

**Design, Synthesis and Characterization of Hyperbranched
Polymers and Hybrid Organic-Inorganic Particles for Oil/Gas
Drilling Applications**

BY

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DEDICATION

To my parents, thank you for your prayers, support, and the values you have taught me.

To my wife and children- none of this would have been possible without your love and support.

I Dedicate this work to:

My Father,

My Mother,

My Wife,

My Children,

My Brothers,

My Sisters, and

My Family

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LIST OF ABBREVIATIONS

EDX	Energy-Dispersive X-ray
FTIR	Fourier Transformation Infrared Spectroscopy
LCST	Lower Critical Solution Temperature
R3	3 reading revolutions per minutes, cP
R300	300 reading revolutions per minutes, cP
R6	6 reading revolutions per minutes, cP
R600	600 reading revolutions per minutes, cP
SEM	Scanning Electron Microscopy
TGA	Thermogravimetric Analysis
PV	plastic viscosity, cP
YP	yield point, cP

ABSTRACT

Full Name : [Abdullah Saleh Al-Yami]
Thesis Title : [Design, Synthesis and Characterization of Hyperbranched Polymers and Hybrid Organic-Inorganic Particles for Oil/Gas Drilling Applications]
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Our pursuit to replace oil-based drilling fluids with more efficient alternatives has led us to focus on three crucial objectives. The first is to develop polymers that can withstand high-temperature environments, the second is to minimize environmental impact, and the third is to ensure acceptable shale inhibition. We have successfully synthesized families of hyperbranched and hybrid polymers that not only meet these objectives but also synergize with conventional polymers, significantly enhancing temperature stability and shale inhibition.

Our research involved three major experimental phases, each contributing to the development of water-based drilling fluids as a viable alternative to oil-based ones. The first phase focused on polymer synthesis and characterization, utilizing a solution ring opening polymerization set-up. The second phase involved formulation and performance testing, specifically at a temperature of 300 °F. The third and final phase was dedicated to shale inhibition performance testing and formulation optimization, as required.

In our synthesis process, we chose branched PEI as our macroinitiator for several reasons. Its interaction with conventional polymers used in drilling operations, such as XC polymer and HPAM, through acid-base reactions leads to electrostatic solid interaction and ionic bond formation. Additionally, it can interact with PEI via a transamidation mechanism, resulting in cross-linking and enhanced viscosity. This interaction also leads to elevated hydrogen bonding, a crucial factor for water solubility and shale inhibition. The use of branched PEI allows us to grow a higher number of functional groups, including degradable ones like glycidol and Maleic anhydride, enhancing the versatility of our synthesized polymers.

Our choice of PEI as the macro-initiator is a testament to our innovative approach. The mechanism we employ is a form of ring-opening multibranching polymerization (ROMP), with the cyclic monomer being Glycidol. We are pushing the boundaries of polymer modification by introducing an additional layer of non-toxic polymer to the PEI. This modification not only enhances the polymer's density of functional groups but also facilitates cross-linking with ease.

The first synthesis of family of hyperbranched polymers utilizes branched PEI as a macroinitiator and glycidol as a cyclic minor. Different ratios were used to find the optimum PEI: glycidol weight ratio. The polymerization mechanism is anionic ring-opening polymerization. ^1H NMR spectroscopy shows two main regions in the synthesized polymer. Region 1 corresponds to the methylene protons ($-\text{CH}_2-$) of PEI and region 2 represents the methylene and methine protons ($-\text{CH}(\text{OH})-$) of the glycidol unit. ^{13}C NMR has been utilized to investigate the synthesized hyperbranched polymers. hyperbranched

polymers that contain branched units display a peak in the ^{13}C NMR spectrum approximately at 79-80 ppm. ^{13}C NMR spectra show PEI in the shift range of 36-58 ppm and Glycidol subunits appear as peaks above 60 ppm. As the certain ratio of PEI to Glycidol we will have better opportunities to create branched subunits (dendritic). Interpretation of ^{13}C NMR of synthesized polymer with ratio of 4:1 PEI to Glycidol shows glycidol on the surface of PEI as mainly linear with terminal subunits. Interpretation of ^{13}C NMR of synthesized polymer with ratio of 1:15 PEI to Glycidol shows dendritic branching.

