

SYNTHESIS AND INVESTIGATION OF COPOLYMER
GRAPHENE OXIDE COMPOSITE AS SHALE HYDRATION
INHIBITORS IN WATER BASED DRILLING FLUID

BY

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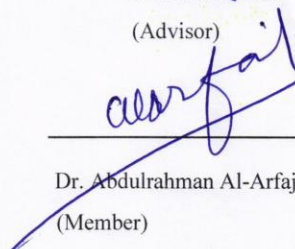
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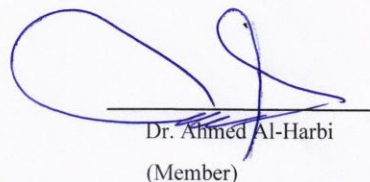
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Dedication

I humbly dedicate this work to Allah, and to my beloved family—especially my wife and child—whose patience and support during this challenging time mean the world to me.

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TABLE OF CONTENT

ACKNOWLEDGMENT.....	V
TABLE OF CONTENT.....	VI
LIST OF TABLE.....	X
LIST OF FIGURES.....	XI
LIST OF ABBREVIATIONS.....	XIV
ABSTRACT.....	XVI
ملخص الرسالة.....	XVIII
1 INTRODUCTION	1
1.1 Background.....	1
1.2 Problem statement	3
1.3 Objective of the study:	4
1.4 Significance of the studies:	5
1.5 Scheme of research findings reporting	5
2 LITERATURE REVIEW	7
2.1 Shale formation and composition.....	7
2.2 Shale hydration and Well drilling challenges.....	9
2.3 Mechanisms of Shale hydration and Swelling	12
2.4 Shale hydration inhibitors and mechanism of inhibition	15
2.5 Drilling fluids and the types of drilling fluids.	17
2.5.1 Oil based drilling fluid (OBDFs).....	19
2.5.2 Synthetic based drilling fluids (SBDFs).....	19
2.5.3 Pneumatic fluids.....	20

2.6	Method of making drilling fluid.....	20
2.7	Properties of drilling fluid:	21
2.8	Shale hydration inhibitors for WBDFs.....	22
2.8.1	Inorganic Salts.....	22
2.8.2	Graphene.....	22
2.8.3	Silicates.....	23
2.8.4	Organic Amines.....	23
2.8.5	Surfactants.....	24
2.8.6	Asphalts.....	25
2.8.7	Organic Polymers.....	25
2.8.8	Nanoparticles.....	27
2.9	Additives for water-based drilling mud.	36
2.9.1	Additives for viscosity control	36
2.9.2	Additives for density control	36
2.9.3	Filtration and rheology (viscosity) control additives.....	37
2.9.4	Other additives	37
2.10	Characterization of shale inhibition.....	38
2.10.1	Shale recovery test.....	39
2.10.2	Linear swelling test	39
2.10.3	Anti-swelling ratio.....	40
2.10.4	Pore pressure transmission test	40
2.10.5	Capillary suction test.....	41
2.10.6	X-ray diffraction (XRD)	41
2.10.7	Plate soaking test.....	42
2.10.8	Contact angle test	42
2.10.9	Scanning electron microscope.....	43
2.10.10	Thermogravimetric analysis.....	43
2.10.11	Zeta potential measurements	43
2.10.12	Water adsorption test	44
2.10.13	Cation exchange capacity	44

3	SYNTHESIS AND INVESTIGATION OF A GRAPHENE OXIDE GRAFTED WITH COPOLYMER OF ACRYLIC ACID AND ACRYLIC AMIDE AS SHALE HYDRATION INHIBITOR FOR WATER BASE DRILLING FLUIDS.	46
3.1	Introduction	46
3.2	Material and Methods.....	50
3.2.1	Materials	50
3.2.2	Material Preparation	50
3.3	Evaluation Method.....	53
3.3.1	Shale recovery test	53
3.3.2	Plate soaking Experiment	53
3.3.3	Contact angle test	53
3.3.4	Thermogravimetric analysis (TGA)	54
3.3.5	H-NMR Analysis.....	54
3.3.6	Anti –swelling test	55
3.3.7	Scanning Electron Microscope (SEM)	55
3.3.8	X-ray Diffraction (XRD).....	56
3.4	Result and discussions.....	56
3.4.1	Characterization of GO, Poly-(AAAm) and Poly-(AAAm)-GO	56
3.4.2	Evaluation of inhibition performance.....	61
3.5	Proposed mechanism of inhibition	77
4	SYNTHESIS AND EXAMINATION OF GRAPHENE OXIDE GRAFTED WITH COPOLYMER OF MALEIC ACID AND ACRYLIC ACID AS A SHALE HYDRATION INHIBITOR FOR WATER BASE DRILLING FLUID	79
4.1	Introduction	79
4.2	Materials and methods	83
4.2.1	Materials.....	83
4.2.2	Material Preparation	83
4.3	Evaluation Methods	86
4.3.1	Shale recovery test	86
4.3.2	Plate soaking Experiment	86

4.3.3	Contact angle test	86
4.3.4	Fourier Transforms Infrared Spectroscopy (FT-IR)	87
4.3.5	Thermogravimetric analysis	87
4.3.6	H-NMR Analysis	87
4.3.7	Anti –swelling test.....	87
4.3.8	Scanning Electron Microscope (SEM)	88
4.3.9	X-ray Diffraction (XRD)	88
4.4	Results and discussion	89
4.4.1	Characterization of GO, Poly-(AAMA) and Poly-(AAMA)GO	89
4.4.2	Evaluation of the inhibition performance	94
4.5	Proposed mechanism of inhibition:.....	110
5	CONCLUSION.....	112
	References	114
	Vitae	127

LIST OF TABLES

Table 2.1: An overview of recent chemical compounds investigated as water based drilling fluid inhibitors.	29
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LIST OF FIGURES

Figure 2.1 Schematic diagram of arrangement of atomic composition of clay [9].....	8
Figure 2.2 Schematic diagram of a drilling system[7]	10
Figure 2.3 Schematic diagram of wellbore instability [16]	11
Figure 2.4 swelling is described as follows: (a) Osmotic swelling (b) Crystalline swelling [8] ...	14
Figure 2.5 Inhibition and hydration mechanism [28].....	16
Figure 2.6 classification of the various drilling fluids	18
Figure 3.1 Reaction scheme of free radical polymerization of the copolymer of acrylic acid and maleic acid/ Graphene oxide (Poly-(AAAm)-GO) (I), and free radical polymerization of the copolymer of acrylic acid and maleic acid (II)	52
Figure 3.2 NMR spectrum for Poly-(AAAm) and monomer solution,	58
Figure 3.3 FT-IR spectrum for GO, Poly-(AAAm), and Poly-(AAAm)-GO	59
Figure 3.4 TDA curves Poly-(AAAm), and Poly-(AAAm)-GO	60
Figure 3.5 shows images of bentonite pallets at different time interval [1=30 min, 2=1 hr, 3=7 hr, 48 hr] in a. DI, b. 10 % KCl solution, c. 4 % Poly-(AAAm) solution, and d. 4 % Poly- (AAAm)-GO solution.	62
Figure 3.6 shows the shale recovery test in water, 10 % wt KCl, 4 % Poly-(AAAm), and 4 % Poly-(AAAm)-GO	64
Figure 3.7 shows the anti-swelling ratio of 10 % wt KCl, 4 % Poly-(AAAm), and 4 % Poly- (AAAm)-GO.	66
Figure 3.8 shows the TGA plot of pristine Na-Bt, Na-Bt/Poly-(AAAm), and Na-Bt/Poly- (AAAm)-GO	68
Figure 3.9 shows the XRD plots for Na-Bt, Na-Bt-Poly-(AAAm), and Na-Bt-4 % Poly-(AAAm)- GO	70

Figure 3.10 SEM images for a. Na-Bt/H ₂ O, b. Na-Bt/4 % Poly-(AAAm), and c. Na-Bt/4 % Poly-(AAAm)-GO	72
Figure 3.11 water contact angle; a. pristine Na-Bt, Na-Bt/4 % Poly-(AAAm), and Na-Bt/4 % Poly-(AAAm)-GO	74
Figure 3.12 FT-IR plotting; Na-Bt, Na-Bt-4 % Poly-(AAAm), and Na-Bt-4 % Poly-(AAAm)-GO	76
Figure 3.13 An illustration of Poly-(AAMA)-GO's hydration inhibition mechanism.....	78
Figure 4.1 Reaction scheme of free radical polymerization of the copolymer of acrylic acid and maleic acid/ Graphene oxide (Poly-(AAMA)GO) (I) and free radical polymerization of the copolymer of acrylic acid and maleic acid (II).....	85
Figure 4.2 Shows NMR spectrum of Poly-(AAMA) and monomer solution	91
Figure 4.3 FT-IR spectrum of Poly-(AAMA)-GO, Poly-(AAMA) & GO	92
Figure 4.4 TGA curves of Poly-(AAMA)-GO and Poly-(AAMA).	93
Figure 4.5 . Pictures of Na-Bt plates soaked in pure water and different inhibitor solutions for 548hr : (a) pure water, (b) 10.0 wt % KCl, (c) 4.0 wt % Poly-(AAMA), (d) 4.0 wt % Poly-(AAMA)-GO.....	95
Figure 4.6 Contact angle of (a) pristine Na-Bt, (b) modified NaBt with 10 wt % KCl, and 4.0 wt % (c) Poly-(AAMA) solution and Na-Bt plate (d) Poly-(AAMA)-GO and Na-Bt.....	97
Figure 4.7 Percentage recovery of shale after hot-rolling in pure water and different inhibitor solutions at a concentration of 120°C for 16 h.	99
Figure 4.8 Thermal stability curve of pure Na-Bt and Na-Bt/inhibitor composites.	101
Figure 4.9 shows anti-swelling ratio of various inhibitors.....	103
Figure 4.10 FT-IR spectra of Na-Bt, Na-Bt/ Poly-(AAMA) and Na-Bt/ Poly-(AAMA)-GO composites.....	105

Figure 4.11 SEM images of (a) Na-Bt (b) Na-Bt/ Poly-(AAMA) (c) Na-Bt/ Poly-(AAMA)-GO composite.....	107
Figure 4.12 XRD patterns of Na-Bt, Na-Bt/ Poly-(AAMA) and Na-Bt/ Poly-(AAMA)-GO composite.....	109
Figure 4.13 shows the mechanism of Poly-(AAMA)-GO inhibiting shale hydration swelling...	111

LIST OF ABBREVIATIONS

AA	: Acrylic Acid
AAm	: Acrylic Amide
API	: American Petroleum Institute
APS	: Ammonium PerSulfate
AR	: Anti swelling Ratio
AP	: Apparent Viscosity
CaCl₂	: Calcium Chloride
CaSO₄	: Gypsum
CEC	: Cation Exchange Capacity
CMC	: Carboxy Methyl Cellulose
DI Water	: Deionized Water
EDA	: Ethylenediamine
FTIR	: Fourier-Transform Infrared
GBM	: Gas Based Mud
IR	: Infrared
KCl	: Potassium Chloride
KPS	: Potassium Persulfate
KHCO₃	: Potassium Bicarbonate

MD	:	Mud Density
Na₂CO₃	:	Sodium Carbonate
Na-Bt	:	Sodium Bentonite
NMR	:	Nuclear Magnetic Resonance
OBDFs	:	Oil Based Drilling Fluids
OBM	:	Oil Based Mud
PV	:	Plastic Viscosity
Poly-(AAMA)	:	poly (Acrylic Acid-co-Maleic Acid)
Poly-(AAMA)-GO	:	Copolymer of Acrylic Acid and Maleic Acid/ Graphene Oxide
Poly-(AAAm)	:	Poly (Acrylic Acid-co-Acrylamide)
Poly-(AAAm)-GO	:	Copolymer of Acrylic Acid and Acrylamide/ Graphene Oxide
SBM	:	Synthetic Based Mud
SEM	:	Scanning Electron Microscope
TGA	:	Thermo Gravimetric Analysis
WBDFs	:	Water Based Drilling Fluids
WBM	:	Water Based Mud
XRD	:	X-Ray Diffraction

ABSTRACT

Full Name : MOMODOU A JALLOW

Thesis Title : SYNTHESIS AND INVESTIGATION OF COPOLYMER GRAPHENE
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Most wellbore stability problems in water-based drilling fluids are caused by the hydration of the underground shale formation, which makes up over 75% of drilled formations. Consequently, developing a high thermal stability inhibitor to prevent shale hydration is crucial. This research focus on synthesizing copolymer graphene oxide composites as an effective and low-cost inhibitor with higher thermal stability than their pure polymer counterpart through free radical polymerization in aqueous solution. We reported the synthesis of a copolymer of acrylic acid and acrylic amide/ graphene oxide composite (Poly-(AAAm)-GO), and a copolymer of acrylic acid and maleic acid/ graphene oxide composite poly-(AAMA)-GO to provide high thermal stability inhibitor for water-based drilling fluids.

Both inhibitors were tested for inhibitory properties through anti-swelling, immersion, and shale recovery tests, with a comparison made to KCl, a standard industry inhibitor. The poly-(AAAm)-GO and poly-(AAMA)-GO greatly retarded the swelling of bentonite, with anti-swelling ratios of 82 and 78 % respectively, compared to KCl with 58 %. Both Poly-(AAAm)-GO and poly-(AAMA)-GO exhibited enhanced thermal stability compared to their pure polymer counterpart Poly-(AAAm) and Poly-(AAMA), attributed to the graphene oxide component. The poly-(AAMA)-GO exhibited excellent temperature

stability up to 250 °C, indicating potential applications in high-temperature well drilling. Contact angle, FT-IR, SEM, and XRD results indicate that both inhibitors form a protective film, adsorbed onto the surface of the bentonite by electrostatic attraction thereby making the surface more hydrophobic. Therefore, both Poly-(AAAm)-GO and Poly-(AAMA)-GO prevent hydration and swelling of bentonite by preventing water molecules from invading the interlayer spacing.

ملخص الرسالة

الاسم الكامل: مامودو أ. جالو

عنوان الرسالة: تحضير ودراسة مركب أكسيد الجرافين مع بوليمر مشترك كميثبات ترطيب الطفل في سوائل الحفر المائية

التخصص: الكيمياء

تاريخ الدرجة العلمية: ديسمبر 2024

تُعزى معظم مشكلات استقرار الآبار في سوائل الحفر القائمة على الماء إلى ترطيب التكوينات الصخرية تحت الأرض، والتي تشكل أكثر من 75% من التكوينات المحفورة. وبالتالي، فإن تطوير مثبط عالي الثبات الحراري لمنع ترطيب الصخر الطيني يُعد أمرًا بالغ الأهمية. تركز هذه الدراسة على تخليق مركب كوبوليمر أكسيد الجرافين كعامل مثبط فعال ومنخفض التكلفة يتميز بثبات حراري أعلى من نظيره من البوليمرات النقية من خلال بلورة الجذور الحرة في محلول مائي.

قمنا بالإبلاغ عن تخليق كوبوليمر من حمض الأكريليك وأكريلاميد/مركب أكسيد الجرافين لتوفير (Poly-(AAMA)-GO) وكوبوليمر من حمض الأكريليك وحمض الماليك/مركب أكسيد الجرافين (Poly-(AAAm)-GO). مثبط عالي الثبات الحراري لسوائل الحفر القائمة على الماء.

تم اختبار كلا المثبتين من حيث خصائصهما المثبطة من خلال اختبارات مقاومة الانتفاخ، والانغماس، واسترجاع Poly-(AAAm)-GO، المثبط القياسي في الصناعة. أظهر كل من KCl والصخر الطيني، مع إجراء مقارنة بمادة فعالية كبيرة في تقليل انتفاخ البنتونيت، حيث بلغت نسب مقاومة الانتفاخ 82% و 78% Poly-(AAMA)-GO و Poly-(AAAm)-GO الذي بلغت نسبته 58%. أظهر كل من KCl على التوالي، مقارنة بـ ، ويُعزى Poly-(AAAm) و Poly-(AAMA) ثباتًا حراريًا محسنًا مقارنة بنظيريهما من البوليمرات النقية GO. ذلك إلى مكون أكسيد الجرافين.

استقرًا حراريًا ممتازًا حتى 250 درجة مئوية، مما يشير إلى إمكانيات استخدامه Poly-(AAMA)-GO أظهر إلى XRD، SEM، و FT-IR في حفر الآبار ذات درجات الحرارة العالية. تشير نتائج اختبارات زاوية التماس، و أن كلا المثبتين يشكلان طبقة واقية، يتم امتصاصها على سطح البنتونيت عن طريق الجذب الكهروستاتيكي، مما ترطيب Poly-(AAAm)-GO و Poly-(AAMA)-GO يجعل السطح أكثر كرهًا للماء. وبالتالي، يمنع كل من. وانتفاخ البنتونيت عن طريق منع جزيئات الماء من التغلغل في الفراغات بين الطبقات.

CHAPTER 1

INTRODUCTION

1.1 Background

Drilling fluid is alternatively referred to as drilling mud. The material helps suspend cuttings, manage pressure, stabilize exposed rock, offer buoyancy, cool the drill bit, and lubricate the drill bit during drilling in wellbores [1]. Drilling fluids' chemical interactions with shales contribute to the instability of wellbores; therefore, selecting the right fluid is crucial [1]. A synthetic-based drilling mud (SBM), oil-based drilling mud (OBM), and a water-based drilling mud (WBM) are three types of drilling fluids [1].

Drilling shale with OBM and SBM is the best option whenever possible [2]. Environmental legislation and high costs, however, limit OBM and SBM's use in drilling applications [2]. When used in offshore drilling, they are known to pollute the environment and are complex to treat [3]. The development of WBM became inevitable in drilling engineering since WBM are simple in composition, inexpensive, and easily accepted by the environment [2]. When WBM is used, the shale formations become seriously soaked with water [4].

Comprehending shale hydration is crucial for developing effective shale inhibitors. Shale refers to a thinly layered sedimentary rock abundant in clay minerals, like montmorillonite (MMT). Water-based drilling fluids lead to significant saturation and invasion of shale formations. Individual layers of clay become negatively charged when metal atoms are substituted within the lattice. Ca^{2+} and Na^{+} are usually found in the interlayer spaces to balance this charge. Osmotic hydration and crystalline hydration are the two distinct ways clay minerals hydrate. Across all clay mineral types, crystalline hydration is possible. The

swelling is caused by the direct adhesion of water molecules to the crystalline surface, causing localized swelling to occur over a short distance. In the case of complete crystalline swelling, the interlayer space can be expanded by 10 to 20 Å. As cations in an interlayer exceed those in the surrounding water, a diffusion effect is created that pulls water molecules into the interlayer. This process is known as osmotic hydration. As a result, swelling occurs to a considerable or significant degree. Water content increases as osmotic effects result in a steep rise, accommodating 35 to 40 Å. A repulsive diffuse double layer continuously grows the volume to several hundred angstroms [4],[3]. Achieving successful drilling necessitates the effective management of shale hydration. A borehole's diameter can be reduced by excessive hydration and swelling of the shale, altering stress distribution around it, and diminishing its mechanical resilience [3]. To ensure that drilling operations are smoothly progressing, drilling fluid must be environmentally friendly and capable of inhibiting shale hydration. Water-based drilling fluids are primarily inhibited by potassium chloride (KCl). It operates by substituting sodium ions with less hydrated potassium ions within the montmorillonite (MMT) layer, thus impeding clay hydration. Due to the high concentrations of KCl required for effective inhibition, large amounts of chloride ions are introduced into the mud. High KCl concentrations are, however, adversely impacting ecosystems causing contamination and environmental concerns [5]. Polyacrylamides, polyglycols, and silicates have been added to KCl to enhance inhibition, resulting in synergistic effects. Nonetheless, these additives may alter the mud's rheology. Researchers have delved into diverse materials in literature to assess their potential in inhibiting shale formation. In addition to nanomaterials and graphene, ionic liquids, natural products, and composites are included in these materials [5]. Clay minerals' irregular shapes, variable

particle sizes, and different charges have prevented any of the developed shale inhibitor compounds from completely stabilizing boreholes [2]. To overcome the challenges and instability caused by shale hydration during drilling, it is imperative that other materials with active and efficient chemistry be explored.

By using addition free radical polymerization, the research aims to synthesize affordable, environmentally friendly copolymers, and graphene oxide modified with copolymers. The subsequent steps involve characterizing the synthesized material and testing its efficacy in inhibiting shale hydration.

1.2 Problem statement

As a result of the significant amount of water in water-based drilling fluids, they pose a number of challenges during application. Several issues can arise as a result of infiltration of water into the formation, including contamination, hydration and swelling of the shale, and collapse.

Reducing water sensitivity damage to reservoirs with a low permeability can be achieved by using clay inhibitors. Shale hydration and dispersion have been inhibited by a variety of inhibitors previously examined in research.

Clay inhibitors at present are mostly salts such as KCl, which are usually inorganic. The KCl weakens shale hydration through ion exchange. Potassium chloride, however, has several shortcomings, including relatively high concentrations, inconsistencies with environmental protection requirements, high liquid waste disposal costs, and corrosion of downhole drilling tools. Despite partial success, wellbore instability problems remain and

using high concentrations of KCl for environmental reasons is undesirable because of its toxicity to benthic organisms [6].

There have been a number of inhibitors used in previous studies to inhibit the hydration and dispersion of shale. Shales have been stabilized using chemicals such as silicates, organic amines, surfactants, and nanoparticles. Despite their effectiveness as shale inhibitors, they still have some limitations, such as high costs and toxicity concerns. The exploration of other materials with active and efficient chemistry is imperative to overcome the challenges and instability caused by shale hydration during drilling.

1.3 Objective of the study:

This project involved developing inexpensive yet highly effective shale hydration inhibitors that could be used as substitutes for conventional KCl in drilling fluids. Following are the specific objectives that will help us accomplish this:

- Synthesize affordable, environmentally friendly low molecular weight copolymers graphene oxide composite using addition free radical free polymerization reaction.
- Characterize the synthesized copolymers, and copolymer graphene oxide composite using Fourier Transform Infrared Spectroscopy (FT-IR), Proton Nuclear Magnetic resonance spectroscopy (H-NMR), and Thermo-gravimetric Analysis (TGA).
- Investigate the efficiency of the products as shale hydration inhibitors in water-based mud using American Petroleum Institute (API) Standard methods.

1.4 Significance of the studies:

Various polymer systems have been used to solve the issue of high electrolyte concentrations in WBDFs. Polymers can be used to modify rheological properties such as viscosity, yield stress, and gel strength. To maintain their rheological properties, drilling fluids must be formulated with high molecular weight polymers resistant to salt. The essence of synthesizing the copolymers modified with graphene oxide is to enable the inhibitor to withstand high temperature beyond its pure polymer counterpart. By grafting the polymer onto the surface of graphene oxide, the polymer exerts its toughness as well as combining the advantages of graphene, and greatly reducing the amount of graphene used.

1.5 Scheme of research findings reporting

To facilitate reading and understanding, the thesis report is organized and structured into the following five chapters:

- **Chapter 1:** describes the problem of shale formation hydration, the essence of copolymers, and the advantages of using copolymer graphene oxide composite to inhibit shale formation hydration. A discussion of the problem statement, significance of the study, and the research plan follows.
- **Chapter 2:** provides an overview of the current literature on shale hydration mechanisms and shale inhibition.
- **Chapter 3:** synthesis and investigation of a copolymer of acrylic acid and acrylic amide graphene oxide composite as a shale hydration inhibitor for water base drilling fluids.

- **Chapter 4:** Synthesis and examination of graphene oxide grafted with copolymer of maleic acid and acrylic acid as a shale hydration inhibitor for water base drilling fluid
- **Chapter 5:** A summary of the study's findings is presented.

CHAPTER 2

LITERATURE REVIEW

2.1 Shale formation and composition

Oil and gas exploration often encounters mudstones that form impermeable caps to oil sources [7]. Mudstone is a sedimentary rock rich in clay and made up mainly of consolidated clay minerals, natural cracks, and nanopores [7]. An aluminosilicate mineral classified as phyllosilicates, shale is composed of layers of negatively charged aluminosilicates stacked in two-dimensions [7]. Using chemical analysis, it has been determined that the mica crystals consist of tetrahedral or octahedral sheets [8]. The octahedral sheet contains six oxygen atoms encircling a central metal atom, mainly aluminum, while the tetrahedral sheet contains four oxygen atoms surrounding a silicon atom (see figure 1) [9]. There is a cleavage plane between platelets due to weak Van Der Waal forces between oxygen atoms. Mineral clay contains a variety of different arrangements of tetrahedral and octahedral sheets. Mineral clays are called 1:1 clay (T-O clays) if they contain one tetrahedral and one octahedral sheet [10]. Those clays consisting of two tetrahedral sheets sandwiched between two octahedral sheets are called 2:1 clays (or T-O-T clays) [10].

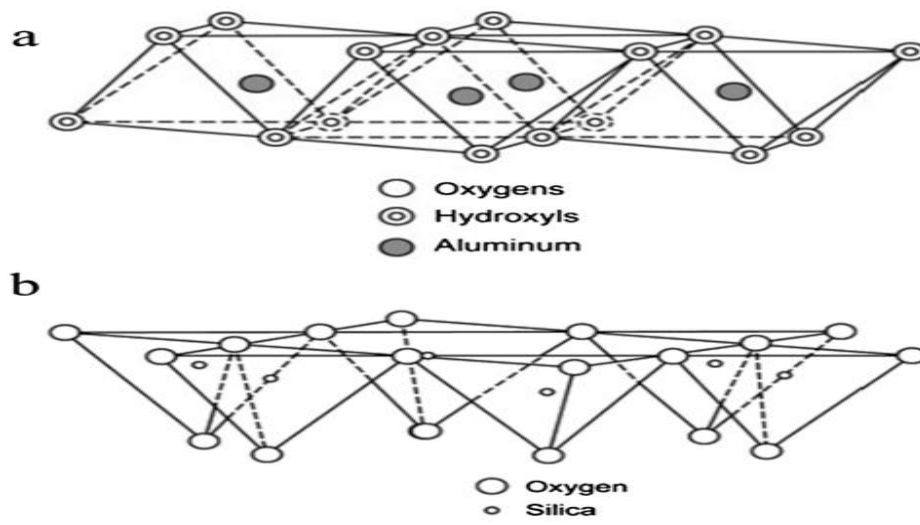


Figure 2.1 Schematic diagram of arrangement of atomic composition of clay [9]

2.2 Shale hydration and Well drilling challenges

The oil and gas industry is experiencing a boom, which requires new technologies and drilling for ultra-deep, highly deviated, and horizontal wells in challenging subsurface environments [11]. Drilling fluids are required for a variety of functions in oil and gas well drilling: lubricating the drilling bit, maintaining fluid rheology, preventing the swelling of shale formations, preventing the invasion of fluid loss into formations, transporting rock cuttings to the surface, and managing hydrostatic pressure in the wellbore [11]. Oil base drilling fluid (OBDFs), synthetic base drilling fluid (SBDFs), and water base drilling fluid (WBDFs) along with various chemical additives, are the three most common types of drilling fluids [12]. OBDFs and SBDFs are known to have excellent lubricity, high temperature stability, and superior inhibition properties [12]. However, the use of OBDFs and SBDFs is limited because of concerns about toxicity, pollution, and cost. Low cost, environmental friendliness, remarkable rheological properties, and excellent performance makes WBDFs a popular alternative [13].

