building piles in pre-bored holes. Subsequently, its bored hole is filled with concrete after reinforcement. Furthermore, it is suitable to be used for piles with long lengths. It has low vibration and noise during its pile formation, which makes it ideal for the development of an urban area. Besides, its constituent is simple, such as sand, gravel, water, cement, and others. However, it has issues regarding the poor inspection of concreting formation. Its drilling operations are affected when there is rainy weather or worse. In general, a bored pile is selected for the pile foundation in the drilling process due to its low noise and vibration during the construction of the foundation, as well as its pile suitability applied in a deep foundation. Besides, its pile length can be adjusted conveniently, making it suitable for use in residual soil (Chen et al., 2019). The following section will further elaborate on the information about bored pile drilling fluid and its operating mechanism.

Table 2.3: Advantages and disadvantages of the bored pile and driven pile.

Type of pile	Advantages	Disadvantages
Bored pile	-Suitable for large diameters and depths of the pile (Toprak et al., 2018). -The length of the pile can be extended. -Low vibrations and noise, which is beneficial when working in the city centre (Chen et al., 2019; Toprak et al., 2018) -The required material is easily accessible, for example, sand, gravel, water, cement, and reinforcement (Toprak et al., 2018).	-Non-displacement piles. -Inspection of concreting is not possible. -Rainy weather or worse condition hinders drilling operations (Toprak et al., 2018).
Driven pile	-Structural capacity is high. -Can be adjusted and spliced in the field to overcome variations in subsurface conditions (Hannigan et al., 2016). -Displacement pile.	-Corrosion is possible. -Vibration and noise during driving. -Cost is relatively high.

2.5.1 Bored pile drilling fluid

Historically, bentonite was the most prevailing material that was utilised in the construction of bored piles and diaphragm walls (Ejezie et al., 2021; Lam et al., 2015; Lam & Jefferis, 2016b). Negatively charged particles of bentonite can interact chemically with the positively charged water surface through electrostatic attraction forces as a result of its excellent swelling capacity (Ahmad et al., 2017; Barry et al., 2015; Gamal et al., 2019). It can absorb around 7 – 10 times more than its weight and swell up to around 18 times of its volume (Gamal et al., 2019; Temraz & Hassanien, 2016). Besides, it can form gelling agents when it reacts chemically with several organic materials. It is a well-known fluid loss controller and viscosifier in drilling fluid technology (Kusrini et al., 2018; Needaa et al., 2016). It can rapidly form a thin filter cake and minimise filtration due to the base fluid loss (Saboori et al., 2019). Further, the filter cake can be effectively used as the membrane to protect the borehole sidewalls due to its high density (Yoo & Han, 2019).

The synthetic polymer used in water-based drilling fluid has become popular for all types of ground in bored pile construction because it has benefits such as a lower site footprint, fluid mixing simplicity, and improved concrete sand interference resistance (Lam & Jefferis, 2016b; Yang et al., 2020; Yoo & Han, 2019). Normally, a pile foundation requires a space with a large diameter and length, which causes land space scarcity. The hair-shaped strand in synthetic polymer contributes to a smaller space compared to the plate-like one in bentonite clay (Lam & Jefferis, 2016b). Furthermore, the synthetic polymer slurry preparation in construction is simple and easy with a lower concentration, unlike bentonite, which needs separate slurry preparation with a high concentration (Shrivastava et al., 2016). Meanwhile, the synthetic polymer is eco-friendly as there is a proper waste disposal practice during drilling operations.

The synthetic polymer has a high molecular weight; hence, it is easily mixed during drilling operations. Then, it can be dissolved in water to form a non-Newtonian fluid for drilling slurry (Lam & Jefferis, 2016b). Due to this reason, its settling rate is faster than bentonite, which can lead to soil squeezing and stabilisation. Furthermore, it does not form a gel when there is negligible yield stress or a lack of disturbance (Lam & Jefferis, 2016b), and it also does not form a filter cake, unlike bentonite (Yoo & Han, 2019). However, it is not feasible to stabilise the excavation of coarse ground with the lower particle holding capacity and poor viscosity of the polymer drilling fluid. Due to this reason, the formation of a “soft toe” at the pile foundation is triggered by the excessive solid that increase collapse risk (Lam et al., 2015; Lam & Jefferis, 2018).

Over the last 30 years, synthetic polymer fluids have also been utilised successfully at geotechnical and building sites; however, the physical and chemical properties of the polymer fluids are not well understood (Ejezie et al., 2021). Even though innovative polymer for drilling fluid exists, it is still underutilised as there is a lack of deep knowledge regarding the polymer's interaction with in-situ soils (Yang et al., 2020). The industry-standard guidance and specifications for geotechnical and construction sites are also poor. It can be noted that none of the basic polymer properties detail was provided by the Institute of Civil Engineering (ICE) in the United Kingdom. Similarly, for European standards, there is no guidance on polymer usage in excavation. Further, it was only denoted as a possible medium for drilling. Other countries also experience a similar situation. Despite that, the American Association of State Highway and Transportation Officials (AASHTO), United States, provides some basic details with regard to the specified ranges of properties, such as density, viscosity, pH, and sand content. The specified ranges for each property of polymer are usually suggested by the material supplier (Lam & Jefferis, 2016b).

2.5.2 Bored pile drilling operations with its construction mechanism

The mechanism of the bored pile drilling operations is illustrated in Figure 2.3. Typically, the process starts with drilling before reinforcement insertion is carried out. Then, the concrete is cast and followed by the pile formation lastly. The drilling stage and the proper reinforcement stage require that each construction detail is followed accordingly before proceeding with the concrete casting and pile formation (Feng, 2021). According to Chen et al. (2019), there is an empirical method that is practised locally for bored pile design in residual soil. The empirical method uses the Standard Penetration Test (SPT-N) to assess the unit shaft friction in the subsoil. The empirical formula is shown in Equation (2.1) and (2.2) as below:

$$f_s = K_s N \tag{2.1}$$

$$f_b = K_b N \tag{2.2}$$

where f_s is the unit shaft friction in kPa, f_b is the base resistance in kPa, N is the standard penetration tests blow count, K_s is the empirical factor for shaft friction, and K_b is the empirical factor for base resistance.

The mobilised shaft friction (f_s) and the ultimate base resistance (f_b) for a pile constructed using polymer (PTP-1A) are higher than those of bentonite (PTP-1), as shown in Figure 2.4 (Chen et al., 2019). Chen et al. (2019) recommended polymer to be used as the stabilising fluid in drilling fluid rather than the usage of bentonite due to polymer's mobilised shaft friction and the ultimate base resistance performance. They also concluded that the empirical method for the polymer-based drilling fluid in bored pile foundation had the following limits in Equation (2.3) and (2.4):

$$f_s = 2\ N \leq 150\ \text{kPa} \tag{2.3}$$

$$f_b = 20\ N \leq 5000\ \text{kPa} \tag{2.4}$$

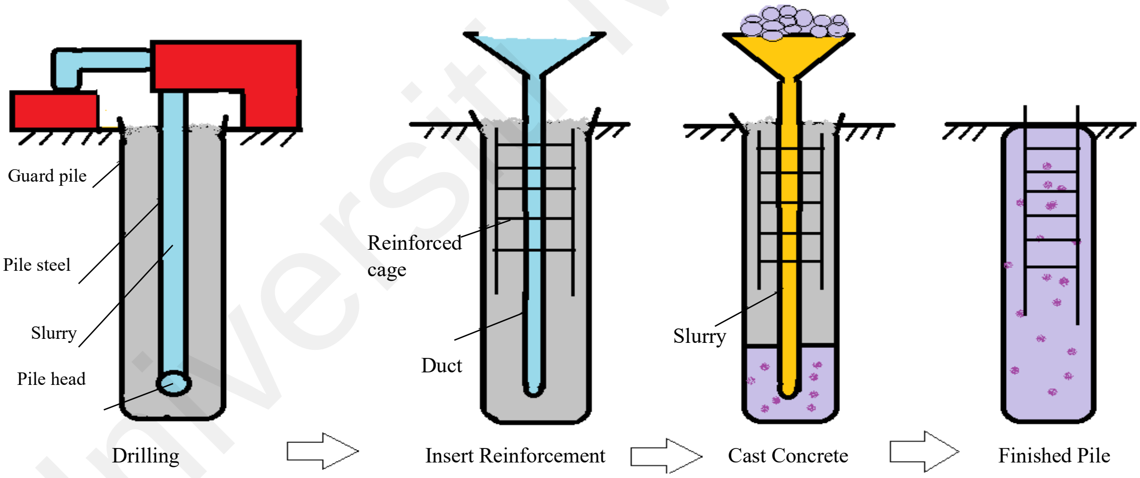

Figure 2.3: Mechanism of bored pile construction (Feng, 2021).

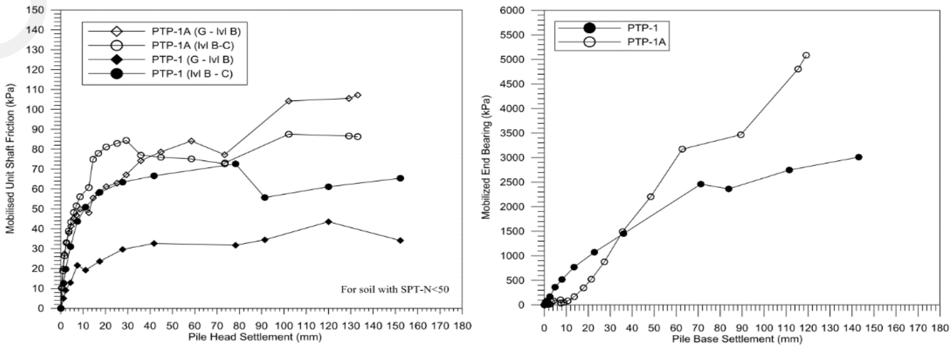

Figure 2.4: Mobilised unit shaft friction and mobilised base resistance according to Chen et al. (2019). Reprinted with permission Ref. from Chen et al. (2019). © 2019 Southeast Asian Geotechnical Society.

2.6 Polymer

The term ‘polymer’ is linked to ‘poly’, which denotes ‘many’ and ‘meros’. This word was invented in 1833 by Swedish chemist Jacob Berzelius, who explained the compound with very high relative molecular mass (Jensen, 2008; Sen et al., 2019). Generally, a polymer is a large molecule comprising a repeating structural unit known as a monomer, which is connected to each other through covalent bonds. In 1922, Hermann Staudinger defined them as “macromolecules” having many small molecules linked together to form long chains (AlMaadeed et al., 2020; Jensen, 2008; Sen et al., 2019). Polymer, such as oils, tars, resins, and gums, has been exploited in the last few centuries. This indicates the technical brilliance of polymer in daily life from the past till now.

2.6.1 Classification of polymer

Polymers can commonly be divided into two broad categories, which are natural polymers and synthetic polymers. Both natural and synthetic polymers are essential in various applications such as transportation, medicine, communication, and fashion to develop a comfortable lifestyle (AlMaadeed et al., 2020). For example, cables of electrical appliances, plastic utensils in the kitchen, car body design in transportation, and other applications have relied on polymer nowadays. This is due to the physical, mechanical, and chemical properties of the polymer. Due to their physicochemical properties, both types of polymers in the drilling industry can be utilised as filtration reduction and fluid loss additives. Details of both polymers and their application in drilling fluid technology will be discussed in the following section.

2.6.1.1 Natural polymer

The natural polymer was discovered when cellulose was extracted from natural plants around the 1810s (AlMaadeed et al., 2020; Sen et al., 2019). In the first industrial revolution, natural rubber production became commercialised for daily needs, such as shoes, gloves, and others. It prompted the development of vulcanisation in the nineteenth century. As a result, the durability improvement of existing natural polymer rubber was achieved to replace the older and established industries, such as the metal industry (AlMaadeed et al., 2020). Due to it being environmentally friendly and easily accessible, it was used in water-based drilling fluid systems in the past, for example, maleic anhydride derivative, polyacrylate, guar gum, xanthan gum, and cellulose. However, it is weak in terms of thermal stability and salt resistance in the drilling process, which leads to its higher construction cost (Huo et al., 2018).

2.6.1.2 Synthetic polymer

Around the 1900s, the first synthetic polymer, named bakelite, was invented by a Belgium chemist, Leo Baekeland (Sen et al., 2019). Then, synthetic polymers, such as plastic, fiberglass, nylon, and many other products, became common in modern society. In the drilling industry, synthetic polymer can act as a filtration reduction and fluid loss additive (Betiha et al., 2020; Ma et al., 2017), which leads to it being the preferred option compared to natural polymer since synthetic polymer has few significant advantages such as biodegradability, stability, water solubility, and economic efficiency (Huo et al., 2018).

Nevertheless, there are still issues with the traditional synthetic polymer, including high operating costs, low stability, high reactivity, and corrosiveness. Additionally, the high-temperature drilling operations can cause traditionally synthesised polymers to degrade easily. This situation can subsequently affect the rheological and filtration properties of the drilling fluid. The traditional synthetic polymer is unable to withstand a temperature of more than 150 ºC. Thus, drilling fluid technology and its performance can benefit from the improvement brought about by synthetic polymer in terms of temperature resistance and salt resistance (Huo et al., 2018). Furthermore, the modification of the polymer will be discussed in the following section.

2.6.2 Polymer in drilling fluid technology

Drilling fluid formulations are varied; some involve natural polymer, synthetic polymer, and their modification (Ahmad et al., 2018; Moghaddam & Saadatabadi, 2020). Additionally, the polymer modification can be in various forms such as copolymer, graft polymer, semi-synthetic (natural polymer with synthetic polymer), and others.

Starch, xanthan gum, and other biopolymers are examples of natural polymers used in drilling fluid technology. However, they have a limitation with regard to salt and temperature resistance (Ma et al., 2020). The most common natural polymer in drilling fluid is polysaccharides such as cellulose, starch, and guar gum (Ma et al., 2020; Ma et al., 2017). Nasiri et al. (2018) stated that starch was the most common in the drilling industry because of its solubility in water. Starch can also reduce fluid loss but its rheological performance is poor in HPHT conditions (Nasiri et al., 2018). Starch can minimise the thickness of the filter cake but its stability is low, causing its degradation easily in a drilling fluid model at a temperature higher than 115 ºC (Davoodi et al., 2019). Starch can be modified with a new additive like mono ethanol amine (MEA) to enhance the thermal stability of drilling fluid up to 160 ºC (Nasiri et al., 2018). Hence, natural polymer modification or synthetic polymer usage is an alternative source in drilling fluid technology.

Additionally, cellulose is one of the widely available natural resources that can be used in the drilling system. Its chemical composition contains many hydroxyl groups, which can be disrupted easily by many reactive functional groups. Methylcellulose derived from cellulose can form viscous fluid due to its hydrophobic properties but its mechanical strength is limited in drilling applications, where it is unable to meet the necessary drilling performance. Betiha et al. (2020) fabricated ionic liquid cellulose silica hydrogels by methylation of cellulose, which was followed subsequently by silica grafting of methylcellulose. This fabrication was optimised with proper thermal stability and good salt resistance through response surface methodology (RSM).

Huo et al. (2018) developed the polymer Poly(SSS/AM/AMPS) by using 2-acrylamido-2-methylpropanesulphonic acid (AMPS), acrylamide (AM), and sodium p-styrene sulphonate (SSS) through an inverse emulsion polymerisation process. This study investigated the thermal stability and rheological properties of the drilling fluid after the traditional synthetic polymer modification. As a result, this modified polymer can withstand a temperature of up to 160 ºC. Further, its rheological performance also improved as the values of Yield Point (YP), and Point Value (PV) met the requirement of the American Petroleum Institute (API) standard based on Figure 2.5. As the modified polymer concentration increased, the AV and PV also increased significantly. That was why the adsorption effect of this modified polymer was improved due to the huge number of non-ionic amide and sulphonic acid groups. Subsequently, the clay particles were easily dispersed in the drilling fluid (Huo et al., 2018; Ma et al., 2017). Thus, the rheological properties of drilling fluid can be enhanced through the modification of the polymer.

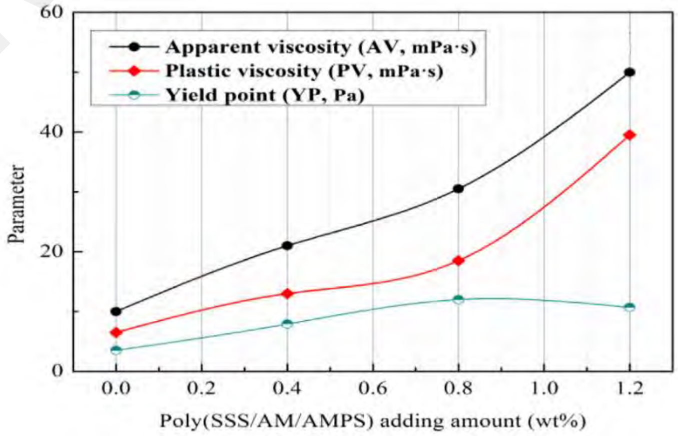

Figure 2.5: The rheological profile of the modified synthetic polymer by Huo et al. (2018). Reprinted with permission Ref. from Huo et al. (2018). © 2018 Elsevier.

Chami et al. (2021) modified a graft polyacrylamide using xanthan through a microwave-assisted graft copolymerisation process. The viscosity losses of the graft polymer were better controlled than that of the natural polymer (xanthan) due to the resistance in a saline environment at a temperature of 65 ºC. Thus, the limitation of the natural polymer is with regard to the temperature. Furthermore, Saboori et al. (2018) developed the carboxyl methylcellulose/polystyrene core-shell nanocomposite through a miniemulsion polymerisation process. A comparison in terms of filtration and rheological properties was investigated between the three additives, which were carboxyl methylcellulose, nano carboxyl methylcellulose, and core-shell nanocomposite. The mud cake thickness of the nanocomposite (30 - 60%) was significantly reduced when compared to the conventional nano carboxyl methylcellulose (20 - 50%). Fluid loss for the three different additives had a sharp declining trend, especially when 6 g of additive was added to each drilling fluid system. Meanwhile, there was an insignificant change in mud weight and pH for all three additives. From these results, it can be noted that the thickness of polymer nanocomposite is thinner than that of bare polymer, which leads to better filtration properties.

Although natural polymer can be used as a fluid loss additive similar to synthetic polymer, modified synthetic polymer exhibits higher thermal resistance and salt resistance than natural polymer (Mao et al., 2020a). For instance, Davoodi et al. (2019) reported that copolymer synthesis could produce reliable results at high-pressure-high-temperature conditions. Vinyl sulphonates-based polymers and acrylamide-based polymers are common examples of fluid loss control additives among synthetic polymers. Likewise, Mao et al. (2020a) developed an anionic polymer that consisted of acrylamide (AM, 99%), N-vinyl-2-pyrrolidone (NVP, 99%), 2-Acrylamido-2-methylpropane sulphonic acid (AMPS, 98%), and 2,2'-Azobis (2-methylpropionamide) dihydrochloride (AIBN, 97%) through a radical polymerisation process. The fluid loss test on this drilling system found that anionic polymer can resist about 4.5 x 105 ppm of Cl^-, 4 x 105 ppm of Ca^{2+}, and 1.5 x 104ppm of Mg^{2+} at low pH by adding the acidic gas together at 180 ºC. Thus, it can withstand the temperature of drilling fluid up to 180 ºC.