Linear PEI was also used as an initiator to demonstrate the importance of branched PEI in the synthesis. No branching was observed, and the yield was too low to utilize for water-based formulation and testing. This underscores the complexity and intricacy of the research. Looking at the ^1H NMR, we had about 1 unit of glycidol per PEI unit due to steric hindrance. The implications of this steric hindrance on the synthesis process are significant

The second synthesis of family of hyperbranched polymers utilizes branched PEI as a macroinitiator and glycidol as a cyclic minor and Maleic Anhydride as a cross linker. There are three mechanism steps here. The first is the ring opening of Malick anhydride, the second step is Micheal addition, and the third and final step is the polymerization by anion ring opening of glycidol monomer, The ^1H NMR provides a clear view of the glycidol and PEI region, as previously indicated in the synthesis. Additionally, a small peak at 5.9 ppm is observed, indicating the successful reaction of the majority of the double bond due to Micheal's reaction.

The synthesized hyperbranched polymers, used as additives for water-based drilling fluids, have shown excellent resistance in high-temperature environments. We

have designed and tested over 100 formulations and iterations using these polymers, which have been successfully used to formulate water-based drilling fluids. They are a promising alternative to oil-based fluids. Our findings underscore the practical need for these polymers to achieve acceptable viscosity measurements, providing reassurance about their effectiveness.

Our successful development of a high-performance polymer water-based drilling fluid, capable of withstanding high-temperature conditions and being environmentally friendly, brings us to the final requirement for replacing oil-based drilling fluids—good shale inhibition. To understand this requirement, we conducted a shale characterization study. A recovery factor above 90% is considered acceptable for drilling applications. We have collected representative shales from typical formations that are drilled with oil-based fluids. The first shale is from the Qusaiba Formation, and the second is from the Sudair Formation.

Kaolinite is a clay mineral with the chemical formula $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$. Illite dominance, a condition where illite, a type of clay mineral having the chemical formula $[(\text{K}, \text{H}_3\text{O})(\text{Al}, \text{Mg}, \text{Fe})_2(\text{Si}, \text{Al})_4\text{O}_{10}[(\text{OH})_2, (\text{H}_2\text{O})]]$, absorbs more water compared to kaolinite, has significant implications for shale properties. The presence of potassium ions between the Illite layers weakens the bonding between the Illite layers. Salts generally have more water affinity, so more water absorbed by Sudair Illite due to the presence of the potassium ion will even weaken the bonding between the layers and cause the shale to disperse more than Qusaiba Kaolinite. An ion exchange mechanism is not an option here since the potassium is fitted between the layers rather than on the surface.

The third complex synthesis utilized nano silica and nano titanium dioxide for hybrid hyperbranched polymerization. We embarked on this journey, initially exploring the use of the hydroxyl group of the silica as an initiator to open up the glycidol ring. However, the results revealed a challenge- we could not achieve the required dispersity. Undeterred, we proceeded with surface modification of the post-functionalized nano silica using APTES. The hydrolyzed APTES would condense the hydroxyl group from the nano-silica surface and bind with it. The presence of an amino group in the APTES proved beneficial in the ring-opening polymerization of the glycidol, as Amines are stronger nucleophiles than the hydroxyl groups. This led to an improvement in the dispersion of the hybrid polymer. However, the performance testing for shale inhibition was unacceptable for Qusaiba shale. Similarly, dispersion testing did not meet the desired standards when the post-functionalized nano-silica was used in water-based drilling formulation.