Shale exhibits different water sensitivity due to clay porosity differences, structure of crystal, composition and development of fissures [13]. Approximately 75% of the world's drilling formations are shale, and 90% of wellbore instability results from troublesome shale [13], [14]. When clay is in contact with water, it hydrates, swells, and disperses [14]. Shale hydration in wellbore creates instability and results to problems such as disintegration and collapse [14]. This accounts for the increasing costs and non-production time associated with WBDFs [14], [15]. This is an indication that the hydration, dispersion, swelling of shale formation in WBDFs is undesired. It is therefore crucial to develop

economical, safe, and environmentally friendly hydration inhibitors for use in WBDFs [15].

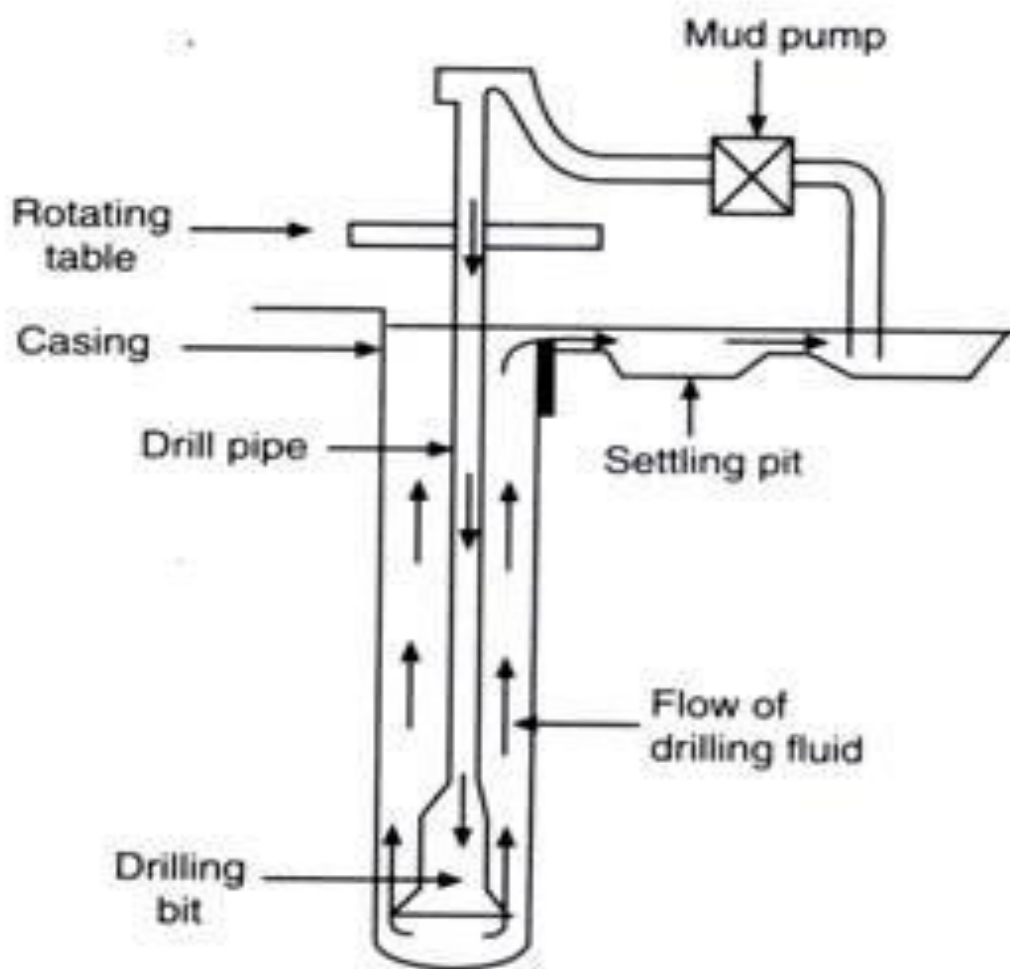


Figure 2.2 Schematic diagram of a drilling system[7]

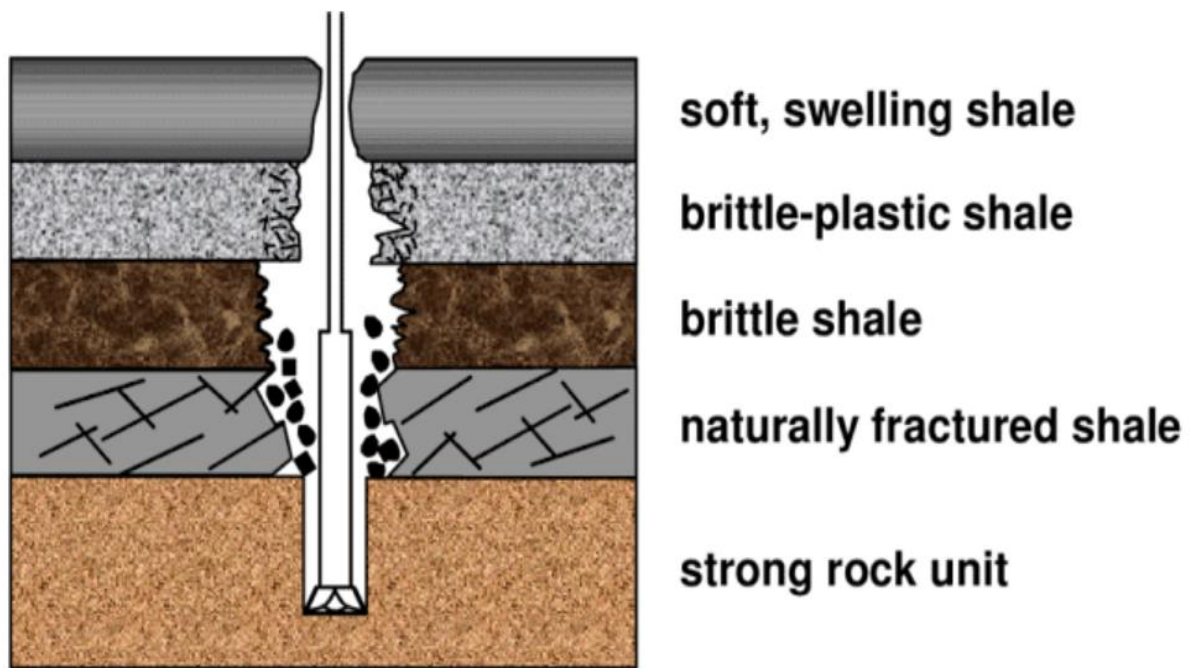


Figure 2.3 Schematic diagram of wellbore instability [16]

2.3 Mechanisms of Shale hydration and Swelling

Understanding the mechanism involve in shale hydration will ensure the development of effective inhibitors with efficient inhibitory capabilities [15],[17]. Shale material hydrates, disperses, and swells due to the hydrated clays in the formation [17]. Because bentonite clay can swell ten times its original volume, it is considered a main factor in shale instability [17], [18]. As clay gets wet, its cations become hydrated, which causes it to swell up [18].

Generally three types of mechanism enhance the hydration clay mineral; surface hydration force, osmotic hydration force, and capillary action [18], [19]. When molecules of water are adsorbed on to the crystals of the clay surface they tend to bond on to the clay surface through hydrogen bond with oxygen [19]. As more water molecules get adsorbed to the hydrated clay surface, this result in the formation of multi layers of hydrate [19],[20]. Adsorption of water molecules caused surface hydration, which is sometimes referred to as crystalline swelling [20]. In the case of a complete surface hydration the interlayer space can be expanded by 10 to 20 Å [20], [21].

The type, size, and charges of cations within the interlayer spacing can also affects clay swelling [21]. Cations with high hydration capacity such Na^+ , have high swelling potentials [21],[22]. As cations in an interlayer exceed those in the surrounding water, a diffusion effect is created that pulls water molecules into the interlayer [22]. This process is known as osmotic hydration. As a result, swelling occurs to a considerable or significant degree [22], [23]. Water content increases as osmotic effects result in a steep rise, accommodating 35 to 40 Å [23]. Furthermore, shale hydration and swelling is also caused by capillary

actions. Liquid intrusion into the shale formation can results from the spontaneous inhibition of shale which is caused by capillary activities [23], [24].

The hydration mechanism of shale formations shows that many factors affects the hydration and swelling of clay such as capillary forces of the formation, types and concentration of cations and the clay type [24]. Inhibitors are selected based on their mechanism of inhibition and the shale type. Thus, two mechanisms exist for inhibiting hydration, such as substituting high-hydration cations with lower-hydration ones or applying macromolecules to coat the clay surface and block water intrusion [25], [26].

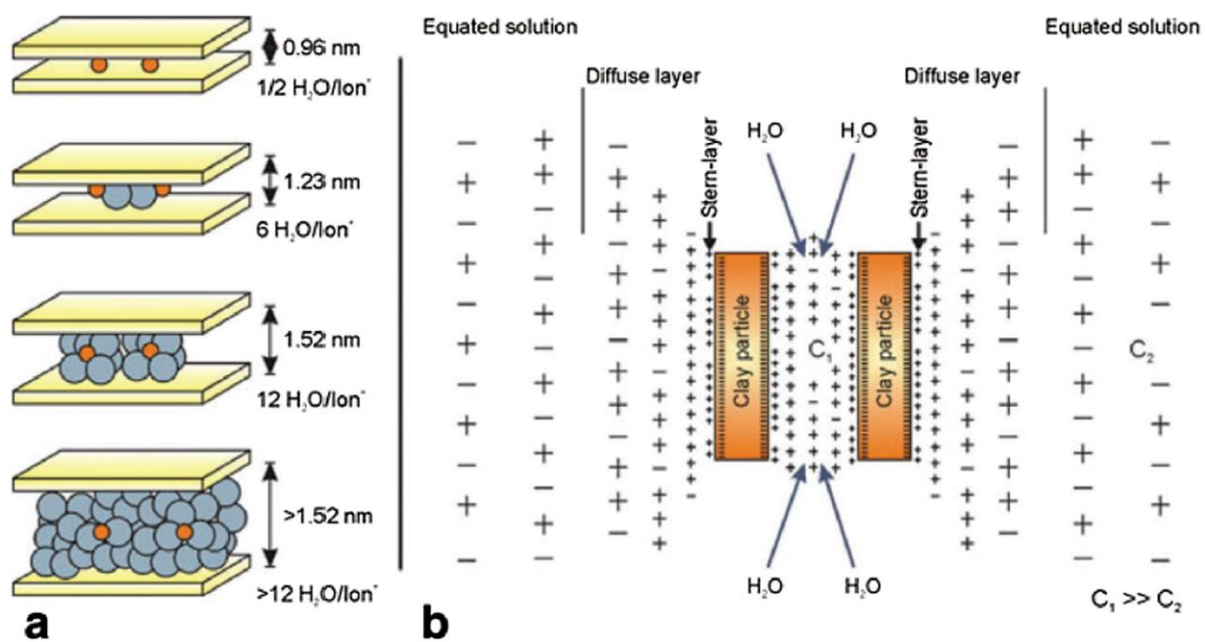


Figure 2.4 swelling is described as follows: (a) Osmotic swelling (b) Crystalline swelling [8]

2.4 Shale hydration inhibitors and mechanism of inhibition

Traditionally used inhibitor in WBDFs includes chlorides salts such as potassium chloride (KCl) [26]. This inhibits shale hydration by exchanging the strongly hydrated capacity cation, Na^+ with a lower hydration capacity cation, K^+ [26], [27]. Various concentrations of electrolytes are used based on the type of shale formations. Most times Massive quantity of KCl is used in order to achieved the desired inhibition [27]. A high concentration of KCl electrolyte results in flocculation of clay mineral and alter the rheology of the drilling mud. On the other hand, massive concentration of KCl affects ecosystems and are detrimental to the environment [27],[10].

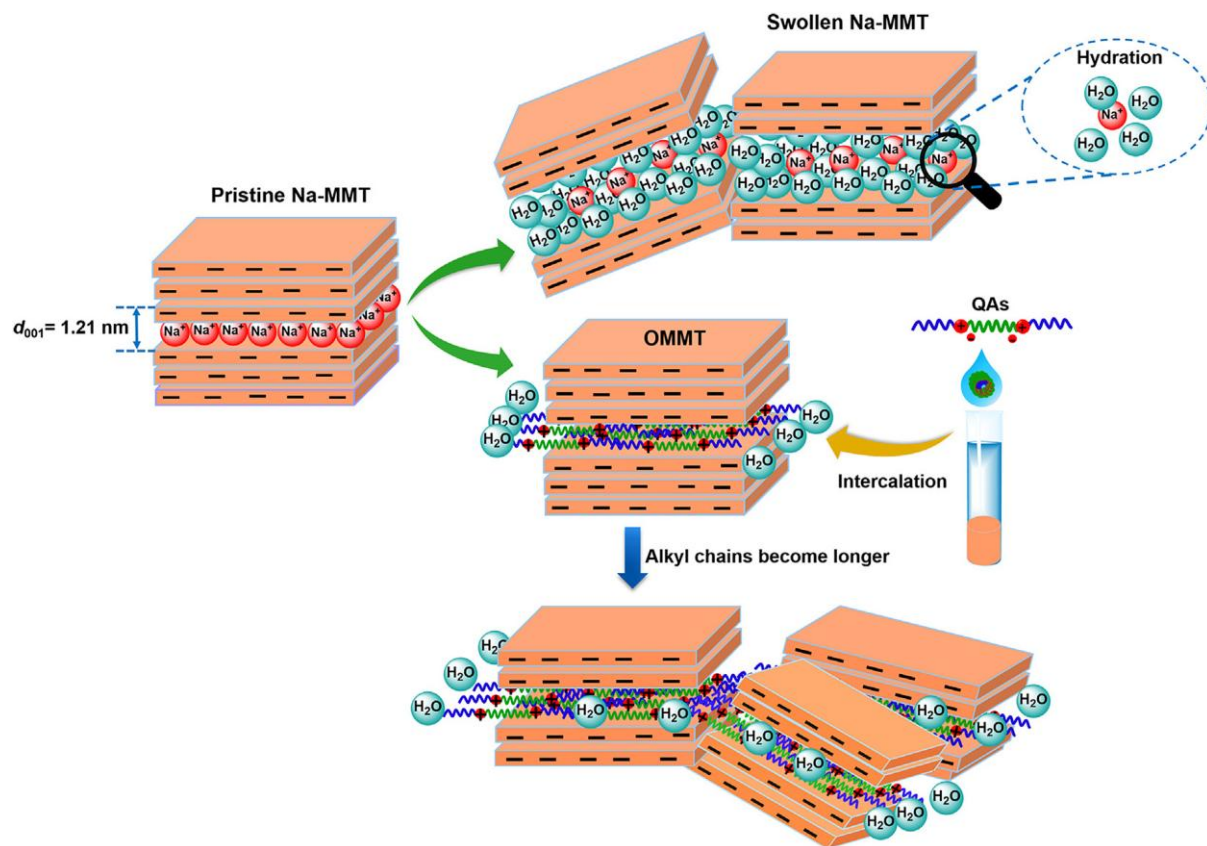


Figure 2.5 Inhibition and hydration mechanism [28]

2.5 Drilling fluids and the types of drilling fluids.

Any fluids that circulates through a wellbore in order to extract shale cuttings from a well are considered as drilling fluids [29]. Through the nozzles of the bit the fluids are pumped down the drill pipes and returned back carrying the shale cuttings generated by the bit action and brought to the surface [29]. The main function is to reduced friction thereby lubricate and clean the hole while drilling. Drilling fluids also serves as a coolant to the drilling bits, control well pressure, and maintain the rheology of the formations [29],[30]. As a complex mixture, drilling fluids are formed from solids, liquids, chemicals and even gases. Drilling mud a type of drilling fluid is often defined as a composition of liquids that help in the process of drilling petroleum wells and depend on the specific requirement of drilling [30], [31].

Typically, drilling fluids contain a base fluid, or solvent, and some additives (chemical agents) to obtain certain properties. Even though drilling fluids can be classified in a variety of ways, the most standard and conventional method is based on the type of based fluid.

As indicated in fig drilling fluids in oil gas exploration can be classified into three Oil based drilling (OBDFs), Synthetic based drilling fluids (SBDFs) and water-based drilling fluids (WBDFs) [31].

Classifications Of Drilling Fluids

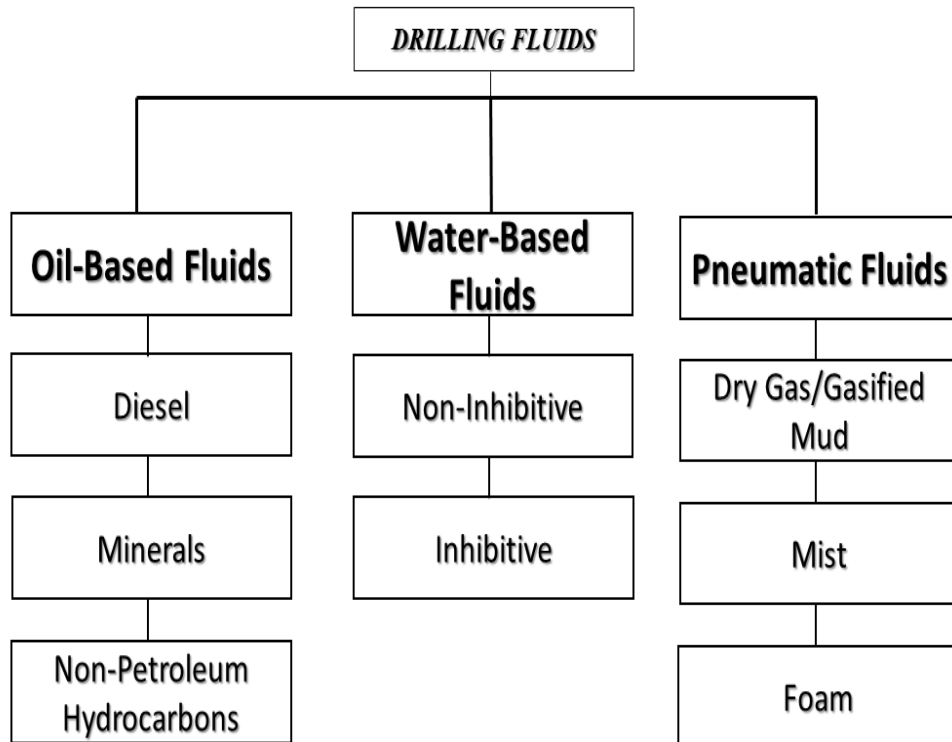


Figure 2.6 classification of the various drilling fluids

2.5.1 Oil based drilling fluid (OBDFs)

The main composition of OBDFs are petroleum hydrocarbons along with other additives such as clay, emulsifiers, polymers and other materials created for drilling [32],[33]. It was introduced in the 1960s to help solve several drilling problems; contaminants, stuck pipes, regulate downhole temperature etc [32]. Its unmatched performance for drilling OBDFs has a special advantage [32]. They are more inhibitive than WBDFs and are effective against all types of corrosion. OBDFs have other advantages such as high temperature stability, reduction in production damage, and resistance to chemical contaminants [33]. In offshore-drilling the discharge generated by OBDFs is processed and shipped to shore for disposal and this results in excessive cost on operations [33], [34].

2.5.2 Synthetic based drilling fluids (SBDFs)

is another form of drilling mud applied in drilling operations. This has synthetic liquids as the external phase instead of oil [34],[35]. It is known to be an inverted emulsion with lower toxicity than OBDFs [35]. Synthetic drilling fluid has performance as good as OBDFs and complies much better with environmental regulations. In offshore drilling, shale cutting from SBDFs is approved to be disposed of into waters because they biodegrade faster [35],[36]. In response to growing environmental legislation demands and excessive costs, OBDFs and SBDFs have been restricted in their applications [36]. Due to the desire for more environmentally friendly drilling fluids, expatriates have adopted the use of water-based drilling fluids (WBDFs) in drilling operations [36], [37]. This type of drilling fluid has water as its external phase which contains additives to enhance drilling operations [37]. Due to their remarkable rheological properties, environmentally friendly nature, and excellent

performance, Water-based drilling fluids are commonly used in drilling operations [37],[38].

As a result of water coming into contact with shale formation, there are undesirable concerns. Formation hydrates, swell, and disperse, resulting in the collapse of the wellbore [38]. To prevent drilling mud from hydrating, various chemical additives are added to drilling mud in order to achieve the performance required by WBDFs [38],[39]. One of the oldest and most widely used inhibitor for WBDFs is potassium chloride (KCl). This inhibits shale hydration by exchanging the highly hydrated sodium ion (Na^+) with a weakly hydrated potassium ion (K^+) [39], [40]. In order to achieve a desired inhibitory effect, large amounts of KCl are required, and as a result ecosystem are negatively affected and the environment is damaged. Scientists now find it necessary to develop effective environmentally friendly inhibitors so as to eliminate or limit the use of KCl in this process [32].

2.5.3 Pneumatic fluids

These are another form of drilling fluid. This form of drilling fluids is generally used in areas where using conventional drilling fluids won't give the desired outcome [41]. To ensure safety in the use of pneumatic drilling operation, many specialized equipment is used to ensure safe management of the cuttings [41], [32].

2.6 Method of making drilling fluid.

A process known as in-line with recirculation is used to produce drilling mud [42]. In the first step, some water is stored in a tank and add 120 to 150 pounds of salt. The calcium ion is reduced by adding 5.0 to 1 pound of soda and then 12 to 14 pounds of starch, stirring well until they are completely combined [42]. The final step is to add the necessary amount

of barite and ferrobar. Water and saturated salt are the primary ingredients in heavy drilling mud, along with starch, barite, slag, and lime [42], [43].

2.7 Properties of drilling fluid:

Oil well drilling is highly dependent on the drilling mud due to these properties. The mud plays an important role in ensuring the efficiency and stability of the wells [44], [45], [46].

- **Well Stabilization:** Stabilization is one of the main features of drilling fluid. Drilling mud, which consists of a variety of compositions, stabilizes the well and prevents the condensation of petroleum material near the earth surface.
- **Adhesion:** During drilling, mud materials have the characteristic of adhesion, which means they stick and stabilize sedimentary materials to the well wall due to their interaction with the surface.
- **Thermal stability:** This feature is especially important in drilling wells with high or low temperatures. Depending on the working temperature, drilling mud materials must be stable.
- **Density:** Density of drilling mud material is important to stop oil and gas from flowing freely into the earth.
- **Surface tensions:** In order for drilling mud to perform effectively, it must be able to withstand surface tensions and not fail.
- **Adjusting the flow of materials:** The flow of drilling mud materials should be adjustable so that drilling productivity can be increased.

2.8 Shale hydration inhibitors for WBDFs

In order to achieve the required performance by WBDFs with effective hydration inhibition capabilities various chemical inhibitors have been used. Inorganic salts, organic polymers, are various inhibiting materials that have been utilized to ensure the wellbore stability in drilling shale formations [47], [48]. Shale hydration swelling is inhibited during drilling in WBDFs in three ways; (i) the exchange of strongly hydrated Na^+ in the shale formation with a weaker hydrated ion in the inhibitor, (ii) formation of a protective film onto the surface of the shale formation, and (iii) the insertion of small organic molecules within the interlayer spaces of shale formations [49], [50], [51].

2.8.1 Inorganic Salts

Potassium chloride (KCl), and other metallic chlorides are inorganic salts that have been used widely as inhibitors in water-based drilling mud. They work by exchanging the strongly hydrated Na^+ in the shale formation with a weaker hydrated ion in the clay mineral. Unfortunately, a high concentration of the inorganic salts is required to achieve the desired inhibition. This is known to affect the ecosystem and being detrimental to the environment [52],[45], .

2.8.2 Graphene

Graphene a single atomic layer thickness with two-dimension makes it impermeable to liquids. Shale hydration can be inhibited by graphene using an innovative approach in the oil and gas industry. Graphene is highly effective at blocking shale nanopores due to its unique properties, such as its flexibility and nanoscale structure. It is challenging to dispersed graphene as a inhibitor in WBDFs since it lacks hydrophilic groups. Researchers have recently become interested in Graphene oxide (GO) because it retains the two-

dimensional structure of graphene while containing hydrophilic groups, enabling it to disperse in water. GO has the ability of sealing the pores and microcracks in the formation thereby making it an excellent inhibitor [53], [54], [55].

2.8.3 Silicates

Silicates are group of minerals or compounds that consists primarily of silicon and oxygen. Mechanisms of inhibition of silicates in WBDFs is by adsorbing on the surface of the shale formation, forming adsorption membrane, and blocking the pores of the shale formation. As a result, shale is protected from water penetration, reducing dispersion and maintaining wellbore stability. Sodium silicate and potassium silicate are different types of silicates that are used as inhibitor in water-based drilling fluids [56]. Studies on the use of hybrid silicates have being explored by researchers. This combines different compositions of silicates to enhance effective inhibition of the inhibitors. A dense quartz film was form on shale surface from the application of a synthesize hybrid silicate, a combination of lithium silicate and potassium methyl silicate, providing superior inhibition. A novel shale hydration inhibitor with aminated nano-silica has been investigated and has shown superior hydration inhibition than traditional potassium chloride [57], [58].

2.8.4 Organic Amines

Organic amines ability to interact with clay minerals makes them indeed applicable as shale hydration inhibitor in WBDFs. These inhibitors are particularly useful since they help in improving shale recovery rate hydration and reducing the linear expansion which are key indicators of their effectiveness. There have been a variety of amine compounds utilized as inhibitors ranging from small molecular amines to more complex molecules. They inhibit shale hydration by adsorbing onto the surface of the shale material forming a protective

film which prevent water from penetrating into the mineral [59], [60]. N,N,N',N'-tetrakis(2-hydroxyethyl)ethylenediamine (THEED), a polyhydroxy organic amine has been used and it has shown promising result in preventing bentonite swelling and maintaining wellbore stability . It works by intercalating into the bentonite layers, thereby prevents water intrusion. low molecular weight amines $-NH_2$ have been found to completely inhibit hydration by entering in between the bentonite layers and displacing exchangeable ions. Oil-based drilling fluids can be hazardous to the environment, which is why organic amines are often preferred since they offer a balance between performance and environmental safety [61],[62], [63].