In addition, the method of polymerisation affects the filtration and rheological properties of the drilling fluid. The inverse emulsion polymerisation method had better performance in terms of solubility (4 times better dissolution rate), salt tolerance (Na^+ and Ca^{2+}), as well as rheological and filtration properties when compared to the solution polymerisation method (Ma et al., 2020). Similarly, Li et al. (2020) stated that the multicopolymer can act as a filtrate reducer. They invented the anionic terpolymer for drilling fluid, which involved synthesising with N, N-Dimethylacrylamide (DMAA), p-styrene sulphonate (SSS), and itaconic acid (IA) through a watery solution free-radical polymerisation process. Based on their investigation, 1.5 wt% multicopolymer in drilling fluid contributed to 17.0 and 35 ml of filtrate loss volume after the thermal rolling test of API and HTHP, respectively, at 240 ºC for 16 h. Furthermore, the anionic terpolymer in drilling fluid exhibits interactions among the sulphonic group, dicarboxylic group of polymers, and salt ions (Ca^{2+} and Na^+). In short, anionic terpolymer addition can enhance the anti-high temperature performance and salt resistance of drilling fluid. Therefore, polymer modification in drilling fluid technology is required as there are few limitations in using unmodified natural and synthetic polymers.

2.7 Polyacrylamide (PAM)

Polyacrylamide is a water-soluble polymer that is known as a ghost crystal. It is a synthetic linear, cross-linked structure, a mixture of acrylamide and acrylic acid, typically using N.N'-methylenebisacrylamide (Kanna et al., 2017). It is an excellent thickening agent involved in water solubility, chemical flooding, plugging agents, and others (Lyu et al., 2019). Further, it is the most common flocculant in wastewater treatment (Shaikh et al., 2021). It is also commonly used in pulp and paper manufacturing, agriculture, food processing, and mining (Lyu et al., 2019). It degrades thermally between 175 and 300 °C and can also be photodegraded (Europe et al., 2005).

In general, the appearance of polyacrylamide is in white colour. It is in the form of dry granular powder and can be used to form a liquid emulsion that disperses at a speedy rate (Lam & Jefferis, 2014). Its solid content is >90% and is insoluble at 0.3%. Its bulk density is 780 kg/m^3. Its degree of hydrolysis is 35 to 40%. The pH for a 0.2% solution is 7 to 8. The superabsorbent gel particles in cross-linked polyacrylamides can restrain the high losses in the coarse ground during drilling operations (Ejezie et al., 2021; Lam & Jefferis, 2014). Hence, it is an earth-stabilising fluid that is designed for a variety of applications in the geo-construction industry, such as tieback anchors, diaphragm walls, horizontal drilling, tunnelling, slurry trenching, drilled shafts/bored piles, and others.

2.7.1 PAM in drilling fluid technology

A good drilling performance depends on the rheological properties. The polymer selection and its concentration in the drilling system are interrelated with the pumping cost and the cutting effect in the drilling operations mechanism (Mudaser et al., 2021). Besides, plastic viscosity allows it to practically meet the high drilling rates required to avoid pumping difficulties and the increasing energy consumption in the drilling operations. The lower molecular weight of the polymer allows a suitable and reasonable viscosity to be determined in the drilling study (Magzoub et al., 2021). The polymer with higher concentration can obstruct the drilling cutting, which increases the pumping cost (Mudaser et al., 2021). However, polyacrylamide with high molecular weight can be a good candidate at lower concentrations to meet the drilling requirements. The viscosity of polyacrylamide at all concentrations decreases with increasing temperature, according to Magzoub et al. (2021). This situation can lead to poor fluid loss due to increased temperature applied to the drilling fluid (Ahmad et al., 2018). There have been reported by various studies on polyacrylamide-based drilling fluid, including its modification and improvement, in recent years.

Magzoub et al. (2021) utilised the anionic polyacrylamide-based drilling fluid that was formed by a polymerisation process of acrylamide monomer. This polymerisation also involved a bifunctional crosslinking agent, polyethyleneimine (PEI). PEI was used as a loss circulation treatment for polymer-based mud, but PEI was not a good viscosifier due to its slight increase in viscosity performance in this study. Thus, crosslinker such as PEI is inefficient in the rheological study. Meanwhile, Magzoub et al. (2021) also studied the addition of bentonite and aluminium acetate as crosslinker agents in the polyacrylamide-based drilling fluid, which can enhance the gel strength and plastic viscosity to improve the carrying capacity and hole-cleaning capability of the polymer-based mud. The result showed that the gel strength of bentonite was insignificant when low concentrations of bentonite (0.5 to 1 wt%) were used after the crosslinking between aluminium acetate and 7.0 wt% polyacrylamide drilling fluid at a pH of 5 (Magzoub et al., 2021). Flocculation of fine bentonite particles may occur when cationic polyacrylamide is added to the drilling fluid because of the charge in polyacrylamide. Moreover, its flocculation can cause its particles to form an open and loose network, which consequently increases filtration and lowers the performance of bentonite (Needaa et al., 2016). Furthermore, the mixing order is crucial for most drilling fluid additives. The polymer should be mixed first before the addition of bentonite later, as this order will affect the hydration of bentonite (Magzoub et al., 2021). In brief, a crosslinking agent such as aluminium acetate is ineffective in terms of drilling performance. Additionally, the mixing order of the additive becomes a concern in the drilling study.

Similarly, Xie et al. (2021) enhanced hydrophobic polyacrylamide using polyethyleneimine (PEI) as a crosslinker. It was synthesised through a micellar copolymerisation process involving HMP of acrylamide, 2-acrylamide-2-methyl propane sulphonic acid, and octadecyl acrylate. The crosslinker-PEI in this polymer drilling fluid exhibited better gel strength, elasticity, and thermal stability at 140 ºC. When the crosslinker concentration was 1.2 wt%, its gel samples had the strongest gel strength. In conclusion, a stronger gel strength depends on the concentration of the cross-linking agent, which leads to a lower loss of volume.

Hamza et al. (2021) stated that mud-weight window shrinkage is a problem when there are high-pressure and high-temperature conditions, exhausted reservoirs, and fractured formations. This situation is due to the lost circulation, which increases drilling operations costs. Hence, the polymeric formulation has been employed as lost circulation materials for wellbore enhancement in drilling. For instance, the polyacrylamide-based drilling fluid can be incorporated with an organic and inorganic crosslinker. Hamza et al. (2021) utilised aluminium acetate as the crosslinker in the polyacrylamide drilling fluid. Since the inorganic crosslinkers are pH sensitive and can readily form a gel at low pH, the acetate group is the optimum chemical group for enhancing gelation and retardation effect. Besides, the aluminium-based crosslinker is environmentally friendly compared to toxic chromium acetate. Research results showed that the size reduction of aluminium acetate particles could enhance the drilling fluid significantly. In addition, it sped up the gelation process of a 7 wt% polyacrylamide-based drilling fluid to 17 minutes when its temperature was at 75 ºC, and pH was at 5. Thus, the crosslinker agent in polyacrylamide-based drilling fluid can improve its gelation performance.

The polymer has a shear-thinning property. This property is known as thixotropy, which can be a problem when the polymer is used in drilling fluid. Alizadeh et al. (2015)

improved the polyacrylamide by synthesising alumina/polyacrylamide nanocomposite through a solution polymerisation process. As a result, the viscosity of the drilling fluid was more than 300 cP for freshwater mud at 4 wt% and about 100 cP for saltwater mud at 2 wt%, respectively. After adding nanoparticles to both fresh and saltwater-based mud, the thixotropic rate was reduced by more than 5%. Thus, nanocomposite polymer can improve the thixotropic behaviour of drilling fluid.

Jain et al. (2015) developed a polyacrylamide-grafted-polyethylene glycol/silica nanocomposite-based drilling fluid through a free radical polymerisation process using potassium persulphate. Compared to drilling fluid based on bare partially hydrolysed polyacrylamide polymer (PHPAs), its nanocomposite-based drilling fluid had lower formation damage, higher shale recovery, and higher thermal stability. The low damage was due to the high return permeability value (74%). In nanocomposite-based drilling, the high shale was formed due to the increased shale recovery rate (87 to 97.4%). Meanwhile, its shale inhibition can be enhanced significantly through the effect of K^+ ions, polyacrylamide, and glycol molecule in the drilling system. When thermal testing was carried out between 200 and 300 ºC, the weight loss of polymer nanocomposite (16%) was lower than that of the partially hydrolysed polyacrylamide (49%). This implies that the thermal stability of polymer nanocomposite is higher than that of the bare polymer due to the dispersed silica nanoparticles in the modified polymer.

The most suitable polymer for borehole stabilisation and shale encapsulation is partially hydrolysed polyacrylamide. At the wellbore, its stability problem can be alleviated by using polyacrylamide to form a thin film cake that acts as a filter membrane. Moreover, shale inhibitors such as Polyethylene glycol (PEI) can constrain shale in drilling operations. Based on the molecular study of glycol molecules, its cloud point effect inhibits the hydrogen bonding between the water and shale surface. It can disrupt the hydrogen molecule from interacting with water, which inhibits the shale surface. To optimise the shale inhibition performance in drilling operations, the silicate mud systems can trigger the protective film formed on the shale surface through the reaction between potassium salt and silica particles. This situation can prohibit the entry of solid particles and filtrate of drilling fluids from going into the micro-pore of shale. Therefore, the appearance of nanoparticles in the composite can enhance the shale inhibition performance of drilling fluid (Jain et al., 2015). In conclusion, synthetic polymers and nanoparticles can enhance rheological properties, mechanical strength, and thermal stability as both components have synergistic performances in drilling operations.

2.8 Functionalised material as potential dopants in drilling fluid technology

2.8.1 Functionalised material in drilling fluid technology

Functionalised material is conducive to various applications, especially in science and technology explorations. Unlike other industries, functionalised material usage in drilling technology is not an exception to the norm in the last few years. The functionalised particle size and shape can influence the fluid loss package, which can affect the fluid-rock interaction in the drilling system (Belayneh & Aadnøy, 2016). Thus, functionalised particle is the most promising material for drilling fluid that is designed with tailor-made properties to achieve the necessary downhole environmental requirement (Vryzas & Kelessidis, 2017).

Correspondingly, it is suggested that polymer with thermo-thickening properties can be used to regulate the viscosity and structure of drilling fluid, although this form of polymer has low thermal stability, according to Xie et al. (2018). There is a concern that the low thermal stability of polymer can lead to the degradation of polymer and high cost of the process. Therefore, SiO_2 particles are recommended to be implemented in drilling fluid technology to enhance further the thermal stability of the drilling fluid

(Vargas et al., 2019). Several functionalised particles in drilling fluid were investigated by several researchers, which are summarised in Table 2.4.

2.8.1.1 Carbon nanotubes

Anoop et al. (2019) studied the rheology properties of colloidal suspension, which was derived from carbon nanotubes (CNT) in water-based drilling fluid, at ambient conditions (P: 170 mPa; T: 180 ºC). They found that the addition of CNT to the drilling fluid can increase its viscosity as shown in Table 2.4. This can make the fluid particles become more stable and homogeneous, where the CNT chains will be linked with the drilling fluid. However, there will be an agglomeration effect if there is further addition of functionalised particles due to the long chains of the functionalised particles, even for the separation of water from the drilling fluid (Anoop et al., 2019).

Ismail et al. (2018) investigated the lubricity and rheology of a drilling fluid that used multi-walled carbon nanotubes derived from carbon nanotubes (CNT). This study revealed that the coefficient of friction increased from 38% to 59% before heating, which improved the lubrication behaviour of the drilling fluid. Additionally, the rheology properties of drilling fluid improved in terms of plastic viscosity, yield point, and fluid loss as detailed in Table 2.4. In short, the rheological performance of CNT-based drilling fluid can be enhanced up to a particular maximum concentration of CNT.

2.8.1.2 Zinc oxide

AlBajalan & Haias (2021) evaluated a conventional water-based drilling fluid by adding zinc oxide into drilling fluid model. This study showed that the plastic viscosity decreased when the zinc oxide increased because of the distribution of zinc oxide particles in the drilling fluid, which minimised the internal friction force between the particles. This can enhance the drilling fluid’s rheological characteristic, which contributes to the borehole cleaning and drill cutting suspension as the decrease in viscosity leads to a thin filter cake. Furthermore, Aftab et al. (2016) improved the rheological performance of composite acrylamide-based drilling fluid by adding zinc oxide, as detailed in Table 2.4. They also concluded that the shale swelling properties could be enhanced at elevated temperatures.

The yield point also declined when the zinc oxide concentration increased. Hence, its high fluid density can result in a larger decline in the yield point. Additionally, the fluid loss of drilling fluid decreased over 30 minutes when different concentrations of zinc oxide were used in the drilling fluid. The permeability of fluid was reduced when there was a reduction in the filtration volume. In short, the addition of zinc oxide in water-based mud results in better improvement than bare mud, which is 0 wt% of zinc oxide in drilling fluid. To enhance the hole-cleaning efficiency of drilling mud, Salehnezhad et al. (2018) optimised the mud formulation using zinc oxide. Thus, the zinc oxide amount influences the rheological parameter. The summary of this study is shown in Table 2.4

2.8.1.3 Zeolite

Ozkan & Ozkan (2019) studied the impact of adding clinoptilolite-rich zeolite to the water-based drilling fluid. This study's result revealed that the rheological properties increased in terms of plastic viscosity (from 18 to 24 cP), yield point (from 24 to 39 lb/100 ft^2), and apparent viscosity (from 30 to 43.5 cP) when there was increasing clinoptilolite-rich zeolite concentration from 0 w/v to 7 w/v %, as summarised in Table 2.4. However, there was a reduction in filtration volume from 10 mL to 7 mL, while the thickness of the filter cake increased from 0.16 to 0.65 mm. The filtration loss can affect the cost and drilling operations time since the thick filter cake can cause a tight borehole, which damages the rig pump pressure. Thus, lowering the filtration loss of drilling fluid is necessary for cost minimisation in drilling operations.

2.8.1.4 Other functionalised material

Aftab et al. (2020) developed a TiO_2 functionalised particles-bentonite, which was added to the drilling mud. The functionalised particles involved in drilling fluid exhibited better lubricity than conventional drilling fluid without additives. It can also help to keep the thin layer of mud cake and clay intact with shale swelling. This is due to the surface mechanism of the functionalised particles in the drilling fluid. Sadeghalvaad & Sabbaghi (2015) synthesised the TiO_2 functionalised particles-polyacrylamide-based drilling fluid. This study revealed that the rheological performance is improved after the addition of TiO_2. Similarly, Parizad et al. (2018) enhanced the rheological performance of polymer-based drilling fluid by adding TiO_2, as detailed in Table 2.4.

Li et al. (2018) also studied cellulose nanocrystals (CNCs) in the drilling fluid. The filtration and rheological properties of carboxylated CNCs were more effective than the cationic CNCs. This can be observed from the thickness of the filter cake and the filtration rate in the comparison between 0.5 wt% cationic CNCs (thickness: 0.75 m; filtration rate: 14 x 10^{-3} cm^3/s) and 0.5 to 2 wt% carboxylate CNCs (an increase of the thickness: 0.12 - 0.20 m; a reduction of filtration rate: 7 x 10^{-3} to 5 x 10^{-3} cm^3/s). In short, the surface characteristic of the functionalised particle is the factor that contributes to the development of lower solid content in the drilling fluid, according to Li et al. (2018).

Furthermore, the composite drilling fluid is also sensitive to temperature and pressure. Barry et al. (2015) synthesised a drilling fluid that included iron-oxide functionalised particles. The fluid loss was reduced at low temperatures and low pressures, as well as at high temperatures and high pressures. This situation is attributed to the alteration of the clay structure in the drilling fluid. Similarly, Needaa et al. (2016) experimented with sepiolite in drilling mud design. Sepiolite can improve the rheological properties, including yield point, plastic viscosity, and bored pile stability, regardless of whether fresh water or brine-based mud was used during drilling operations. At reservoir pressure and temperature, it also lowers fluid loss and reduces the permeability of drilling fluids.

Huang et al. (2021) investigated laponite in the drilling fluid. There is an incline of apparent viscosity, yield point, and gel strength but the plastic viscosity was not influenced significantly when the concentration of laponite increased. Besides, its fluid loss declined from 22.8 mL to 13.2 mL when its laponite concentration increased from 0 to 2 wt%. Similarly, Xiong et al. (2019) also studied the impact of laponite applied in drilling fluid. It was observed that the 2 wt% laponite dispersion showed well thickening properties at high temperature, which was demonstrated the fluctuation of apparent viscosity in the range 22 – 24 mPa.s happened when its drilling temperature is increased from 200 to 240 °C.

However, it has poor salt resistance but is relatively better than clay, as highlighted by Xiong et al. (2019). Ahmed et al. (2020) enhanced the rheological performance of drilling mud by adding garamite. They found that the addition of garamite can stabilise drilling operations by reducing the sagging effect. Additionally, the optimised dosage of garamite (1.25 g) improved the rheological properties as observed in the incline of yield point and yield point/plastic viscosity ratio with the reduction of filtration volume and filter cake thickness, as detailed in Table 2.4. Similarly, Mohamed et al. (2020) studied the addition of 3 lb/bbl perlite to improve water-based drilling mud's rheological performance, which showed a similar trend as Ahmed et al. (2020).

Table 2.4: Utilisation of various functionalised materials in drilling fluid by previous researchers.

Type of functionalised material	Purpose of research	Percentage of functionalised material	Parameter	Findings	References
Carbon nanotubes	Study the rheology of water-based drilling fluid at high pressure and high temperature.	0.027 – 0.22 wt%	Viscosity, thermal stability	- With 0.22 wt% carbon nanotubes loading, the viscosity values increased fivefold when compared to that of base mud at ambient condition (170 mPa; 180 ºC).	Anoop et al. (2019)
	Enhancement of lubricity and rheological properties of water-based drilling fluid	0.01-0.04 ppb	Plastic viscosity, yield point, fluid loss, coefficient of friction	- There was a marginal increment in plastic viscosity, especially at a concentration of 0.02%. - Before heating, the yield point showed unusual behaviour with fluctuating data when increasing the concentration of carbon nanotubes. After heating, the yield point increased from 36 to 42 lb/100 ft^2 when the concentration of carbon nanotubes increased from 0.01 to 0.03%. - Filtrate volume increased with a longer time retention. The addition of carbon nanotubes in drilling fluid resulted in lower filtrate volume than that of base mud. This can prevent swelling in the shale formation. - Addition of carbon nanotubes resulted in the reduction of the coefficient of friction from 38 to 59% before heating. The trend changed to increasing after heating as the carbon nanotubes were dispersed at high temperature.	Ismail et al. (2018)

Table 2.4, continued.