The fourth synthesis utilized dopamine, which is an influential anchor group. Dopamine's versatility lies in its ability to bind to various surfaces, including silica and titanium. It also interacts with the shales due to the presence of aluminum silicate layers. Dopamine's strong hydrogen bonding properties further enhance shale inhibition. We used PEI as a macroinitiator in these syntheses, glycidol as our monomer, and Maleic Anhydride as a cross-linker in some of the synthesized polymers. Dopamine served as the anchor group, and we also incorporated different nanomaterials, namely Nano Silica and Titanium Dioxide. The incorporation of these nanomaterials adds an intriguing dimension to our research. In the case of Titanium Dioxide, I conducted both situ and post-functionalization synthesis. Post-functionalized TiO_2 refers to the nanomaterial being prepared separately

from the polymerization step, while in situ functionalization involves preparing the nanomaterial using a precursor during the synthesis of the polymerization solution.

We have multiple steps in this synthesis. First is the oxidization of Dopamine due to the high pH of the PEI. This oxidation will convert Dopamine from its enol form to keto form. Next, we have a mixture of mechanisms, namely the Micheal and Schiff base reactions, between the Dopamine and the PEI. We also have the anionic ring-opening polymerization of the glycidol monomer. The last step in this synthesis is the addition of the nanomaterial. If the nanomaterial is nano-silica, the Dopamine will bind to its surface by condensation of the OH group on the nano-silica surface. If the nanomaterial is titanium oxide, the binding will be due to the chelation of the TiO_2 by Dopamine. The TiO_2 surface is under-coordinated so that the Dopamine will attach to the TiO_2 surface. A dark black conversion indicates this interaction.

The hybrid polymer and hybrid hyperbranched polymer, particularly when utilizing TiO_2 , demonstrated exceptional performance inhibiting Qusaiba shale. All the synthesized polymers in this study outperformed oil-based drilling fluids in the case of Qusaiba shales. For Sudair, the most promising outcome was achieved with TiO_2 , boasting a recovery factor of 66%. SEM images clearly show the nanomaterials effectively sealing the shale pores. This underscores the mechanism of shale inhibition, where the hybrid hyperbranched polymers, in conjunction with the nanomaterials and Dopamine, play a crucial role. Significantly, the hydrogen bonding facilitated by the PEI and the Dopamine significantly contributes to the shale inhibition, a finding of utmost significance.

With the successful achievement of the three requirements to replace oil-based drilling fluids for Qusaiba, we were presented with two viable options: either to employ a combination of hyperbranched polymer for viscosity and another hybrid hyperbranched polymer for shale inhibition, or to subject the hybrid hyperbranched polymer to comprehensive testing for all the requirements (viscosity and shale inhibition). The hybrid hyperbranched polymers, synthesized with utmost precision in this study, were then formulated in water-based drilling fluids and rigorously tested at high-temperature environments, producing excellent results. The viscosity obtained was more than sufficient for effective drilling application, even after the fluid was exposed to 300 F. The practicality of these formulations is underscored by the fact that they were finalized after several meticulous attempts.

ملخص الرسالة

الاسم الكامل: [عبدالله صالح اليامي]

عنوان الأطروحة: [تصميم وتوليف وتوصيف البوليمرات شديدة التشعب والجسيمات العضوية غير العضوية

الهجينة لتطبيقات حفر النفط / الغاز]

المجال الرئيسي: [الكيمياء]

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لقد دفعنا سعينا لاستبدال سوائل الحفر القائمة على النفط ببدائل أكثر كفاءة إلى التركيز على ثلاثة أهداف حاسمة. الأول هو تطوير البوليمرات التي يمكن أن تصمد أمام البيئات ذات درجات الحرارة العالية ، والثاني هو تقليل التأثير البيئي ، والثالث هو ضمان تثبيط الصخر الزيتي المقبول.

لقد نجحنا في تصنيع عائلات من البوليمرات فائقة التفرع والهجينة التي لا تلبي هذه الأهداف فحسب ، بل تتأزر أيضا مع البوليمرات التقليدية ، مما يعزز بشكل كبير استقرار درجة الحرارة وتثبيط الصخر الزيتي.

تضمن بحثنا ثلاث مراحل تجريبية رئيسية ، تساهم كل منها في تطوير سوائل الحفر القائمة على الماء كبديل قابل للتطبيق للسوائل القائمة على النفط. ركزت المرحلة الأولى على تخليق البوليمر وتوصيفه ، باستخدام إعدادات بلمرة فتح حلقة المحلول.