2.8.5 Surfactants

By reducing the surface tension between the molecules of water and oil, surfactants have the capabilities of reducing the surface tension of this immiscible liquids. In mitigating issues of shale swelling during drillings in WBDFs using surfactants as hydration inhibitors has become an effective method. Surfactants has inhibitors are known to reduced fluid loss improve the rheological properties, and enhance wellbore stability. The tendency of clay minerals absorbing water and swell is reduced by the surfactant ability to interact with the mineral surface. Hydrophobic barrier is created by the surfactant when it is adsorbed onto the surface of clay particles thereby preventing water intrusion. Both cationic and anionic surfactants have been used to inhibit hydration. A cationic surfactant Cetyltrimethylammonium bromide (CTAB), is effective in inhibiting shale hydration because it binds to the surfaces of the shale formations which is negatively charged. The effective application of surfactants as inhibitors is influence by several factors such as clay type, concentration of surfactant and the composition of drilling fluid [64], [65], [66].

2.8.6 Asphalts

The use of asphalt during drilling operations is an effective way to prevent shale swelling and maintain wellbore stability. Similarly, modified asphalt forms a hydrophobic membrane on the shale surface by adsorption, thereby inhibiting intrusion of water into the shale formation through blocking the micro-pores, and cracks. Shale expansion was reduced by 56.3% and shale recovery was improved by 97.8% with a modified 3% asphalt solution, according to a study. As a result, modified asphalt offers some promise for drilling in shale gas formations, especially when using water-based drilling fluids [67], [68].

2.8.7 Organic Polymers

It was the desire to increase penetration rate that initially sparked the evolution of polymer drilling fluids. With advancing well depth, temperatures, pressures, and instability zones, the design of drilling fluid have become more robust, resistant to harsher conditions, and environmentally friendly with changing subsurface conditions [69]. Polymers performed various functions when used as a component in water-based drilling mud. Polymers has the ability of inhibiting shale hydration, controlling viscosity and suspension ability of drilling fluids, and also modified the rheology of shale formation [69], [8]. Inhibition occurs when polymers break hydrogen bonds between water molecules and clay molecules, thereby adsorbing onto mineral surfaces and preventing water from interacting with the clay material. Inhibitors based on polymers are broadly classified into anionic polymers, cationic polymers, and nonionic polymers [8].

polypropylene oxide (PPO) and polyethylene glycol (PEG) are non-ionic polymers that have shown effective inhibitory capability when used in WBDFs [28], [3]. Shale hardening is a process through which these polymers reduce clay swelling. This is when the shale

becomes harder and less prone to swelling and dispersion. Non-ionic polymers are highly preferred due to their environmental friendliness, low cost and good lubrication. Low molecular non-ionic polymers such as glycols are highly preferred in this category since they have the ability of penetrating into the shale matrix and create a strong binding film on to surface [70]. Inorganic salts such as KCl has been combine with PEG to enhance inhibition due to the combine adsorption on the clay mineral and it also limit the excess quantity of mineral salt used. This has help to mitigate the impact on the environment when excess KCl used to inhibit hydration. Hydrophobically modified PEGs have been synthesized recently to create a water-repellent barrier on the shale surface to enhance inhibition performance [4]. In comparison with linear polyglycerols, hyperbranched polyglycerols have shown superior inhibition properties due to their unique structure and increased hydrophobicity compared to linear polyglycerols [2].

In water-based drilling fluids, ionic polymers, including cationic and anionic polymers, are widely used as shale inhibitors to prevent clay swelling and enhance wellbore stability [71]. The inhibition mechanism of ionic polymers is by adsorbing onto clay surface or encapsulate the clay particle through electrostatic interactions, creating a polymer barrier that prevent water interaction with the mineral. A cationic polymer like polyacrylamide (PAM) or partially hydrolyzed polyacrylamide (HPAM) is effective in preventing clay hydration and dispersion, as they are able to adsorb onto the negatively charged surfaces of the clay. Among these polymers, copolymers and terpolymers are effective in environments with high salinity and temperature. Several nitrogen-based polyamines, such as polyether amines and polyamido amines, are effective shale inhibitors due to their hydrogen bonding capabilities and electrostatic interactions with clay. Zwitterionic

Terpolymer P(AM-DMC-AMPS), a low molecular weight encapsulant that forms a protective layer on shale surfaces through hydrogen bonding and electrostatic interactions, reducing dispersion and hydration [72],[73].

Anionic polymers are less commonly used as additive in water-based drilling fluid. Among the potentially useful anionic polymers is P(ANAN), which is synthesized from acrylamide, N-vinyl-2-pyrrolidone, and 2-acrylamide-2-methylpropanesulfonic acid. As a result of its excellent performance in high-temperature and high-salinity conditions, this polymer is suitable for drilling deep wells and ultra-deep wells. Fluid loss is reduced as a low-permeability filter cake forms on the walls of the wellbore [8],[71].

Certain nano-modified polymers have shown excellent performance at extreme temperatures (200 °C) and high salinity environment. Nano-silica-modified co-polymers can improve the inhibition properties of drilling fluids significantly by stabilizing the wellbore through preventing shale hydration and swelling [1]. These composites inhibit by increasing the hydration layer between clay particle and drilling fluid is thickened and the colloidal stability of the drilling fluid is maintained [74], [75].

2.8.8 Nanoparticles

Enhance surface area to volume ratio and quantum effect are unique mechanical properties of nanoparticles (NP). Mechanical structures such as intra granular structure and an enhanced grain boundary can be improved when NPs are added to materials. The shale formations in wellbore is strengthened by NPs by preventing the development of micro-nano-scale fractures [76]. Gao et al investigated the impact of aluminum nanoparticles on shale formation in the USA. Results showed that nanoparticles size, 10 nm - 30 nm played crucial role in inhibiting shale hydration. The quality of the filter flakes is significantly impacted

by the size and distribution of the nanoparticles. When the filter cakes are too small (4-9 nm), fluid loss cannot be controlled. The density of filter cakes formed by nanoparticles with a larger particle size distribution can increase fracture reopening pressure and reduce fluid loss, in contrast to the density formed by nanoparticles with a smaller distribution of particle size [77]. Smith et al. reported the use of aluminum nanoparticles significantly improving the thermal stability of WBDFs and decreasing the fluid loss due to high temperature.

Literally, nanoparticles are nanomaterials (1-100nm size) that have a very large surface area and can have a tremendous effect on fluid properties when they are present in very small concentrations. The particles have a distinctive size and hydro dynamism that allows them to interact with shale formations in inhibiting hydration and swelling. Some examples of the nanomaterials based inhibitors that have been tested in water-based drilling fluids include; nanosilica, nanopolymers, multiwalled carbon nanotubes, graphene nanoplatelets, laponite, and polymer-silica nanoparticle composites among others [78],[79],[80].

Table 2.1: An overview of recent chemical compounds investigated as water-based drilling fluid inhibitors.

Inhibitor	mechanism	Rheological properties/Compa tibility	Advantages	Environmentally friendly/ or Not	Reference
hydrophobic graphene oxide (HGO)	electrostatic attraction	Not mention	stronger hydration inhibition capability compared to commercial shale inhibitors KCl and PA.	Not mention	[81]
nano-blocking agent (PKSHN)	forming a tight layer on shale surface through bridge plugging	Maintains good rheological properties	High thermal stability	Not mention	[82]

	and filling accumulation				
modified nano biochar on polyarginyl lysine	Hydrogen bonding	Not mention	Thermal stability of 220 °C	promising environmentally friendly shale inhibitor	[83]
acylated inulin	Hydrogen bonding	Not mention	super hydration-inhibition at low concentration	non-toxic and biodegradable	[84]
hyperbranched polymer nanocomposite (HBPN)	electrostatic interaction and hydrogen bonding	Not mention	superior shale inhibition performance compared with KCl, PDA, and PEI at the same concentration	Not mention	[85]
polymer grafted with dopamine	hydrogen bonding and	Not mention	thermal stability below 200°C	Not mention	[86]

derivatives, P(AM-DA)	electrostatic interaction				
Janus silica nanoparticles (JNPs)	Electrostatic interaction, compression of double layer, and hydrophobic property	No significant impact on the rheological properties	Good inhibition at low concentration of wt0.5 %	Not mention	[87]
nanoparticle- enhanced water-based drilling fluid (NP-WBDF)	bridging and sealing shale core-pore and microcracks	Not mention	demonstrated excellent thermal stability.	Not mention	[88]
Gemini surfactant	Encapsulation through	Not mention	Exhibit Good inhibition at low concentration	Not mention	[89]

	electrostatic interaction				
ionic liquid copolymer shale inhibitor (PIL)	Hydrophobic film, and lowering surface tension	good compatibility with bentonite slurry	better inhibition performance than the inhibitor D230	Not mention	[90]
shell-coated metal oxide nanoparticles (MONPs),	electrostatic and hydrogen bonding	Not mention	good thermal stability, and dispersion stability	Not mention	[91]
amphoteric polysiloxane (SC-POTD)	Forming hydrophobic barrier through adsorption	low harm to the rheology of Na- Bent slurry	impressive heat resistance,	Not mention	[92]

chitin nanofibers (ChNFs)	hydrogen bonds and electrostatic interactions	compatibility with bentonite water-based drilling fluids and significantly improved the rheological properties	High thermal stability	environmentally friendly	[93]
polyionic polymer inhibitor, (TIL-NH ₂)	electrostatic and hydrogen bonding	Not mention	High thermal stability exceeding 300 °C at low concentration	Not mention	[94]
Crosslink polymer, of DMA, AMPS,	Inhibit hydration through ionic cross-linking and	good rheological properties at 160 and 0 °C	Favorable rheological behavior under high temperature,	Nontoxic and Environmentally friendly	[95]

and CNF, (PADC)	sealing shale pores		high-pressure conditions		
ANS	electrostatic and hydrogen bonding interactions,	Not mention	stronger plugging capability compared to nano-silica	Not mention	[96]
Low-melting mixture solvents (LoMMSs)	Electrostatic interaction	Not mention	demonstrating superior performance compared to commercial inhibitors.	Not mention	[97]
paraffin wax microemulsion (PM)	electrostatic and hydrogen bonding interactions	Not mention	Shows better sealing and inhibition properties than commonly used shale stabilizers	Not mention	[98]

amine-based clay mineral surface hydration intercalation inhibitor (ODBB)	electrostatic and hydrogen bonding interactions	Not mention	Superior inhibition than common inhibitors	Non toxic	[99]
hydrophobic nanosilica (HNS)	Electrostatic interaction.	Increase in rheological properties	Excellent Inhibition at low concentration and ensures stability under various temperature conditions.	Not mention	

2.9 Additives for water-based drilling mud.

Bentonite serves as the primary component in drilling fluid which gives it its thixotropic traits. A range of additives is included to give it the necessary rheological property range to accomplish best drilling operations and well stability. Such characteristic properties include lubricity, gel strength, mud density (MD), plastic viscosity (PV), apparent viscosity (AV), yield point (YP), mud filtrate loss volume, and gel strength [100], [101]. It is essential that the right combination be selected in order to provide enhanced shale inhibition. Bentonite forms filter flakes with low permeability which helps in the reduction of fluid loss, provides viscosity, enhances hole stability, and decreases water seepage into the shale formations [102], [103].

When additives are selected correctly at the right proportion, key parameters like less corrosivity, acceptable pH, heat stability, and minimal thickness are also achieved [104]. Following is a discussion of typical drilling fluid additives.

2.9.1 Additives for viscosity control

Typical additives for viscosity include thickeners like starch, carboxymethylcellulose, glycol Xanthan gum, and polyanionic cellulose [105]. To support the transportation of cuttings during drilling, these viscosity additives are vital in achieving the required rheology. However, flocculants are used to reduce the viscosity to the desired level. Calcium chloride (CaCl_2), Sodium carbonate (Na_2CO_3), acrylates, gypsum (CaSO_4), polyphosphates, and lignosulfates are the common flocculants used in reducing drilling fluid viscosity [105].

2.9.2 Additives for density control

Density-enhancing agents include materials like barite and calcium carbonate, iron oxides, dolomite, hematite, and magnetite are incorporated into drilling fluid to raise its overall

density. [106], [107]. In other to prevent formation damage and aid in the removal of dry pipes, sufficient bottom-hole pressure is maintained. Sufficient density is required for Filter cakes to be form on the wall of the wellbore. Buoyant effect on cutting carrying effect is increase with adequate mud density. An excessive density of mud, however, may result in high costs, overbalance, induced fractures, and reduced penetration [108].

2.9.3 Filtration and rheology (viscosity) control additives

A variety of drilling fluids such as WBDFs and OBDFs are treated with these additives in order to reduce fluid loss. These additives are also used when drilling at high temperatures [109]. Carboxy methylcellulose, low and high polyanionic cellulose, xanthan gum, guar gum, and bentonite modified starch in WBDFs while gilsonite and organophilic lignite in OBDFs are various materials used as filtration and rheology control additives [110]. As well as its primary function of encapsulating shale and thickening drilling mud, partially hydrolyzed polyacrylamide may also serve as a filtration control material [111]. When fluid flow is poor, circulation may be lost, penetration may be reduced, holes can be filled by cutouts and wells may be enlarged. Adsorption of water into permeable formations is the primary role of WBM filtration control additives for stabilizing holes and minimizing fluid loss. Stabilization of the shale formation can be achieved with the utilization of gilsonite as an additive [112]. Additionally, it improves fluid loss and aids suspension properties of oil-based fluid systems, as well as maintaining high thermal and high-pressure stability [112].

2.9.4 Other additives

Wetting agents, emulsifier, defoamer and fluid loss control additives are additional additives used in drilling fluid. There are three types of emulsifying agents: anionic,

cationic, and neutral chemical substances that facilitate the mixing of immiscible liquids into a homogeneous mixture [113]. In WBDFs, common emulsifiers include surfactants, soaps, detergents, and organic acids. In OBDFs, amines and fatty acids are used [114]. In addition to improving emulsion stability these additives can enhance the thermal stability of the mud, boost viscosity, and aid in filtration. In highly salinized environments, such as brackish and saturated salt water, defoamers reduce foaming in the drilling mud [115]. There are also thinning agents, which can be used to modify viscosity and solids content. Using them will improve fluid permeability by reducing thickness [116]. Lignosulphonate and lignite are examples of such additives. Additionally, lubricants and antiscaling or antispotting agents are widely used as drilling additives [116]. As a part of the drilling operation, they reduce friction, drag, and torque. In order for muds to be lubricating and anti-scaling, Stuck pipe-free oils, drilling detergents, and lubricants are essential materials to include. Bentonite is commonly mixed with polymers in the range of 0.1 to 2% based on the chemical composition and the impact of the polymer on the ultimate fluid composition [117], [118].

2.10 Characterization of shale inhibition

Drilling operations pose many challenges that may cause severe damage or even cause the operation to be shut down entirely. As a result of the use of water-based drilling fluids (WBDF), wellbore instability is among the most common problems encountered by drilling engineers. Due to the presence of active clay minerals in shale formations, WBDFs can be destabilized once they encounter hydration and swelling. Inhibitors have been employed to combat the menace posed by these active clays. This makes it extremely important to evaluate and characterize these inhibitors' ability to inhibit shale hydration. Shale swelling

in the presence of inhibitors is being investigated with standard physical and chemical methods developed by the American Petroleum Institute (API). Following are the methods being used to achieve the purpose:

2.10.1 Shale recovery test

To examine the hydration inhibition performance of drilling fluids in preventing the hydration and breakdown of shale cuttings, shale recovery test is employed. In this test shale samples are grinded into fine particles and sieved through a 20-30 mesh screen. The cuttings are then transfer into a steel cell along with a specific volume of the inhibitor solution. The cell is then placed in a roller oven and hot roll for 16 hours at temperature of 120 °C. The cuttings are then filtered and washed with distilled water and passed through a 50-mesh screen. The retain cuttings are dried in an oven at 60 °C. The percentage recovery is calculated with the formula;

$$\% Recovery = \frac{M_2}{M_1} \times 100$$

M_2 is the mass of shale cutting after hot rolling, and M_1 is the mass prior to hot rolling. High percentage recovery indicates minimum hydration with low dispersion and vice versa.

2.10.2 Linear swelling test

This is also another test employed to test performance inhibition of drilling fluid. It investigates bentonite capability to resist swelling when soaked in drilling fluid. In this test an examination is done on the linear swelling of bentonite pallet as a function of time. Bentonite samples are press with a hydraulic press at a pressure of 10 MPa for 5 min to form a cylindrical disc. The disc is placed in swelling meter with a specific volume of the

inhibitor solution. Reactivity of the bentonite disc and the inhibitor solution determines the inhibition capacity. The linear height is measured by the linear swelling meter. The inhibitor with the lowest linear swelling height is considered as a good inhibitor whereas the inhibitor with a high linear swelling height is considered as a poor inhibitor.

2.10.3 Anti-swelling ratio

Standard anti-swelling tests are conducted to determine the effect of inhibitors on Na-bentonite stabilizers in drilling fluids. We use it to test the swelling resistance of bentonite samples in drilling fluids. Specific masses of bentonite is place in a centrifuge tubes and filled with inhibitor solution. The tubes are thoroughly stirred and shaken then centrifuge for 15 minutes at 1500 r/min to ensure all the residue settles at the bottom of the tube. The change in volume of the bentonite is recorded. The anti-swelling ratio is measured using the formula:

$$AR = \frac{V_b - V_a}{V_b - V_o} \times 100$$

V_a and V_b represent variations in the volume of bentonite in the inhibitor solution and water respectively. V_o indicates the change in volume in the kerosene sample.

2.10.4 Pore pressure transmission test

Pore pressure of shale increases when fluid from WBDFs invades into the shale formation. During swelling mechanisms, wellbore instability occurs due to abnormal pore pressure. It is reported that the addition of inhibitors can block shale pores and decrease pore pressure transmission by up to 97%. To record downstream pressure over time hydraulic gradient and osmotic pressure are applied. Pressure regulating systems are commonly utilized to manage upstream and downstream pressures. The clay sample is positioned in the holder

and permitted to contact the upstream pressure valve. Based on the inhibition capability of the fluid, Pressure transmission curves capture the variations in downstream pressure.

2.10.5 Capillary suction test

An apparatus used for capillary suction tests (CSTs) measures the time it takes for clay slurry or shale to pass through filter paper. Results from the capillary suction test can be used to evaluate the reactivity of shale samples and to evaluate various drilling fluids inhibition characteristics. This experiment uses a cylinder containing filter paper of a particular thickness and 5 ml of clay dispersion containing an inhibitor. Two electrodes, both linked to a timer, are positioned 0.5 cm and 1 cm from one edge of the cylinder. A timer measures the amount of time it takes for free water to travel from one electrode to another. A short capillary suction timer indicates low interaction between water and the shale sample. High capillary suction timer indicates that there is great interaction between water and the shale sample which is a prove that the water molecules are attached onto the surface of the clay mineral. Drilling fluids with short capillary suction timer is a prove of a good inhibition whereas those with high capillary suction are considered poor inhibitors.

2.10.6 X-ray diffraction (XRD)

XRD analysis is one of the important techniques to assess the hydration inhibition potential of drilling fluids. Inhibitor solution is mixed with a sample of bentonite and the mixture is stirred for 24 hr to ensure complete equilibrium absorption. The sample is then filtered and the residue is dried in an oven at temperature of 40 °C. The sample is grinded into fine powder and then XRD analysis conducted to measure the interlayer spacing (d-spacing). In the presence of the inhibitor the analysis indicates decrease in the interlayer spacing which implies the shale inhibitor prevent water intrusion and better inhibition. While in the

absence of the inhibitor the analysis shows increase in interlayer spacing which indicates there is bentonite swelling and significant hydration has occurred [119].

2.10.7 Plate soaking test

When shale formation is significantly hydrated it can result to wellbore instability such as shrinkage and collapsed of the wellbore. The plate soaking test mimics the free hydration and swelling of shale formation in downhole. In this analysis a pressure device is used to pressed bentonite into pallets at 10 MPa for five minutes. The pallets are then placed in petri dish containing the inhibitor solution. Photographs are taken at different interval to assess the swelling disintegration of the bentonite in different solutions. The disintegration and swelling of the pallets imply that significant hydration has occurred indicating poor hydration. Whereas pallets that did not disintegrate nor swells can be illustrates good inhibition [120].

2.10.8 Contact angle test

Bentonite is hydrophilic in nature which translate to a surface high in free energy. This makes it draws water easily, hydrates and then swells. When bentonite is modified with polymer inhibitor it tends to bind on the surface and forms a hydrophobic film on the surface of the mineral. This serves as barrier that expel water molecules intruding the bentonite minerals. We used contact angle tester to determine the hydrophilicity of the bentonite after modification with inhibitor. High contact angle illustrates good inhibition which shows the bentonite free energy has been reduced. Low contact angle shows poor inhibition demonstrating the bentonite having high tendency to adsorb water [71].

2.10.9 Scanning electron microscope

The interaction of bentonite and water in the drilling fluid results in hydration which causes rough and porous morphology. To get a clear picture on the degree of hydration SEM can be used to get a detailed picture to analyzed the morphology of the mineral. In this analysis a sample of bentonite is placed in beaker and the inhibitor solution is added. The mixture is stirred for 24 hours to obtain maximum absorption. The slurry is filtered and the residue is dried in an oven at 60 °C and the dried sample is then analyzed with a scanning electron microscope. Rough and porous morphology reflects significant hydration and swelling in the clay mineral whereas smooth morphology denotes low hydration and good inhibition [3].

2.10.10 Thermogravimetric analysis

TGA is perform to evaluate the rate at which bentonite mineral absorbed free water in various inhibitor solution. Specific masses of bentonite are weighed into beakers containing various inhibitor solution and the mixture is stirred for 24 hours to obtain maximum absorption. The samples are then filtered and the residue is dried in an oven at 60 °C. TGA analysis is used to determine absorption of water into the bentonite clay. A sharp and significant drop in the curve at 100 °C implies strong hydration in the bentonite manifesting poor inhibition. A lesser steepness in the curve demonstrate low hydration of the bentonite suggesting excellent inhibition [121],[8].

2.10.11 Zeta potential measurements

Because of isomorphous substitutions in their octahedral structure, bentonites have a negative charge. layers and bentonite forms stable suspension in water. Adding inhibitors with varying charges, functions, and molecular compositions affects the potential of clay

particles. The typical zeta potential of pristine bentonite in distilled water is highly negative. With the addition of various concentration of inhibitors, the zeta potential value increases by approaches zero indicating strong adsorption of inhibitor. Strong inhibitors have the capabilities of neutralizing the negative charges clay particle [4],[122].

2.10.12 Water adsorption test

A hydrometer that indicates the relative humidity of a shale sample is used for taking measurements for the water adsorption test. This test described the reactivity of shale in drilling muds, and to calculate water adsorption, relative humidity is expressed as a percentage. The sample is put in water for a specific period in order to measure water adsorption. The weight of the shale is recorded both before and after it is immersed in water.. In comparison with lesser active shale, active shale adsorbs more water, resulting in a higher mass [8], [1].

2.10.13 Cation exchange capacity

Magnesium, calcium, sodium, potassium and iron are the most commonly available cation in a shale sample. Mineral clay contains these cations in its interlayers in order to neutralize the negative charges which is as a result of the isomorphic substitution of cations. The exchangeable cations present in a shale sample are measured in the cation exchange capacity test. Montmorillonite and bentonite, which are reactive clays, exhibit high cation exchange capacity expressed in milliequivalents per 100 g. As API standard, methylene blue test (MBT) is used in determining the cation exchanging capacity of shale samples. In addition to sulfuric acid and hydrogen peroxide, a small mass of shale powder is mixed with water. Titration with methylene blue solution is performed after boiling the mixture for a few minutes. In the end, a light green or blue halo color forms around the droplet after

the mixture is poured onto filter paper. Upon interacting with water, the reactive clays demonstrate high cation exchange capacity and display hydration and swelling affinity. The less reactive clay shows less affinity to hydration and swelling which translate to good inhibition [8], [2].

CHAPTER 3

SYNTHESIS AND INVESTIGATION OF A GRAPHENE OXIDE GRAFTED WITH COPOLYMER OF ACRYLIC ACID AND ACRYLIC AMIDE AS SHALE HYDRATION INHIBITOR FOR WATER BASE DRILLING FLUIDS.

3.1 Introduction

Performance of drilling fluids greatly contributes to the success of drilling operations [123], [124]. Drilling fluids are used in drilling oil and gas wells for lubricating drill bits, maintaining hydrostatic pressure, transmitting sensor readings, removing rock cuttings, and preventing swell in clay-based shale formations [5], [6]. A fluid of this kind must be engineered to operate effectively in challenging conditions while not damaging the formations that are being drilled [125]. One of the key causes of wellbore instability is chemical interaction between drilling fluids and shales; therefore, choosing the right drilling fluid is critical to a successful drilling operation [126], [1].

There are many types of drilling fluids available for different drilling conditions, including water-based drilling fluids (WBDF), oil-based drilling fluids (OBDF), and synthetic drilling fluids (SBDF) [28], [124]. For reducing hydration and swelling problems in shale, OBDF and SBDF are usually preferred due to their extremely low friction coefficients. Its adoption is however hindered by its high costs and negative environmental impact [71] [120]. As a result of its simple preparation, cost effectiveness, and environmental friendliness, water-based drilling fluids have emerged as the most widely used option [127]. In WBDF applications, clay swelling poses a significant challenge to drilling operations, leading to increased well construction costs [128], [129].

In order to develop effective shale hydration inhibitors, we need to understand how shale swelling occurs WBDFs. Various clay minerals are found in shale, including bentonite, montmorillonite (MMT), illite, mixed illite/montmorillonite layer, and kaolinite [130]. Clay easily hydrate and swells if it comes in contact with water [130]. There are two distinct mechanisms by which clay minerals hydrate: crystalline hydration and osmotic hydration. Crystalline hydration occurs in all types of clay minerals and involves water molecules directly adsorbing onto the crystal surface, causing swelling in a short distance [131]. When cation concentration in the interlayer exceeds that in surrounding water, osmosis occurs, resulting in water molecules diffusing into the interlayer. This results in significant swelling [4]. Many shale inhibitors have been found to be effective in water-based drilling fluids for this reason.