Zinc oxide	Rheology and mud filtrate properties	0.25 – 1 wt%	Plastic viscosity, yield point, mud filtration	- The plastic viscosity and yield point decreased when concentration increased from 0.25 to 1 wt%. - The mud filtration volume was reduced by 30% when concentration increased from 0.25 to 1 wt%.	AlBajalan & Haias (2021)
	Efficiency of drilling hole cleaning	0.1 – 1 wt%	Yield point, plastic viscosity, shear-thinning, consistency index, flow behaviour index	- The optimised mud's yield point (YP) was about 66.08 mPa, plastic viscosity (PV) was about 3.44 mPa.s, shear-thinning characteristic (YP/PV) was about 19.43 mPa/mPa.s, consistency index (K) was about 45.56 mPa.s, and flow behaviour index (n) was about 0.48.	Salehnezhad et al. (2018)
	Rheological performance zinc oxide in acrylamide-based drilling fluid	0.028 – 0.28 w/v %	Yield point, gel strength, filter cake thickness, shale swelling	- Incline of yield point from 7 to 12.8 Pa at 150 F when the addition of zinc oxide from 0 to 0.28 w/v %. - Incline of 10-min gel strength insignificantly from 4 to 5 Pa when concentration increase from 0.25 to 0.28 w/v %. - Filter cake thickness reduced from 0.97/32 to 0.90/32 inches after addition of zinc oxide. - Improvement of shale swelling behaviour at the elevated temperature condition.	Aftab et al. (2016)

Table 2.4, continued.

Zeolite	Rheology properties	0 – 7 w/v %	Plastic viscosity, yield point, apparent viscosity, filtration loss, cake thickness	- The effect of zeolite addition in drilling mud increased plastic viscosity by 33%, apparent viscosity by 45%, and yield point by 62.5%. - The filtration loss decreased, and mud cake thickness increased with the addition of zeolite with increasing concentration into the drilling fluid.	Ozkan & Ozkan (2019)
TiO_2	Enhancement of lubricity	0.1-1g	Lubricity	- 0.8 g titanium oxide functionalised particles-bentonite was added in 350 ml drilling mud, and the lubricity performance was 35%.	Aftab et al. (2020)
	Enhancement rheological performance	0 – 0.2625 lb/bbl	Yield point, shale recovery consistency index, flow behaviour index	- The rheological properties are affected after the concentration of titanium oxide increased as below: - Incline of yield point. - Decline of filtration volume by 26 % in HTHP and 27 % in LPLT. - Shale recovery increased by 97.2 %. - Incline of the consistency index by 300 % and decline of flow behaviour index by 22 % after 2.625 lb/bbl TiO_2.	Parizad et al. (2018)
	Enhancement rheological performance on water-based drilling fluids	2 – 4 w/v %	Viscosity, fluid loss, thickness of filter cake	- Viscosity, plastic viscosity and yield point increased when the concentration of titanium oxide increased. - Decline of fluid loss by 81 % from 53 to 10 ml. - Decline of filter cake by 63 % from 1.58 to 0.58 mm.	Sadeghalvaad & Sabbaghi (2015)

Table 2.4, continued.

Cellulose nanocrystals	Enhancement of rheological and filtration properties	0.5 – 2 wt% carboxylate CNCs; 0.5 wt% cationic CNCs	Filtration, thickness of filter cake, filtration	- The thickness of the filter cake and the filtration rate in the comparison between 05 wt% cationic CNCs (thickness: 0.75 m; filtration rate: 14 x 10^{-3}cm^3/s) and 0.5 to 2 wt% carboxylate CNCs (increase of the thickness: 0.12 – 0.20 m; reduction of filtration rate: 7 x 10^{-3} to 5 x 10^{-3} cm^3/s). - CNCs with two unique surface characteristics (cationic carbon nanotubes with anionic carboxyl content of 0.18 mmol/g and carboxylated carbon nanotubes with cationic 2,3-epoxypropyl trimethyl ammonium chloride (EPTMAC) content of 0.43 mmol/g) were considered. Both can be used as modifiers.	Li et al. (2018)
Sepiolite	Enhancement of fluid loss and sandstone permeability	0.2 – 2.5 w/v %	Yield point, plastic viscosity, fluid loss, permeability	- The addition of sepiolite functionalised particles can improve the plastic viscosity and yield point. - The addition of sepiolite functionalised particles can minimise the fluid loss of bentonite-based mud by 15% at reservoir temperature and pressure. - The sandstone permeability of drilling mud can be decreased by adding sepiolite functionalised particles. As a result, its permeability was lower than that of mud without sepiolite functionalised particles by 23.4%.	Needaa et al. (2016)

Table 2.4, continued.

Iron-oxide	The ability to withstand low-temperature low-pressure (LTLP) and high temperature high pressure (HTHP)	0.5 wt%	Fluid loss, thermal stability	- The experiment was conducted with low temperature low-pressure (LTLP: 25 ºC, 6.9 bar) and high-temperature high-pressure (HTHP: 200 ºC, 70 bar), where it was shown that the fluid loss reduced as much as 37% and 47%, respectively.	Barry et al. (2015)
Laponite	The effect of laponite in water-based drilling fluids	0 -2 wt%	Apparent viscosity, yield point, gel strength, fluid loss	- Adding laponite into drilling fluid led to better rheological properties as below: - No significant to plastic viscosity in range 3-5 mPa.s - Increment of apparent viscosity from 6 to 34 mPa.s. - Increment of yield point from 2 to 27 Pa. - Increment of 10 s-gel strength (1 to 25 Pa), and 10 minutes-gel strength (4 to 47 Pa). - Decline of fluid loss from 22.8 to 13.2 mL.	Huang et al. (2021)
	Investigation of laponite in mud-making for drilling application	0.5 – 2.5 wt%	Apparent viscosity, thermal resistance, salt resistance	- With 2 wt% laponite loading, the apparent viscosity showed fluctuation in the range 22 – 24 mPa.s when the aging temperature increased from 200 to 240 °C. - Salt resistance of laponite showed better than that of other clays (attapulgite, sepiolite and sodium bentonite), but it is still poor salt resistance.	Xiong et al.(2019)

Table 2.4, continued.

Garamite	Study of garamite in drilling mud	0 – 1.5 g	Yield point, yield point/plastic viscosity (YP/PV), filtration volume, filter cake thickness	- The optimised dosage of garamite in drilling fluid led to better rheological performance as below: - Increment of yield point by 152 % from 19 to 48 lb/100 ft^2. - Increment of yield point/plastic viscosity ratio by 102 % from 1.34 to 2.71. - Decline of filtration volume by 8 % to 3.4 cm^3. - Decline of cake thickness by 16 % from 2.69 to 2.26 mm.	Ahmed et al. (2020)
Perlite	Study of perlite in water-based mud	3 lb/bbl	Yield point, yield point/plastic viscosity (YP/PV), filtration volume, filter cake thickness	- The perlite in drilling fluid led to better rheological performance as below: - Increment of yield point by 70 % from24 to 41 lb/100 ft^2. - Increment of yield point/plastic viscosity ratio from 1.31 to 2.58. - Decline of filtration volume by 64 % from 6.7 to 2.4 cm^3. - Decline of cake thickness from 4 to 2.7 mm.	Mohamed et al. (2020)

2.8.2 Functionalised SiO_2-based composite in drilling fluid technology

The functionalised particles used in drilling fluid can minimise the cost of the operations. At the time of this study, the SiO_2-based composite is still a relatively new technique in drilling fluid technology. Herein, Table 2.5 shows various studies that are related to SiO_2-based composite. Inturi et al. (2019) investigated PAM with functionalised SiO_2 using SDS. The rheological performance was changed significantly after the addition of SiO_2 to PAM-based drilling fluid, such as the fluid viscosity reduction by two orders of magnitude. Mohd Saparti et al. (2018) designed a water-based drilling fluid with the functionalised SiO_2. This study demonstrated the filter cake thickness becoming thinner after adding hydrophobic functionalised SiO_2. However, the filtrate volume also improves with the fluid loss reduction at 25 % and 44 % after using hydrophilic and hydrophobic SiO_2, respectively. Thus, the low permeability in drilling fluid can lead to better fluid loss control after adding hydrophobic functionalised SiO_2. Corredor-rojas et al. (2018) also investigated the modified PAM and xanthum gum with the functionalised SiO_2. The viscosity of the polymer was decreased after the addition of functionalised SiO_2 as a cross-linker between the polymer chains. Unmodified functionalised SiO_2 was unable to mitigate the viscosity reduction when temperature increased. Similarly, Al-Yasiri et al. (2019) also enhanced the rheological performance of xanthan-based drilling fluid after the addition of functionalised SiO_2, as detailed in Table 2.5. It resulted in the improvement of swelling inhibition by using composite fluid.

Kumar et al. (2020) studied the stability of functionalised SiO_2 in PAM-based drilling fluid with a saline environment. The result revealed a maximum pH value of 8 with 2 wt% of SDS in that drilling fluid maintained loading up to 3 wt% NaCl. They concluded that the viscosity reduction is due to the salt involvement in that drilling fluid. Minakov et al. (2019) studied the effect of functionalised SiO_2 added to the drilling fluid. This study can observe that the functionalised particles can influence the filtration loss value. At 1.0 wt% silicon oxide, there is a maximum reduction of filtrate loss decrease from 42 to 25 ml shown in Table 2.5. There is a 40 % decrease from the original value. According to Minakov et al. (2019), the addition of functionalised particles also influences the filter cake thickness with its surface structure. Thus, the pore formation in the filter cake after the addition of functionalised particles can promote filtrate loss reduction. Besides, Afolabi et al. (2017) optimised the rheological properties of the drilling fluid by using SiO_2 particles in drilling fluid technology via response surface methodology (RSM). Moreover, they studied the shear stress limit of 1.5 wt% SiO_2 particles that were treated with 6.3, 13, and 15 wt% bentonite mud, and the results were 22.27, 72.62, and 171.3 Pa, respectively.

Table 2.5: Utilisation of SiO_2 by previous researchers.

Purpose of research	**Percentage of SiO_2**	**Parameter**	**Findings**	**References**
Study of stability and viscosity of nanosilica fluid in saline environment	0 - 2 wt%	Viscosity	- Nanosilica fluid with a maximum pH value of 8 and 2 wt% SDS concentration maintained loading up to 3 wt% NaCl. - Viscosity was reduced due to salt inclusion.	Kumar et al. (2020)
Enhancement rheological properties of polyacrylamide-based drilling	0-1.5 wt%	Fluid viscosity	- Fluid viscosity was reduced to two orders of magnitude after adding functionalised particles.	Inturi et al. (2019)
Study rheological behaviour between bentonite-based and bentonite/xanthan based drilling with their modifications	0.28 w/v%	Apparent viscosity, plastic viscosity, yield point, gel strength	- The rheological of bentonite-based drilling fluid improved after the addition of SiO_2 as below: The incline of apparent viscosity (from 6.5 to 7 Pa.s), yield point (from 2.5 to 4 Pa), 10 s-gel strength (from 6 to 8 Pa) and 10 minutes-gel strength (from 14 to 16 Pa) after addition of SiO_2. But it has a decline of plastic viscosity insignificantly from 4 to 3 Pa.s. - The rheological of bentonite/xanthan-based drilling fluid improved after the addition of SiO_2 as below: The incline of apparent viscosity (from 22.5 to 23.5 Pa.s), Plastic viscosity (from 7 to 9 Pa.s), 10 s-gel strength (from 17 to 19 Pa) after addition of SiO_2. But it has a decline of yield point (from 15.8 to 14.8 Pa) and 10 minutes gel strength (from 37 to 23 Pa). - Shale inhibition improved after the addition of SiO_2.	Al-Yasiri et al. (2019)

Table 2.5, continued.

Filtration loss of drilling fluid	0.25 – 4 wt%	Filtration loss	- The maximum decline of filtration loss was obtained at 1 wt% silicon oxide, dropping from 42 to 25 ml.	Minakov et al. (2019)
Study rheological behaviour of modified silica in partially hydrolysed polyacrylamide and xanthum Gum solution	0.5 - 2 wt%	Viscosity	- The viscosity of fluid was decreased after the addition of modified functionalised SiO_2. - The unmodified functionalised SiO_2 in polymer drilling fluid cannot mitigate the viscosity reduction when the temperature increase from 25 to 70 °C.	Corredor-rojas et al. (2018)
Enhancement of shear stress limit and rheological properties	0.5 – 1.5 wt%	Shear stress limit	- The addition of SiO_2 functionalised particles up to 1.5 wt% improved the shear stress limit and rheological properties through its modification.	Afolabi et al. (2017)

2.9 Surface modification of functionalised materials towards the development of modified polymer

2.9.1 Silane coupling agent

The silane coupling agent is the most common modifier in chemical treatment; for instance, gamma-glycidoxypropyltrimethoxysilane (GPTMS), Octyltriethoxysilane (OTES), Tetraethyl orthosilicate (TEOS), 3-methacryloxypropyltrimethoxysilane (MPS), 3-glycidoxypropyl-triethoxy silane (GPTS). With the utilisation of a silane coupling agent, the organic functionality on the surface of the functionalised material can be altered through covalent bonding, or physical bonding. However, it is easily condensed by silylation (Corredor-rojas et al., 2018; Hajiabadi et al., 2021; Wu et al., 2016; Yegane et al., 2020; Hajiabadi et al., 2021). Thus, there is a limitation on the preparation and storage of silane coupling agents (Corredor-rojas et al., 2018).

2.9.2 Organic modifier

The organic modifier is a compound consisting of organic functional groups such as alcohols, thiols, sulphonic, carboxylic acids, and amines (Vengatesan & Mittal, 2015). Several organic modifiers, such as dodecanedioic acid (DDDA), oleic acid, and stearic acid, have been studied in the surface modification of functionalised material for drilling operations by Corredor-rojas et al. (2018). The interaction between the organic modifier and functionalised material is usually with cross-linking structure. The recycling step is required before being used in the polymer composite; thus, there is an additional recovery cost. Additionally, it is easily polluted if it does not have proper disposal or recycling steps.

2.9.3 Surfactant

Surfactant is the one type of adsorption of polymeric dispersants that is the easiest method to enhance the dispersion behaviour of functionalised material in the drilling system. The anionic or cationic polymer dispersant can be used with hydrophilic functionalised particles. For instance, SDS is an example of a surfactant that can be used in the surface modification of functionalised materials. Due to environmental and cost concerns, the surfactant is the most potential modifier that can be used in the surface modification of functionalised materials (Qiao et al., 2016). It is not causing pollution if the modification process is not used with any organic modifier. In short, there is a concern about the well-equipped process and practice in industrial usage. Surfactant is considered easy to prepare and does not require further washing steps, unlike the organic solvent or silane agent applied in surface modification of functionalised material.

2.10 Factors affecting the polymer composite

2.10.1 The effects of water volume on polymer composite

Water content is crucial in the formulation of drilling fluid. Water-based drilling mud comprises 80 per cent water and 20 per cent drilling additives. Lesser water content in drilling fluid can minimise shale swelling. On the contrary, the high water content in drilling fluid may have drawbacks such as high shale, friction, and mud filtrate volume with low plastic viscosity. These situations lead to the wellbore instability issue (Aftab et al., 2017).

Drilling fluid with low solid content may have high water content, which offers several benefits, such as the enhancement of drilling penetration, small thickness of the cake, and good friction loss with shale inhibition improvement. However, drilling fluid with low solid and high water content has a weak carrying capacity (Gamal et al., 2019), contributing to the bored pile instability problem, according to Lam et al. (2015).

2.10.2 The effects of thermal stability on polymer composite

The thermal stability of the polymer can influence the ability of the polymer to resist heat because the degradation of the polymer can affect the rheological properties of the drilling fluid (Huo et al., 2018). Xing et al. (2017) studied the graphene oxide

(GO)/styrene-butadiene rubber composite had exothermic peaks at the range 190-200 ℃ through differential scanning calorimetry. At 210 ℃, pure graphene oxide had exothermic peaks due to thermal reduction. Furthermore, the curing process of polymer composite was below the exothermic peak through a rheometer, which can determine the cross-linking between graphene oxide and polymer after curing with optimum temperature, according to Xing et al. (2017).

Huo et al. (2018) used monomers such as 2-acrylamido-2-methylpropanesulphonic acid (AMPS), acrylamide (AM), and sodium p-styrene sulphonate (SSS) to modify the water-based drilling fluid for rheology study, including the thermal stability study of monomers maintained at the optimised temperature of 160 ℃ through Thermogravimetric and Derivative Thermogravimetric.

Gautam & Guria (2020) modified polyanionic cellulose-based drilling fluid maintained its rheology at 250 ℃. This modification of the functionalised particles involved alpha glycol functionalised fly ash with monomers (AMPS, AM and SSS). In summary, several synthetic polymer-based fluids can maintain their rheology properties when exposed to high-temperature and high-pressure conditions. However, most of these drilling fluids can be exposed to temperature that is less than 200 ℃ only.

2.10.3 The effects of pH sensitivity on polymer composite

A pH sensitive polymer is a polymeric material that responds to pH changes in drilling fluid. Different drilling fluid formations have different pH requirements, according to Olatunde et al. (2012). Gamal et al. (2019) found that pH significantly impacted the rheological properties of water-based drilling fluid, such as a decrease in yield point (from 85.7 to 15.8 lb/100 ft^2) and plastic viscosity (from 62.4 to 29.3 cP) when the pH of the drilling mud was increased from 8 to 12. Additionally, the filter cake thickness was increased from 2.0 to 3.6 mm when the pH of the drilling mud inclined from 9 to 12.

A study by Yao et al. (2017) showed that the grafted graphene oxide composite solution was sensitive to pH. The dispersion of the composite was good in an aqueous solution with pH 2.0, which showed a high value of 32.5 mV in zeta potential. On the other hand, there was aggregation when its medium had a pH of 5.0, which decreased to 5.7 mV in zeta potential. When further increasing the pH from 5 to 10, its zeta potential can be found to be a negative value of -7.2 eV, indicating poor particle suspension stability in a drilling fluid. Moreover, Kosynkin et al. (2012) found that methylated graphene oxide in drilling fluid was stable in a saline environment. Similarly, Kusrini et al. (2020) reported that phosphorylated graphene oxide in drilling fluid contributed to a low pH value that was close to 4, which can degrade the properties of the polymer and contribute to the poor performance of the drilling fluid.

2.10.4 The effects of cutting on polymer composite

The drilling fluid can remove the cutting particles formed at the borehole to its surface. (Ghayedi & Khosravi, 2020; Kanna et al., 2017; Li et al., 2015; Saparti et al., 2018; Vryzas & Kelessidis, 2017). Additionally, the rheological performance of drilling fluid is influenced by its cutting properties related to the rock type loading in drilling fluid, according to Bageri et al. (2020).

Besides, Li et al. (2015) studied the non-Newtonian fluid with good shear-thinning properties that can contribute to the good drilling cutting in the cellulose composite drilling fluid. Furthermore, Vryzas & Kelessidis (2017) stated that the drilling fluid with thixotropic properties has gelling formation behaviour that helps to suspend cuts. Likewise, Medhi et al. (2021) studied the thixotropic behaviour of graphene oxide composite-based drilling fluid controlled the cutting carrying capacity as its drilling fluid with 0.5 wt% of graphene oxide demonstrated the lesser deposition of cutting, among others.