تضمنت المرحلة الثانية اختبار الصياغة والأداء ، وتحديدًا عند درجة حرارة 300 درجة فهرنهايت. وخصصت المرحلة الثالثة والأخيرة لاختبار أداء تثبيط الصخر الزيتي وتحسين التركيب، حسب الاقتضاء.

في عملية التوليف لدينا ، اخترنا PEI لدينا لعدة أسباب. يؤدي تفاعله مع البوليمرات التقليدية المستخدمة في عمليات الحفر ، مثل XC polymer و HPAM ، من خلال تفاعلات الحمض القاعدي إلى تفاعل صلب إلكتروستاتيكي وتكوين رابطة أيونية. بالإضافة إلى ذلك ، يمكن أن يتفاعل مع PEI عبر آلية transamidation ، مما يؤدي إلى الربط المتقاطع واللزوجة المحسنة. يؤدي هذا التفاعل أيضا إلى ارتفاع الترابط الهيدروجيني ، وهو عامل حاسم للذوبان في الماء وتثبيط الصخر الزيتي.

يسمح لنا استخدام PEI المتفرعة بتنمية عدد أكبر من المجموعات الوظيفية ، بما في ذلك المجموعات القابلة للتحلل مثل glycidol و Maleic anhydride ، مما يعزز تنوع البوليمرات المركبة لدينا. إن اختيارنا PEI كبادئ كلي هو شهادة على نهجنا المبتكر. الآلية التي نستخدمها هي شكل من أشكال البلمرة متعددة الفروع ذات الفتح الحلقي (ROMP) ، مع كون المونومر الدوري هو Glycidol.

نحن ندفع حدود تعديل البوليمر من خلال إدخال طبقة إضافية من البوليمر غير السام إلى PEI. لا يعزز هذا التعديل كثافة المجموعات الوظيفية للبوليمر فحسب ، بل يسهل أيضا الربط المتقاطع بسهولة. يستخدم التوليف الأول لعائلة البوليمرات شديدة التفرع PEI كبادئ كبير والجليسيدول كقاصر دوري. تم استخدام نسب مختلفة لإيجاد نسبة وزن الغليسيدول المثلى PEI. آلية البلمرة هي بلمرة فتح الحلقة الأنيونية. كما تم استخدام PEI الخطي كبادئ لإثبات أهمية PEI المتفرعة في التوليف. لم يلاحظ أي تفرع ، وكان العائد منخفضا جدا بحيث لا يمكن استخدامه في التركيب والاختبار المائي. هذا يؤكد على تعقيد وتعقيد البحث. بالنظر إلى $^1\text{H NMR}$ ، كان لدينا حوالي وحدة واحدة من الجليسيدول لكل وحدة PEI بسبب عائق ستيريك. الآثار المترتبة على هذا العائق الستيريك على عملية التوليف كبيرة

يستخدم التوليف الثاني لعائلة البوليمرات شديدة التفرع PEI المتفرعة كبادئ كبير والجليسيدول كثنائي دوري وأنهيدريد المالتيك كرابط متقاطع. هناك ثلاث خطوات آلية هنا. الأول هو فتح حلقة أنهيدريد مالتك ، والخطوة الثانية هي إضافة ميشيل ، والخطوة الثالثة والأخيرة هي البلمرة بواسطة فتح حلقة أنيون لمونومر الجليسيدول