Generally, WBDFs inhibitors fall into two categories based on their inhibitory mechanism: chemical inhibitors and sealing agents [4]. Inhibitors of WBDFs include potassium chloride (KCl), one of the oldest and most commonly used chemicals. When used, KCl inhibits hydration in montmorillonite (MMT) by exchanging its sodium ions (Na^+) with less hydrated potassium ions (K^+) [28], [132]. Thus for an effective inhibition state, large quantities of KCl are required, resulting in a large concentration of chloride ions in the mud which can cause contamination and serious environmental issues [133], [69], [134]. In addition, high concentrations of electrolytes like KCl in drilling fluids result in flocculation of clay minerals, which negatively affects fluid properties, such as causing high fluid loss volume and thixotropy loss [135], [136], [8]. The development of environmentally friendly

and cost-effective materials and formulas for inhibiting clay mineral hydration is therefore an urgent need for water-based drilling fluids.

A number of amino-containing chemicals have been found to inhibit shale hydration by acting as alternative organic cations [99]. In many industries, natural biopolymer like gelatin is widely used as a hydration inhibitor in WBDFs [137]. Gelatin and gelatin/KCl composites have been used to prevent MMT swelling by being absorbed onto the surface [4]. In the presence of this encapsulation, the hydrophobic properties of the MMT are enhanced to some extent, acting as a sealing agent to eliminate water and reduce the space between the layers [4], [119], [8]. Studies have also been conducted on the use of polyalcohols and sealing agents, such as nanoparticles, asphaltenes, graphites, silicates, and others [138] [2], [8], [139], [140]. Nevertheless, many of these inhibitors are expensive, poorly dispersed, and unstable at high temperatures [3], [141].

Using polymerized organic chemicals, which coat the MMT with a protective layer, swelling can be prevented, and the original appearance of the shale preserved [8], [3]. The properties of polymers can be used not only to inhibit shale formation, but also to enhance drilling fluid rheology and filtration [139]. Between the water/polymer and the shale matrix, hydrogen bonds act as the mechanism behind shale inhibition. By competing for interlayer spaces and forming hydrogen bonds with silicates and aluminates, polymers disrupt hydrogen bonds between water molecules and clay minerals. As a result of the attachment, shale hydration is inhibited by preventing further interaction between water and clay minerals [142], [2].

Drilling at high temperatures and high salt levels presents significant challenges in using polymers as inhibitors for WBDFs. Studies indicate that high temperatures compromise the stability of these polymers [128], [143], [124], [144]. Modifying the polymer to make it more stable and resistant to harsh conditions is therefore crucial. In other studies, graphene oxide has been shown to inhibit water intrusion into shale due to its high surface area, which allows it to form a protective layer on shale surfaces [37] [124]. Studies have shown that graphene oxide, due to its thermal and mechanical stability, has excellent inhibitory properties [37], [145]. Also, graphene can improve wellbore stability by filling microspores and fractures in shale, thereby preventing water infiltration [145]. The main disadvantage of graphene in water-based drilling fluids (WBDFs) is its poor dispersion as an inhibitor [145], [146] .

With stricter environmental protection standards being enforced, it is more important than ever to develop drilling fluids that are low toxicity and biodegradable. Researchers have recognized polymer/graphene oxide composites as possible shale hydration inhibitors, but this application is still in its infancy. Using free radical polymerization, we synthesized a copolymer of acrylic acid and acrylamide/ Graphene oxide (Poly-(AAAm)-GO) composite to serve as an effective and low-cost inhibitor. The pristine copolymer, poly (acrylic acid-co-acrylic amide) (Poly-(AAAm)), was also synthesized and its inhibitory properties were compared to the polymer graphene oxide composite. Tests were conducted to evaluate the inhibitory quality of the prepared Poly-(AAAm)-GO and (Poly-(AAAm)), using anti-swelling, immersion test, and shale recovery tests. Industry-standard inhibitor KCl was used in the comparison.

3.2 Material and Methods

3.2.1 Materials

Acrylamide (AAM) ($\text{C}_3\text{H}_5\text{ON}$, $M_r=71.08$ g/mol, ≥ 99 % purity), ammonium persulfate (APS) ($(\text{NH}_4)_2\text{S}_2\text{O}_8$, $M_r = 228.18$ g/mol, ≥ 98 % purity) and acrylic acid (AA) ($\text{C}_3\text{H}_4\text{O}_2$, $M_r = 72.063$ g/mol, 99 % purity) were purchased from Sigma-Aldrich. Sodium bentonite (Na-Bt) 100% pure was purchased from Belle Chemical. We used potassium chloride (KCl, $M_r = 74.55$ g/mol, 99 % purity) purchased from Fisher Scientific Company for the purpose of comparison. Shale cutting were provided by the geology department of KFUPM. In all experiments, chemicals of analytical grade were used as they were received, as well as deionized water.

3.2.2 Material Preparation

The Polymer graphene oxide composite was prepared by a free radical polymerization in aqueous solution [147],[124],[121]. The procedure for the synthesis is as follows; 50 mL deionized water was added into a 250 mL dry three-neck flask, equipped with a N_2 gas inlet, magnetic stirrer, and a reflux condenser. 500 mg of graphene oxide produced by modified Hummers method [148] was added into the flask. The mixture was stirred with a magnetic bar to ensure proper dissolution and dispersion of the GO. 2 g of AAm and 0.504 g of AA were added in to the flask to achieved a mole ratio of 4:1 respectively. The mixture was stirred and heated under reflux to 60 °C to obtained a homogenous mixture. Trace amounts of APS (≈ 5 mg) was added into the flask to initiate the polymerization of the monomers. We continuously purged nitrogen into the flask and kept the conditions for 5 hours for complete polymerization. We precipitated macromolecular product, Poly-(AAAm)-GO by washing it in three-fold volumes of absolute ethanol. In the following step, the precipitate

was dialyzed in deionized water for 24 hours, thereby removing any unreacted monomers. The final product was then freeze dried to get rid of the solvent used. the same synthesis procedure was used to obtain GO-free polymers (Poly-(AAAm)).

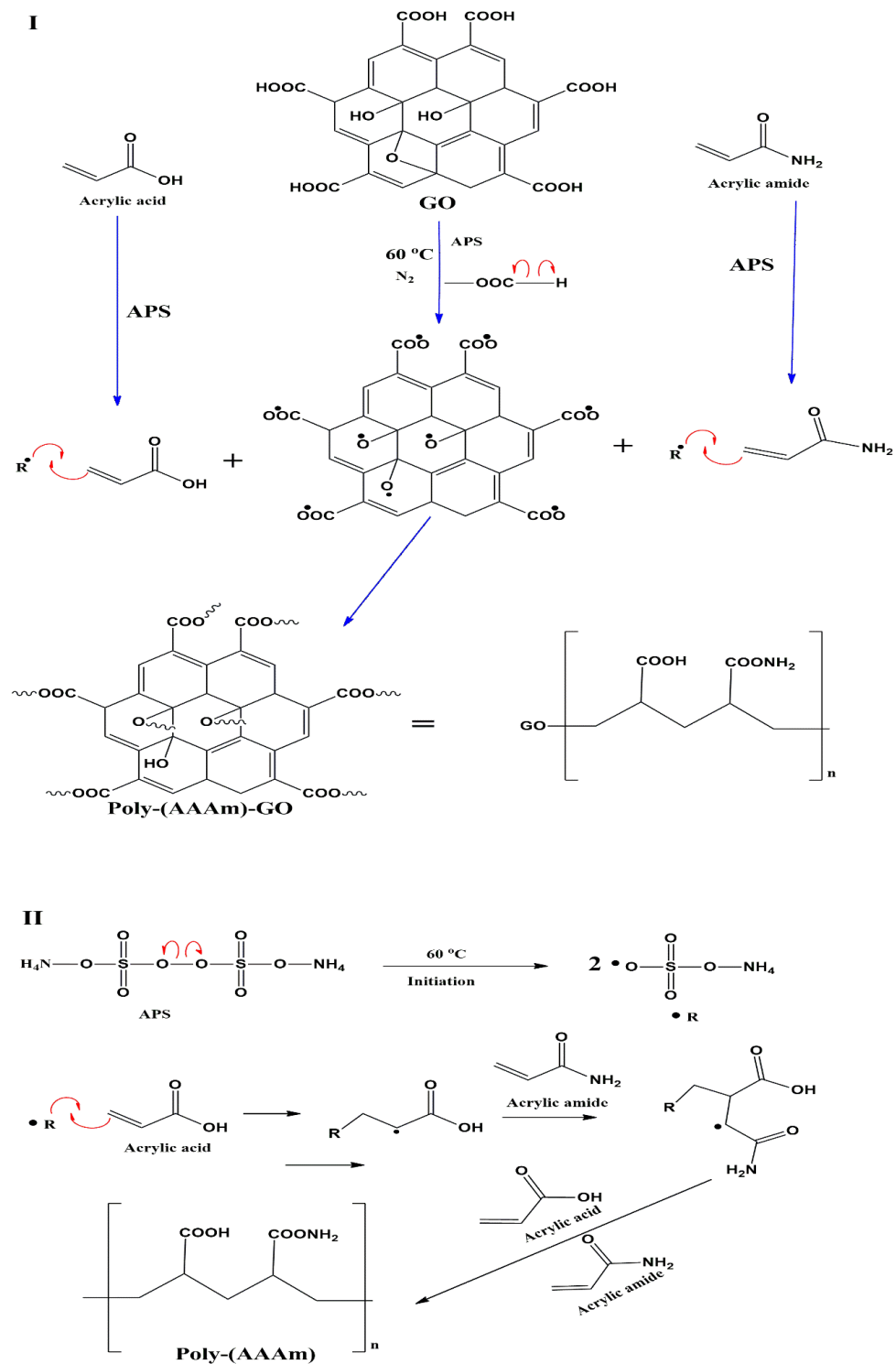


Figure 3.1 Reaction scheme of free radical polymerization of the copolymer of acrylic acid and maleic acid/ Graphene oxide (Poly-(AAAm)-GO) (I), and free radical polymerization of the copolymer of acrylic acid and maleic acid (II)

3.3 Evaluation Method

3.3.1 Shale recovery test

Using a sealed pressure vessel, shale cuttings were mixed with a prepared inhibition solution to determine their dispersion degree. High recovery percentages indicate better ability to inhibit shale cutting dispersion. 5 g of shale cuttings with a mesh size of 6-10 were placed in sealed vessels containing 35 mL distilled water, 35 mL 10% KCl in solution, and 35 mL of 4% Poly-(AAAm) and Poly-(AAAm)-GO in solution. The sealed tanks were then hot rolled for 16 hours at 120 °C in a roller oven. The cuttings were washed with deionized water, filtered, and dried at 100 °C. Using the formula,

$$Recovery = \frac{M_2}{M_1} \times 100$$

the percentage recovery was calculated. M2 is the mass of shale cutting after hot rolling, and M1 is the mass prior to hot rolling.

3.3.2 Plate soaking Experiment

Bentonite samples were pressed into pallets using a pressure device. We weighed 5 g of sodium bentonite screen through a mesh sieve. Then, the material was pressed under 10 MPa for five minutes. The compacted pallets were immersed in petri dishes containing 25 mL distilled water, 25 mL 10% KCl solution, and 25 mL 4% wt in solution of inhibitor. Photographs were taken at 5 min, 30 min, 1 h, 3 h, 7 h, 24 h, and 48 h intervals to record the hydration process of the compacted pallets at room temperature.

3.3.3 Contact angle test

5 g bentonite were added to measuring cylinders containing 50 mL distilled water, 50 mL 10% KCl solution, and 50 mL 4% wt inhibitors in solution and stirred for 24 hours to reach

equilibrium adsorption. After filtering and drying at 90 °C, the residue was pressed under 5 MPa to form smooth pallets. We used contact angle tester to capture the images after a micro injector on a Kruss Goniometer DSA25 was utilize to drop distilled water onto the pallets.

Fourier Transforms Infrared Spectroscopy (FT-IR): About 400 mg KBr and 3 mg sample were mixed to make homogenous mixture. Then, the mixture was poured into molds and pressed under 3 MPa pressure. We recorded the spectral analysis of (Poly-(AAAm)), (Poly-(AAAm))-GO, Pristine Na-Bt, and polymer modified bentonite composite using a Nicolet is10 FT-IR spectrometer in the range between 400-4000 cm^{-1} .

3.3.4 Thermogravimetric analysis (TGA)

TGA analysis was performed on the prepared polymer and polymer/graphene to evaluate the thermal stability of the inhibitors. Also, the TGA was performed to evaluate the thermal stability of the polymer mixed bentonite. 5 g of bentonite were weighed into beakers, followed by 100 mL of distilled water and 100 mL 4 % wt inhibition in solution. In order to achieve maximum absorption, the mixtures were thoroughly mixed for 24 hours using a magnetic stirrer. At a heating rate of 10 °C/min, we performed TGA analyses on pure bentonite and bentonite/inhibitor using a STARe System TGA/DSC 3+ machine at high purity Ar atmosphere.

3.3.5 H-NMR Analysis

In order to acquire the proton Nuclear Magnetic Resonance data for (Poly-(AAAm)), a 600 MHz (JEOL, Japan) spectrometer was used. The signals were compared with those from the residual protonated solvent at 4.79 ppm. Individual NMR tubes were used for sample containing (Poly-(AAAm)) and monomer solution dissolve in D₂O. The synthesis was

enhanced with the acquisition of distinct spectra for the monomer solution and (Poly-AAAm)).

3.3.6 Anti –swelling test

A standard method for testing the inhibitors' influence on Na-bentonite stabilizers in drilling fluids is anti-swelling tests. Approximately 1g of Bentonite was weighed and placed in a centrifuge tube filled with 20 mL inhibitor solution. After the tubes were thoroughly stirred and shaken, they were left to stand for two hours. We measured the change in volume of bentonite after centrifuging the mixture for 15 minutes at 1500r/min. According to the equation below, the anti-swelling ratio (AR) was calculated:

$$AR = \frac{V_b - V_a}{V_b - V_o} \times 100$$

The variation in volume of bentonite in the inhibitor solution and water is represented by V_a and V_b . V_o indicates the change in volume of kerosene.

3.3.7 Scanning Electron Microscope (SEM)

3 g of bentonite sample were placed in empty beakers followed by 50 mL inhibitor solution. Slurry was formed by stirring the mixture for 24 hours to ensure equilibrium absorption. After the samples were filtered, the residue was dried in an oven at a temperature of 60 °C. The specimen was glued to a tape and coated with gold for characterization. Using a Thermo Scientific™ Quattro ESEM in high vacuum mode the morphology of dried shale samples treated with distilled water was compared with another dried shale samples treated with inhibitor solution.

3.3.8 X-ray Diffraction (XRD)

Beakers containing 3 g of bentonite were filled with 50 mL of inhibitor solution. The mixtures were stirred for 24 hours for complete equilibrium absorption. Both water-treated and inhibitor-treated bentonite powders were dried at 90°C and grinded. Another portion was treated and dried at 40 °C to maintain its muddy state. At a range of 2⁰ to 10⁰ and a 2θ scanning angle, an Ultima IV X-Ray diffractometer was used to record the XRD pattern. To calculate d001 interlayer spacing, Bragg's equation was used.

$$d = \frac{n\lambda}{2\sin \theta}$$

3.4 Result and discussions

3.4.1 Characterization of GO, Poly-(AAAm) and Poly-(AAAm)-GO

3.4.1.1 NMR

The polymer was characterized with H-NMR, which was conducted with D₂O as a solvent in a Joel 600 Hz NMR apparatus. As shown in the figure 2(a), 1.4-1.8 ppm is attributed to 4H of CH₂ whereas 2.0-2.5 can be attributed to the 2H of CH. The peak at 4.8 is the solvent peak of D₂O. No peak appeared for the proton of –COOH and –NH₂ since D₂O is used as a solvent. This is due to hydrogen-deuterium exchanged [149]. The absence of -HC=CH proton peak at 5.5-6.2 is an indication of the polymerization of the monomers.

3.4.1.2 FT-IR

In Fig. 2(b) FT-IR was used to determine various functional groups in GO, Poly-(AAAm), and Poly-(AAAm)-GO. In the GO FT-IR spectrum, 1720 cm⁻¹ is assigned to the C=O stretching vibration, 1648 cm⁻¹ is the absorption peak for un-oxidized C=C. The bands at 3200 cm⁻¹ and 1288 cm⁻¹ were assigned to the stretching vibration of –OH and C-O-C respectively [145]. As can be seen from the FT-IR spectrum of Poly-(AAMA) in the figure,

the carboxyl carbonyl group has a transmittance bands at 1660 cm^{-1} . Bands ranges from 3000 to 3350 indicate and overlap stretching of FT-IR peaks of -OH and -NH_2 , while bands at 1599 indicates bending FT-IR peaks of -NH_2 . The formation of hydrogen bond between GO and Poly-(AAMA) is evidence by the shift of -C=O , -OH , and -NH_2 peaks [124]. There is an identical FT-IR spectrum between Poly-(AAMA) and Poly-(AAAm)-GO, which can be attributed to the small amount of GO used.

3.4.1.3 TGA

Figure 2(b) shows the thermal stability of Poly-(AAAm) and Poly-(AAAm)-GO. Utilizing a TGA instrument can provide a general analysis of the thermal stability of drilling fluid materials. A slight drop in Poly-(AAAm) at below 100 degrees Celsius is attributed to the evaporation of the polymer's solvent. At 120 to 200 °C, Poly-(AAAm) starts showing a sharp drop which is attributed to functional groups decomposition. Above 200 °C indicates the next sharp drop in the curve this is ascribed to the main chain of the polymer decomposing. There is a slight drop in mass at 200 °C, suggesting good thermal stability for the graphene modified polymer Poly-(AAAm)-GO. Comparing the curves of the two polymers Poly-(AAAm)-GO has shown a better thermal stability than Poly-(AAAm). This is as a result of the GO content in the polymer material.

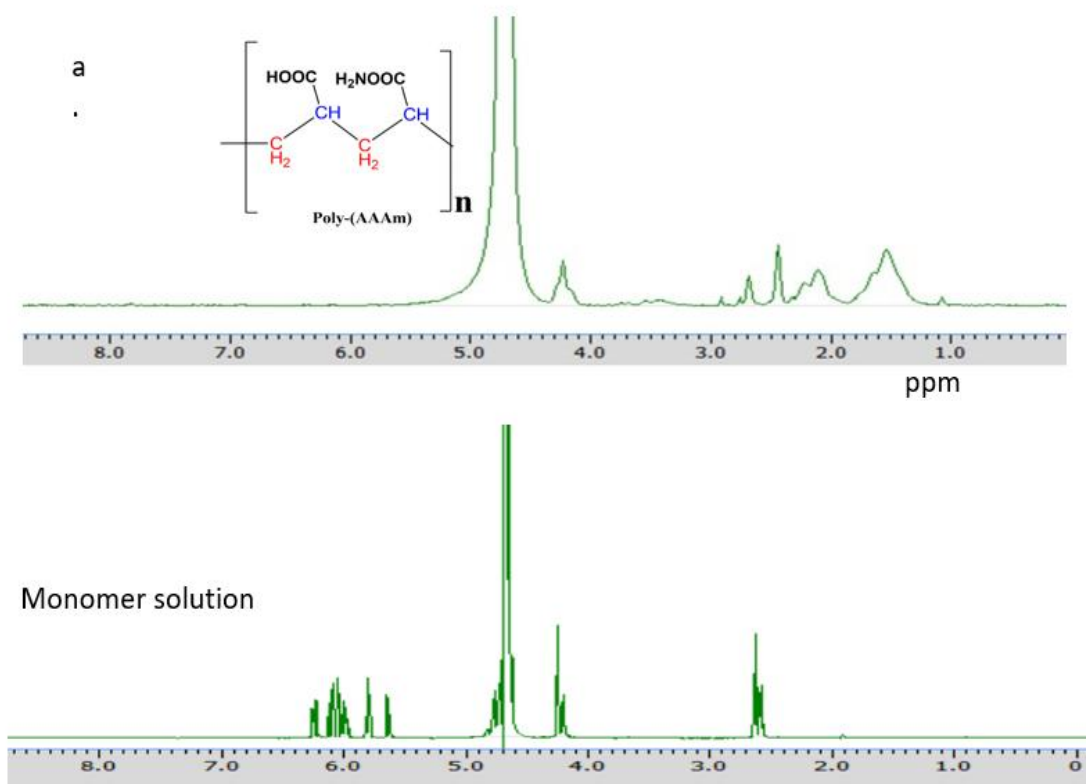


Figure 3.2 NMR spectrum for Poly-(AAAm) and monomer solution,

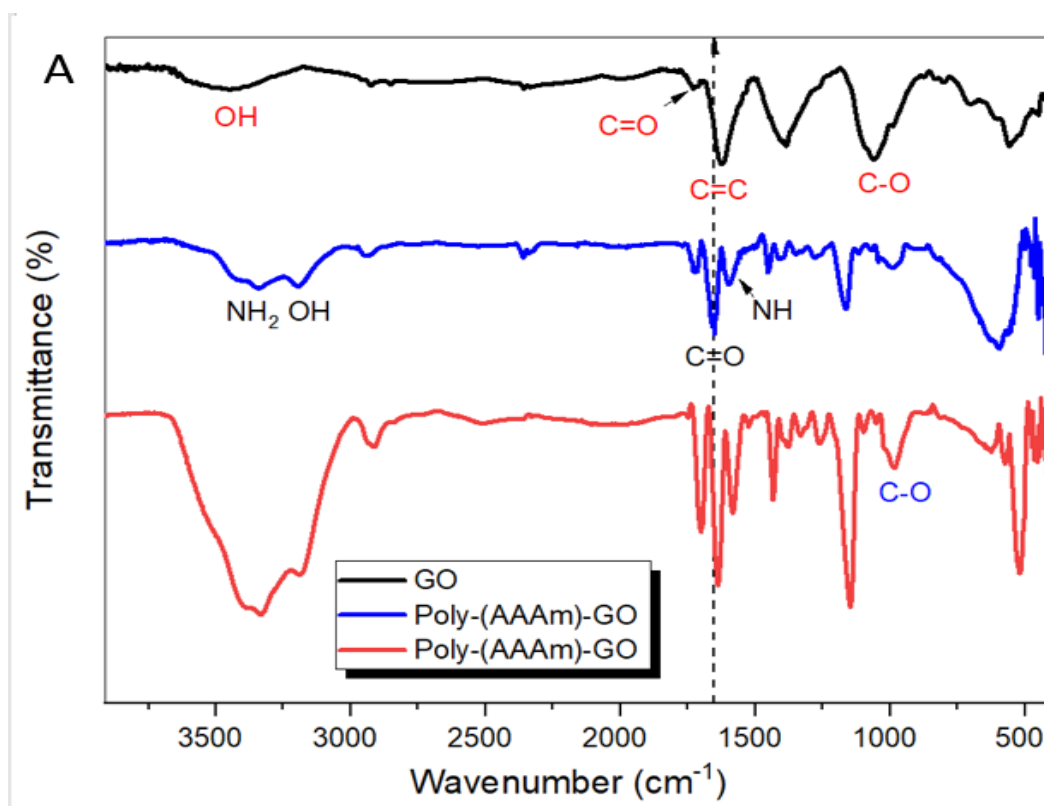


Figure 3.3 FT-IR spectrum for GO, Poly-(AAAm), and Poly-(AAAm)-GO

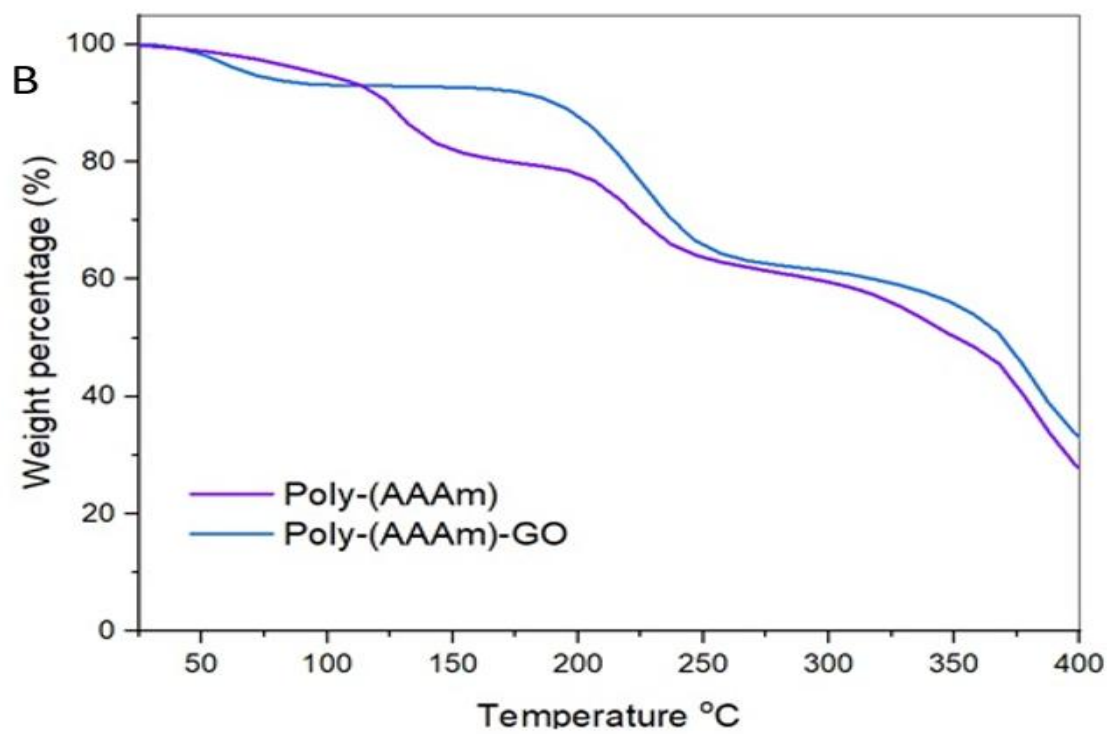


Figure 3.4 TGA curves Poly-(AAAm), and Poly-(AAAm)-GO

3.4.2 Evaluation of inhibition performance

3.4.2.1 Plate soaking test

wellbore instability such as shrinkage and collapsed can result from the intrusion of drilling fluids into shale formations. The soaking test helps in mimicking the hydration and free swelling action of shale in downhole [142]. The soaking test photographs of Na-Bt in distilled water, 4 % KCl solution, 4% of Poly-(AAAm) in solution, and 4 % Poly-(AAAm)-GO in solution are displayed in fig 3. when the bentonite is soak in distilled water as shown in the fig 3(a), with increase in soaking time, water molecules gradually enters the interlayer spacing. The intruding water destroys the interlayer binding force as this resulted in great hydration and expansion of the bentonite. The bentonite immersed in potassium chloride solution in fig 3(b) resulted in K^+ breaking the interlayer binding force. The pallet collapse from its initial cylindrical shape but good to note that no hydration occurs. This proves that KCl being an excellent inhibitor. Fig. 3(c) and (d) is the Na-Bt immersed in Poly-(AAAm) and Poly-(AAAm)-GO solution respectively. With the increase in soaking time both pallets maintain their original shapes indicating there was no water intrusion and no swelling. The polymers got adsorbed and forms a sealing film on to the surface of the bentonite. This shows that the polymer and the polymer graphene oxide composite being good inhibitors of hydration in water based drilling fluid than the traditional KCl inhibitor.