Rheological properties (such as plastic viscosity, yield point, and gel strength) are the concerns of the drilling cutting effect on the borewell (Ghayedi & Khosravi, 2020; Vryzas & Kelessidis, 2017). A higher plastic viscosity with higher shear stress can enhance the cleaning of the cutting in graphene oxide-zinc oxide composite drilling fluid, according to Ghayedi & Khosravi (2020). Besides, Belayneh & Aadnøy (2016) studied that the functionalised SiO_2 polymer composite has a good cutting transport effect with the reduction of filtration loss. Likewise, Betiha et al. (2021) investigated the shear thinning behaviour using the yield point/plastic viscosity ratio (YP/PV) of graphene oxide-amino-based drilling fluid, which showed the increase of its YP/PV ratio represents the improvement of drilling cutting removal. Therefore, the drilling fluid's rheological performance is related to the drilling cutting effect.

CHAPTER 3 INFLUENCE OF POLYACRYLAMIDE CONCENTRATION ON DRILLING FLUID: A CHARACTERISATION AND RHEOLOGICAL STUDY

3.1 Introduction

This chapter begins with the background of several rheological studies regarding the influence of polyacrylamide (PAM) involved in drilling fluid in the past. This section also presents several studies that demonstrated different concentrations of PAM and the rheological profile of fluid. Therefore, this chapter aims to investigate the effect of PAM concentration on the rheological study. Detailed experimental procedures and investigation are reported in Sections 3.3 and 3.4, respectively, followed by the conclusion at the end.

3.2 Background

The polymer has dominated the industrial field in the last century. Nowadays, the technology related to polymer has matured in most applications, such as packaging, the rubber tyre industry, coating, and others. Meanwhile, the concept of "green chemistry" has engaged in the foundation field to minimise the environmental footprint and contribute to cost-effectiveness. Such as polyacrylamide (PAM), which is a common additive in geotechnical drilling. However, the use of polymer is fraught with concerns, such as the lack of official guidelines, incompatibility with salt water, and other factors (Jefferis & Lam, 2013). With these concerns, the fluid performance may worsen in drilling fluid technology, which can cause additional costs in facilities and operations. Further, the guideline of polymer usage is related to the concentration of polymer, which can subsequently affect the drilling performance. Therefore, polymer concentration in drilling fluid is vital in this study to achieve a better rheological profile of PAM-based drilling fluid.

Several researchers have investigated several formulations of PAM in drilling operations, as summarised in Table 3.1. For instance, Chami et al. (2021) studied the rheological properties of grafted PAM by varying concentrations of PAM (0.05 to 0.2 w/v). This study demonstrated pseudoplastic behaviour and shear thinning characteristics of a grafted PAM-based drilling fluid. Hamza et al. (2021) studied cross-linking agents in PAM modification. They stated that the low polymer concentration causes a long gelation time. They reported that 7 wt% PAM was the optimum polymer concentration, facilitating gelation time and gel strength of drilling fluid. Similarly, Magzoub et al. (2021) investigated the comparison of rheological study between PAM and cross-linked PAM. They reported 7.5 wt% PAM achieved similar apparent viscosity and plastic viscosity with 20 lb/bbl bentonite but varied from the yield point between them.

However, Xie et al. (2021) studied the cross-linked PAM. They recommended that the polymer concentration be considered due to the pumping properties of the fluid. They reported that a higher polymer concentration caused a longer gelation rate, shorter gel time, and enhanced gel strength. Another study on the nano-PAM composite in drilling also reported that the polymer concentration influences the consistency index and flow behaviour index. The high value of the consistency index and flow behaviour index due to the low concentration of PAM can promote the hole cleaning efficiency and shear thinning characteristic, respectively (Gudarzifar et al., 2020). Yegane et al. (2020) investigated the rheological behaviour of PAM solutions. They explained that the higher polymer concentration caused the polymer molecules' deformation by shear forces.

As summarised from the review, most studies nowadays focus on modified PAM rather than bare PAM in drilling operations. In geotechnical excavation, there is a general guideline on polymer concentration (0.5 to 2 kg/m^3), but the optimal dosage of PAM is poorly specified in drilling (Jefferis et al., 2011). Therefore, this study aimed to optimise the concentration of PAM in drilling operations according to the general guideline of polymer concentration.

Table 3.1: Comparison of drilling research in terms of PAM concentration.

Author	**PAM concentration**	**Aims**
Current study	500 – 2000 ppm (Equivalent to 0.05 to 0.2 w/v%)	Study of the effect of polymer concentration on rheological studies of PAM. 1000 ppm was the critical association concentration of PAM
Chami et al. (2021)	0.05 – 0.2 w/v%	Study of grafted PAM. The grafted PAM showed pseudoplastic flow and shear thinning behaviour.
Hamza et al. (2021)	5 – 7.5 wt%	Study of cross-linking agent in PAM modification. 7 wt% PAM was an ideal formulation to facilitate gelation time and strength.
Magzoub et al. (2021)	5 – 12.5 wt%	Comparison of rheological properties between PAM and cross-linked PAM. 7.5 wt% PAM corresponded to the best result for the reference bentonite in terms of plastic viscosity and apparent viscosity. However, the yield point for all concentrations of PAM was lower than that of the reference bentonite. In addition, the high molecular weight of PAM resulted in a relatively higher viscosity than that of the reference bentonite.
Xie et al. (2021)	1 – 1.2 wt%	Study of cross-linked PAM. A higher concentration of polymer caused a longer gelation rate with shorter gel time and enhanced the gel strength.
Gudarzifar et al. (2020)	0.01 – 0.08 wt%	Study of nano-PAM composite in drilling. Consistency and flow behaviour index were decreased when the increase of concentration.
Yegane et al. (2020)	0 – 0.5 wt%	Study of PAM in rheological properties. A high concentration of PAM caused the deformation of polymer molecules by shear forces.
Yang (1999)	0– 0.5 wt%	Study rheological behaviour of PAM solution. The viscosity of PAM declined when increased of concentration of PAM.

3.3 Materials and Methods

Materials involved in this experiment are PAM powder as a bare polymer which was provided by Synergy Lite Sdn Bhd, Puchong.

This experiment's first step was optimising various bare PAM concentrations in the rheological studies. The material characterization of bare PAM is the last step in understanding the physical and chemical properties of bare PAM.

3.3.1 Synthesis of bare PAM

The bare PAM samples were prepared in 350 ml of distilled water with a specified amount of PAM powder, as detailed in Table 3.2. The samples were mixed well using Joanlab overhead stirrer at 700 rpm.

Table 3.2: Formulation of PAM.

Fluid formulation, ppm	Distilled water, ml	PAM, g
500	350	0.175
750	350	0.263
1000	350	0.350
1500	350	0.525
2000	350	0.700

3.3.2 Materials characterisation of bare PAM

Several characterization techniques were performed on the optimised concentration of the bare PAM. The bare PAM underwent the techniques to identify its chemical structure, contact angle, and surface tension characteristics. The chemical structure of bare PAM was conducted using Fourier Transform Infrared Spectroscopy (FTIR). This test was performed via a spectrometer (Model: FTIR-Spectrum 400, Perkin Elmer) with KBr pellet technology. Approximately 2 g of sample was used in this test under the wavelength ranging from 500 to 4000 cm^{-1}.

The surface tension of bare PAM was measured using Sigma 700 Force Tensiometer. This testing was applied with a Du Noüy ring technique. Firstly, the process involved immersing a platinum-iridium ring into the bare PAM. Subsequently, that ring was pulled up slowly from the liquid interface. This testing can evaluate the surface tension of the bare PAM. The measurement was performed at room temperature.

Besides, the contact angle was measured using Attension® Theta Lite Optical Tensiometer. This testing was applied with a syringe to put a droplet of bare PAM onto the glass surface. The camera recorded the image. Finally, the contact angle was analysed using OneAttension software. All the measurement was conducted at room temperature.

3.3.3 Rheological studies of bare PAM

All the samples (500 – 2000 ppm) were investigated in the rheological studies using HDT-6ST 6-speed rotational viscometer, Qingdao Heng Taida. All the related rheological properties were determined by using the below equation as follows:

$$\text{Apparent Viscosity, AV} = 0.5\ \Phi600 \tag{3.1}$$

$$\text{Plastic Viscosity, PV} = \Phi600 - \Phi300 \tag{3.2}$$

$$\text{Yield Point, YP} = (2\Phi300 - \Phi600)/2 \tag{3.3}$$

where Φ600 is the dial reading at 600 rpm and Φ300 is the dial reading in mPa.s.

The gel strength (τ, Pa) is measured according to API 13 D. For 10-second gel strength in the rheological testing procedure, the sample was stirred at 600 rpm for 10 seconds and turned off the viscometer subsequently for around 10 seconds. Lastly, the sample was proceeded to stirring at 3 rpm till the gel breaks and recorded their maximum deflection. Additionally, the 10 mins-gel strength is followed in the same manner; however, the only difference in viscometer turnoff is around 10 minutes. The gel strength is formulated as Equations (3.4) and (3.5).

$$\tau_0 = 0.511\ \Phi3 \tag{3.4}$$

$$\tau_f = 0.511\ \Phi3 \tag{3.5}$$

where τ_0 is 10 s-gel strength, τ_f is 10 mins-gel strength, and Φ3 is the dial reading at 3 rpm in mPa.s.

3.4 Research findings

3.4.1 Physical properties of bare PAM

The surface tension of liquid shows the reflection of the physical and chemical properties of liquid as well as its material composition. In general, the surface tension of a liquid is related to cohesive forces between the liquid molecules that contribute to the cohesion of liquid molecules associated with the film of the surface. The unit in surface tension is typically analysed in mN/m. The surface tension of water is usually 72 mN/m at room temperature.

The wettability of the sample with the interaction between three phases (the solid, liquid, and gas) can be determined by the contact angle measurement. Generally, the solid surface is hydrophilic when the water contact angle is less than 90 °, whereas the solid surface is hydrophobic when the contact is more than 90 °.

The surface tension of PAM was 43.834 mN/m, which had different than water's surface tension (Zhang et al., 2020). The contact angle of polymer fluid to glass as a substrate is shown in Figure 3.1. The shale inhibition of PAM can be evaluated through the contact angle test. This test showed that the droplet of fluid made the mean angle of 42.19, which shows the hydrophilicity of polymer PAM (Ahmed et al., 2019).

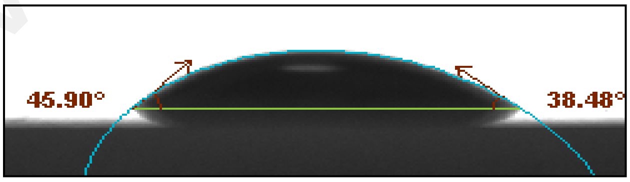

Figure 3.1: Contact angle of bare PAM.

3.4.2 Chemical properties of bare PAM

The FTIR analysis allows for the determination of the chemical nature of the material as a result of understanding the bonding types existing within the sample. A sample is exposed to infrared radiation transmission via FTIR equipment. Further, the vibration or rotational energy can be transformed from the absorbed radiation as a result of the spectrum for the chemical identification of the sample. Generally, a spectrum at the detector usually appears in the ranges from 400 to 40000 $cm^{-1,}$ and each chemical structure or molecule demonstrates a distinct spectral fingerprint in a chemical substance or compound. Hence, FTIR analysis is a fantastic technique for identifying specific chemicals.

Based on the FTIR analysis of PAM, as depicted in Figure 3.2, the carbonyl group stretching and amide group stretching vibration were found at the peaks of 1650 cm^{-1} and 3424 cm^{-1}, respectively. 2905 cm^{-1} and 2974 cm^{-1} were the peaks that corresponded to the C-H bond stretching vibration. The peak at 1378 cm^{-1} was for C-N stretching, whereas the peak at 1449 cm^{-1} was for the ring structure vibration of methyl C-H bend (Haruna et al., 2019).

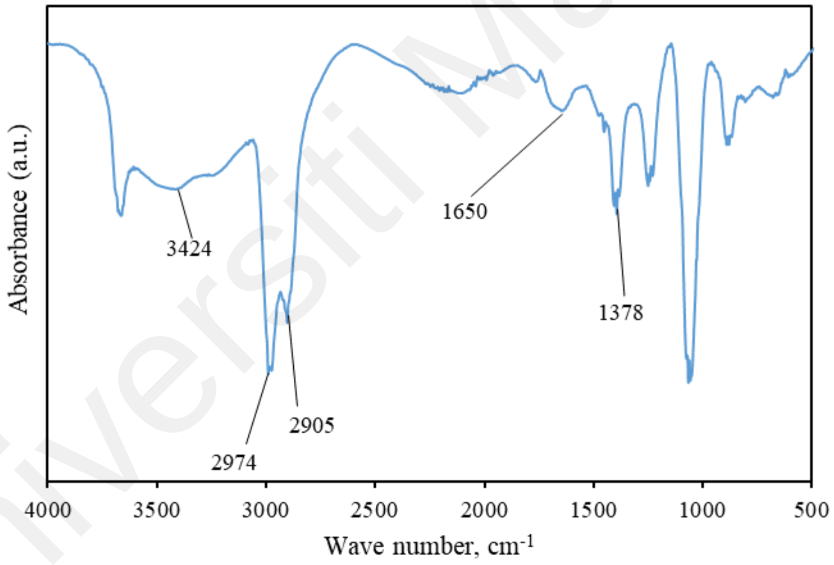

Figure 3.2: FTIR analysis of bare PAM.

3.4.3 Rheological properties of bare PAM

In order to understand the rheological behaviour of bare PAM in drilling operations, a 6-speed rotational viscometer is an advanced technique to study the flow behaviour of drilling fluid that meets the American Petroleum Institute (API) standards. This drilling standard is accredited by the American National Standards Institute.

A 6-speed rotational viscometer involves the outer cylinder rotating at a constant speed, and the viscous drag of the fluid on the inner cylinder or bob imposes torque that is shown on a calibrated scale. This viscometer is designed to fulfil the Bingham plastic model, which can simulate the plastic viscosity and apparent viscosity, as well as the yield point of a plastic material. Therefore, a 6-speed rotational viscometer can be applied in drilling measurement to determine the Bingham plastic rheological parameters for bare PAM.

Over various concentrations of PAM, the rheological behaviour of PAM, including dynamic viscosity, apparent viscosity (AV), plastic viscosity (PV), yield point (YP), and gel strength, had a similar trend, as depicted in Figure 3.3(a), (b), and (c). Below 1000 ppm, each rheological parameter fluctuated. Subsequently, all rheological parameters increased sharply above 1000 ppm.

With the aid of Figure 3.3 (d), it can be observed that the rheological behaviour of the drilling fluid was affected by the dispersion stability of the polymer. When the polymer concentration increased, there was an alternation between the stabilisation and the flocculation during the polymer dispersion. The steric stabilisation of particles occurs when there is sufficient polymer covering the surface of the particles. The depletion flocculation occurs at moderate to high polymer concentrations due to the existence of a non-adsorbing polymer. A high polymer concentration can lead to the depletion stabilisation in a fluid system, which provides colloidal stability (Kuroiwa et al., 2015).

In this study, the rheological performance of the drilling fluid was high at 2000 ppm PAM due to the effect of dispersion stability in the polymer. Therefore, 1000 ppm PAM was the critical association concentration of the polymer used in this study.

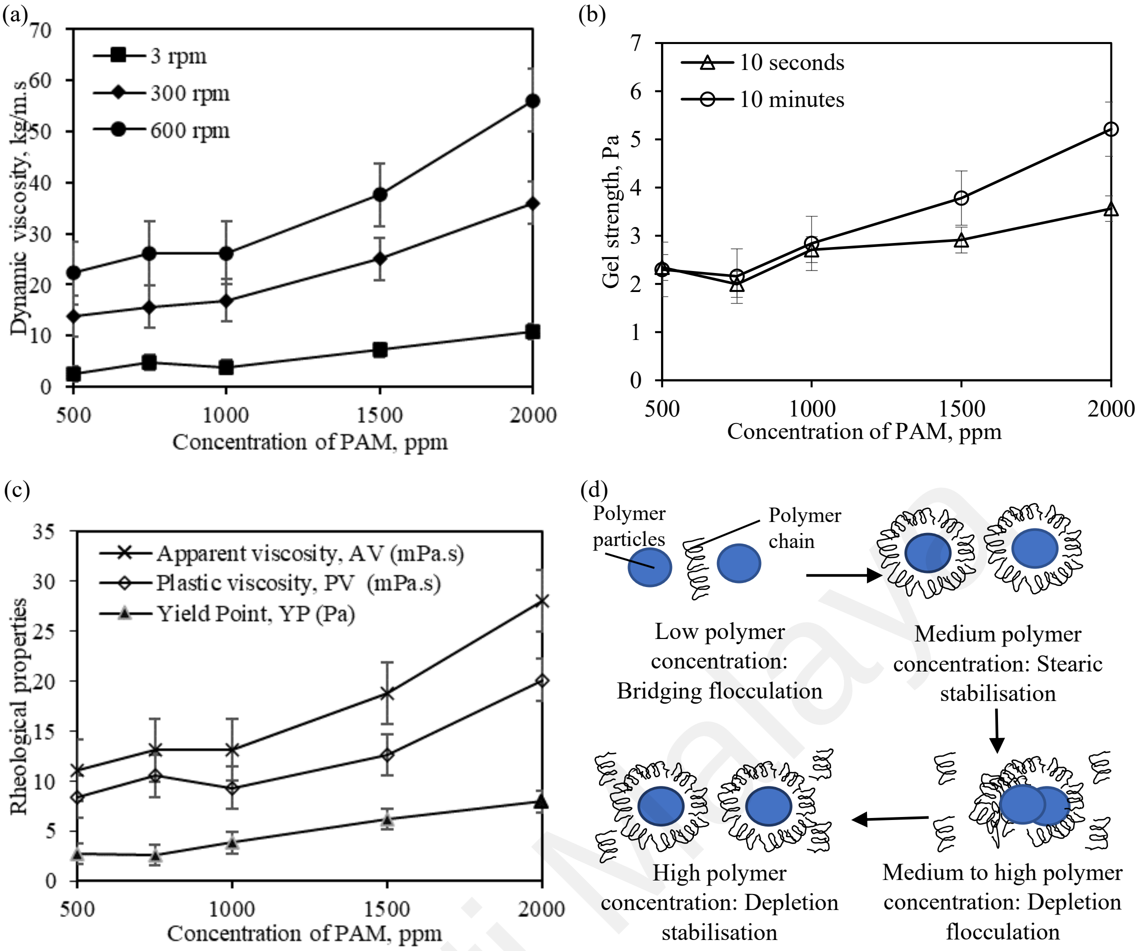

Figure 3.3: Effects of PAM concentration on the (a) dynamic viscosity, (b) rheological properties, (c) gel strength, and (d) dispersion stability of the polymer, which is redrawn from Kuroiwa et al. (2015).

3.5 Discussion

In this section of the study, the effect of PAM concentration was investigated with regard to the rheological properties of bare PAM. After optimisation, the bare PAM was further characterised by FTIR and tensiometer. FTIR has shown the identity of bare PAM, which fulfils the chemical nature of the polymer. Investigation of the rheological data with the explanation of dispersion stability of polymer (Section 3.4.3), the viscosity-increases due to PAM concentrations demonstrated a transition from bridging flocculation to depletion flocculation that contributed to the drilling fluid flow behaviours of the PAM. With this explanation, the rheological performance of PAM-based drilling fluid is related to the effect of PAM concentration and the dispersion stability of the polymer concept.