أظهرت البوليمرات المتفرعة للغاية ، المستخدمة كإضافات لسوائل الحفر القائمة على الماء ، مقاومة ممتازة في البيئات ذات درجات الحرارة العالية. لقد قمنا بتصميم واختبار أكثر من 100 تركيبة وتكرارا باستخدام هذه البوليمرات ، والتي تم استخدامها بنجاح لصياغة سوائل الحفر القائمة على الماء. إنها بديل واعد للسوائل القائمة على الزيت. تؤكد النتائج التي توصلنا إليها على الحاجة العملية لهذه البوليمرات لتحقيق قياسات لزوجة مقبولة ، مما يوفر الطمأنينة بشأن فعاليتها. إن تطويرنا الناجح لسائل حفر عالي الأداء قائم على الماء من البوليمر ، قادر على تحمل ظروف درجات الحرارة العالية وكونه صديقا للبيئة ، يقودنا إلى المتطلبات النهائية لاستبدال سوائل الحفر القائمة على النفط - تثبيط الصخر الزيتي الجيد. لفهم هذا المطلب ، أجرينا دراسة توصيف الصخر الزيتي. يعتبر عامل الاسترداد فوق 90٪ مقبولا لتطبيقات الحفر. لقد جمعنا الصخر الزيتي التمثيلي من التكوينات النموذجية التي يتم حفرها بالسوائل القائمة على النفط. الصخر الزيتي الأول من تكوين القصيبة والثاني من تكوين

سدير

استخدم التوليف المعقد الثالث السيليكا النانوية وثاني أكسيد التيتانيوم النانوي للبلمرة الهجينة شديدة التشعب. شرعنا في هذه الرحلة ، واستكشفنا في البداية استخدام مجموعة الهيدروكسيل للسيليكا كبادئ لفتح حلقة الجليسيديل. ومع ذلك ، كشفت النتائج عن تحد - لم نتمكن من تحقيق التشنت المطلوب. دون رادع ، شرعنا في تعديل سطح السيليكا النانوية بعد التشغيل باستخدام APTES. ستقوم APTES المتحللة بالماء بتكثيف مجموعة الهيدروكسيل من سطح السيليكا النانوية والارتباط بها. أثبت وجود مجموعة أمينية في APTES أنه مفيد في بلمرة الجليسيديل ذات الفتح الحلقي ، حيث أن الأمينات هي نيوكليوفيلات أقوى من مجموعات الهيدروكسيل. هذا أدى إلى تحسن في تشنت البوليمر الهجين. ومع ذلك، فإن اختبار الأداء لتثبيت الصخر الزيتي لم يكن مقبولا بالنسبة لصخر القصيبة. وبالمثل ، لم يستوف اختبار التشنت المعايير المطلوبة عند استخدام السيليكا النانوية بعد التشغيل في صياغة الحفر القائمة على الماء.

استخدم التوليف الرابع الدوبامين ، وهو مجموعة مرساة مؤثرة. يكمن تنوع الدوبامين في قدرته على الارتباط بالأسطح المختلفة ، بما في ذلك السيليكا والتيتانيوم. كما أنه يتفاعل مع الصخر الزيتي بسبب وجود طبقات سيليكات الألومنيوم. تعمل خصائص الترابط الهيدروجيني القوية للدوبامين على تعزيز تثبيت الصخر الزيتي. استخدمنا PEI كبادئ كبير في هذه التوليفات ، والجليسيديل كمونومر لدينا ، وأنهيدريد المالنك كرابط متقاطع في بعض البوليمرات المركبة. كان الدوبامين بمثابة مجموعة مرساة ، وقمنا أيضا بدمج مواد نانوية مختلفة ، وهي نانو سيليكا وثاني أكسيد التيتانيوم. يضيف دمج هذه المواد النانوية بعدا مثيرا للاهتمام لأبحاثنا. في حالة ثاني أكسيد التيتانيوم ، أجريت توليفا في الموقع وما بعد الوظيفة. يشير TiO_2 بعد التشغيل إلى المادة النانوية التي يتم تحضيرها بشكل منفصل عن خطوة البلمرة ، بينما يتضمن التشغيل في الموقع تحضير المادة النانوية باستخدام سلائف أثناء تخليق محلول البلمرة.

لدينا خطوات متعددة في هذا التوليف. الأول هو أكسدة الدوبامين بسبب ارتفاع قيمة الرقم الهيدروجيني في PEI. هذه الأكسدة سوف تحول الدوبامين من شكل enol إلى شكل كيتو. بعد ذلك ، لدينا مزيج من الآليات ، وهي تفاعلات قاعدة مايكل وشيف ، بين الدوبامين و PEI. لدينا أيضا بلمرة فتح الحلقة الأنيونية لمونومر الجليسيديل. الخطوة الأخيرة في هذا التوليف هي إضافة المادة النانوية.