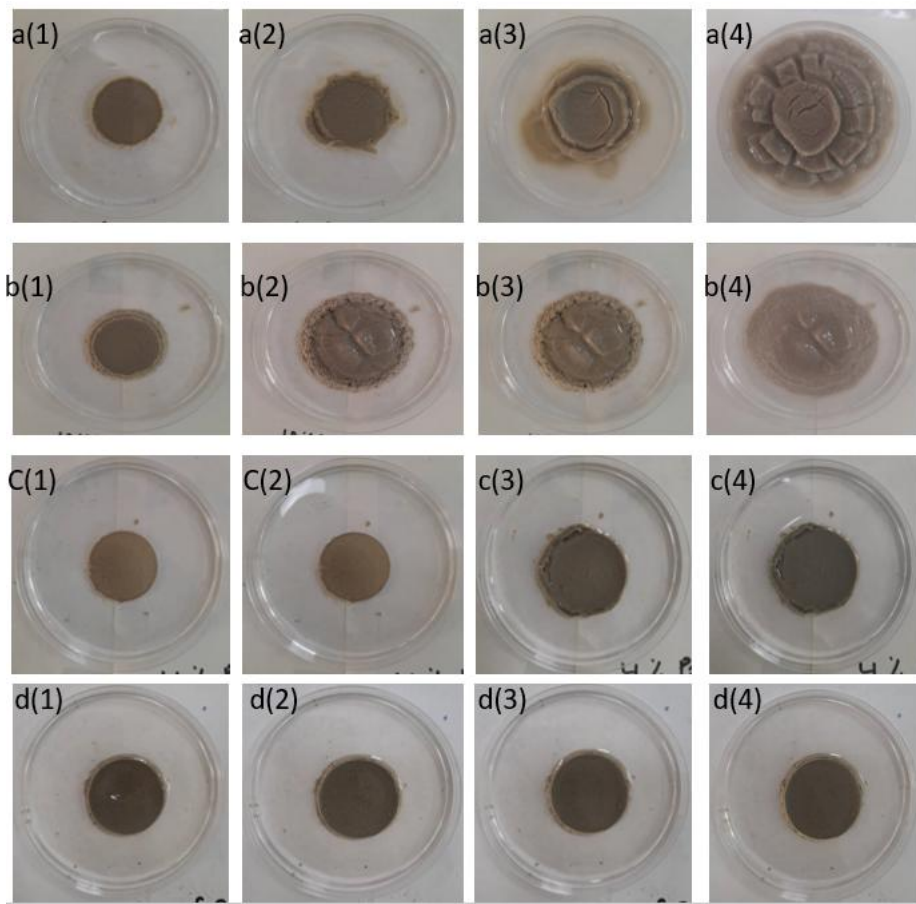


Figure 3.5 shows images of bentonite pallets at different time interval [1=30 min, 2=1 hr, 3=7 hr, 48 hr] in a. DI, b. 10 % KCl solution, c. 4 % Poly-(AAAm) solution, and d. 4 % Poly-(AAAm)-GO solution.

3.4.2.2 Shale recovery test

Hot rolling recovery was used to test the dispersion of shale cuttings in inhibitor solution. The purpose of this test is to assess a drilling fluid's inhibitory capabilities in mimicking shale cuttings disintegrating from a drill bit to the surface. Without an inhibitor the shale cuttings disintegrate easily in drilling fluid [132]. As a result, drilling becomes unsafe, ineffective and inefficient, and the rheology of shale formations deteriorates. Fig 4 shows the results of the recovery test. The percentage recovery of the shale in Poly-(AAAm), and Poly-(AAAm)-GO is compared with water and KCl. As shown in the figure, the remaining shale in distilled water after hot rolling accounts for 25 %. This signifies great hydration and dispersion of the cuttings. Poly-(AAAm) and Poly-(AAAm)-GO indicates a percentage recovery of 82 and 85 % respectively. Compared to KCl with a recovery of 56 %, the polymers have greatly hindered the hydration of the shale cuttings. A correlation is found between this observation and the anti-swelling test results, which show that Poly-(AAAm) and Poly-(AAAm)-GO enhance wellbore stability.

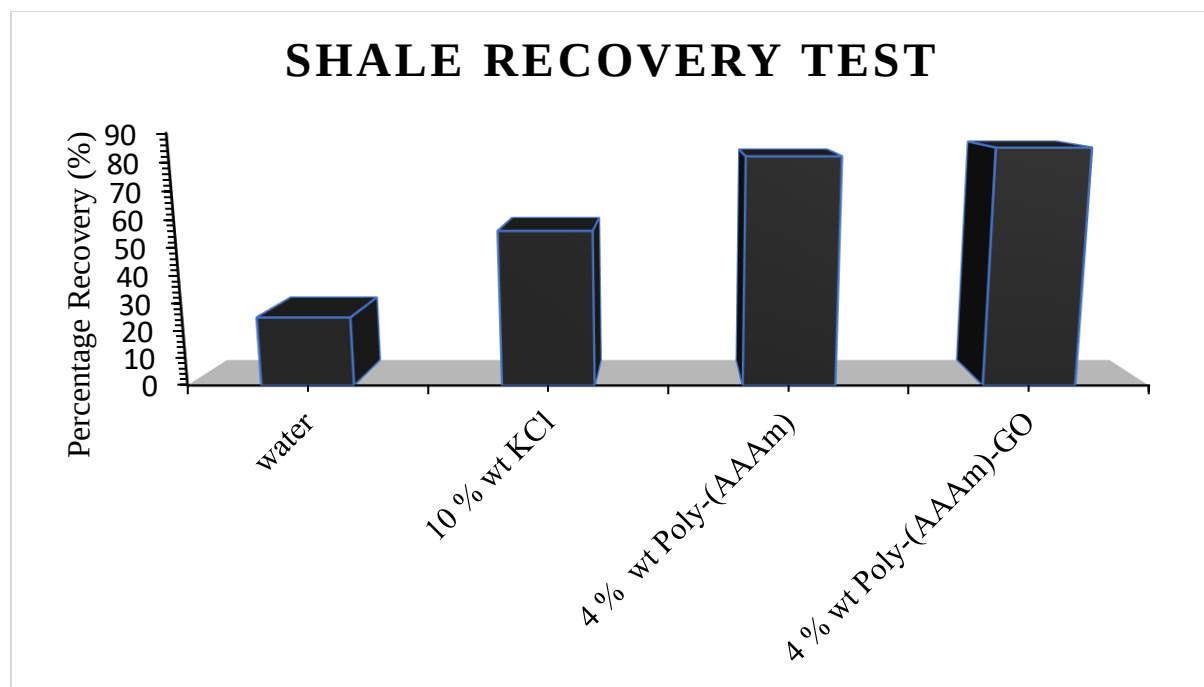


Figure 3.6 shows the shale recovery test in water, 10 % wt KCl, 4 % Poly-(AAAm), and 4 % Poly-(AAAm)-GO

3.4.2.3 Anti-swelling Ratio

Fig. 5 illustrate the anti-swelling ratio of Na-Bt in the four solutions. In distilled water with no effective inhibitor, bentonite swells which indicates high hydration levels. When the water penetrates the bentonite layers, it breaks the interlayer bonds, causing the minerals to swell. We can determine the ability of inhibitors to suppress bentonite hydration and swelling by using the anti-swelling ratio test [150]. The anti-swelling capabilities of 4 % Poly-(AAAm) and Poly-(AAAm)-GO in solution were evaluated and compared to 10 % KCl in solution which is a standard use in industries for drilling shale formations. In fig a Poly-(AAAm) and Poly-(AAAm)-GO show anti-swelling ratio of 80 % and 82 % respectively. When compare to KCl ,57 % anti-swelling ratio, the polymers have better capabilities in inhibiting the expansion of the bentonite. Water is prevented from penetrating Bentonite's surface by the inhibitors that is adsorbed on its surface and forming a thin film. This reveals that Poly-(AAAm) and Poly-(AAAm)-GO has good effect on inhibiting shale expansion.

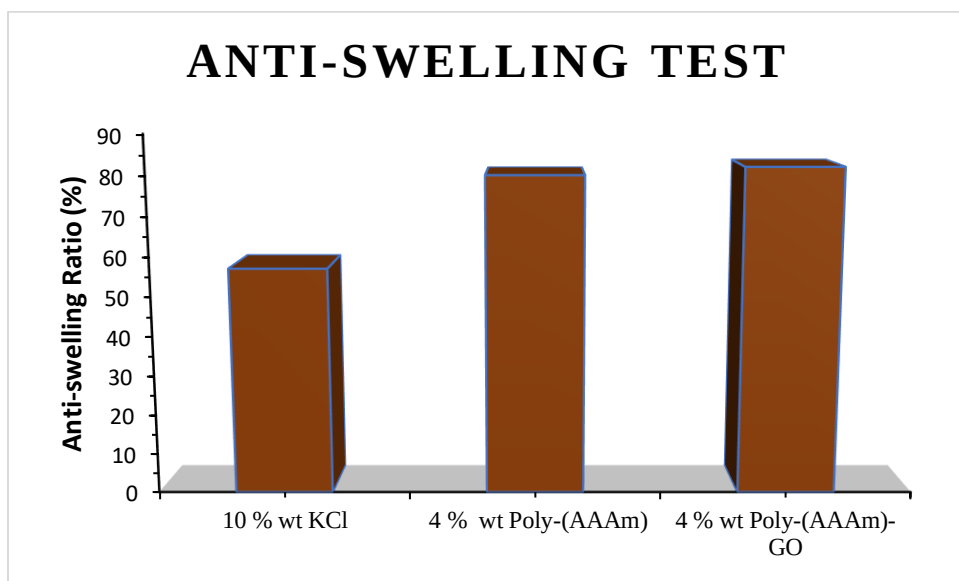


Figure 3.7 shows the anti-swelling ratio of 10 % wt KCl, 4 % Poly-(AAAm), and 4 % Poly-(AAAm)-GO.

3.4.2.4 TGA

The thermo-gravimetric curves in fig. 6 shows the decomposition of pristine Na-Bt, and bentonites modified with Poly-(AAAm) and Poly-(AAAm)-GO. By using TGA analysis, we are able to determine the amount and rate at which bentonite absorbs free water [151]. At room temperature to 100 °C the pristine Na-Bt soaked in water shows a sharp drop in the curve. Nearly 15 % of the sample's weight has been lost. At this temperature, this significant loss in mass can be attributed to the evaporation of absorbed water by the bentonite, which indicates significant hydration in the absence of an inhibitor. Bentonite modified with Poly-(AAAm) and Poly-(AAAm)-GO shows a lesser degree of steepness. Approximately 7 % and 5 % of mass were lost at 100 °C by the bentonite modified with Poly-(AAAm) and Poly-(AAAm)-GO respectively. Which indicates a low content of absorbed free water due to the effective inhibition of the polymer inhibitors. Comparing the three samples free Na-Bt absorbed more free water. As a result, Poly-(AAAm) and Poly-(AAAm)-GO inhibit water absorption, which is beneficial to clay particle stability.

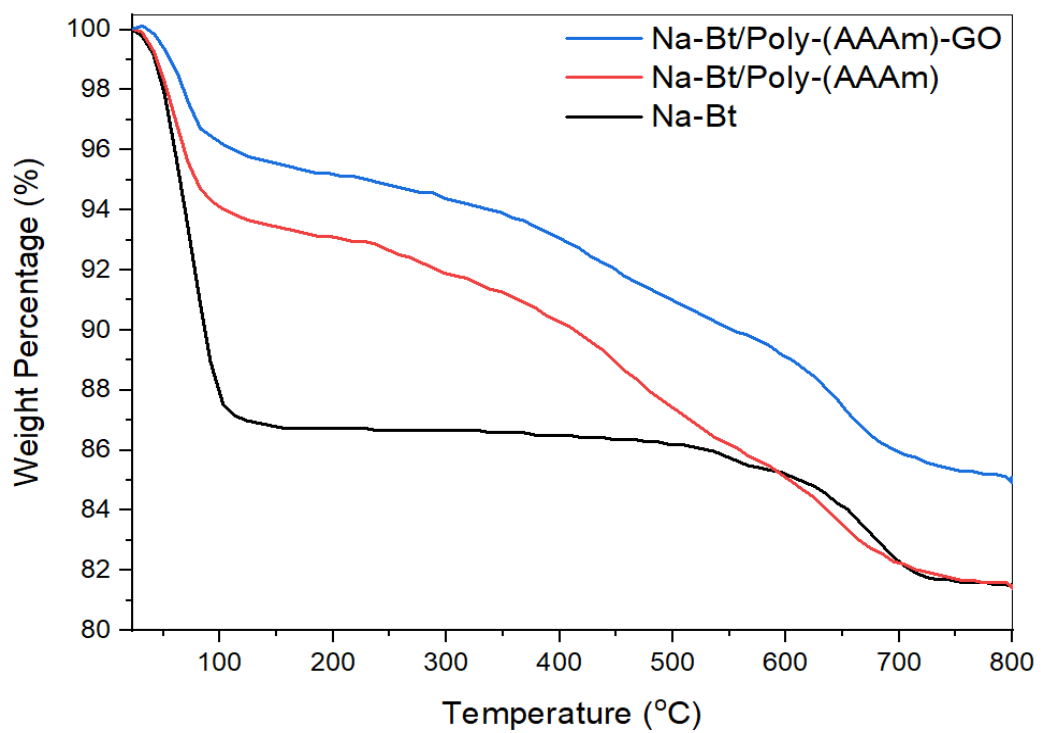


Figure 3.8 shows the TGA plot of pristine Na-Bt, Na-Bt/Poly-(AAAm), and Na-Bt/Poly-(AAAm)-GO

3.4.2.5 XRD

The plot in fig. 7 shows the XRD pattern of pristine Na-Bt, and bentonite modified with Poly-(AAAm) and Poly-(AAAm)-GO. When bentonite interacts with water, it breaks the binding force between layers, increasing the interlayer spacing. Depending on the degree of hydration and swelling, the spacing will expand. By using XRD, we can determine how much expansion has occurred within the interlayer spacing when the drilling fluid interacts with the bentonite. A low d-value which corresponds to a high 2θ indicates that interlayer spacing increases by a small amount and vice-versa [135]. Pristine Na-Bt soak in water shows an interlayer spacing of 14.7 Å. The interlayer spacing analysis of Poly-(AAAm) and Poly-(AAAm)-GO in solution at 4 % weight shows 12.8 Å and 11.8 Å, respectively. Comparing the spacing the bentonite soak in water shows an increase of approximately 25 %. However, Poly-(AAAm) and Poly-(AAAm)-GO's interlayer spacing demonstrates that they effectively prevent water intrusion. As such, it is a direct indication that both inhibitors are anti-swelling agents. The polymer material adsorption onto the bentonite formed a protective film that protected it from water intrusion. Therefore, Poly-(AAAm) and Poly-(AAAm)-GO can be classified as good hydration inhibitors in water base drilling fluids.

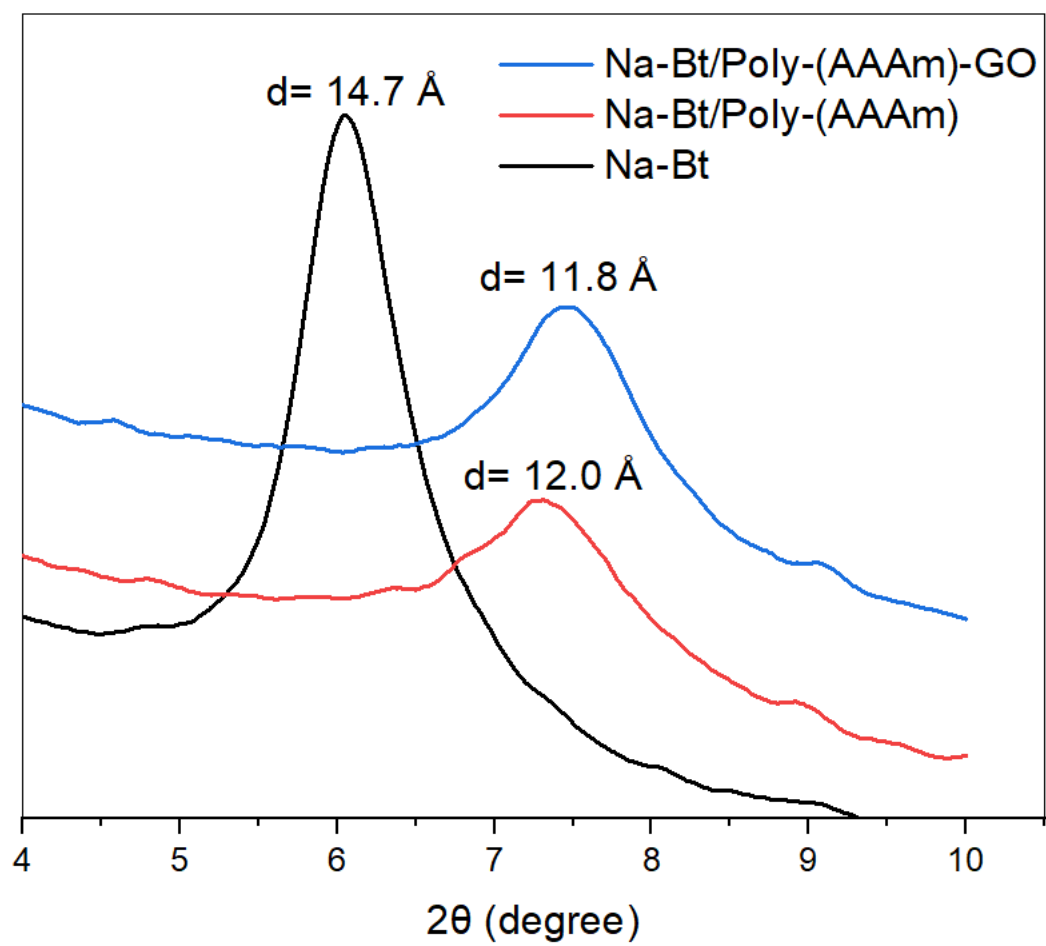


Figure 3.9 shows the XRD plots for Na-Bt, Na-Bt-Poly-(AAAm), and Na-Bt-4 % Poly-(AAAm)-GO

3.4.2.6 SEM:

When bentonite interacts with water in drilling fluids it gets hydrated, which result to a porous and rough morphology onto the surface of the bentonite. SEM can be use in getting a comprehensive detail on the degree of hydration by getting clear image on the morphology of the bentonite [152]. Fig 8 shows the SEM image of pristine bentonite and bentonite modified with Poly-(AAAm) and Poly-(AAAm)-GO. Fig 8(a) represents the Na-Bt immersed in distilled water. The morphology is rough and porous and the plats became loosely distributed. This indicates the bentonite was significantly hydrated. This expansion and bulging blocks pore channels of oil and gas reservoirs, and then decreases production. Fig 8(b) and 8(c) shows the bentonite treated with Poly-(AAAm) and Poly-(AAAm)-GO respectively. The modified bentonite shows a smooth and compact morphology which indicates mild hydration. This demonstrated that Poly-(AAAm) and Poly-(AAAm)-GO effectively inhibited bentonite hydration swelling. Both were capable of forming a polymer film that is closely adsorbed on the surface of the bentonite, restraining hydration and swelling.

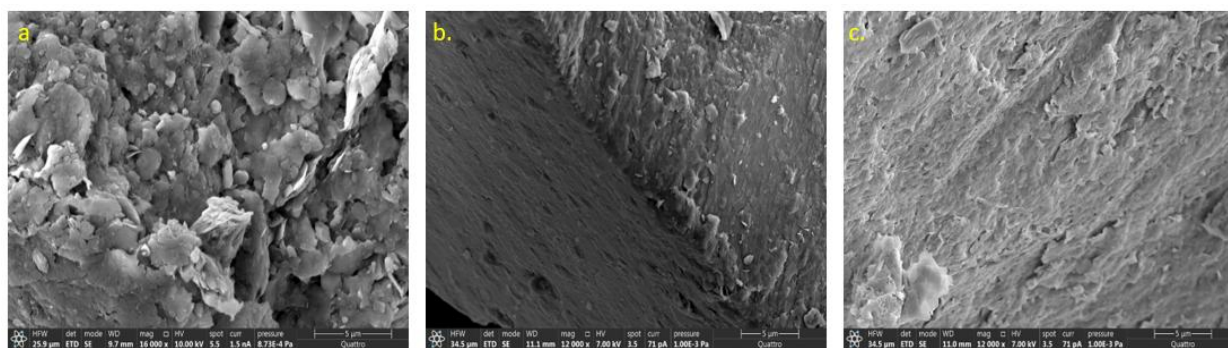


Figure 3.10 SEM images for a. Na-Bt/H₂O, b. Na-Bt/4 % Poly-(AAAm), and c. Na-Bt/4 % Poly-(AAAm)-GO

3.4.2.7 Contact angle test

High surface free energy shale molecules often have a high affinity for water, which translates into bentonite's hydrophilic nature [133]. Fig 9 shows the contact angle test on pristine bentonite, bentonite modified in 10 % wt KCl solution, and bentonite modified in 4 % wt Poly-(AAAm) and Poly-(AAAm)-GO. As can be seen from Fig 9(a), the pristine Na-Bt contact angle was 19.2° as measured by a contact angle tester. In this case, it indicates that the mineral has significant free energy, which translates into high hydrophilicity. Fig 9(b) shows the bentonite modified with KCl. With an increase in contact angle to 38.7° , KCl was able to reduce the free energy, thus increasing the hydrophobicity. Na-Bt modified with Poly-(AAAm) and Poly-(AAAm)-GO is shown in figure 9(c) and 9(d), respectively. There is a higher contact angle in both samples as shown in the figure. As a result, the surface was less able to absorb water molecules because the free energy was reduced. Poly-(AAAm) and Poly-(AAAm)-GO form a polymer protective film onto the surface inhibiting hydration and stabilizing the bentonite. As a result, Poly-(AAAm) and Poly-(AAAm)-GO show better inhibitory properties than traditional KCl.

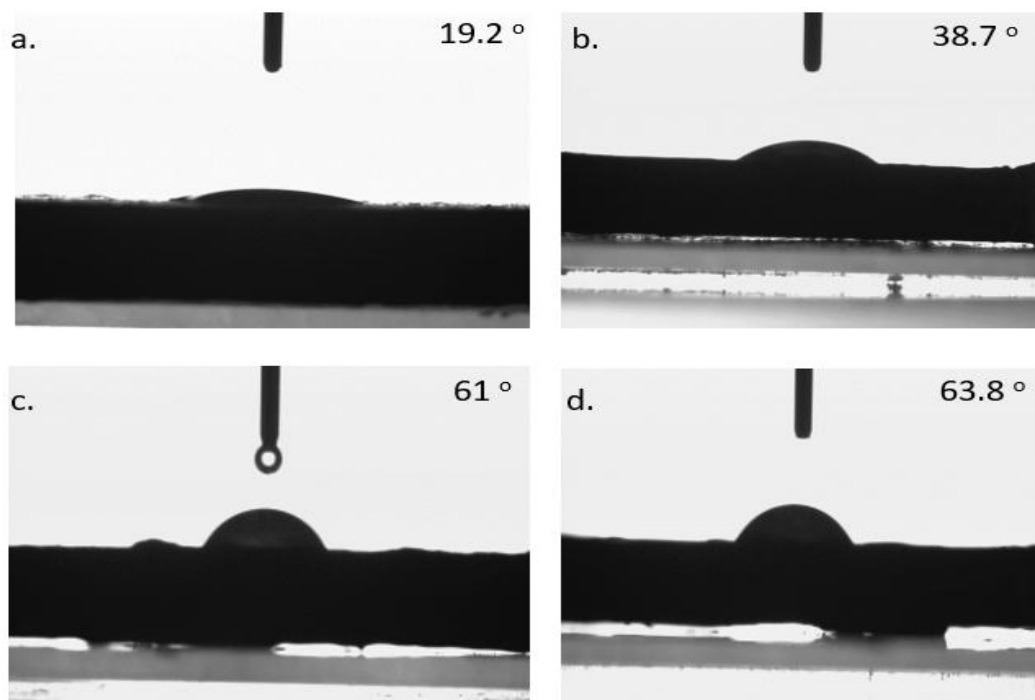


Figure 3.11 water contact angle; a. pristine Na-Bt, Na-Bt/4 % Poly-(AAAm), and Na-Bt/4 % Poly-(AAAm)-GO

3.4.2.8 FT-IR

The infrared spectra of pristine Na-Bentonite and bentonite modified with Poly-(AAAm) and Poly-(AAAm)-GO are shown in figure 10. Na-BT spectra indicates a typical characteristic of Na-Bentonite groups. Following Peaks of absorption can be seen in the plotting: Al-Al-OH peak (917 cm^{-1}), stretching band of quartz, Si-O-Si (1121 cm^{-1}), deformation band of Al-O-Si (537 cm^{-1}), the stretching band of Si-O (1030 cm^{-1}), water deformation band (1634 cm^{-1}) and the stretching band -OH (3370 cm^{-1}). For the bentonite modified with Poly-(AAAm), peaks such as 1713 cm^{-1} and 1555 cm^{-1} belongs to -C=O and -NH_2 bending vibration respectively. The broad spectra at 3000 to 3350 indicate and overlap stretching of peaks of -OH and -NH_2 from Poly-(AAAm). A shift of the water deformation from 1634 cm^{-1} to 1630 indicates the weakening of the bond. This translate the electrostatic attraction between the polymer and the bentonite, confirming the adsorption of the polymer [151]. Since the quantity of GO is not much different between Na-Bt- Poly-(AAAm)-GO and Na-Bt-Poly-(AAAm), the spectrum shows a similarity between the two.