Based on the analysis obtained from the rheological properties of bare PAM with respect to the concentration of PAM, the fact that found the dispersion stability of the polymer could be reasonably prompted by the adsorption of a particle on the surface of the polymer. At a low polymer concentration, particle agglomeration is unstable when the molecule absorption occurs onto the surface of the polymer. When the polymer concentration is exceeded the saturation adsorption, the excess polymer chains in the solution phase form a three-dimensional network through associative interactions (Malkin et al., 2017). Further, the polymer agglomeration is probably also caused by the excess polymer chains in the solution since the polymer is exceeded the saturation adsorption. Therefore, the dispersion ability of polymeric in a colloidal system depends on the concentration of the polymer.

Further, several researchers studied that the relative viscosity of polymer suspension decreases dramatically with increasing polymer concentration. This finding could be explained by the relationship between the particle-particle attraction and the association network presented in a colloid system. Usually, the particle-particle attraction is relatively poor in the medium in which the association network is generated, and the systems are widely distributed. Therefore, the bridging conformation and flocculation level change dramatically with polymer concentrations (Geonzon et al., 2022; Malkin et al., 2017; Otsubo & Horigome, 2003). The result of this study can be observed from 500 ppm to 1000 ppm PAM in the rheological study, which has low polymer coverage and unstable association networking between polymer chains. It can be concluded that the low concentration of polymer with unstable networking contributes to the weak rheological profile in this study.

However, this rheological study of bare PAM increased dramatically when polymer concentration was applied from 1000 ppm to 2000 ppm. This result is probably due to the PAM concentration not exceeding the saturation adsorption, which is related to the transition from a stearic stabilisation to a depletion stabilisation in a colloidal system. Certain studies showed that the increase in polymer viscosity is attributed to the appearance of aggregates induced by the polymer bridging in a system (Murray et al., 2018; Zaman & Delorme, 2002). In addition, the changes from the intramolecular to the intermolecular association are contributed by the increased hydrophobic group from the non-adsorbing polymer with the increased concentration of PAM. Hence, the agglomeration of supramolecular within fluid was developed, and fluid viscosity was increased significantly above 1000 ppm, defined as the critical association concentrations (Lei et al., 2021; Lu et al., 2010). Hence, this study was mainly interrelated with the stearic stabilisation and the bridging flocculation in the mechanism of dispersion in a polymer fluid system (Section 3.4.3), which was induced by the absorption of polymer or macromolecule. Hence, the polymer adsorption in control measures the stability and the rheology of drilling fluid, and the experiment provides new insight into the relationship between PAM concentration and critical association concentration in drilling applications.

One concern about the findings of this study was the limited method analysis of the critical association concentration of PAM in this study. This method of analysis in this study is known as the viscosity method via a 6-speed rotational viscometer. Although a 6-speed rotational viscometer is a precise measurement, it is labour-dependent and time consumption. Further, the extent to which it is possible to the critical association of bare PAM is less explored, as well as insufficient information on the literature review regarding the critical association concentration of PAM in the past. Therefore, other than the viscosity method, the fluorescence method via fluorescence Spectrometry and the micro-pore method via resistance factor are the optional way for further research in the verification of the critical association concentration of PAM (Lu et al., 2010). Therefore, the critical association concentration of PAM can be adequately identified before proceeding with drilling operations. Besides, this can save time in defining the critical association concentration of PAM.

3.6 Conclusion

The analysis of the results can be concluded that the dispersion stability can influence the rheological properties of PAM. In this study, 1000 ppm PAM was identified as the critical association concentration of PAM due to the rheological behaviour with the dispersion stability concept in a polymeric material. However, the generalisability of the results is limited by the method identification of critical association concentration of PAM with its literature review. In the future, other methods can further enhance the verification of the critical association concentration of PAM.

CHAPTER 4 FABRICATION AND CHARACTERISATION OF A NOVEL MODIFIED FUNCTIONALISED SILICA/POLYACRYLAMIDE COMPOSITE FOR ADVANCED WATER-BASED DRILLING DESIGN

4.1 Introduction

This chapter explores the modification of PAM to improve the drilling using functionalised silica (SiO_2) and sodium dodecyl sulphate (SDS). First, this chapter begins with the literature review regarding the mishandling of the polymer fluid in the bored pile, the previous studies reported on the modification of PAM using SiO_2 and SDS with a brief summary of the previous research. Next, Section 4.3 reports the effect of functionalised SiO_2 concentration with a constant SDS as an exploratory optimisation of functionalised SiO_2 study on the PAM modification. The details of the experimental procedure, analysis, and discussion are also demonstrated in that section. Subsequently, the optimised concentration of functionalised SiO_2 was applied to the experiment regarding the effect of SDS concentration on the rheological performance of PAM (Section 4.4). It is also followed by the data findings with its analysis and discussion at the end of that section. Lastly, a short conclusion is presented in Section 4.5.

4.2 Literature review

As urbanisation continues, improved infrastructures are desired by many communities. Due to land scarcity, high-rise buildings can be constructed with innovative piling. PAM has been widely used with advantages such as a lower environmental footprint, easily accessible, and resistance improvement when used with concrete sand in a foundation. However, the pile stability in a foundation is a concern since problems can occur due to the mishandling of the polymer fluid, such as the failure to utilise the polymer according to the supplier’s recommended concentration, viscosity degradation caused by fluid recirculation, limited research publications on the polymer with other additives in the market, and others (Jefferis & Lam, 2013; Koh et al., 2022; Lam &

Jefferis, 2017b). Usually, the polymer utilisation with its concentration is suggested by the supplier, but it fails to follow the supplier's recommendations. The recommendation of polymer viscosity is usually greater than that of bentonite. However, the consumer misuses the polymer by lowering the concentration to obtain a low viscosity. Besides, the consumer also likes to recycle polymer usage due to the temptation of saving costs. The repeated usage of polymer can cause the loss of active polymer concentration. Hence, the polymer usage in the study is freshly prepared since there is a concern about the loss of active polymer concentration. Although PAM was introduced more than 30 years ago, there is less exploration of the modified PAM with additives in the bored pile foundation, which is incredible in the drilling market.

To date, drilling research mainly focuses on oil and gas applications to fulfil the global energy demand. However, current research has utilised the functionalised material in the water-based drilling fluid. The high molecular weight of PAM and the specific surface structure of functionalised materials can be hybridised into a functionalised composite (Aliabadian et al., 2018; Liu et al., 2021). Hence, the effect of functionalised SiO_2 on the rheological properties of PAM for water-based drilling fluid was investigated extensively in this study. In previous research, most studies demonstrated the synergistic effect of functionalised SiO_2 and sodium dodecyl sulphate (SDS) on a polymer in drilling applications, as summarised in Table 4.1. Most of the previous drilling research focused on enhanced oil recovery with this type of hybridisation in PAM modification. Previous research has reported different findings using this type of hybridisation in PAM modification. For instance, Kumar et al. (2020) reported that the viscosity was slightly decreased due to the high critical micelle concentration (cmc) value. Since there is involved of surfactant in this study, cmc is the factor that can affect the viscosity of the drilling fluid. Corredor et al. (2019)

investigated that the improvement of the interfacial tension between oil and water was caused by the presence of SDS and SiO_2 in the PAM complex.

Further, Sharma & Sangwai (2017) reported that the result of the drilling study was a reduction of interfacial tension after PAM modification with this type of hybridisation. Besides, Inturi et al. (2019) and Sharma et al. (2016) found that the drilling model in their study had a reduction in viscosity in their rheological study. However, Inturi et al. (2019) and Sharma et al. (2016) also reported that this drilling model had different findings, such as shear thinning behaviour and better wettability, which were achieved by reducing surface adsorption. A study reported that this drilling model could act as the thermally stable Pickering emulsion in oil-water drilling because there is a synergistic effect between the nanoparticles and surfactants in polymer, providing a better stabilised dispersion in the Pickering emulsion compared to surfactant/polymer emulsion solely. In short, these few investigations showed that the functionalised SiO_2 in PAM had thickening behaviour, reduced viscosity, and improved interfacial tension. These past research findings can be explained by Figure 4.1, showing the interaction between SiO_2, SDS, and PAM in a drilling fluid. Besides, the rheological performance comparison between the bare polymer and modified polymer can provide insight into the design in bored pile drilling.

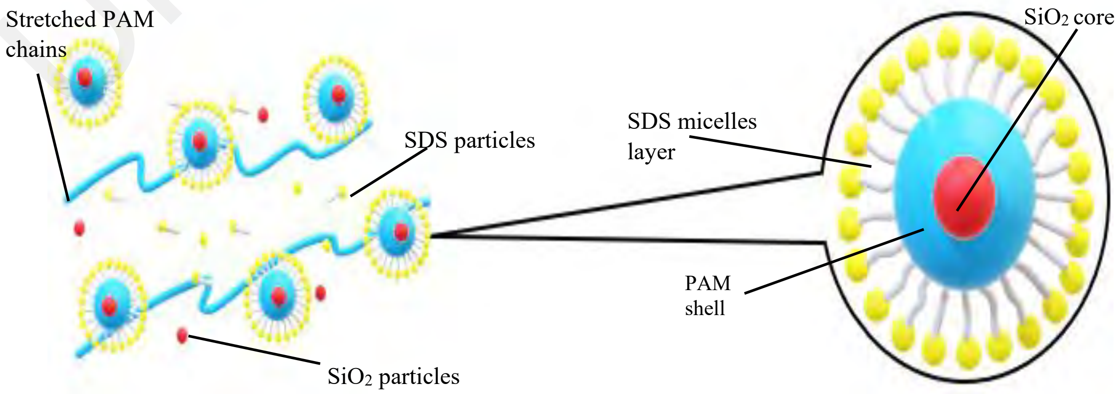

Figure 4.1: A surface modification of PAM. Redrawn with permission from Kumar et al. (2020).

Table 4.1: Previous studies on functionalised SiO_2/PAM-based drilling.

Concentration of SDS, wt%	Concentration of SiO_2, wt%	Concentration of PAM, wt%	Aims & Findings	Author
0 – 2	0.5	0.1	To design enhanced oil recovery. Viscosity was slightly decreased due to the cmc value being too high. The cmc value of SDS was 0.15 wt%.	Kumar et al. (2020)
0.1	0.2	0.4	To design grafted PAM for enhanced oil recovery. The improvement of the interfacial tension between oil and water due to the presence of SDS and SiO_2 in PAM complex was observed.	Corredor et al. (2019)
0.14	0 – 1.5	1	To develop enhanced oil recovery. Reduction of viscosity and shear thinning behaviour were observed.	Inturi et al. (2019)
0.1	0.5 – 2	0.4	To enhance the drilling model. Reduction of viscosity was observed.	Corredor -rojas et al. (2018)
0.05 – 0.14	0.5 – 2	0.1	To formulate the enhanced oil recovery. Reduction of interfacial tension was observed. The cmc value of SDS was 0.14 wt%	Sharma & Sangwai (2017)
0.14	0.5 – 2	0.1	To design the enhanced oil recovery. Reduction of viscosity and better wettability were achieved by reducing surface adsorption. The cmc value of SDS was 0.14 wt%	Sharma et al. (2016)

Table 4.1, Continued.

0.1 – 0.22	0.1 – 10	0.08 – 0.25	To formulate a thermally stable Pickering emulsion in oil-water drilling. A synergistic effect between the nanoparticles and surfactants in polymer provided a better stabilised dispersion in the Pickering emulsion compared to surfactant/polymer emulsion solely. The cmc value of SDS was 0.22 wt% in 0.1 wt% PAM.	Sharma et al. (2015)

4.3 Effect of Functionalised Silica (SiO_2) concentration in the modification of PAM

The drilling fluid additive is necessary for optimal rheological performance in drilling fluid technology. For this reason, the improvement in surface properties of PAM could be conducive to using combined doping with the hybridisation approach. Therefore, a preliminary study on improving the drilling fluid of PAM using functionalised silica (SiO_2) and sodium dodecyl sulphate (SDS) was explored. Moreover, the concentration of functionalised SiO_2 was optimised with a constant SDS concentration in the modification of PAM and presented in this section. After optimisation of functionalised SiO_2 in this section, the following section (section 4.4) presents the optimisation of SDS in PAM modification with a constant optimised SiO_2 concentration.

4.3.1 Materials and Methods

PAM was obtained from Synergy Lite Sdn Bhd. Functionalised silica (SiO_2) was purchased from Sigma-Aldrich, whereas sodium dodecyl sulphate (SDS) was purchased from Merck & Co.

The experiment in this section focuses on the rheological studies on the effect of functionalised SiO_2 concentration. Besides, there is a characterisation study on the physical properties of functionalised SiO_2. Besides, the physical and chemical properties of modified PAM with the effect of functionalised SiO_2 were also presented at the end of the characterisation study.

4.3.1.1 Synthesis of bare PAM and modified PAM

Bare PAM fluid was synthesised according to optimised concentration, as mentioned in section 3.3. On the other hand, modified PAM was synthesised by directly mixing the optimal concentration of PAM with a specified amount of functionalised SiO_2 (0-2 wt%) and a constant of 0.1 wt% SDS concentration in 350 ml distilled water, formulated with several samples, as shown in Table 4.2. In this way, the stirring speed and mixing time were demonstrated in the same manner, as mentioned in Section 3.3.

Table 4.2: Formulation of bare PAM and modified PAM with a specified amount of Functionalised SiO_2 and SDS in 1000 ppm polymer solution.

Fluid denoted as	Distilled water, ml	SDS, g	SiO_2, g
Bare PAM	350	0	0
0 wt% SiO_2	350	0.35	0
0.5 wt% SiO_2	350	0.35	1.75
1 wt% SiO_2	350	0.35	3.5
1.5 wt% SiO_2	350	0.35	5.25
2 wt% SiO_2	350	0.35	7

4.3.1.2 Material characterisation

After the analysis of the bare PAM (Section 3.3.3), the material characterizations were also performed on silica. First, the morphology of the silica was observed using a Field Emission Scanning Electron Microscope (FESEM, Model: Quanta FEG 450). The FESEM with an energy-dispersive analysis system (EDS)/electron back scatter diffraction (EBSD) was used to identify an insight into the bulk elemental composition of the silica. Next, the simultaneous thermal analyser (STA) was performed on the silica to determine its thermal stability and change in residue weight. A simultaneous thermal analyser (Model: Perkin Elmer. STA6000) was used to analyse the silica with approximately 5 g. The sample was heated in the crucible from room temperature to 950 °C at 10 °C/min under 20 ml/min N_2 atmosphere. This program was monitored by Pyris Software.

The material characterizations were also performed on the modified PAM with silica. All samples were characterised by using FTIR (Spectrum 400), Force Tensiometer (Sigma 700), and Optical Tensiometer (Theta Lite), as listed in Section 3.3.3.

4.3.1.3 Rheological studies of modified PAM

The rheological studies investigated all the samples using an HDT-6ST 6-speed rotational viscometer, Qingdao Heng Taida. First, the calculation of rheological properties is followed according to the equations in Section 3.3.2.

4.3.2 Data Analysis

4.3.2.1 Physical properties of Functionalised SiO_2

Electron microscopy techniques can identify the morphology of the silica as applied with the electrons in the instrument, such as Field Emission Scanning Electron Microscopy (FESEM), which depend on the energy of the electron beam. Further, the micrograph image is captured by the reflection of the electrons on the sample.

Figure 4.2(a) and (b) present SEM images for the functionalised SiO_2 in the magnification of 2 400 x with a 50 μm scale of length and the magnification of 10 000 x with a 10 μm scale of length, respectively. The micrograph illustrates that functionalised SiO_2 is composed of irregular-shaped particles with ~1 to ~40 μm. Therefore, this functionalised SiO_2 has micro-features that can improve the rheological performance of polyacrylamide-based drilling fluid.

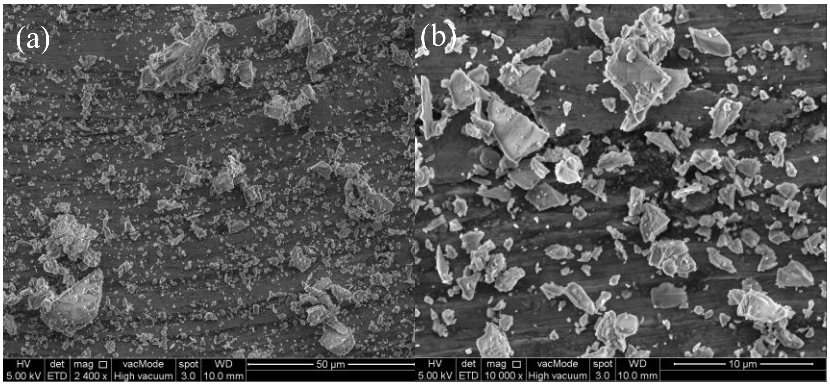

Figure 4.2: SEM of Functionalised SiO_2 in (a) 2 400, and (b) 10 000 magnification.

As depicted in Figure 4.3, Simultaneous Thermal Analyser analysis of functionalised SiO_2 was investigated in a nitrogen atmosphere to demonstrate the thermal stability of functionalised SiO_2. The weight is gained from 0 to 420 °C by 0.94%. About 0.08% weight loss was achieved from 420 to 950 °C. Therefore, there is no significance in weight gain and loss in functionalised SiO_2. Therefore, it can be used as a promising candidate in the high-temperature additive.

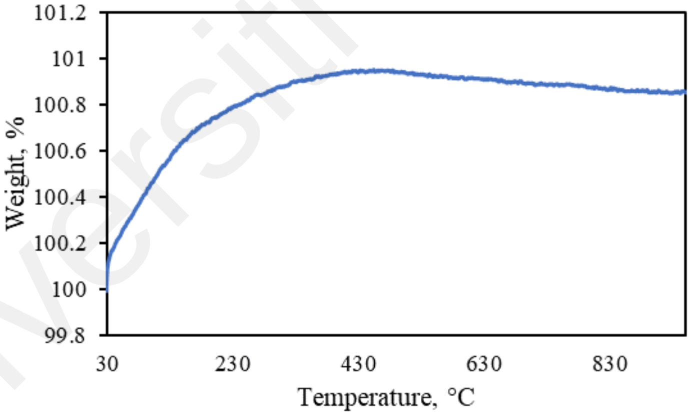

Figure 4.3: Simultaneous Thermal Analyser analysis of Functionalised SiO_2 under nitrogen atmosphere.

4.3.2.2 Effect of Functionalised SiO_2 on the chemical properties and physical properties of PAM

As depicted in Figure 4.4, the spectrum of PAM was well defined as seen from the C=O stretching (1650 cm^{-1}), NH_2 group stretching vibration (3424 cm^{-1}), C-N stretching vibration (1378 cm^{-1}), methyl C-H bends with ring structure vibration (1449 cm^{-1}), and C-H bond stretching vibration (2905 cm^{-1}, 2974 cm^{-1}) (Haruna et al., 2019; Jain et al., 2015). However, all the modified PAM spectra were defined from -OH vibration (3280 cm^{-1} and 1630 cm^{-1}), implying that the modified PAM spectra deviated from the PAM peaks (3424 cm^{-1}, 1650 cm^{-1}) to a lower wavenumber and indicating a stable dispersion of functionalised SiO_2 into PAM. Therefore, the bonding of the modified PAM can be enhanced (Muhamad et al., 2015).