إذا كانت المادة النانوية هي السيليكا النانوية ، فإن الدوبامين سوف يرتبط بسطحه عن طريق تكثيف مجموعة OH على سطح السيليكا النانوية. إذا كانت المادة النانوية هي أكسيد التيتانيوم ، فسيكون الارتباط ناتجا عن استخلاص TiO_2 بواسطة الدوبامين. سطح TiO_2 غير منسق بحيث يلتصق الدوبامين بسطح TiO_2 . يشير التحويل الأسود الداكن إلى هذا التفاعل.

أظهر البوليمر الهجين والبوليمر المفرط التشعب، خاصة عند استخدام TiO_2 ، أداء استثنائيا في تثبيت صخر القصيبة. تفوقت جميع البوليمرات المركبة في هذه الدراسة على سوائل الحفر القائمة على النفط في حالة صخر القصيبة. مع النجاح في تحقيق المتطلبات الثلاثة لاستبدال سوائل الحفر القائمة على النفط في القصيبة ، تم تقديم خيارين قابلين للتطبيق: إما استخدام مزيج من البوليمر فائق التفرع للزوجة وبوليمر هجين آخر مفرط التفرع لتثبيت الصخر الزيتي ، أو إخضاع البوليمر الهجين مفرط التفرع لاختبار شامل لجميع المتطلبات (اللزوجة وتثبيت الصخر الزيتي). ثم تمت صياغة البوليمرات الهجينة شديدة التفرع ، التي تم تصنيعها بدقة قصوى في هذه الدراسة ، في سوائل الحفر القائمة على الماء واختبارها بدقة في بيئات ذات درجات حرارة عالية ، مما أدى إلى نتائج ممتازة. كانت اللزوجة التي تم الحصول عليها أكثر من كافية لتطبيق الحفر الفعال ، حتى بعد تعرض السائل ل 300 فهرنهايت. ومما يؤكد الطابع العملي لهذه الصيغ حقيقة أنها وضعت في صيغتها النهائية بعد عدة محاولات دقيقة.

CHAPTER 1

INTRODUCTION

Water-based drilling fluids utilize freshwater, seawater, and brines. The selection of optimum chemicals is critical to maximize the well's productivity and reduce drilling costs without damaging equipment or the surrounding environment. Drilling fluids must be evaluated before drilling to ensure technical and environmental requirements. There is always a strong relationship between the performance of wells and the chemicals used in drilling and completion. For instance, formation permeability is significant for fluid filtration properties. Water sensitivity and temperature stability will determine the most suitable polymer types. Selecting suitable polymers is essential to provide sufficient carrying capacity and minimal filtration losses.

Filtration loss, viscosity, and shale stability are all controlled with different polymers. Because salt limits polymer hydration, some polymers will not work well in salt solutions. At high temperatures, some polymers degrade and lose their viscosity. A viscosifier is an additive used to build up the viscosity of drilling fluids to carry the cuttings generated while drilling. Another issue we see in drilling operations is stuck pipes due to improper shale inhibition. Shale inhibitors should provide long-term inhibition, especially when drilling across loss circulation zones.

Oil-based drilling fluids have been the ideal fluid to use in high-temperature environments. If high shale content is encountered, then switching from water-based

drilling fluids to oil will be the ideal solution. However, oil-based drilling fluids are considered environmentally toxic and expensive. When oil-based drilling fluids are used in water aquifers or offshore environments, excellent care and attention must be followed. Contamination of environments are always a significant concern when it comes to oil-based drilling fluids. Drilled cuttings from offshore drilling operations must be disposed of properly and not be dumped in the sea to avoid contamination of marine life.