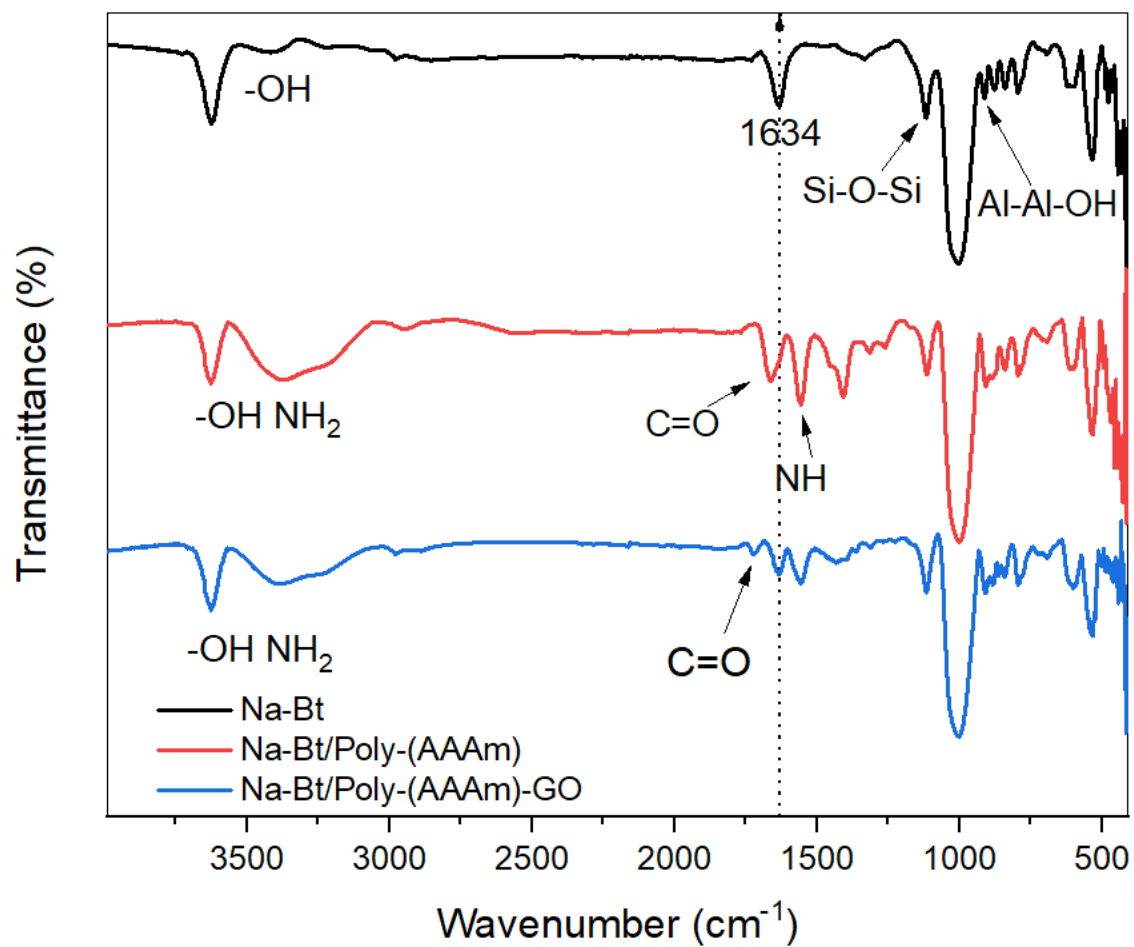


Figure 3.12 FT-IR plotting; Na-Bt, Na-Bt-4 % Poly-(AAAm), and Na-Bt-4 % Poly-(AAAm)-GO

3.5 Proposed mechanism of inhibition

Water enters the shale formations due to the positive pressure difference and capillary force. This result in shale hydration, strength reduction, wellbore instability, and well collapse. A wellbore can remain stable if the intruding water is effectively reduced in the shale reservoir. Isomorphic substitution of metal atoms generates negative charges onto the bentonite and this is compensated by exchangeable cations in the interlayer. This results in high hydrophilicity and draws water into the bentonite. Thus bentonite absorbed water and gets hydrated due to crystalline or osmotic hydration. Chemical effects such as ion exchange, electrostatic neutralization, and physical actions such as sealing, can be used to inhibit hydration.

Fig 11 shows the proposed mechanism of inhibition of Poly-(AAAm)-GO. We have proposed the inhibition mechanism with reference to range of characterization techniques, in this work and in other works. With there being carboxyl and amides functional groups in the polymer chain of Poly-(AAAm)-GO, there exist electrostatic interactions, hydrophobic interaction and hydrogen bonds. This enables the polymer composite to form hydrogen bond with the bentonite material and get adsorbed on to high free energy surfaces. The mechanism of Poly-(AAAm)-GO that inhibit shale hydration includes forming a protective film on to the surface of the bentonite. The polymer skeleton and the graphene oxide are a source of rejecting water molecules within the composite. In this way, water molecules are not able to directly contact bentonite particles, thus inhibiting hydration because of the film form onto its surface.

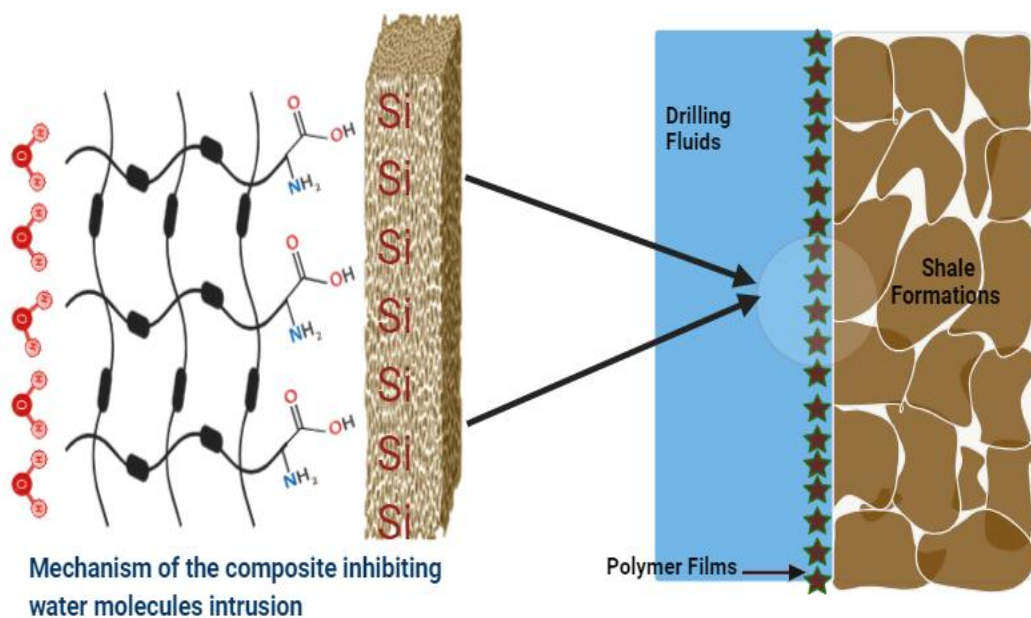
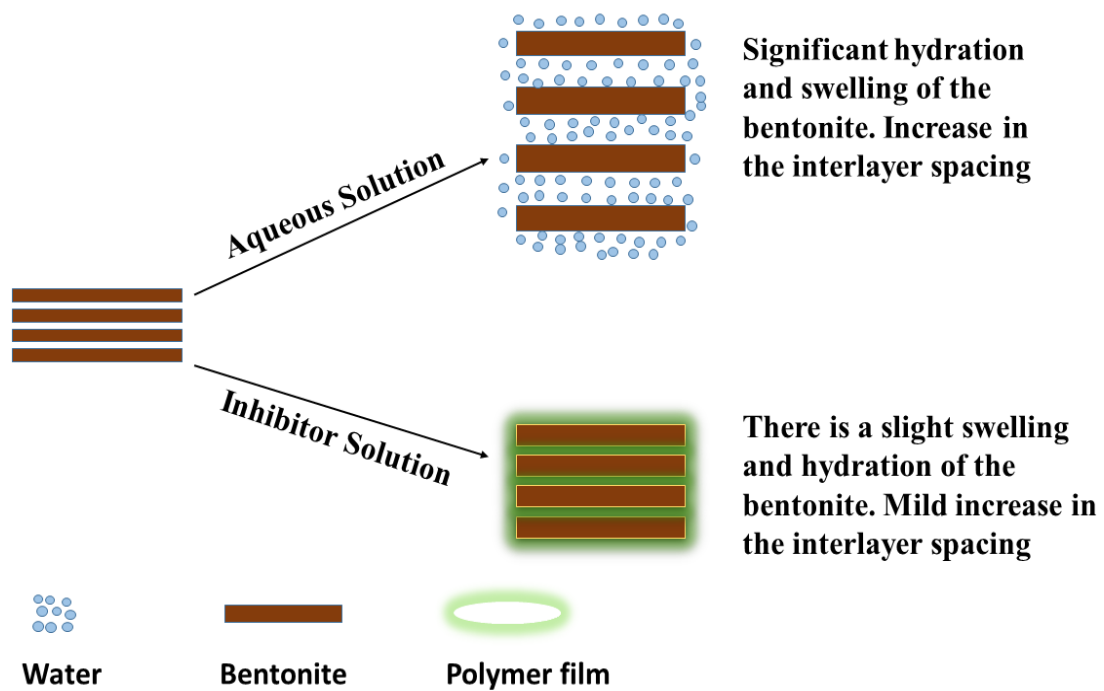


Figure 3.13 An illustration of Poly-(AAMA)-GO's hydration inhibition mechanism.

CHAPTER 4

SYNTHESIS AND EXAMINATION OF GRAPHENE OXIDE GRAFTED WITH COPOLYMER OF MALEIC ACID AND ACRYLIC ACID AS A SHALE HYDRATION INHIBITOR FOR WATER BASE DRILLING FLUID

4.1 Introduction

In oil and gas drilling, telescopic holes are drilled from surface to reservoirs that can be kilometers long. Drilling is accomplished with the help of a drill bit attached to a string of drill pipe [125]. As drilling fluids circulate from the surface through the drill pipe to the bit face, the formation pressure is maintained, cuttings are conveyed, and drilling equipment is cooled and lubricated as well [28]. Various drilling fluids can be used under various drilling conditions, including oil-based drilling fluids (OBDFs), synthetic-based drilling fluids (SBDFs), and water-based drilling fluids (WBDFs) [153] [28]. Generally, OBDFs and SBDFs are considered more efficient when drilling in shale areas since they do not hydrate clay material content in the shale. However, they have disadvantages such as high costs, environmental unfriendliness, and limited logging capabilities, which prevent them from complying with increasingly stringent environmental regulations and cost-control standards [154],[119]. OBDFs and SBDFs Are now being replaced by WBDFs, because they are the cheapest and the most environmentally friendly [8],[28].

When WBDFs are used, shale is prone to hydration and dispersion problems [119]. As the contact time between the drilling fluids and the formation increases, the hydration problem of the shale gets worse [127], [120]. Most wellbore stability issues are caused by shales, which account for more than 70% of all drilled formations. These include wellbore

diameter reduction, collapses, stuck pipes, and even possible interruptions of drilling operations [132], [99], [69], [119]. It has been shown that clay volume expansions and interlayer spacing expansions are the most important internal factors contributing to the loss of rock strength and indentation hardness, which directly affects cementation strength [155], [130].

Developing effective shale inhibitors requires an understanding of how shale swells when WBDFs are used. Due to their significant clay mineral content, including montmorillonite, water invades and soaks the shale formations seriously[129]. In clay lattices, isomorphic substitution of metal atoms generates negative charges, which are largely compensated by exchangeable cations in the interlayers [131]. Crystalline and osmotic hydration are the two hydration methods through which clay minerals hydrate. All clay minerals can undergo crystalline hydration. In this type of hydration, water molecules are directly adsorbed onto the crystal surface, leading to short-range swelling. As a result of osmotic hydration, water molecules can move into the interlayer by diffusion if the cation concentration differs from surrounding water. This results in large swelling [4],[1]

The industry has become increasingly interested in shale inhibitors with excellent inhibitory properties, as well as environmental benefits. One of the earliest and most widely used inhibitors of WBDFs is potassium chloride (KCl) [142],[137]. Montmorillonite layers are inhibited from hydrating because sodium ions (Na^+) are replaced with weakly hydrated potassium ions (K^+) [3]. Certain offshore drilling locations may not accept KCl because of its large dosage requirement [136],[4],[128]. This high concentration of electrolytes

prevents water-sensitive shale formation from hydrating and swelling, and it is important to note that high concentrations of these electrolytes result in flocculation of clay minerals in drilling fluids, affecting the drilling fluid's properties, causing loss of fluid volume and thixotropy [150],[133]. Furthermore, salts have a detrimental effect on the rheological properties of drilling fluids based on bentonite, as well as the marine environment and the ability of drilling fluids to lift shale cuttings [8].

The instability of shales has been addressed by a variety of chemical agents, including silicates, organic amines, surfactants, asphalts, Polymer/KCl composite, and nanoparticles [138],[140],[135],[134],[156]. In spite of their effectiveness as shale inhibitors, some limitations persist, including high costs, toxicity concerns, and inadequate temperature resistance [120],[157]. Polymers are beneficial to drilling fluids for a variety of reasons, including controlling viscosity, increasing suspension, and inhibiting the formation of shale [141]. Polymers are not only effective at inhibiting shale formation, but also improve drilling fluid rheology and filtration characteristics [139],[8]. Between the water/polymer and the shale matrix, hydrogen bonds act as the mechanism behind shale inhibition. Because of the tendency of the shale matrix to adsorb water, swelling and dispersion occur within it. Hydrogen bonds between water molecules and clay minerals are disrupted by polymers, which compete for interlayer spaces and form hydrogen bonds with aluminates and silicates. The attachment enhances shale hydration inhibition by preventing further water interaction with clay minerals [2]. The high temperature and high salt conditions experienced during drilling present significant challenges to the use of polymers for shale hydration. Studies indicate that high temperatures compromise the stability of these polymers [128],[143], [124],[144]. This instability can significantly impact the stability of

the drilling fluid. Thus, it is crucial to modify the polymer to enhance its stability and withstand harsh conditions and high temperatures.

Studies have shown that graphene oxide, due to its thermal and mechanical stability, has excellent inhibitory properties. Its high surface area allows it to form a protective layer on the shale surface, preventing water molecules from penetrating [145]. Additionally, graphene can enhance wellbore stability by filling the microspores and fractures in the shale, thereby blocking water intrusion [145]. However, a major drawback of using graphene in water-based drilling fluids (WBDFs) is its poor dispersibility as an inhibitor [145],[146].

Therefore, it is essential to develop a polymer-graphene oxide composite that offers high thermal stability in drilling pits and effectively inhibits shale hydration. An effective shale inhibitor is usually a water-soluble organic macromolecule with hydrophobic and hydrophilic regions as well as electro-functionality such as carboxyl, Amine and hydroxyl groups [119]. While polymer/graphene oxide composites have been recognized by scholars as a possible shale hydration inhibitor, this application is still in its infancy. Using free radical polymerization, we synthesized a copolymer of acrylic acid and maleic acid/Graphene oxide (Poly-(AAMA)GO) composite to serve as an effective and low-cost inhibitor. The special structures of the synthesized Poly-(AAMA)-GO are electrostatic interactions, hydrogen bonds, thus, it is suitable as a shale hydration inhibitor in water base drilling fluids. The pristine copolymer, poly (acrylic acid-co-maleic acid) (Poly-(AAMA)), was also synthesized and its inhibitory properties were compared to the polymer graphene oxide composite. Tests were conducted to evaluate the inhibitory qualities of the prepared

Poly-(AAMA)GO and Poly-(AAMA) using anti-swelling, immersion, and shale recovery tests. A comparison was made using KCl, a commonly used inhibitor in industry.

4.2 Materials and methods

4.2.1 Materials

Sodium bentonite (Na-Bt) 100% pure was purchase from Belle Chemical and Maleic acid (MA) ($C_4H_6O_5$, $M_r = 134.09$ g/mol, 99 % purity) was obtain from Fluka Chemie AG, Industriestrasse. Ammonium persulfate (APS) ($(NH_4)_2S_2O_8$, $M_r = 228.18$ g/mol, ≥ 98 % purity) and Acrylic acid (AA) ($C_3H_4O_2$, $M_r = 72.063$ g/mol, 99 % purity) were purchase from Sigma-Aldrich. Potassium chloride (KCl, $M_r = 74.55$ g/mol, 99 % purity) use for comparison was purchase from Fisher Scientific Company. Shale cutting were provided by the geology department of KFUPM. All the utilize chemicals were of analytical grade. Deionized water was used in all experiments

4.2.2 Material Preparation

The composite was prepared by using free radical polymerization in aqueous solution [147],[124],[121]. 150 mL dry three-neck round bottom flask was equipped with a magnetic stirrer, a reflux condenser, nitrogen gas inlet and dropping funnel. 100 mg of graphene oxide produced by a modified Hummers method [148] was added to 50 mL of deionize water and magnetically stirred to fully dispersed. A mole ratio of 3:1 MA (3 g) and AA (0.62 g) was selected respectively and added into the flask. The temperature was increased to a range of 60 °C to dissolve the components under magnetic stirring to attained a homogenous solution. After the dissolving of the reactants, trace amount (≈ 5 mg) of APS was then added into the solution in batches. The mixture was kept under reflux for 5 hr and three-fold volume absolute ethanol was added to precipitate the macromolecular

product. The obtained product was dialyzed in deionized water to get rid of the unreacted monomer and followed by freeze-dried to get rid of the used solvent (water). The collected copolymer of acrylic acid and maleic acid/ Graphene oxide weight 2.3 g and was given the abbreviation as Poly-(AAMA)-GO. The same method was used to synthesize Poly-(AAMA) without graphene oxide.

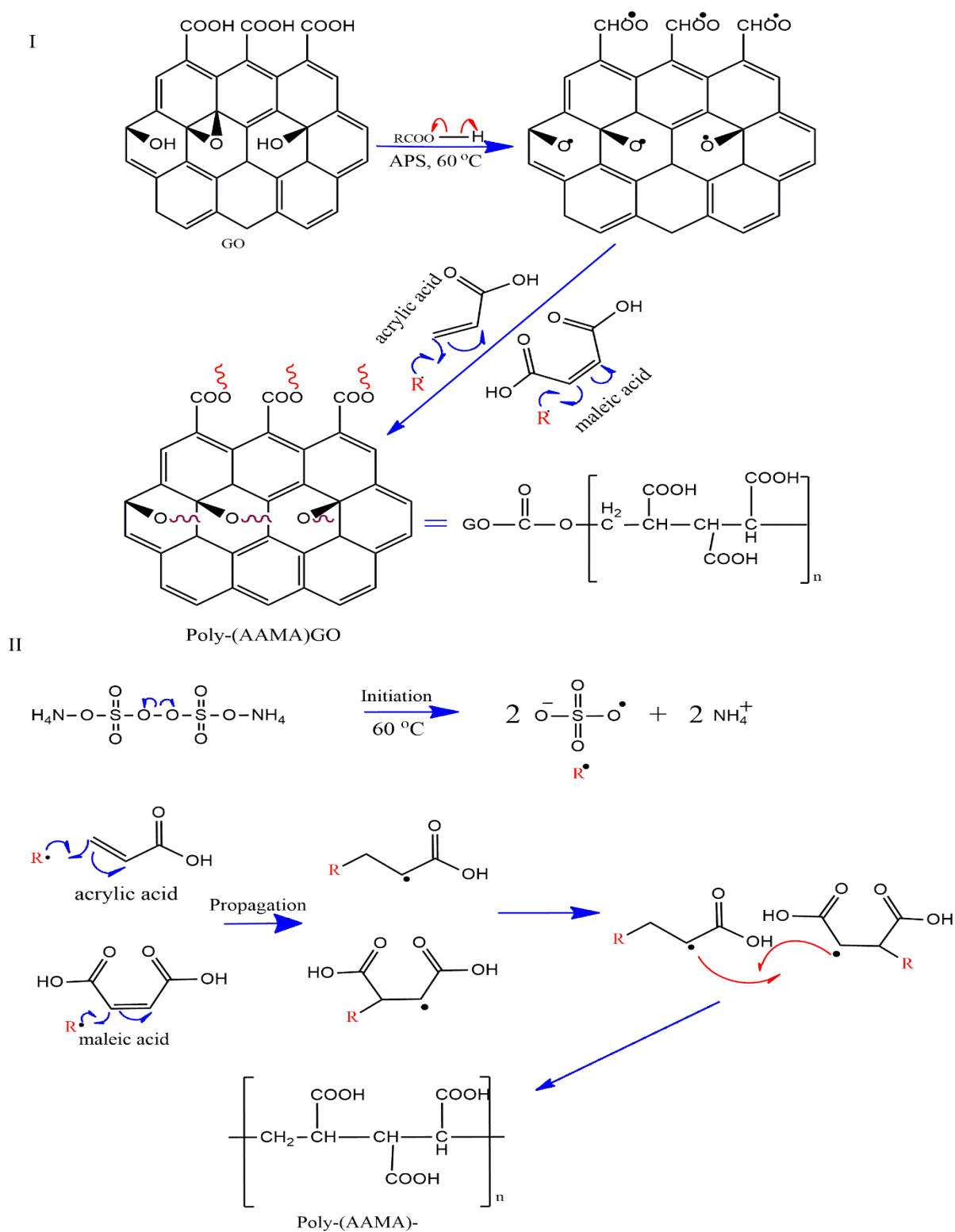


Figure 4.1 Reaction scheme of free radical polymerization of the copolymer of acrylic acid and maleic acid/ Graphene oxide (Poly-(AAMA)GO) (I) and free radical polymerization of the copolymer of acrylic acid and maleic acid (II)

4.3 Evaluation Methods

4.3.1 Shale recovery test

An inhibition solution is prepared and mixed with shale cuttings in a sealed pressured vessel to determine the degree of dispersion. A higher recovery percentage indicated a better property of inhibiting the dispersion of shale cuttings. 5 g of shale cuttings between 6-10 mesh were prepared and put into sealed vessel tanks containing 35 cm³ distilled water, 35 cm³ 10% KCl in solution 35 cm³ of 4% of the inhibitors in solution. The sealed tanks were then placed into a roller oven cell and then hot rolled for 16 hr at a temperature of 120 °C. The mud was then washed with deionized water, filtered and dried at 110 °C. The percentage recoveries were calculated using the formula M_2/M_1 in which M_2 is the mass of shale cutting after hot rolling, whereas M_1 is the mass before hot rolling.

4.3.2 Plate soaking Experiment

Pallets were made from 5 g sodium bentonite (Na-Bt) pressed under 10 MPa for 5 min by a pressure device. The compacted Na-Bt pallets were taken out and fully immersed in petri dishes containing 25 mL distilled water, 25 mL of 10 % KCl solution, and 25 mL of 4 % inhibitor in solution. Conditions were maintained at room temperature for two days in which pictures were captures to record the hydration process of the compacted pallets at 5 min, 30min, 1 hr, 3 hr, 7 hr 24 hr and 48 hr.

4.3.3 Contact angle test

3 g shale Na-Bt was added into 100 mL measuring cylinders containing distilled water, 10 % weight KCl in solution, 4 % weight of inhibitors in solution and the dispersions was stirred for 24 hours to reach adsorption equilibrium. The samples were filtered and dried at 90 °C and the residues were pressed under 5 MPa to form pallets with smooth surface.

Distilled water was drop onto the surface of the pallets with a micro injector on a Kruss Goniometer DSA25 and the images were captured by a contact angle tester.

4.3.4 Fourier Transforms Infrared Spectroscopy (FT-IR)

200 mg KBr and 2 mg sample were fully, poured into a mold and pressed under 3 MPa by hydraulic press. A Nicolet is10 FT-IR spectrometer was used to record the spectral analysis of Poly-(AAMA)-GO, Poly-(AAMA), pristine Na-Bt, and modified Na-Bt samples.

4.3.5 Thermogravimetric analysis

A beaker containing 100 mL of distilled water and 4 % inhibitor in solutions was filled with 5 g of Na-Bt. A magnetic stirrer was used to thoroughly mix the mixtures for 24 hours to achieve maximum absorption. We utilized a STARE System TGA/DSC 3+ machine and a high purity Ar atmosphere to perform TGA analyses on pristine Na-Bt Poly-(AAMA), and Poly-(AAMA)-GO modified NaBt at a heating rate of 10 °C/min.

4.3.6 H-NMR Analysis

A 600 MHz (JEOL, Japan) spectrometer was used to acquire the proton Nuclear Magnetic Resonance data for the monomers in solution, and Poly-(AAMA). To achieve this, individual NMR tubes were utilized for samples containing the monomers and pure Poly-(AAMA), with each sample dissolved in deuterium oxide (D₂O) at room temperature.

4.3.7 Anti –swelling test

As a standard evaluation method for Na-Bt stabilizers in drilling fluids, a test for anti-swelling has been used to test the inhibitors influence on bentonite. 1 g of Bentonite was weighed and placed in a centrifuge tube containing 20 mL of a 4 % inhibitor solution. A 2-hour stand time was followed after the tubes were stirred and shaken thoroughly. The mixture was then centrifuged at a speed of 1500 r/min for 15 min and the change in volume

of the Bentonite was measured. The anti-swelling ratio (AR) was calculated based on the equation:

$$AR = \frac{V_b - V_a}{V_b - V_0} \times 100$$

V_a and V_b represents the variation in the volume of bentonite in the inhibitor solution and water respectively. Whereas V₀ is the change in volume of kerosene in milliliters.

4.3.8 Scanning Electron Microscope (SEM)

In three different empty beakers, 5 g of Na-Bt was placed, followed by 100 mL of distilled water and 100 mL of 4 % inhibitor solutions. For equilibrium absorption, the mixture was stirred for 24 hours to form a slurry. An oven was used to dry the residue after filtering the samples. the specimens were glued to a piece of tape and then coated with a gold layer. The morphology of the dried sample treated with distilled water and the one treated with inhibitor solution was compared using a Thermo Scientific™ Quattro ESEM in high vacuum mode.

4.3.9 X-ray Diffraction (XRD)

XRD patterns of pristine Na-Bentonite sample in distilled water, and bentonite soak in inhibitor solution were recorded with an Ultima IV X-Ray diffractometer. Using copper as a target, the pattern was collected with 2θ angle scanning from 3° to 10°. As part of the preparation process, Na-Bt samples were treated in inhibitor solution and another sample treated with distilled water. 5 g of Na-bentonite was placed, followed by 100 mL of distilled water and 100 mL of 4 % inhibitor solutions. The mixture was stirred for 24 hours to form a slurry. The samples were filtered and dried at 60 °C and ground into powder. In order to calculate d₀₀₁, the interspacing layer was calculated using Bragg's equation.

$$d = \frac{n\lambda}{2\sin \theta}$$

4.4 Results and discussion

4.4.1 Characterization of GO, Poly-(AAMA) and Poly-(AAMA)GO

4.4.1.1 NMR

The structure of the resultant product was characterized using H-NMR spectroscopy. As shown in Figure 2(a) for Poly-(AAMA): the peak at 2.9 ppm can be attributed for 3H, of CH; whereas that of 1.4 ppm for 2H, of CH₂; the H of –COOH does not exhibit a signal in the D₂O solvent, and the peak at 4.70 ppm is ascribed to the solvent (D₂O). Notably, the figure indicates no transmittance for the C=C peak at 5.5 to 6.2 ppm, providing evidence for the polymerization of the monomers [121].