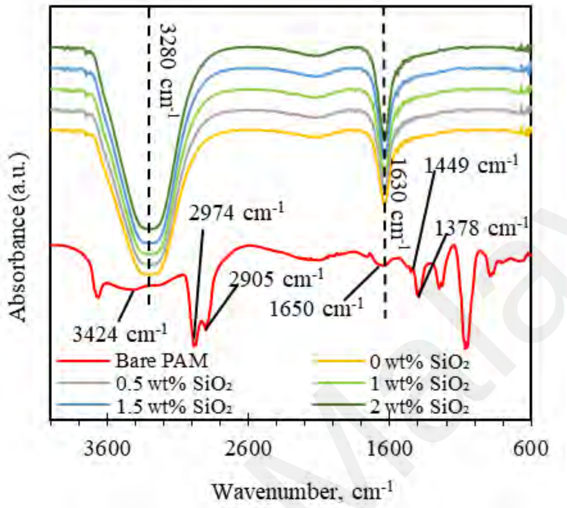

Figure 4.4: Effect of Functionalised SiO_2 on FTIR of PAM.

As depicted in Figure 4.5, there was an undulated surface tension means for all concentrations of functionalised SiO_2. Additionally, all modified PAM demonstrated a lower surface tension that was below 30 mN/m. 0 wt% functionalised SiO_2 had the lowest surface tension of the modified PAM since only 0.1 wt% SDS existed in PAM. However, a decreasing trend in contact angles with increasing concentration of functionalised SiO_2 was observed. Therefore, the hydrophilic nature of PAM was significantly affected by functionalised SiO_2.

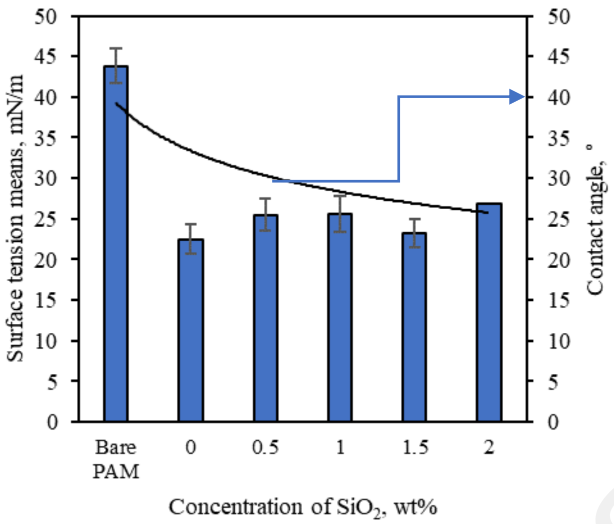

Figure 4.5: Effect of Functionalised SiO_2 on surface tension and contact angle of PAM.

4.3.2.3 Effect of Functionalised SiO_2 on the Rheological Analysis

The rheological properties of PAM had fluctuated over the different concentrations of functionalised SiO_2, as depicted in Figure 4.6(a). Generally, the drilling fluid should facilitate cutting at a reduced flow resistance, such as at low plastic viscosity with a high yield point (Yan et al., 2021). Compared to bare PAM, all rheological properties of the modified PAM had lower apparent viscosity and plastic viscosity, but it showed a similar trend in yield point, hence indicating a better drilling performance.

As depicted in Figure 4.6(b), 2 wt% functionalised SiO_2 in modified PAM demonstrated a ramp-up gel strength (0.84 Pa) between 10 seconds and 10 minutes, indicating progressive gel strength. Additionally, the rest are indicated as flat gel strength because there was a negligible difference in gel strength (0.12 – 0.19 Pa) between 10 seconds and 10 minutes. Hence, 0.5 wt% functionalised SiO_2 in modified PAM had the highest gel strength, which can suspend the cutting efficiently (Akpan et al., 2019; Vryzas & Kelessidis, 2017).

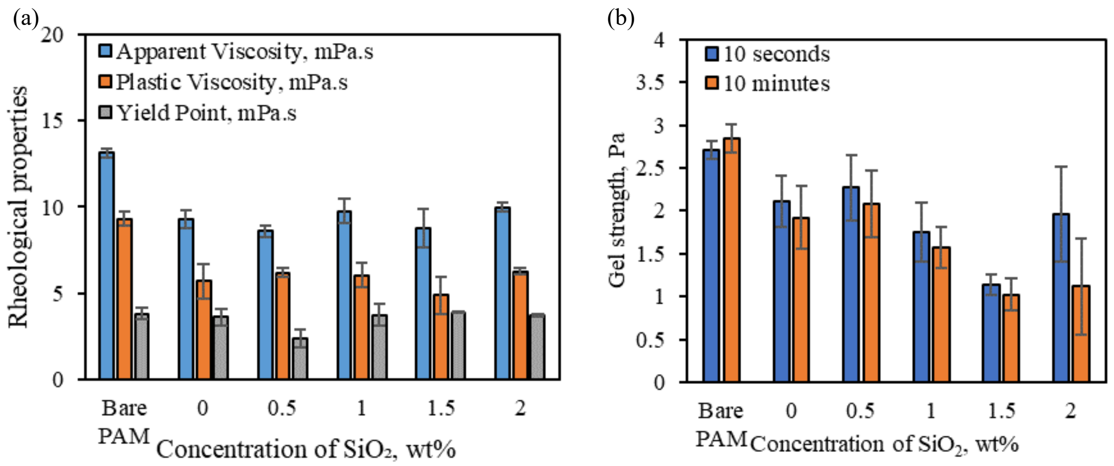

Figure 4.6: Effect of Functionalised SiO_2 on (a) rheological properties (AV, PV & YP), and (b) gel strength of PAM.

4.3.3 Discussion

This experiment investigated the effect of functionalised SiO_2 on the PAM modification to enhance the PAM-based drilling fluid. It was found that the modified PAM introduces the -OH bonding into bare PAM, as shown by a comparison of peaks in the spectrum between bare PAM and modified PAM in Fourier Transform Infrared Spectroscopy analysis (Figure 4.4). This change was triggered by modifying PAM with functionalised SiO_2 and SDS. Nonetheless, no obvious peak was found to indicate the functionalised SiO_2 in all the spectrums of modified PAM because this was due to the low concentration of the functionalised SiO_2 applied during the modification of PAM. Theoretically, the peak at 1130 cm^{-1} was attributed to S=O stretching symmetric, while the peak at 795 cm^{-1} was attributed to the O-Si-O vibration (Yu et al., 2014). Although this functionality of SiO_2 could not be defined clearly in spectrums of modified PAM in the current study, it can be assumed that there was an unclear and tiny peak in the range of 700 -1200 cm^{-1} that possibly indicates SiO_2 exists in the modified PAM.

Further, the surface properties of drilling fluid were also analysed with the effect of the functionalised SiO_2. It was observed that it reconciles the extent of contact angle and surface tension in the modified PAM, which showed lower than that of bare PAM. The reason is the addition of modifiers towards the bare PAM, such as functionalised

SiO_2 and SDS. With the bare PAM accompanied by the functionalised SiO_2 and SDS in this study, the nature of hydrophilicity with the surface properties of modified drilling fluid was influenced. The surface area of the functionalised SiO_2 powder seems like a significant factor contributing higher to the surface area with micropores, as proven in the micrograph via Scanning Electron Microscopic (SEM). O-Si-O groups involved in this modified PAM can hypothesise that there was a bonding formation within the particles in the modified PAM. Besides that, the micropore structure in functionalised SiO_2 can transform and modify the PAM-based drilling model into an advantageous operation model in drilling fluid technology. Additionally, the tiny size of microparticles is beneficial over the macroscale substances such as polymeric material, which can be linked to the concept of large surface volume to ratio generally.

The surface properties of drilling fluid are the main reason contributing to the rheological response of this study. It is evident from the contact angle and surface tension in Figure 4.5, as well as rheological studies in Figure 4.6. Bare PAM was the highest contact angle and surface tension, while all modified PAM had lower contact angles and surface tension than bare PAM. The result showed that the contact angle could be linked with the rheological studies. Furthermore, comparing and analysing the effect of functionalised SiO_2 in rheological testing, all modified PAM also achieved a lower rheological performance than bare PAM. In short, the non-polar behaviour of silica and the polar behaviour of PAM can cause the decline of the surface tension and contact angle of the modified PAM by increasing the functionalised SiO_2 content from 0.5 to 2 wt%. It might be associated with the surface energy of the polar component, which is related to dipole-dipole force contributing to the incline of interfacial polymer filler interactions. Besides, the dispersive components are connected to the Van der Waals forces. Therefore, the rheological studies of the functionalised SiO_2 effect on

PAM were influenced by the surface of functionalised SiO_2, contact angle, and surface tension properties of drilling fluid (Ivanova & Kotsilkova, 2019).

Besides, the most promising formulation of functionalised SiO_2 concentration optimised in this experiment for modified PAM is 0.5 wt% functionalised SiO_2, according to the rheological studies concerning the effect of functionalised SiO_2. There was explained that rheological properties of 0.5 wt% functionalised SiO_2 in modified PAM (Section 4.3.2.3), especially in terms of PV, YP, and gel strength. Usually, the PV relies on the liquid phase viscosity, particle size with shape, and the number of particles; however, the YP is the effect of a long chain of polymeric materials, which is related to the function of electrochemical behaviour. The incline of PV represents that drilled solids are inclining in the drilling fluid, while the incline of YP could represent the degradation of chemicals used or some chemical contamination to maintain the YP. The drilled solids exist much more in drilling fluid, which will drag the power performance and efficiency in drilling operations. YP can be maintained with increasing value for detecting chemical degradation in a drilling fluid. For high gel strength, the fluid tends typically to be solidified in a static condition requiring higher pumping energy for recirculation after stopping. However, low gel strength has weaknesses in suspending the cutting capacity, which can cause the accumulation of cutting beds, stuck pipes, and unbalanced pressure.

In this study, 0.5 wt% functionalised SiO_2 is a potential candidate with low PV and high YP but has limitations such as high gel strength. Because high gel strength can lead to damage if there is over the initiation of pressure during pumping in drilling operations (Ye et al., 2015), thus, the high gel strength of drilling fluid should be monitored closely during the pilot scale testing, as well as using suggested methods for gel strength measurements such as large amplitude oscillation shear (LAOS), nuclear magnetic resonance (NMR), and small amplitude oscillation shear (SAOS). Because these few methods are more conducive than API standards in the current experiment, especially since the gel strength is required at multiple rest periods, according to Ye et al. (2015).

4.4 Effect of Sodium Dodecyl Sulphate (SDS) concentration in the modification of PAM

In the current modification of PAM, the critical micelle concentration (cmc) can reflect the effectiveness in stabilizing the bond between PAM and functionalised SiO_2. When the concentration of SDS exceeds cmc, there will be adverse effects because the formation of micelles of SDS synthesised continuously without inhibition. However, the free molecules of SDS are available for clay inhibition at a low cmc value (Muhammed et al., 2021). Likewise, Sharma & Sangwai (2017) found that the stability of dispersed nanoparticles was unstable at low SDS concentrations.

However, 0.14 wt% SDS in 1000 ppm PAM demonstrated the most stable dispersion, which was reported as the cmc value of the surfactant. Other studies have also investigated SDS in the context of drilling, as shown in Table 4.1 (Corredor et al., 2019; Sharma et al., 2015, 2016). Therefore, the concentration of SDS is a critical formulation in the drilling fluid. In this study, SDS was further investigated by manipulating SDS concentration between 0.1 to 0.5 wt% to explore the effect of cmc on the rheological performance of PAM. Furthermore, this study can be compared with previous studies to understand the impact of cmc on the rheological properties of drilling.

4.4.1 Materials and Methods

PAM was supplied by Synergy Lite Sdn Bhd. Functionalised SiO_2 was purchased from Sigma-Aldrich. SDS purchased from Merck & Co. was used as a surface modifier for the SiO_2/PAM-based drilling fluid.

The experiment in this section focuses on the rheological studies on the effect of SDS concentration. Besides, there is a characterisation study on surface properties and chemical properties of the modified PAM with the effect of SDS concentration.

4.4.1.1 Synthesis of bare PAM and modified PAM

This study required a yield of 350 ml of drilling fluid, which was stirred at a relative speed using a Joanlab overhead stirrer. Bare PAM-based drilling fluid was prepared based on the optimised PAM concentration, according to Section 3.3. The optimised SiO_2 concentration (Section 4.3) acted as a constant parameter in the study of modified PAM. Hence, the preparation of modified PAM drilling fluid was incorporated at a PAM to functionalised SiO_2 ratio of 1:5, with a specified amount of SDS from 0 – 0.5 wt%, as detailed in Table 4.3.

Table 4.3: Formulation of a specified amount of SDS assigned in drilling.

Modified PAM fluid is denoted as	SDS, g
0 wt% SDS	0
0.1 wt% SDS	0.35
0.2 wt% SDS	0.70
0.3 wt% SDS	1.05
0.4 wt% SDS	1.40
0.5 wt% SDS	1.75

4.4.1.2 Material characterisation

The material characterisation for modified PAM with the SDS effect was involved with FTIR (Spectrum 400), Force Tensiometer (Sigma 700), and Optical Tensiometer (Theta Lite), according to the methods mentioned in Section 3.3.3.

4.4.1.3 Rheological studies

Rheological studies of all samples were tested via HDT-6ST 6-speed rotational viscometer, Qingdao Heng Taida. The rheological computations were followed according to the equations in Section 3.3.2.

4.4.2 Data Analysis

4.4.2.1 Effect of SDS on the chemical properties and physical properties of modified PAM

Under the effect of SDS, all modified PAM spectra were confirmed to have a broad peak in the range of 3200 – 3400 cm^{-1}, as depicted in Figure 4.7. This can be observed in the amide group (3424 cm^{-1}) of the PAM spectrum, which was altered with the vibration of the -OH group (3280 cm^{-1}) in the modified PAM spectra. Furthermore, the peak at 1650 cm^{-1} (carbonyl group) of the PAM spectrum was offset marginally to a lower wavenumber with a sharp peak of 1630 cm^{-1} (bending vibration of H-O-H) in all modified PAM spectra. Since these peaks existed in the modified PAM, the dispersion of SDS and SiO_2 in PAM was successful (Muhamad et al., 2015). Unlike the spectrum of bare PAM, there were no peaks at 2905 cm^{-1}, 2974 cm^{-1} (stretching vibration of C-H bonds), 1449 cm^{-1} (ring structure vibration of methyl C-H bend), and 1378 cm^{-1} (stretching vibration of C-N bond) (Haruna et al., 2019; Jain & Mahto, 2015). Refer to Figure 4.7 for more information.

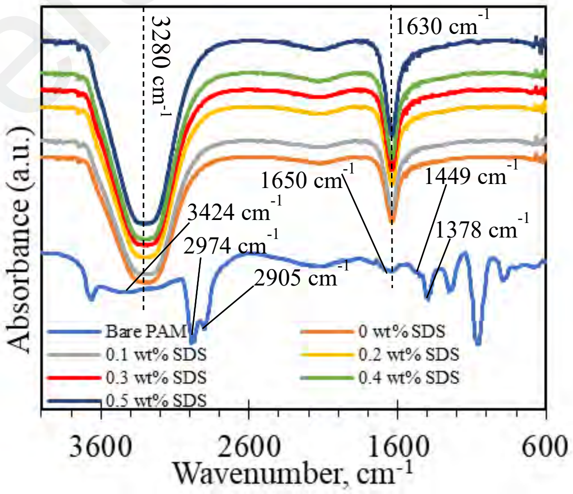

Figure 4.7: Effect of SDS on FTIR of PAM.

As depicted in Figure 4.8, all modified PAM had lower surface tension mean than bare (47.68 mN/m) because that sample was only formulated with 0.5 wt% SiO_2. In contrast, the lowest surface tension was 25.52 mN/m, which was observed in 0.1

wt% SDS in modified PAM. The other modified PAM (0.2 – 0.5 wt% SDS) also had similar surface tension in the range of 30.11 – 31.31 mN/m. Hence the addition of SDS can influence the surface tension of PAM. The drilling risk can be minimised with lower surface tension to achieve better rheological performance and penetration rate. In short, all modified PAM can improve the rheological performance with lower surface tension in drilling operations (Abang et al., 2021; de Sousa et al., 2021). A declining trend was observed in the contact angle of the modified PAM over various concentrations of SDS. Therefore, the polarity of modified PAM was less hydrophobic than bare PAM. Bare PAM and all modified PAM were comprehensively hydrophilic.

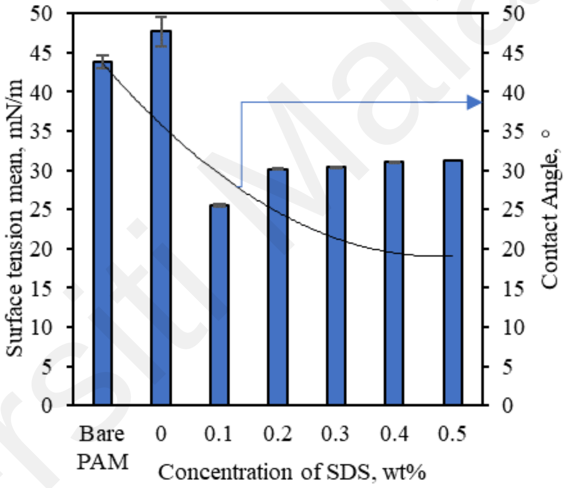

Figure 4.8: Effect of SDS on surface tension and contact angle of PAM.

4.4.2.2 Rheological analysis

As illustrated in Figure 4.9(a), the results of the rheological studies on the drilling fluid were varied. As observed from bare PAM to 0.1 wt% SDS, there was a decreasing trend in apparent viscosity (AV), plastic viscosity (PV), and yield point (YP). Furthermore, there was a comparable trend of AV, PV, and YP from 0.2 to 0.5 wt% SDS in modified PAM. From the results of the rheological studies, it can be concluded that all the modified PAM had lower PV than the bare PAM, which was influenced by the cmc value and the interaction between SDS, PAM, and SiO_2, as illustrated in Figure 4.5. Compared to the research by Sun et al. (2015), the cmc value of SDS in water was 0.23

wt% at 25 °C. When the cmc is exceeded, there are slight or sometimes detrimental effects (Briceño-Ahumada et al., 2021; Muhammed et al., 2021). In this study, 0.1 wt% SDS in PAM demonstrated the poorest rheological performance in drilling. Subsequently, the rheological performance of 0.2 – 0.5 wt% SDS used in PAM was higher than that of 0.1 wt% SDS and had a similar result to 0 wt% SDS. Meanwhile, a lower PV was maintained in the modified PAM than the bare PAM when higher concentrations of SDS were applied. Hence, the modified PAM can maintain better rheological performance over all the considered concentrations of SDS.