This research is about finding an alternative water-based system that can replace oil-based drilling fluids to reduce any potential impact on the environment. Formulations using existing polymers in the market will not produce suitable viscosity in high-temperature conditions. Also, drilling through water-sensitive formations using water-based drilling fluids is challenging. To overcome this challenge, new polymers must be synthesized to formulate water-based drilling fluids for optimum performance and less environmental impact.

CHAPTER 2

LITERATURE REVIEW

There are amide and carboxyl groups in partially hydrolyzed polyacrylamide (HPAM). The carboxyl group imparts water solubility to the polymer by dissociating and leaving negatively charged macro-ions and positively charged counter-ions, which results in the aqueous solution being a polyelectrolyte. This polyelectrolyte property led to higher viscosity when compared to neutral polymers. These negatively charged macro-ions in PHPA absorb and distribute positively charged particles through the force of ionic attraction and certain neutral particles through the force of hydrogen bonding. [1]. Fig.1 shows the hydrolysis reaction of polyacrylamide polymer [2].

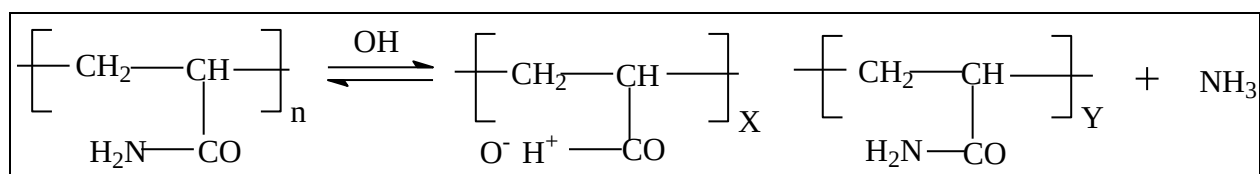


Fig.1: Polyacrylamide polymer hydrolysis reaction, [1]

PAM has a different molecular structure from HPAM. PAM is a nonionic polymer (disregarding hydrolysis in water), so it does not have the polyelectrolytic properties of HPAM. HPAM used in enhanced oil recovery has a 25% to 35% hydrolysis degree. A higher hydrolysis degree means increasing solution viscosity [3-4]. Polymer concentration and cross-linker concentration can affect the gelation time. Increasing cross-linker

concentration will reduce the gelation time. Increasing salt concentration will lead to viscosity reduction. The reason behind this is the presence of more cations in the solution, which will lower the initial degree of hydrolysis and delay the crosslinking process. Increasing temperatures will lead to an increase in hydrolysis degree, which will lead to generating more carboxyl groups and accelerate the crosslinking [5-8]. PAM trivalent metals cross linkers have been used since 1970. However, the issue with the inorganic cross-linkers is the stability under high temperatures (more than 90 °C) [9].

The crosslinking mechanism between PEI and HPAM starts with a nucleophilic amine group attack from PEI on the carbonyl carbon of the amide group within the PAM backbone, Fig.2 [10-11]. Temperature and high pH values accelerate the gelation and the crosslinking. Inorganic salts delay the gelation and crosslinking because of the shielding effect by positive cations that will be attached to the negatively charged functional group on the PAM, preventing the entrance of PEI and delaying the crosslinking [9]. Bentonite can provide better crosslinking between PAM and PEI. The bentonite will also show a reinforcing effect on the crosslinked structure. However, other studies by *Shaikh et al.* [12] mentioned that a high concentration of bentonite will weaken the interaction between PEI and PAM. The reason is that the bentonite positive charge will be placed in some of the free amine groups in the cross-linker. In addition, the PAM will have high adsorption on bentonite, reducing the number of available PAMs that can perform crosslinking. Barite will also delay gelation because it will prevent or mitigate crosslinking between PEI and PAM. In addition, at extremely high pH values of more than 13, using more than 0.5 lb./bbl. The polymers of caustic soda or lignite will not be cross-linkable [9].