4.4.1.2 FT-IR

was used to determine the functional group of GO, in figure 2(b). In the GO FT-IR spectrum, 1720 cm⁻¹ is assigned to the C=O stretching vibration, 1648 cm⁻¹ is the absorption peak for un-oxidized C=C. The peaks at 3200 cm⁻¹ and 1288 cm⁻¹ were assigned to the stretching vibration of –OH and C-O-C respectively [145]. The FT-IR spectrum of Poly-(AAMA) in figure, the transmittance peaks of carboxyl carbonyl groups and hydroxyl groups are located at 1707cm⁻¹ and 3300 cm⁻¹, respectively. The absence of transmittance peak of C=C bonds at 1645-1620 proves the polymerization of the monomers. A similar FT-IR spectrum is observed between Poly-(AAMA) and Poly-(AAMA)GO, which is due to the small amount of GO used. The formation of hydrogen bond between GO and Poly-(AAMA) is evidence by the shift of C=O peak to smaller wave length [124].

4.4.1.3 TGA

Inorganic inhibitors are recognized for their high thermal stability, whereas organic inhibitors, especially polymers tend to degrade at high temperature [3]. hence, it is essential to determine the thermal stability of inhibitors. Figure 2(c) illustrate the thermal decomposition of Poly-(AAMA) and Poly-(AAMA)-GO. Poly-(AAMA) begins to decompose at around 150 °C whereas Poly-(AAMA)-GO start decomposing above 225 °C, indicating a better thermal stability. The improved thermal stability of Poly-(AAMA)-GO is primarily due to the GO content in it.

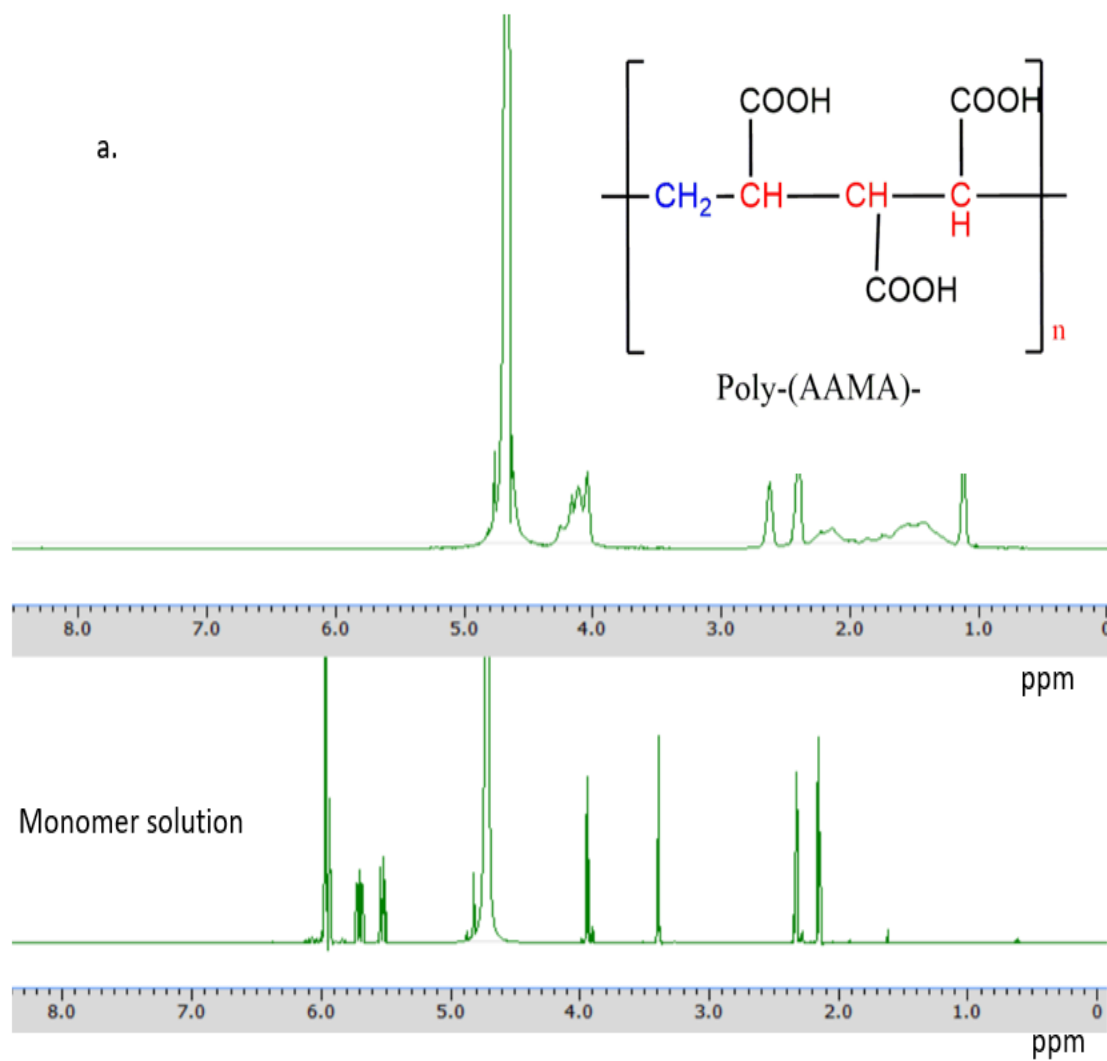


Figure 4.2 Shows NMR spectrum of Poly-(AAMA) and monomer solution

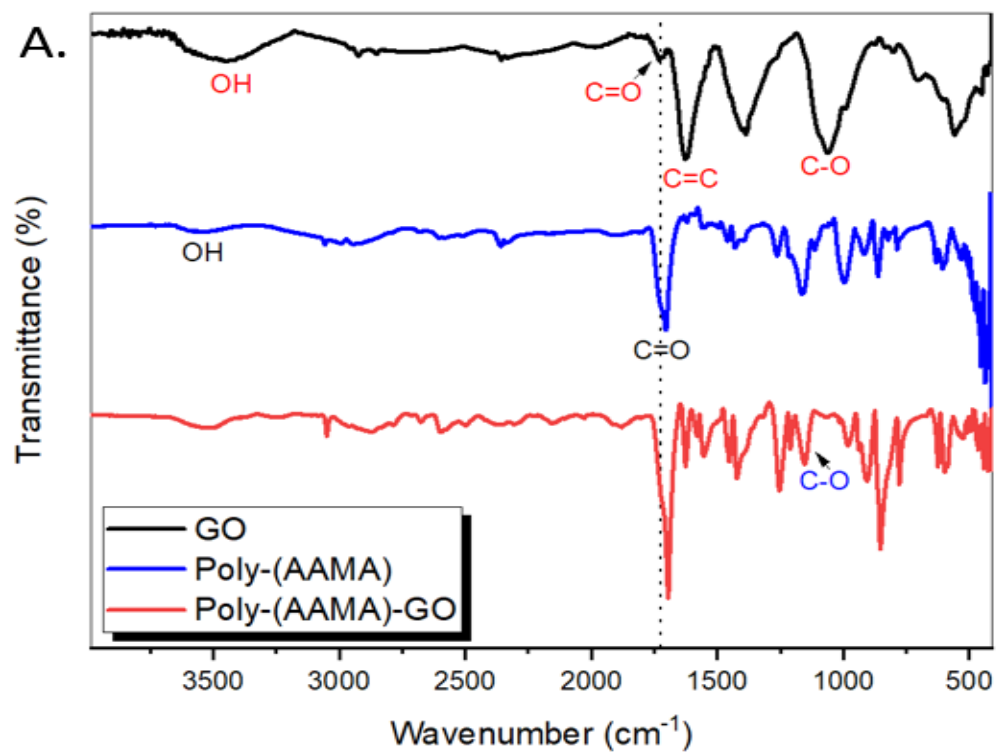


Figure 4.3 FT-IR spectrum of Poly-(AAMA)-GO, Poly-(AAMA) & GO

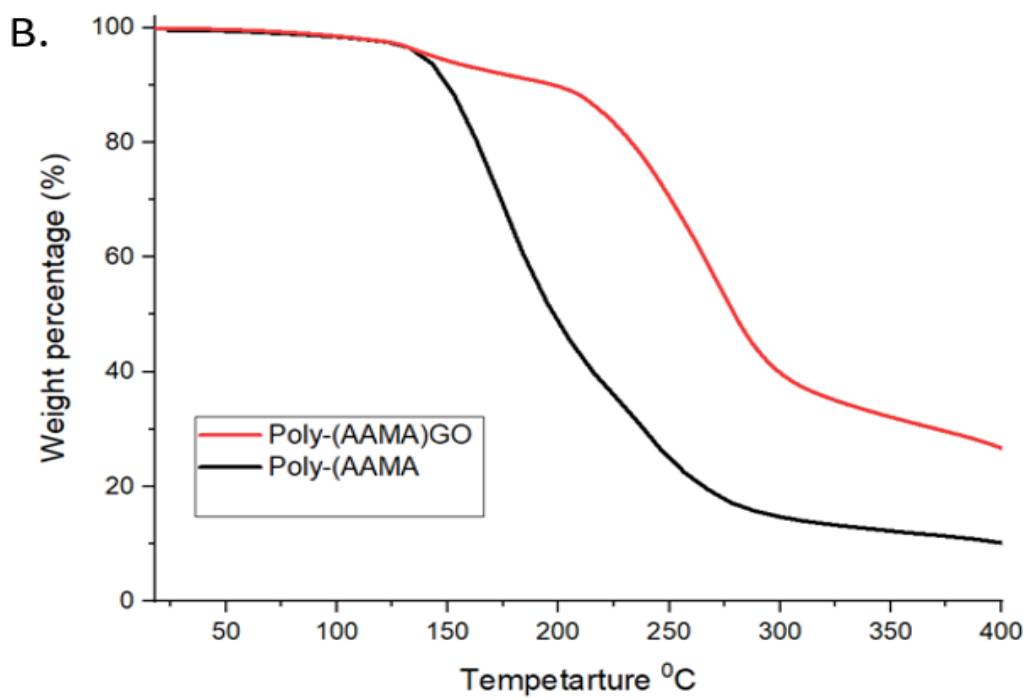


Figure 4.4 TGA curves of Poly-(AAMA)-GO and Poly-(AAMA).

4.4.2 Evaluation of the inhibition performance

4.4.2.1 Plate soaking Experiment:

When drilling fluids enter shale, the wellbore can become unstable, resulting in the collapse of the wellbore. During the plate soaking test, Na-Bt Pallets are exposed to different solutions to simulate free hydration and swelling in downhole [123]. As shown in figure 3, the letters A-D represent pallets in different inhibitor solutions at a time interval of 48 hours. Figure 3(a) shows the Na-Bt palate in distilled water. As it is observed the palate shows great swelling resulting in the palate disintegrating. Figure 3(b) shows a palate in KCl solution in which the palate disintegrated but there was no swelling. This is a prove of KCl being an inhibitor. Figure 3(c) and 3(d) respectively show pallets in the polymer solution and polymer graphene oxide composite solution. Its seen that after 48 hr of soaking, the pallets did not disintegrate and no swelling occurs proving that the synthesize compounds as good hydration inhibitors. Inhibiting hydration with KCl is possible, but stabilizing the pallet with Poly-(AAMA) and Poly-(AAMA)-GO is much more effective. Based on the results of the experiment, it can be inferred that the Na-bentonite pallet is less hydrated and swollen because Poly-(AAMA) and Poly-(AAMA)-GO has merged to its surface, preventing water from entering.

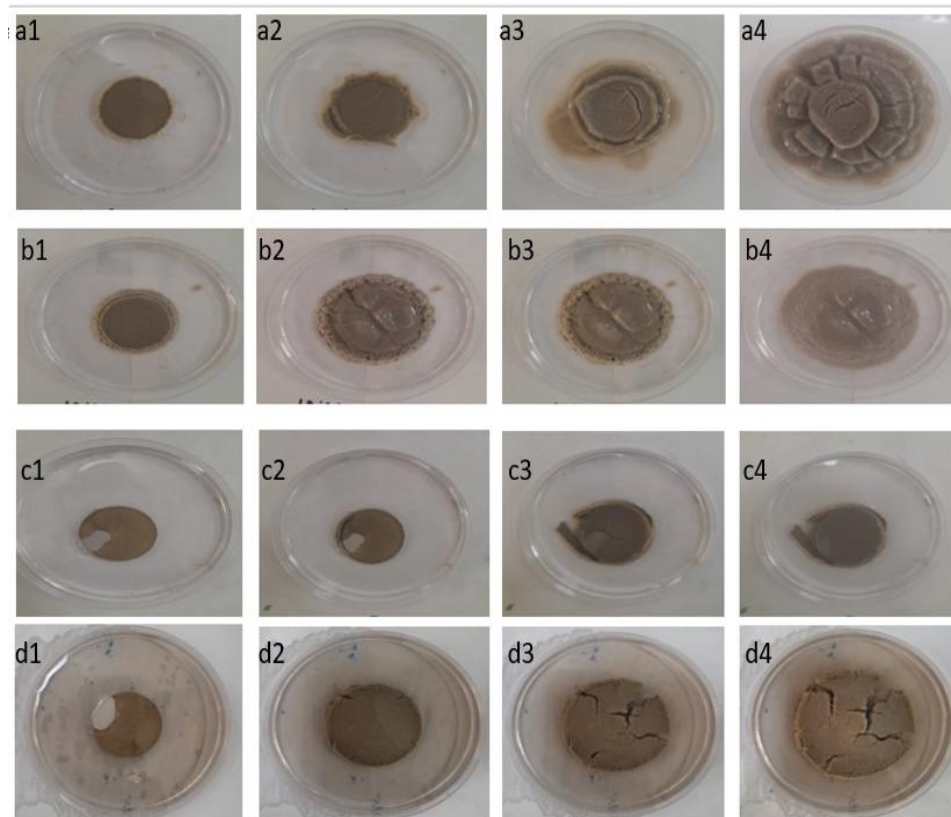


Figure 4.5 . Pictures of Na-Bt plates soaked in pure water and different inhibitor solutions for 5 48hr : (a) pure water, (b) 10.0 wt % KCl, (c) 4.0 wt % Poly-(AAMA), (d) 4.0 wt % Poly-(AAMA)-GO

4.4.2.2 Contact angle test:

In the contact angle test, the direction of the capillary force can be determined. The high hydrophilicity indicates that capillary force drives water into the shale through spontaneous imbibition. A decrease in hydrophilicity and an increase in hydrophobicity leads to an inability of water to enter the pores in the shale, inhibiting hydration [120]. The contact angle labelled A, B, C and D in figure 4 is a representation of pristine Na-Bt, Na-Bt treated with KCl, and Na-Bt modified with Poly-(AAMA) and Poly-(AAMA)-GO. For pristine Na-Bt, an average contact angle of 19.2° was obtained, indicating the material being highly hydrophilic. The sample modified with 10 % weight of KCl in solution resulted in an improve hydrophobicity, which is seen by an increased in the average contact angle to 33° . Samples C and D represent shale modifications with Poly-(AAMA) and Poly-(AAMA)-GO at 4 % concentrations in solution. There is an increase in the Hydrophobicity of the sample as shown in the figure. This is an evident that the synthesize material serves as a superior hydration inhibitor compared to KCl, creating a barrier that hinders water penetration into the shale samples [126].

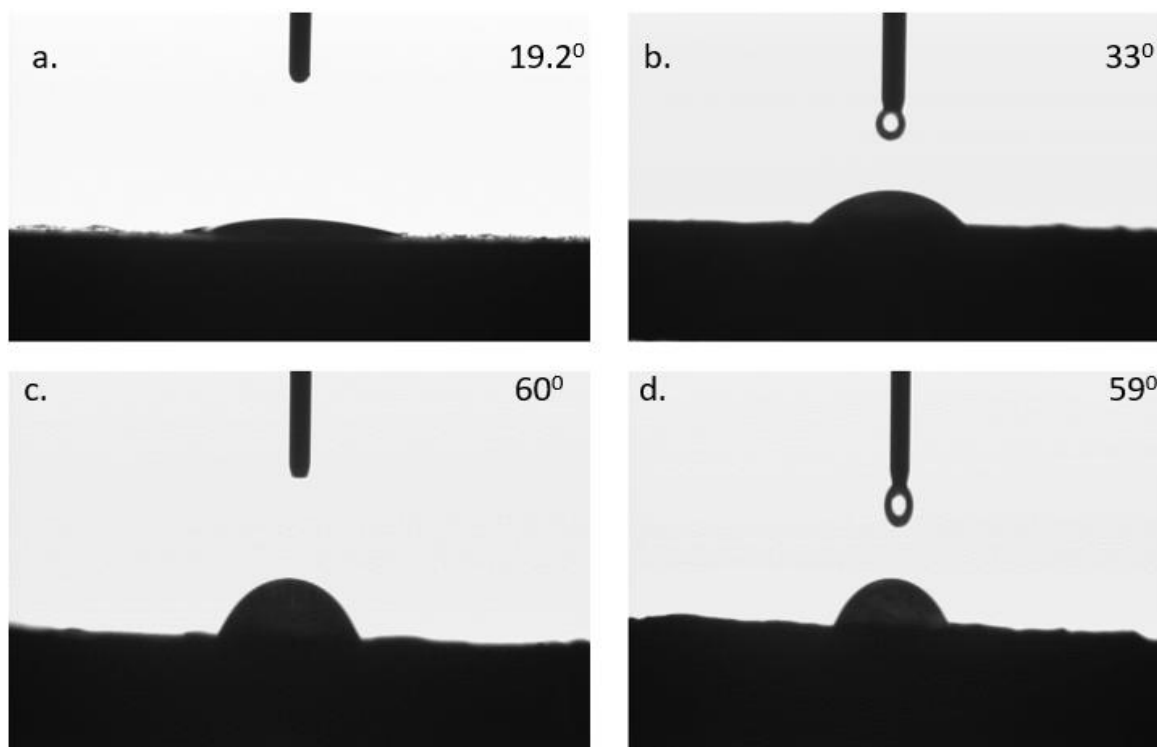


Figure 4.6 Contact angle of (a) pristine Na-Bt, (b) modified NaBt with 10 wt % KCl, and 4.0 wt % (c) Poly-(AAMA) solution and Na-Bt plate (d) Poly-(AAMA)-GO and Na-Bt

4.4.2.3 Shale recovery test:

Shale recovery tests are commonly used to assess the inhibitory properties of drilling fluids in controlling cutting disintegration from the drill bit to the surface. A high temperature dispersion of shale cuttings is mimicked by this inhibitory performance [120]. The result of hot rolling in figure 5 indicates the remaining shale in distilled water has a 25 % shale recovery average. The shale disintegrated and displayed high dispersion, showing high hydration of the shale. In comparison with the KCl solution, an increase of 30 % recovery was observed in the remaining shale. The low recovery shown by KCl is a result of the weak ionic effect on shale samples. The shale recovery was further increased to an average percentage 80 % using a 4 % of the synthesized samples in solution. This improvement indicates that Poly-(AAMA) and Poly-(AAMA)-GO has a strong adsorption capacity on the cuttings of shale and can prevent hydration.

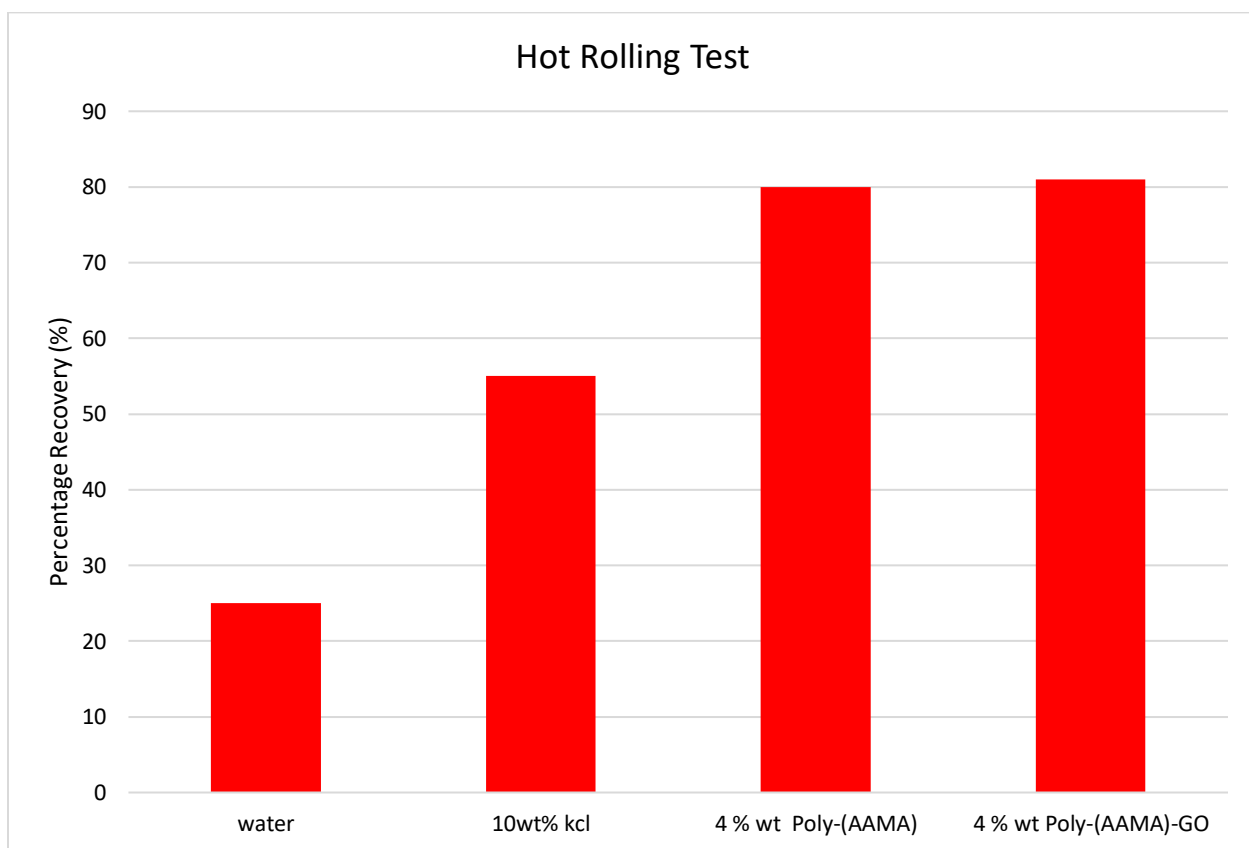


Figure 4.7 Percentage recovery of shale after hot-rolling in pure water and different inhibitor solutions at a concentration of 120°C for 16 h.

4.4.2.4 TGA:

In Na-Bentonite, water exists in three states: free adsorbed water, loosely coupled water, and closely coupled water. The evaporation of these water states in a Na-Bt/inhibitor composite occurs in three stages: below 75 °C, 75–120 °C, and 120–230°C. Therefore, the distribution of water in Na-Bentonite can be determined using TGA [71]. TGA can provide us with information on how much water has been absorbed by the Na-Bt. In figure 6 thermal decomposition curve is shown for Na-Bt samples, and for Na-Bt samples modified with Polymer, and polymer graphene oxide. Pristine Na-Bt samples show fast decomposition as a result of dehydration of much water and it then keeps a slow decomposition pattern. While the modified shale shows a very slow decomposition initially due to its small water absorption compared to the unmodified shale sample. It is evident from the gradual decomposition of modified shale that not much of the sample contains free water. Water absorption is inhibited by the polymer, and polymer graphene oxide composite, proving its inhibitory properties.

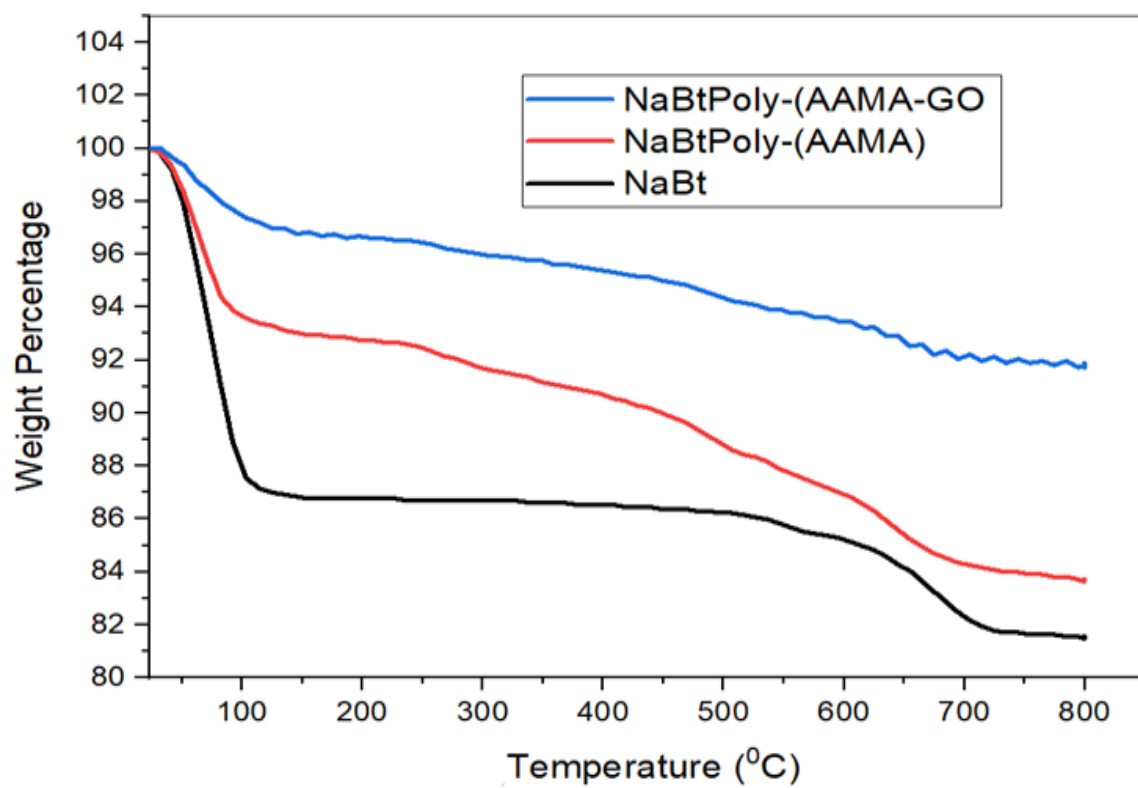


Figure 4.8 Thermal stability curve of pure Na-Bt and Na-Bt/inhibitor composites.