According to Briceño-Ahumada et al. (2021), the adsorption of both surfactants and nanoparticles-surfactant entities at the surface/interface decreases the surface/interfacial tension when there is a low concentration of SDS. SDS is adsorbed on the nanoparticles when there is a high concentration of SDS. The fluid interface is further affected by an incline of the interfacial tension and the depletion of surfactants. Therefore, 0.1 wt% SDS is the cmc value in this research because it evidently had the lowest surface tension and the poorest rheological performance among all modified PAM. Furthermore, a fluctuation was observed in the gel strength of PAM over the different concentrations of SiO_2, as illustrated in Figure 4.9(b). For comparison, between 10 seconds and 10 minutes, the gel strength of 0 wt% SDS in modified PAM went up from 2.3 to 2.9 Pa. Further, the other modified PAM demonstrated that at 10 seconds, the gel strength was higher than that at 10 minutes. Therefore, these observations indicate the behaviour of progressive gel strength. In contrast, at 10 seconds, the gel strength for 0.2 wt% SDS in modified PAM remained constant until 10 minutes, which indicates the behaviour of flat gel strength. Hence, the most promising SDS concentration in modified PAM formulation is 0.2 wt%.

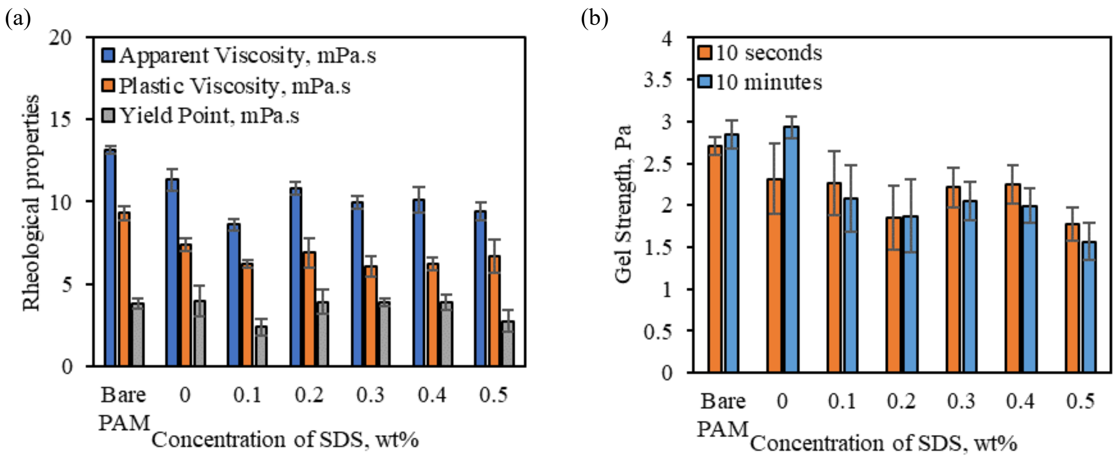

Figure 4.9: Effect of SDS on (a) rheological properties (AV, PV & YP), and (b) gel strength of PAM.

4.4.3 Discussion

After optimisation on the effect of SiO_2 (Section 4.3), this experiment investigated the effect of SDS with an optimised concentration of functionalised SiO_2 in the modification of PAM. FTIR and surface properties analysis in this experiment found a similar trend with the effect of functionalised SiO_2 in modified PAM (Section 4.3.2). No obvious peak was found in the FTIR analysis with the effect of SDS, as shown in Figure 4.7. The reason is due to the low SDS concentration applied in modified PAM. Hafizah et al. (2019) report that the SDS in polymer solution has an obvious peak at 950 -1000 cm^{-1} wavelengths, demonstrating the S=O stretching vibration of SDS. Similarly, Raj et al. (2010) reported 1030 and 1000 cm^{-1} as visible peaks for molecular stretching of SO^{3-}. Compared to the present study, the range between 950 to 1000 cm^{-1} of all modified PAM spectrums had a tiny and unclear peak, which indicates that SDS is possibly involved in PAM.

However, the data analysis of surface tension and contact angle in modified PAM with the effect of SDS differed from the modified PAM with the effect of functionalised SiO_2. It is evident shown in Figure 4.8, which is demonstrated that the value of surface tension increased slightly, and the contact angle decreased over the concentration of SDS from 0.1 to 0.5 wt% with a constant 0.5 wt% of functionalised SiO_2 in modified

PAM. On the contrary, the effect of functionalised SiO_2 on surface tension and contact angle (Figure 4.5) found that the value of surface tension was unstable with a lower value (22 – 26 mN/m) than that of the effect of SDS (47 – 31 mN/m), as well as the contact angle of the effect of functionalised SiO_2 was higher than that of the effect of SDS. Therefore, the surface tension and contact angle properties were significantly impacted by the effect of SDS in modified PAM. Theoretically, the surfactant is usually supposed to decrease the surface tension of the fluid. This study showed the breakthrough of the modification on the surface tension of PAM that demonstrated the bare PAM and modified PAM with 0 wt% SDS had higher surface tension than other modified PAM with 0.1 to 0.5 wt% SDS, as illustrated in Figure 4.8. The surface tension reduction is due to the addition of surfactant in PAM. However, there is a marginal incline of the surface of tension in modified PAM over the concentration of SDS from 0.1 to 0.5 wt%. It can be elucidated that the intermolecular forces within the particles increase in modified PAM. That is why the contact angle of modified PAM had decreased over the concentration of SDS. These surface properties can be interrelated with the rheological study of the effects of SDS on the modified PAM.

Referring to the rheological study in Figure 4.9, the modified PAM also showed lower AV and PV after adding modifiers such as functionalised SiO_2 and SDS. That meant a low concentration of functionalised particles with a low surfactant concentration weakened the intermolecular force, leading to lower viscosity. However, when the concentration of additives increases, the intermolecular force between additives with polymer becomes more substantial due to the shorter intermolecular distance between particles (Maiti et al., 2021). In this study, the effect of SDS demonstrated 0.1 wt% SDS had poor rheological performance, such as low PV but low YP, which is related to the critical micelle concentration. Theoretically, the drilling fluid is surface-active, and forms charged micelles once the concentration in the medium becomes more than cmc. These micelles allow no agglomeration by establishing the electrostatic repulsion between functionalised particles.

This experiment studied increasing SDS concentrations in a functionalised SiO_2/PAM-based drilling fluid. It found that the surfactant behaves more efficiently in reducing the contact angle of drilling fluids in the presence of functionalised particles. This behaviour can be attributed to the electrostatic repulsion between SDS molecules and functional particles, which promotes surfactant adsorption (Vatanparast et al., 2018). Since there is a shorter intermolecular distance between particles caused by the increased concentration of additives such as SiO_2 and SDS, the electrostatic repulsion between the functionalised particles in modified PAM becomes stronger. That is why the short-range forces tend to be repulsive in intermolecular force between particles in drilling fluid. Hence, the surfactant properties of cmc nature are the critical factor affecting the rheological performance of modified PAM in this study.

The limitation of using surfactant is the foam formation and its stability. The foam generated from the high surfactant concentration could increase the surface tension of water with the presence of electrolytes. Further, lowering the surface tension could create stable foam (Ismail et al., 2013). Thus, the surfactant concentration is key to the foam formation and stability, which is part of controlling the surface tension and influencing the rheological properties of the drilling fluid. Foam stability can be determined by the measurement of the electrical conductance of the foam between two fixed electrodes. Since the surfactant involved in this study is anionic, different types of foam are suggested, such as cationic, amphoteric, and non-ionic, for further investigation of the rheological behaviour of PAM-based drilling fluid.

4.5 Conclusion

In the effect of functionalised SiO_2 on modified PAM, PAM and modified PAM were successfully synthesised and characterised using FTIR and tensiometer. Modified PAM with functionalised SiO_2 demonstrated low plastic viscosity and apparent viscosity with a similar yield point to bare PAM. Furthermore, the rheological performance of modified PAM-based drilling was enhanced using functionalised SiO_2. Therefore, 0.5 wt% SiO_2 in modified PAM is the most promising formulation in this study because it achieved the highest gel strength and better rheological properties.

For the effect of SDS, the synthesis and characterisation of PAM and modified PAM were studied. All modified PAM with the effect of SDS results were lower than PAM in terms of surface tension, contact angle, and rheological properties. The value of cmc and the promising formula were defined in this study, which are 0.1 and 0.2 wt% SDS, respectively, for modified PAM.

With all this information regarding modified PAM formulation, the difficulties of in situ bored pile drilling can be addressed in the future. Consequently, the drilling fluid technology can be more effective using polymer composite in pile foundations.

CHAPTER 5 A COMPARATIVE STUDY OF PH AND TEMPERATURE ON RHEOLOGICAL BEHAVIOUR BETWEEN POLYACRYLAMIDE (PAM) AND ITS MODIFIED PAM

5.1 Introduction

This chapter is organised into a few sections as follows. This chapter briefly describes the drilling background on the temperature and pH effect on past rheological studies of PAM-based drilling (Section 5.2). It is followed by the methodology and results with a discussion that compares rheological behaviour between bare PAM and modified PAM. Additionally, the experiment begins with optimising pH and temperature in the rheological study based on bare PAM before further studying the modified PAM. The details of rheological testing are demonstrated in Section 5.3. Further, the detailed data analysis is shown in Section 5.4, followed by the discussion (Section 5.5). A short conclusion is summarised in Section 5.6.

5.2 Literature Review

Temperature and pH are often the rheological problems in drilling. PAM can withstand temperatures below 80 °C because a higher temperature can deteriorate the drilling performance when excessive hydrolysis occurs (Hashmat et al., 2016; Xie et al., 2021). In several studies, the viscosity of PAM or modified PAM declined with inclining temperature (Lyu et al., 2019; Magzoub et al., 2021; Yang, 1999; Yegane et al., 2020). Most studies addressed the effectiveness of modified PAM in terms of viscosity and thermal stability, as summarised in Table 5.1. For instance, Ismail et al. (2022) tested the utilisation of functionalised silica as a calcium carbonate inhibitor in modified PAM. The low dosage of the inhibitor can improve the inhibition efficiency with different temperatures and pH. Chami et al. (2021) designed the grafting of PAM onto xanthan for polymer flooding. The viscosity of grafted xanthan-PAM was higher than those of pure xanthan, which demonstrated a better thermal resistance in the graft copolymer.

Besides, Xie et al. (2021) enhanced modified PAM in high-temperature drilling. The study revealed that the gelation time of the improved polymer was not affected by the temperature at 140 °C. They also reported that PAM was hydrolysed at a temperature above 90 °C. Gudarzifar et al. (2020) investigate the effect of thermal heating and nanoparticles on the rheological performance of modified PAM. The results revealed that heating made the nanoparticles effective in terms of flow resistance with a decrease in apparent viscosity.

Similarly, Lyu et al. (2019) reported a study regarding the effect of graphene oxide composite on the rheological and thermal performance of modified PAM. The result revealed that the apparent viscosity of modified PAM decreased with increasing temperature. Unfortunately, there is insufficient information on the temperature effect on the rheological performance of bare PAM. Therefore, a rheological study was conducted to extensively investigate the effects of temperature from ambient temperature to 80 °C in this study.

A study found that the rheological performance of water-based drilling fluid can be significantly enhanced from pH 9 to 10 (Gamal et al., 2019). Further, Kusrini et al. (2020) discovered the effect of nanoparticles in a bentonite-based drilling fluid. The result showed that the pH could be reduced from 8.36 to 7.78 in a graphene oxide-based drilling fluid. In contrast, Gudarzifar et al. (2020) and Medhi et al. (2019a) studied the nanocomposite-based drilling fluid's rheological performance, where the pH was insignificantly affected. Veritably, previous studies regarding the effect of pH on bare PAM had received less attention, where the focus was more on the effect of additives in drilling, as shown in the comparison in Table 5.1. Therefore, this study investigated the effect of pH on bare PAM extensively.

Therefore, this chapter further investigates the effect of temperature and pH on the optimised formulation of modified PAM in terms of rheological properties. Further, it was targeted that the research will contribute to a deeper understanding of the optimised pH and temperature effects on the optimised concentration of PAM. Due to practical constraints in this research, the rheological study is insufficient to comprehensively overview the effects of pH and temperature at each concentration of PAM. The findings of this study can enrich the knowledge regarding drilling applications and serve as the basis for future research, as well as advocate the concept of “green chemistry” in drilling fluid technology.

Table 5.1: Comparison of drilling research in terms of temperature and pH.

Author	Temperature, °C	pH	Aims and findings
Current study	Ambient to 80	Ambient to 10	To optimise the effect of pH and temperature on bare PAM and further study the effect of optimise pH and temperature on modified PAM. Bare PAM had a better rheological performance at 60 °C and pH 9-10, whereas modified PAM had better rheological properties at 40 and pH 10.
Ismail et al. (2022)	40 – 80	7 - 9	To test the use of functionalised silica as a calcium carbonate inhibitor in modified PAM. The low dosage of the inhibitor can improve the inhibition efficiency with different temperatures and pH.
Chami et al. (2021)	25 – 65	-	To design the grafting of PAM onto xanthan for polymer flooding. The viscosity of grafted xanthan-PAM was higher than those of pure xanthan, which demonstrated a better thermal resistance in the graft copolymer.
Hamza et al. (2021)	75	4 - 6	To study the impact of aluminium acetate on polyacrylamide-based gel with bentonite as a crosslinker. The size of nanoparticles sped up the gelation process of the polymer composite gel at 75 °C and pH 5.
Magzoub et al. (2021)	21 – 96	-	To design loss circulation materials by using PAM with a crosslinker. The viscosity of PAM decreased when the temperature was increased.
Xie et al. (2021)	100 to 150	-	To enhance modified PAM in high-temperature drilling. The gelation time of the improved polymer was not affected by the temperature at 140 °C. PAM was hydrolysed at a temperature above 90 °C.
Gudarzifar et al. (2020)	120	7	To investigate the effect of thermal heating and nanoparticles on the rheological performance of modified PAM. The results revealed that heating made the nanoparticles effective in terms of flow resistance with a decrease in apparent viscosity. However, the pH of the drilling fluid was not impacted by the addition of nanoparticles.
Kusrini et al. (2020)	-	7 - 8	To study the effect of nanoparticles in a bentonite-based drilling fluid. The addition of nanoparticles resulted in a decrease in the pH of the drilling fluid.
Yegane et al. (2020)	25 - 70	-	To study the effect of modified silica/PAM at high temperatures. The results demonstrated that the viscosity of modified silica/PAM decreased with increasing temperature.
Hamad et al. (2020)	180 - 220	-	To compare the various rheology modifiers in a bentonite-based drilling fluid. The results demonstrated that the amphoteric polymer had a better rheological performance at 180 – 220 °C than bare PAM.

Table 5.1, continued.

Medhi et al. (2019a)	80	8 - 10	To study the effect of nanoparticles on the rheological properties of polyamine-based drilling fluid. The addition of nanoparticles did not affect the pH of the drilling fluid.
Lyu et al. (2019)	30 - 120	-	To study the effect of graphene oxide composite on the rheological and thermal performance of modified PAM. The apparent viscosity of modified PAM decreased with increasing temperature.
Gamal et al. (2019)	-	7 - 12	To study the effect of pH on the rheological properties of water-based drilling fluid (bentonite). The results demonstrated better rheology and filtration properties at pH 9 -10.
Yang (1999)	20 -50	-	To study the rheological properties of polyacrylamide. The viscosity decreased with an increase in temperature.

5.3 Materials and Methods

Polyacrylamide was provided by Synergy Lite Sdn Bhd. Sodium dodecyl sulphate was purchased from Merck. Functionalised silica was purchased from Sigma-Aldrich. Soda Ash was purchased from Solvay S.A, which acted as a pH controller.

The experiment in this section was focused on the rheological studies of bare PAM and modified PAM with the effect of temperature and pH. The bare PAM was formulated according to the optimised concentration from Chapter 3, whereas the modified PAM in this section was formulated with the optimised dosage of each modifier – functionalised SiO_2 and SDS from Chapter 4. This study included comparing bare PAM and modified PAM in terms of the effect of the optimised temperature and pH.

5.3.1 Synthesis of PAM and modified PAM

Bare PAM fluid was mixed in 1000 ppm. Besides, 0.5 wt% functionalised SiO_2 and 0.2 wt% SDS were mixed with 1000 ppm PAM as a modified PAM fluid. These were mixed well at a relative speed using a Joanlab overhead stirrer.

5.3.2 Rheological testing

After the optimisation of the concentration of PAM (Section 3.3.3), the optimised bare PAM was further tested in rheological studies with the effect of temperature (ambient to 80 °C) and pH (ambient to 10) separately. This testing was conducted as the exploratory data on the optimisation of the effect of pH and temperature.

Subsequently, modified PAM was further analysed with the optimised pH and temperatures. The testing procedure is followed, according to the American Petroleum Institute (API).

5.4 Data analysis

5.4.1 Effect of temperature

Based on Figure 5.1(a), AV and PV of PAM were decreased from ambient temperatures to 60 °C, while YP of PAM was increased. Subsequently, there was an inverted trend in AV, PV, and YP after further heating at 80 °C. Meanwhile, PAM had the lowest AV and PV with the highest YP after heating at 60 °C, which denoted the maximum thermal stability of bare PAM. The rheological performance of the drilling fluid is influenced by the flocculation and adsorption capacity during endothermic heating. As large gel-like floc formed at high temperatures, this study showed that PV was increased with the increase of heating temperature from 60 to 80 °C (Xiong et al., 2018; Zhang et al., 2015). As shown in Figure 5.1(b), the gel strength in bare PAM-based drilling fluid was not significantly affected by temperature, demonstrating better thermal stability with consistent gel strength from ambient temperatures to 80 °C.

As depicted in Figure 5.2(a), overall showed a fluctuation in AV, PV, and YP between PAM and modified PAM. Compared to bare PAM, the modified PAM had an incline of YP by 2.2% but AV and PV had a reduction of 17.7% and 25.8%, respectively, in ambient conditions. After further heating at 40 °C, modified PAM showed a reduction of AV, PV, and YP by 20.9%, 15.1%, and 30.2%, respectively. After heating at 60 and 80 °C, the modified polymer demonstrated the incline of AV and PV with the decline of YP. Compared to the gel strength of PAM, modified PAM demonstrated lower over all the temperatures in Figure 5.2(b). Overall, it can be concluded that modified PAM can withstand temperature at 40 °C because modified PAM exhibited better rheological performance, especially the reduction of PV.

Therefore, high PV in drilling fluid due to flocculation is undesired, which can influence the wellbore performance (Akpan et al., 2019; Fokuo et al., 2021). This study showed that the inclination of PV is affected by higher heating temperatures.

Thereupon, the large gel-like floc formation that occurs at high temperatures potentially contributes to the higher viscosity with high pumping energy during drilling. Ultimately, the poor rheological performance in drilling operations is caused by aggregation and flocculation at higher temperatures (Fokuo et al., 2021; Guezennec et al., 2015; Makinde et al., 2011).