4.4.2.5 Anti-swelling ratio:

Analyses were carried out on bentonite to determine how inhibitors affected anti-swelling rate. It helps us to determine the capabilities of the inhibitor in suppressing the swelling and dispersion of the bentonite. Water-based drilling operations commonly use 10 % KCl to inhibit swelling, which has been evaluated and compared with 4 % of the inhibitors in solution. As shown in the figure 7, Poly-(AAMA) and Poly-(AAMA)-GO greatly retarded the swelling of bentonite at an average anti-swelling ratio of 75 % and 78 % respectively. When compared to KCl, which shows a 58 % anti-swelling ratio, the polymers and polymer graphene composite is more effective at minimizing shale hydration. The polymer interaction on the bentonite prevented the water molecules from infiltrating to cause significant swelling.

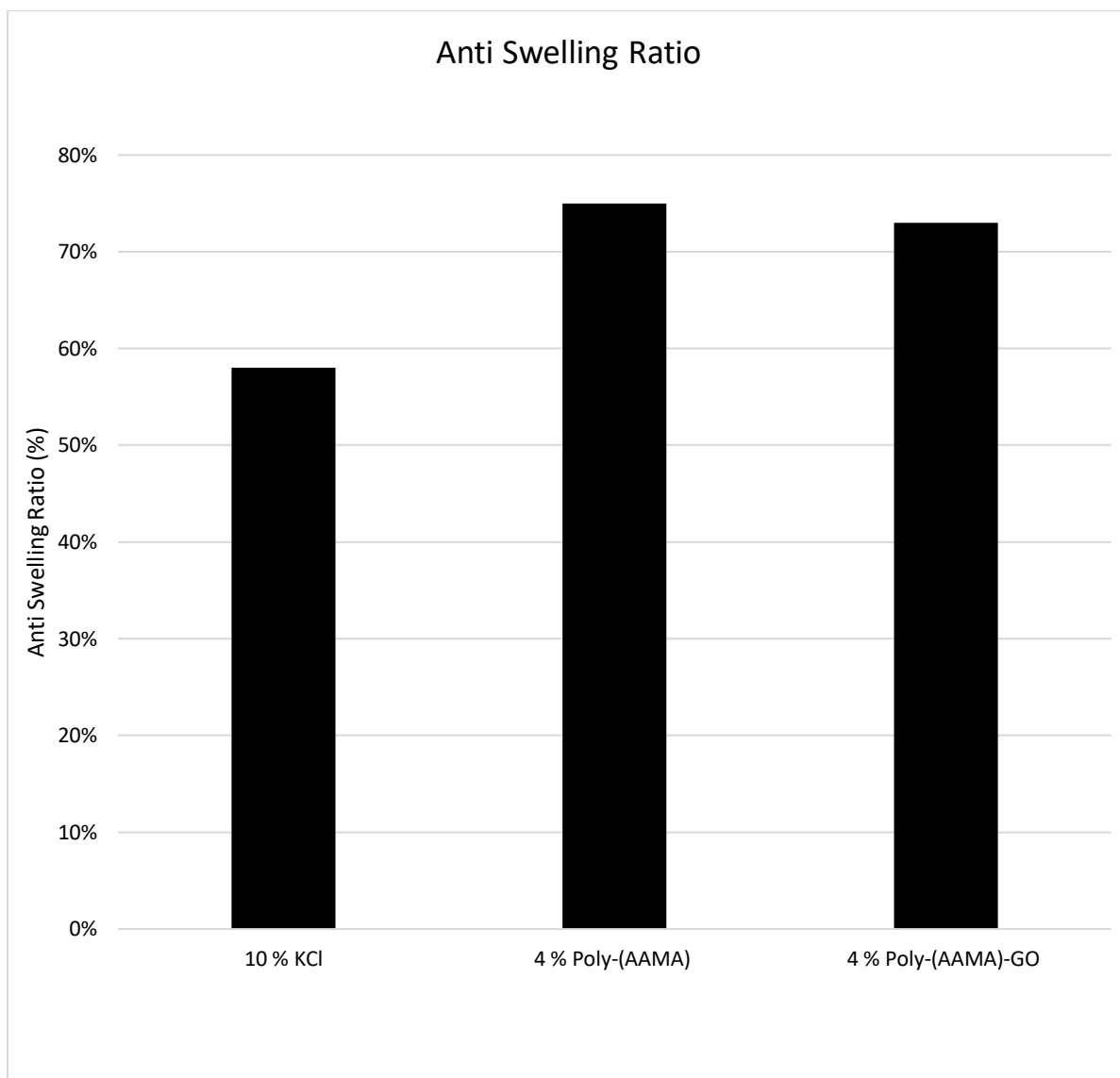


Figure 4.9 shows anti-swelling ratio of various inhibitors

4.4.2.6 FT-IR:

figure 8 shows the infrared spectra for the pristine Na-Bentonite and bentonite modified with Poly-(AAMA) and Poly-(AAMA)-GO. A typical characteristics Na-Bentonite groups was shown by the FT-IR spectra. The following are the absorptions peaks: stretching band of Si-O-Si (469 cm^{-1}), deformation band of Al-O-Si (537 cm^{-1}), the stretching band of Si-O (1030 cm^{-1}), water deformation band (1634 cm^{-1}) and the stretching band -OH (3618 cm^{-1}). For the Na-Bt modified with Poly-(AAMA)., there is a change in the spectra due to the absorption of the polymer into the surface. The stretching band of -OH shifted by 4 cm^{-1} , And Si-O band shifted by 4 cm^{-1} . Moreover, the appearance of a new peak at 1703 cm^{-1} indicates the stretching band of C=O which indicates the incorporation of the polymer into the shale sample. The shifting of these common stretching bands further proves that a hydrogen bond is formed between the bentonite and the polymer. Furthermore, this showed that the inhibitors were well adsorbing on the Na-Bt surface. The same can be said for the sample modified with Poly-(AAMA)-GO.

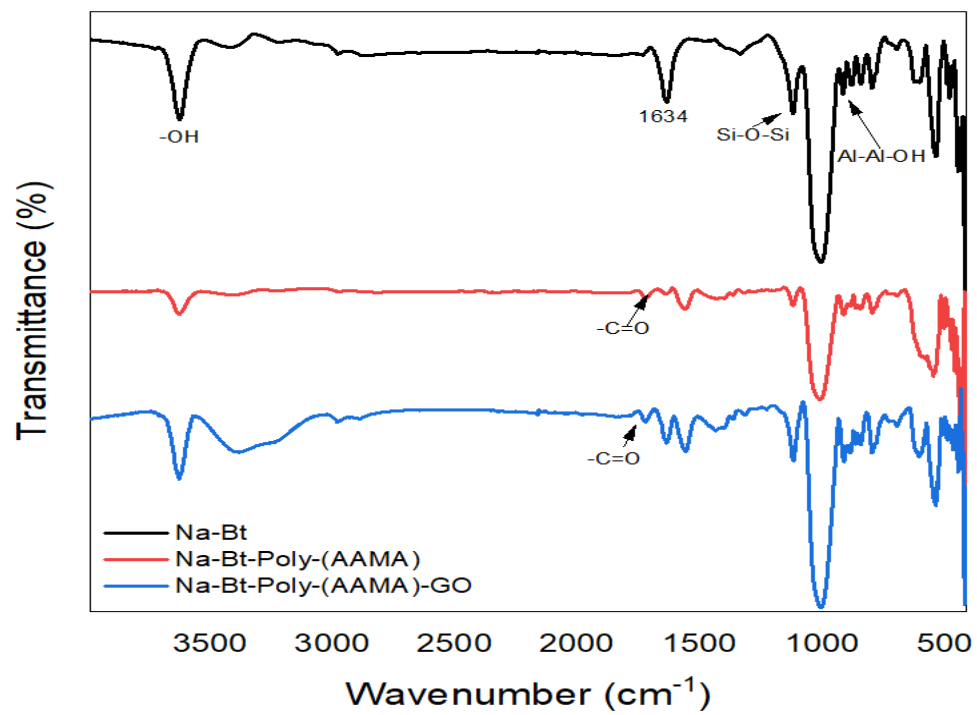


Figure 4.10 FT-IR spectra of Na-Bt, Na-Bt/ Poly-(AAMA) and Na-Bt/ Poly-(AAMA)-GO composites.

4.4.2.7 SEM:

figure 9 shows the SEM images of the microscopic morphology of the Pristine bentonite sample in water and the sample treated with 4 % Poly-(AAMA) and Poly-(AAMA)-GO in solution respectively. In Fig 9(a), the pure shale exhibits a hydrated state, evident from its porous and rough morphology, indicating sodium bentonite hydration. The bentonite expanded and became loose when exposed to pure water. The modified bentonite sample in Figure 9(b) and 9(c) shows more compatibility and less porous which is an indication of less hydration. This outcome demonstrates that the surface of the shale was covered and sealed by the inhibitor, forming a protective film on the surface of the bentonite, thereby preventing hydration.

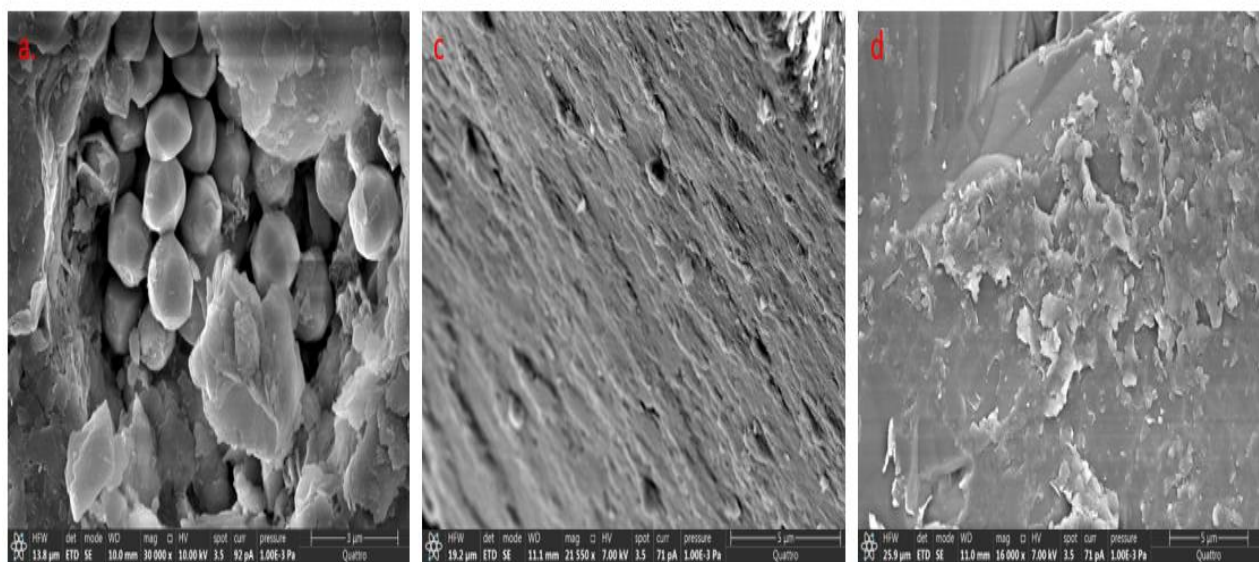


Figure 4.11 SEM images of (a) Na-Bt (b) Na-Bt/ Poly-(AAMA) (c) Na-Bt/ Poly-(AAMA)-GO composite

4.4.2.8 XRD:

It used to assess changes in interlayer spacing as this will help us to determine the hydration level of the Na-Bt when in contact with various inhibitor solution. Figure 10 illustrates the hydration pattern of pristine bentonite in H₂O, and bentonite in various inhibitor solutions. The diffraction peak (d_{001}) of the pure bentonite in water shows a d-value of 14.8 Å, whereas the bentonite samples in inhibitor solution of Poly-(AAMA) and Poly-(AAMA)-GO decrease in interlayer spacing showing a d-value of 12.1 Å and 12.2 Å respectively. Comparing these XRD patterns indicates that the Na-Bt soak in distilled water is highly hydrated which resulted to increase in interlayer spacing. The decrease in d-value of the bentonite in the inhibitor solution infers less hydration indicating that Poly-(AAMA) and Poly-(AAMA)-GO effectively absorbed on to the surface mineral, thereby inhibiting hydration [37].

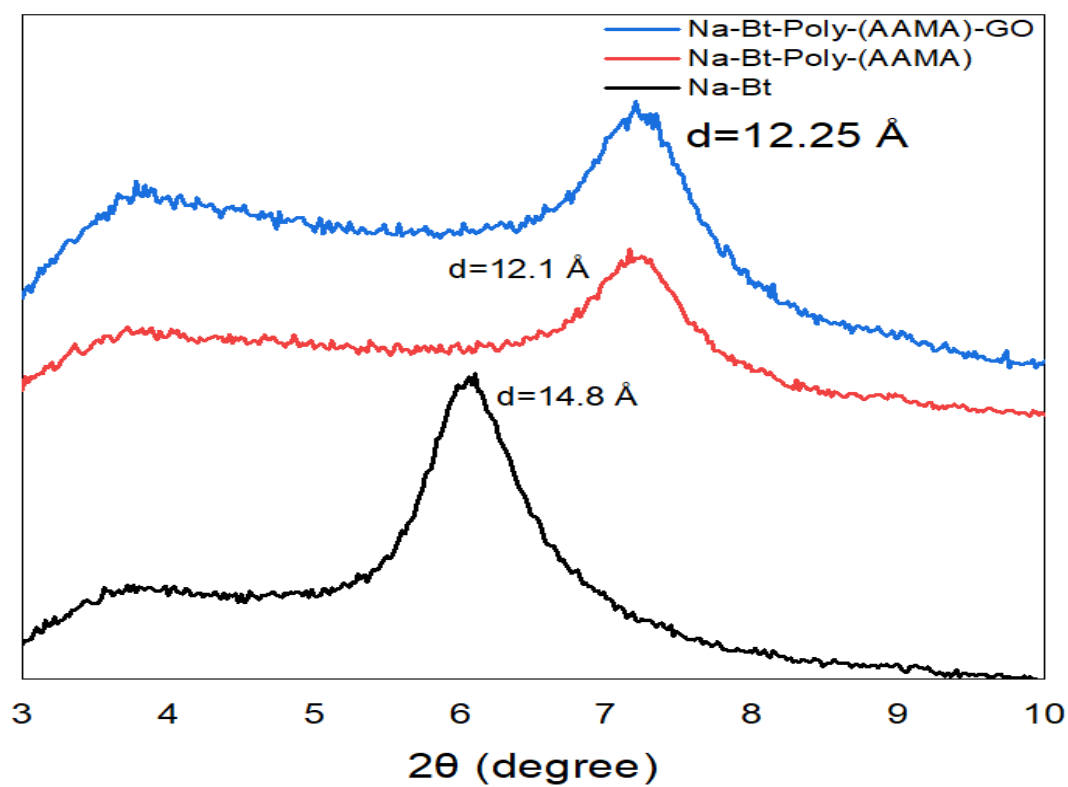


Figure 4.12 XRD patterns of Na-Bt, Na-Bt/ Poly-(AAMA) and Na-Bt/ Poly-(AAMA)-GO composite

4.5 Proposed mechanism of inhibition:

Using characterization techniques, the inhibitors poly-(AAMA) and poly-(AAMA)-GO were investigated for their probable inhibitory mechanism. In water based drilling fluid Shale formations are seriously soaked and invaded with water due to their significant clay mineral content [158]. In clay lattice, negative charges are generated by metal atoms through isomorphic substitution and this is compensated by the exchangeable cations in the interlayer. This results in the surface of the bentonite being highly hydrophilic, thus bentonite absorbs water and gets hydrated seriously through crystalline or osmotic hydration. The hydration of shale can be inhibited through the following approaches; chemical effects, such as ion exchange, electrostatic neutralization, and physical actions such as sealing [159], [151].

For poly-(AAMA) and poly-(AAMA) -GO in solution, the many carboxyl functional groups and backbone chain of the polymers, there exist electrostatic interactions, hydrophobic interaction and hydrogen bonds. These interactions enable the inhibitors to be easily adsorbed onto the surface of the bentonite and forming a polymer film. As shown in fig 11. The polymer film forms an effective shield over the bentonite thus preventing the serious soaking and intrusion of water. Thus poly-(AAMA) and poly-(AAMA) -GO acting as effective inhibitors in water base drilling fluid. The TGA analysis has shown that poly-(AAMA) -GO has better thermal stability than poly-(AAMA), which is due to the incorporation of GO.

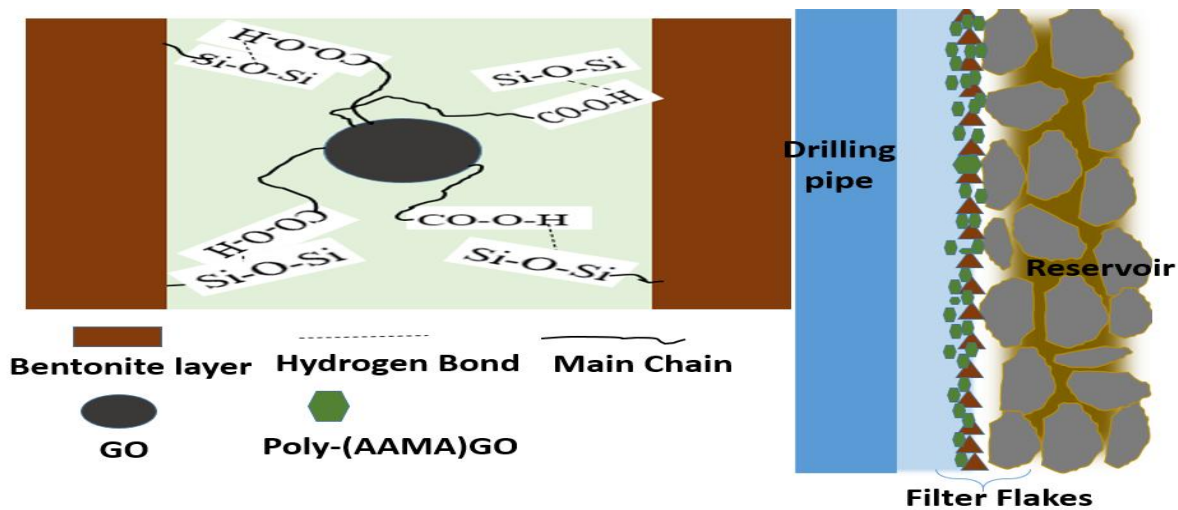
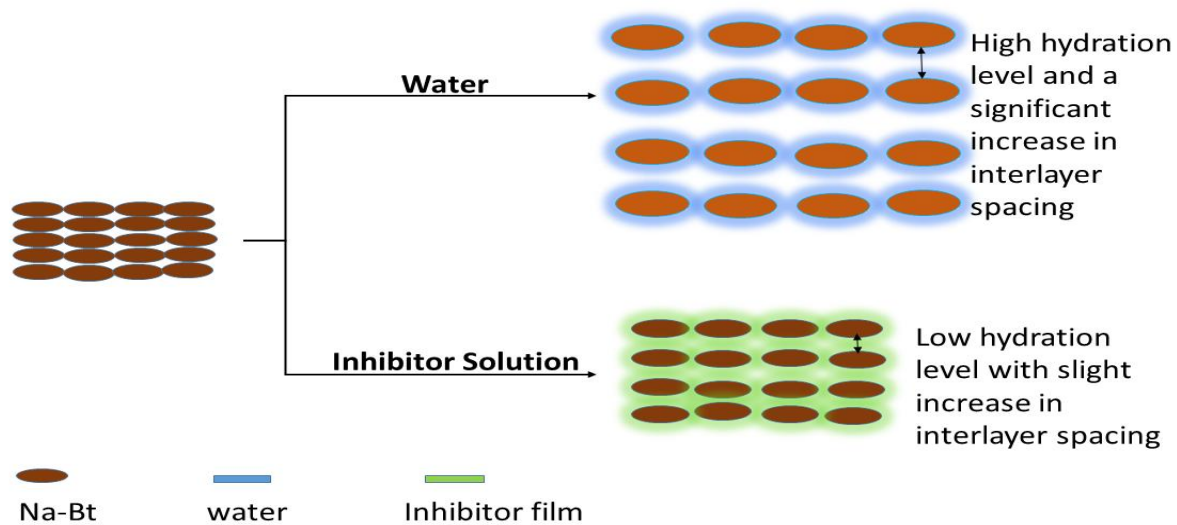


Figure 4.13 shows the mechanism of Poly-(AAMA)-GO inhibiting shale hydration swelling

CHAPTER 5

CONCLUSION

In order to achieve high thermal stability inhibitors for water-based drilling fluids, this study focus on synthesizing co-polymer graphene oxide composites as shale hydration inhibitors. The structure of the synthesize acrylic amide and acrylic acid graphene oxide composite, Poly-(AAAm)-GO and the polymer free GO (Poly-(AAAm)) were confirmed using FT-IR and NMR characterization. Its inhibitory characteristics were evaluated and compared to the standard KCl that is commonly used in the industries. The TGA results indicate that Poly-(AAAm)-GO is thermally stable, which is beneficial when drilling at high temperatures. The average Shale recovery for Poly-(AAAm) and Poly-(AAAm)-GO was 82% and 85%, respectively, demonstrating that, both inhibitors were capable of preventing the disintegration of the shale cutting and preventing the rheology of shale formations from deteriorating. Poly-(AAAm) and Poly-(AAAm)-GO indicates an anti-swelling ratio of 80 and 82% respectively. This shows that both inhibitors were capable of suppressing bentonite hydration and swelling. FTIR, SEM, and TGA were all utilized as methods to evaluate the inhibitory properties of the polymer composite. The results indicate the polymer form a protective film, adsorbed onto the surface of the bentonite through electrostatic attraction thereby making the surface more hydrophobic. This confirms that both inhibitors are capable of preventing water molecules intruding the interlayer spacing to cause hydration and swelling of the bentonite. As a result of their common chemical composition, Poly-(AAAm) and Poly-(AAAm)-GO show similar inhibitory properties

A copolymer of acrylic acid and maleic acid/Graphene oxide (Poly-(AAMA)-GO) composite was also synthesize to serve as an effective and low-cost inhibitor. Its

performance as an inhibitor at high temperatures was evaluated. The increase in shale recovery to 80 %, by adding 4 % of the synthesized inhibitors in solution, shows that the inhibitors have a strong adsorption capacity on shale cuttings. It was found that poly-(AAMA) and poly-(AAMA)-GO both significantly retarded swelling of bentonite, with anti-swelling ratios of 75 and 78 %, respectively, in comparison to KCl which had 58 %. FT-IR characterization of the pristine bentonite and the bentonite/polymer graphene oxide composite revealed that Poly-(AAMA) and Poly-(AAMA)-GO were adsorbed onto the bentonite particles through electrostatic interactions and hydrogen bonds. The inhibitors form a thin film on the surface of the bentonite, increasing its hydrophobicity and thus reducing the amount of water entering the bentonite's interlayer spacing. Poly-(AAMA)-GO demonstrated improved thermal stability compared to Poly-(AAMA), which can be attributed to the presence of graphene oxide in the composite. Despite the difference in thermal stability, both Poly-(AAMA)-GO and Poly-(AAMA) showed similar inhibitory results due to their similar chemical compositions.

To conclude, a thermally stable polymer graphene oxide composite for water-based mud was successfully synthesized. However, the synthesis parameters and components of both inhibitors can be adjusted to make their applications as diverse as possible in water-based drilling fluids. Further studies are needed to assess the environmental impacts of the synthesized inhibitors. There should be further investigation on their compatibility with other additives agents in water-based drilling mud.

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Vitae

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Academic Background

2024: King Fahd University of Petroleum and Minerals (KFUPM). Daharan, KSA. M.Sc. Chemistry; CGPA: **3.75/4.0**
2017-2021 University of The Gambia; BSc Chemistry (**Magna Cum laude**)
2013-2016 The Gambia College; Higher Teacher Certificate (**Distinction**) Main subject: Science and English

Work Experience

2022 to date Graduate Assistant KFUPM, Saudi Arabia

Duties and Responsibility

- Instructing and grading CHEM 101 practical; an introductory chemistry practical course
- Prepare experimental reagents and standards
- Analysis and interpretation of data from experiments as well as reporting and documentation of findings
- Synthesis of polymers and polymer graphene oxide composite.
- Using different analytical techniques including NMR, XRD, SEM, FT-IR among others.

2017- to 2022 Chemistry and General Science Teacher Masroor Senior Secondary School, Yundum, The Gambia

- Establish and enforce rules for behavior and procedures for maintaining order among students.
- Assign and grade class work and homework.
- Prepare materials and classrooms for class activities and setting up the labs for chemistry practical.
- Teach and train students on how to safely conduct Chemistry practical in the lab.
- Setting up the labs for chemistry practical which include the preparation of standard solutions.
- Prepare, administer, and grade tests and assignments to evaluate students' progress.

- Confer with parents or guardians, other teachers, counselors, and administrators to resolve students' behavioral and academic problems.

2016-2017 Chemistry and General Science Teacher, Aji Sukai Senio Ndateh Memorial Senior Secondary School, Bakau The Gambia

Additional Skills

• Advanced verbal and written communications skills • Good research and analytical skills • Proficiency in Microsoft Excel, PowerPoint, Word, Minitab, Chem-Draw. Origin	• Good inter-personal skills • Good presentation skills • Good report writing skills
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Personal Interests And Affiliations

Member of The Gambia Chemical Society.

Member of the Chemistry club of the UTG.

Coordinator of Masroor Science club

A member of Masroor human right club

Sports: Football

Under Review

- Momodou A Jallow, A. Alraw, Tawfik A Saleh, Synthesis and Examination of graphene Oxide grafted with copolymer of Maleic Acid and Acrylic Acid as A Shale Hydration Inhibitor for Water Base Drilling Fluid, PTLRS-D-24-00209
- Momodou A Jallow, A. Alraw, Tawfik A Saleh, Synthesis of Copolymer of Acrylic Acid and Acrylic Amide on Graphene Oxide as Shale Hydration Inhibitor for Water Base Drilling Fluids, POLYMER-D-24-2438