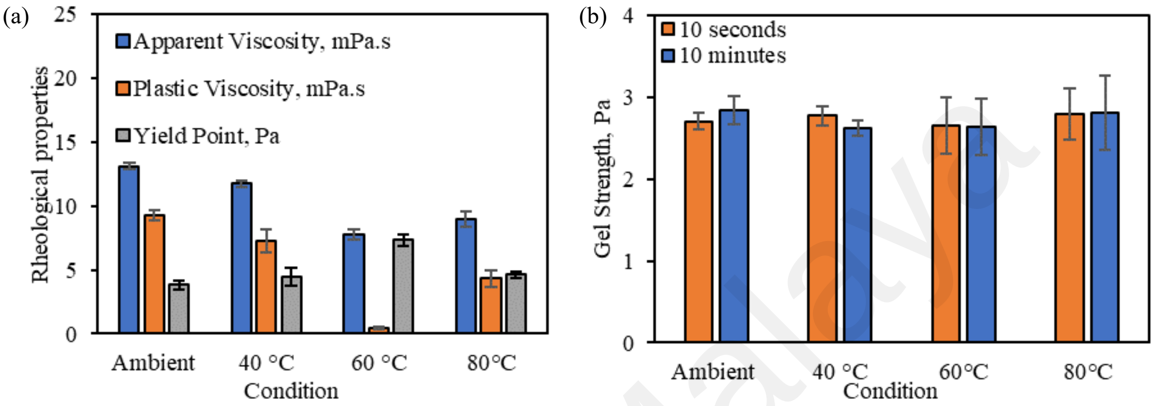

Figure 5.1: Effect of temperature on (a) rheological properties, and (b) gel strength of 1000 ppm PAM.

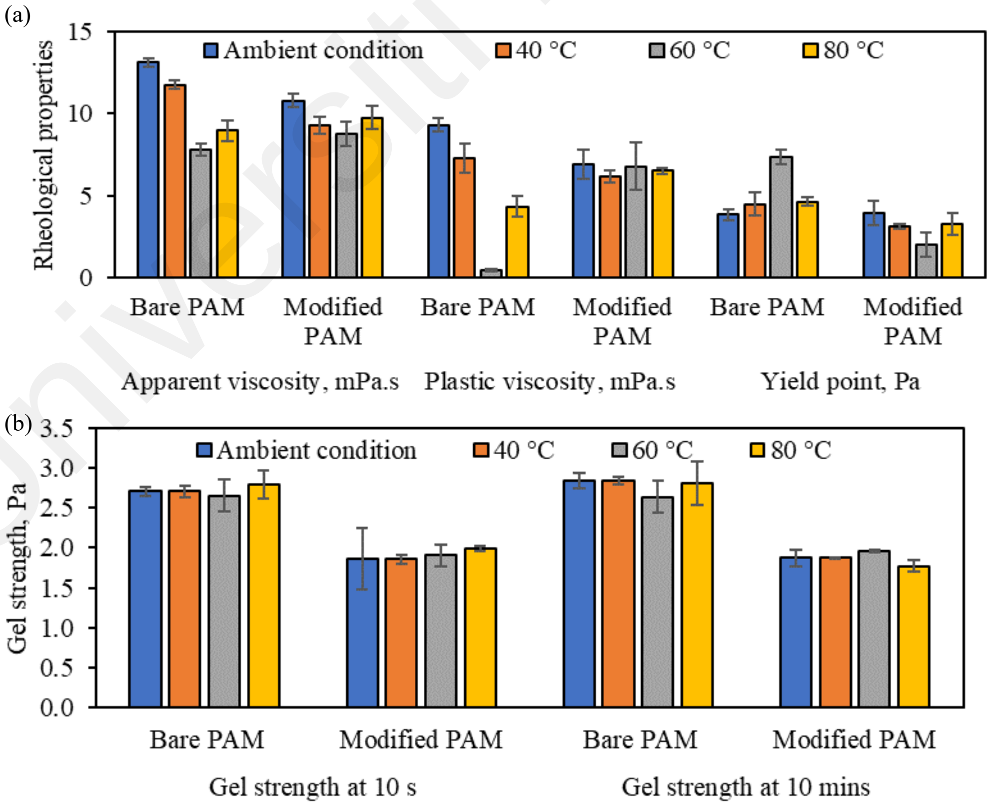

Figure 5.2: Comparison of temperature effect on (a) rheological properties, and (b) gel strength between bare PAM and modified PAM.

5.4.2 Effect of pH

The effect of pH on the rheological studies of PAM is shown in Figure 5.3(a). The ambient condition of PAM is prepared with a pH of distilled water in the range of 5.5 to 6. Drilling design is favourable at pH 10 as the rheological performance of drilling achieved the lowest PV and highest YP. Further, hydroxide and carbonate ions from soda ash can affect the rheological performance under basic conditions. Overall, there was a decreasing trend in AV and PV, with an increasing trend in YP. Compared with the gel strength of PAM at each pH, the desired flat gel strength of PAM is obtained at pH 9 – 10 because there was a negligible difference in gel strength between 10 seconds and 10 minutes, as shown in Figure 5.3(b). Hence, pH 9 and 10 were further investigated to study the rheological behaviour of modified PAM.

The effect of pH on the rheological properties between PAM and modified PAM was compared in Figure 5.4. At pH 9, the modified PAM demonstrated a reduction in AV and YP by 11.6% and 79.8%, respectively. However, modified PAM showed an incline of AV by 6.3 % and a decline of YP by 48.1%, respectively, at pH 10. For PV, modified PAM inclined by 48.1 %, and 89.4%, at pH 9 and 10, respectively. Although the rheological performance of modified PAM was not ideal as that of bare PAM, the plastic viscosity of modified PAM was lower at pH 10. The gel strength of modified PAM was inclined at pH 9 -10. Hence, modified PAM had higher gel strength than bare PAM. Higher gel strength can promote better cutting in drilling (Akpan et al., 2019; Vryzas & Kelessidis, 2017). Further, modified PAM and PAM performed a flat gel strength at pH 10 due to a negligible difference in gel strength between 10 seconds and 10 minutes. Therefore, the drilling fluid performed with better rheological behaviour at pH 10.

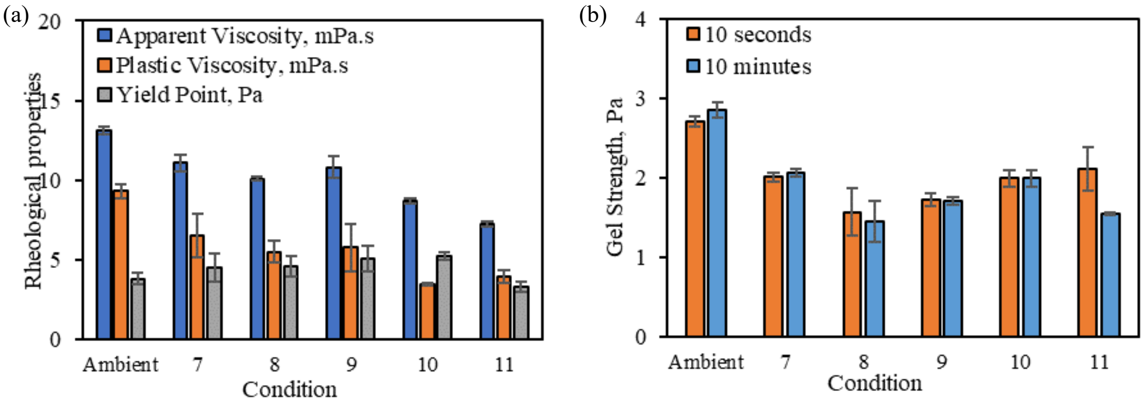

Figure 5.3: Effect of pH on (a) rheological properties, and (b) gel strength of 1000 ppm PAM.

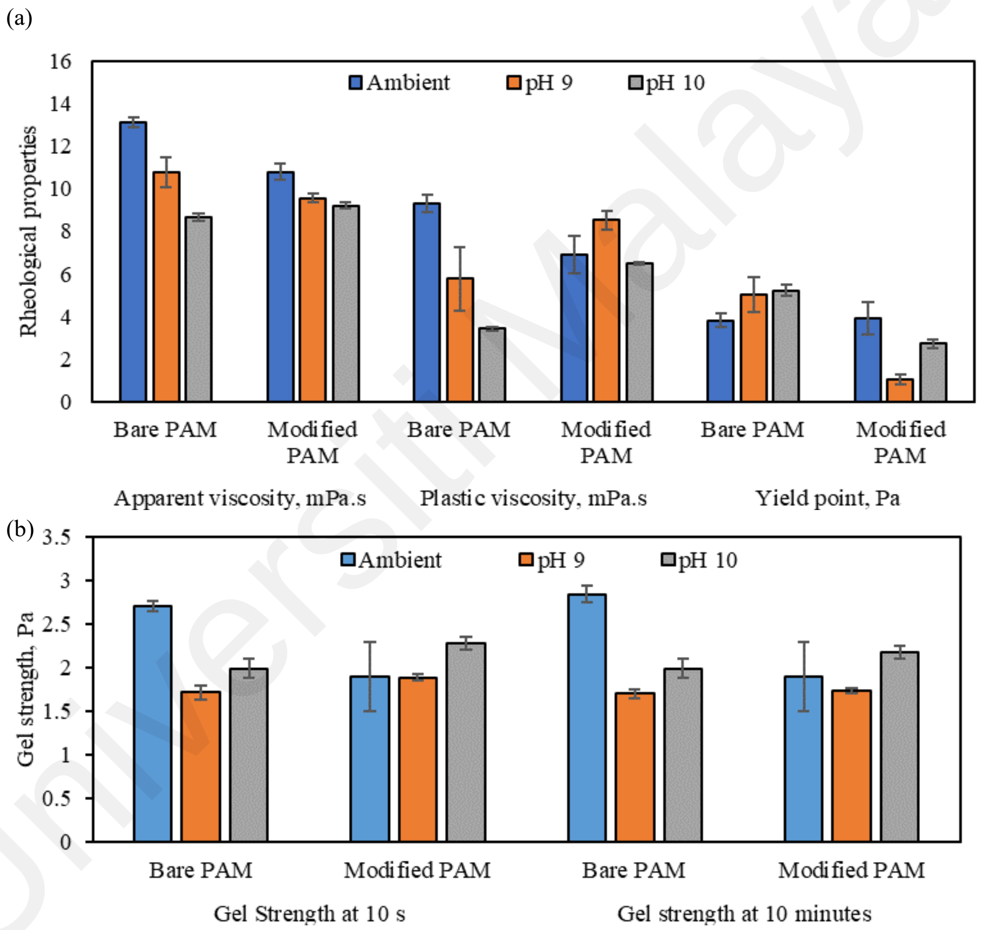

Figure 5.4: Comparison of pH effect on (a) rheological properties, and (b) gel strength between bare PAM and modified PAM.

5.5 Discussion

The temperature and pH effect on this modification of PAM highlighted two main points, i.e., the thermal stability of drilling fluid and chemical sensitivity of drilling fluid, with their limitations in this study. The weak bonding of the particles in a drilling fluid can be elucidated by the increasing temperatures due to the thermal energy, demonstrating the decrease in YP. PV also decreases at high temperatures because of the partial hydration shell, as evident in Figures 5.1 and 5.2. Although the functionalised silica can withstand more than 100 °C, as shown in TGA (Figure 4.3), the drilling fluid sample tested in this study performed below 100 °C due to the boiling point of water. Since the constituent of the drilling model is mainly water, the thermal stability is probably based on the main constituent's effect. However, the modified PAM doping with functionalised SiO_2 and SDS in this study demonstrated that its thermal stability is poorly established as it is maintained at 40 °C. Based on this thermal stability with the rheological study, the bonding in modified PAM is assumed to be weak than bare PAM. The bonding associated with the particles in a drilling fluid model affects the thermal stability of the fluid. This study demonstrated that the chemical bonding between the polymer and silica composite is probably van der Waals or electrostatic forces since it is physical mixing between PAM, functionalised SiO_2, and SDS. According to the interfacial chemistry of substances, a composite with electrostatic or van der Waals forces is poorer than a composite developed through covalent bonding (Baskaran et al., 2022). Additionally, bare PAM can form covalent bonding within the polymer chains and polymer molecules. Therefore, bare PAM has higher strength and higher thermal stability than modified PAM.

A pH of drilling fluid is essential as it mitigates the corrosion of the drill strings during operations. In the wellbore, a decrease in the pH level of the drilling fluid is simulated by an incline in the acid gas level. Acids in water generated from the formation of these acids can adversely influence the pH of drilling fluid, causing problems in fluid properties, such as thickening, dispersion flocculation, and clay separation (Nzerem et al., 2020). Thus, this study uses soda ash to increase the pH of drilling fluid, according to the following equations:

$$Na_2CO_3 + H_2O \rightarrow Na_2O + H_2CO_3 \tag{5.1}$$

$Na_2O + H_2CO_3 \rightarrow H_2O + CO_2 + NaOH$ (5.2)

A polymer chain can release the cations (usually Na^+) followed by the negative charge after the polymer is added to water. Subsequently, the free anionic polymer has existed in hydrate water. Therefore, the polymer can increase its size and viscosity when it hydrates the water. However, the polymer cannot hydrate and expand easily when there is the presence of salt in water. This situation happens due to the lack of hydrogen bonding between the polymer chains and water molecules. Therefore, the gel strength differences between 10 seconds and 10 minutes become negligible at pH 9 – 10 (Alaskari & Teymoori, 2007). Besides that, the viscosity reduction is due to the monovalent cation of Na^+ in soda ash. Although cations enhance the attractive force between particles, monovalent cations prompt a lesser attractive force than divalent cations (Alaskari & Teymoori, 2007). Since there is a contribution of Na^+ from soda ash in PAM-based drilling fluid, this study shows the negligible difference in gel strength between 10 seconds and 10 minutes and the reduction of the rheological parameter such as AV and PV. Therefore, soda ash is essential in pH adjustment to this PAM-based drilling fluid because it can influence the rheological behaviour of drilling fluid in terms of gel strength, AV, and PV. Overall, the drilling fluid in this study achieved a better pH of 9-10.

The limitation of this study is the thermal stability of modified PAM. Possibly modifying with the oil-based additives is required due to the boiling point of material sources. Although PAM and silica can withstand more than 100 °C, the fluid base is water. The liquid base of the drilling fluid model can be suggested by changing to the oil-based drilling fluid to further study the rheological performance compared to water-based fluid.

5.6 Conclusion

The rheological performance of PAM was significantly affected by temperature and pH. High thermal heating can increase the rate of polymer degradation. A more basic pH condition can enhance the rheological performance of polymer-based drilling.

PAM and modified PAM were synthesised, characterised, and utilised in drilling fluid at a specific temperature (ambient to 80 °C) and pH (9 – 10). The modified PAM was investigated to enhance drilling fluid performance, especially in bored pile drilling. The surface characterisation of modified PAM showed more hydrophilic than that of PAM. Besides, the rheological investigation showed that modified PAM performed better than PAM at 40 °C. Further, modified PAM had a better rheological performance at pH 10. In the future, modified PAM can be further tested in the bored pile construction to validate the frictional resistance of drilling fluid.

CHAPTER 6 CONCLUSION

6.1 Preamble

This study was carried out to investigate the effect of functionalised SiO_2 in PAM-based drilling fluid by evaluating the rheological behaviour of drilling fluid. In addition, this study has also sought to know the effect of SDS involved whether able to participate as a surface modifier in functionalised SiO_2, as well as rheological additives. The general literature on the PAM modification and nano-based drilling fluid is insufficient and provides an opportunity for exploration. Therefore, the study sought to achieve the following aims:

(1) To synthesise and characterise PAM and its modified PAM drilling fluid.

(2) To study the effect of PAM concentrations, functionalised SiO_2 concentrations, and SDS concentrations with the rheological study of PAM.

(3) To study the effect of temperature and pH with the rheological study of PAM and modified PAM.

To achieve these aims of this study, the first strategy and second strategy were carried out simultaneously; such could tuning on the properties of PAM, e.g., rheological properties. Finally, the last strategy was to optimise the effect of pH and temperature of drilling mud, concentrating on the relationship between bare PAM and modified PAM. A series of findings synthesis from this study is presented in the following paragraphs.

The study has identified 1000 ppm as a critical association concentration of PAM in Chapter 3. It is due to the polymer's dispersion stability, which is interrelated with the concentration of polymer that affects the rheological properties of PAM. Therefore, the optimised concentration of PAM has been further investigated in a series of experiments in modified PAM.

The effect of functionalised SiO_2 and SDS involved in the modification of PAM were discovered in Chapter 4. 0.5 wt% functionalised SiO_2 and 0.2 wt% SDS were determined as the optimised concentration in the formulation of modified PAM due to the rheological properties study, primarily obtained at low PV and high YP, as well as achieve a flat gel strength. Further, the achievement of rheological performance relies on the non-polar behaviour of functionalised SiO_2 and the surface properties of SDS. This optimised concentration of functionalised SiO_2 and SDS has become a modified PAM formulation in the following study.

Lastly, the effect of pH and temperature between the bare PAM and modified PAM were investigated (Chapter 5). The findings of bare PAM indicate that pH 9 and 10 are optimised while the heating temperature was conducted below 100 °C due to the fluid base that followed the water's boiling point. After further testing with formulated modified PAM, the study has also shown that drilling fluid work well at pH 10 while bare PAM-based and modified PAM-based drilling fluid work well at temperature 60 and 40 °C, respectively.

6.2 Limitations of the study

These findings in this research are subject to at least a few limitations. First, the drilling samples concentration optimises only performed using the viscosity method (viscometer) for identifying the critical association concentration of polymeric material involved in drilling. It is the first step to ensuring the success of drilling formulation in operations. Further, it is time-consuming in this study. Besides that, the pumping power relies on the gel strength of the drilling fluid. Such as PAM was involved in this study, a high gel strength obtained from the viscometer must focus on monitoring in the pilot scale due to the higher pressure required. Subsequently, high pressure applied can potentially cause damage to the operations if it exceeds the pressure required in drilling operations.

The research approach, such as silica modification and PAM modification employed for this study, provided new insight into drilling fluid even though they limited the generalisability of findings. In addition, although a few research reported the enhancement of surface properties of functionalised SiO_2 by applying SDS as a surface modifier, the method has concerns about the foam stability that affects the rheological properties of drilling fluid. Lastly, the thermal stability of modified PAM and bare PAM-based drilling fluid are limited below 100 °C.

6.3 Recommendations

Practitioners should consider the optimisation association concentration of polymeric material using another method, such as the fluorescence method via fluorescence Spectrometry and micro-pore method resistance factor. All these methods are worth further exploring in the future and obtaining a critical association concentration of PAM initially. Further research needs to be conducted to better understand the rheological findings' implications.

Advanced gel strength measurement is essential for proper drilling fluid operations. Hence several recommended equipment can be introduced in future research, such as a large amplitude oscillation shear (LAOS), nuclear magnetic resonance (NMR), and small amplitude oscillation shear (SAOS).

For future studies, water-based drilling fluid can be replaced by oil-based drilling fluid in PAM-based drilling fluid since the thermal stability of the oil is higher than 100 °C. In addition, PAM generally can withstand 175 – 300 °C. Therefore, the use of oil-based drilling fluid is suggested to oversee the trend of rheological behaviour with the effect of temperatures more than 100 °C

6.4 Commercialisation

Generally, PAM-based drilling fluid is not only applied in bored pile foundations. It can be applied to offshore exploration and the oil and gas industry. Besides, the modified PAM provides cutting-edge technology in these fields for concentrating the drilling fluid's rheological behaviour. Therefore, the proper drilling operation of modified PAM-based drilling fluid is lucrative in these fields and provides cost-effectiveness with a green environment for drilling fluid technology.

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