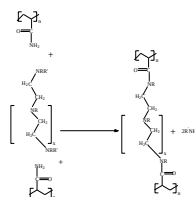


Fig.2: PAM and PEI cross linking mechanism, [9]

A study [13] shows that the drilling rate of penetration was improved when using guar gum or carboxymethyl cellulose compared to polyacrylamide. HPAM has moderate good solubility in water. HPAM is synthesized from acrylamide monomers. HPAM has negatively charged linear chain macromolecules hydrolyzed by an electrolyte, causing repulsion forces among negatively charged polymers in HPAM solution, causing the large viscosity. This viscosity is also controlled by the degree of hydrolysis. Salt content also affects the viscosity of HPAM. For example, a monovalent cationic solution like NaCl can cause the attraction between Na^+ and the negative polymer chain, causing polymer coiling up. This coiling up causes the polymer to precipitate and viscosity to decrease. For the divalent cations like Ca^{2+} , Ba^{2+} , and Sr^{2+} , more severe polymer precipitation and viscosity loss will occur [14-16].

Partially hydrolyzed polyacrylamide (HPAM) has been used as a flocculation agent in drilling fluids since as early as 1958. It is used to support removing the cuttings during drilling operations. The amount of drilled cuttings and size make the HPAM an attractive flocculation agent. HPAM can carry more and smaller cuttings than other additives. HPAM showed a significant impact on improving ROP (rate of penetration). However, there could be some disadvantages, such as concentration sensitivity. We could have flocculation if we

use a concentration of HPAM that is too high. In addition, if we drill through shale formation with montmorillonite, the flocculation will be poor because of sodium ions in these shales. HPAM is used mainly for low-solids drilling fluid for optimum results [17]. HPAM can also work as a shale inhibitor by accumulating cuttings. This research project will also cover testing for shale dispersion using representative formation. In addition, the HPAM has an amide ion group (CONH_2), which has a strong hydration ability, which allows it to work as a fluid loss additive, which will also help minimize the water invasion into the water-sensitive shales.

The current practice for high-temperature drilling is to utilize starch for temperatures up to 230 °F. For higher temperatures, no good viscosifier can be utilized. We can switch to oil-based drilling fluids at high temperatures. However, oil-based drilling fluids are expensive and can cause environmental and operational issues. An intensive literature review [18-32] has shown that HPAM and cross-linkers were used for different applications than drilling, such as EOR (Enhance Oil Recovery) or production.

Applications of hyperbranched polymers can be found in a range of sectors, including optical, electrical, and magnetic applications, as well as coatings, additives, supramolecular chemistry, and biomedicine. Other fields that make use of hyperbranched polymers (HBPs). Because of the three-dimensional globular structure that HBPs possess and the ease with which they can be synthesized compared to dendrimers, they have garnered much interest as potential methods for the administration of drugs. This is because HBPs can be made relatively quickly. HBPs have had their compositions, structures, and functions altered in order to make the process of administering medications more effective. This was done to improve the efficiency of drug delivery [33].

When compared to linear polymers, the advantages of HBP include a higher degree of inherent solubility, a lower tendency for chain entanglement, a smaller hydrodynamic radius, a lower degree of inherent viscosity, and a high degree of branching (DB) that results in a large number of terminal functional groups, Fig.3. The uneven topologies of these macromolecules, which consist of dendritic, linear, and terminal units that are randomly interspersed, are what cause them to have significant molecular weight distributions in comparison to dendrimers. Dendrimers have a uniform distribution of molecular weight across their entire molecule. The production of HBP can be done in a single pot, making the process more efficient and cost-effective than the multi-step approach used to make dendrimers. This is because the production of dendrimers requires purification after each coupling reaction, whereas the production of HBPs does not require this step. Dendrimers will probably be more complex than the functionalization of HBPs, although this remains to be seen. This occurs due to the steric barrier presented by dendrimers [34-48]. Utilizing high-density functional groups that are located on the exterior of HBP makes it possible to introduce functions. These groups are located outside of HBPs [49], which significantly increases the overall number of terminal functional groups, Fig.4.

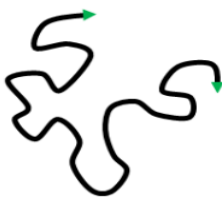
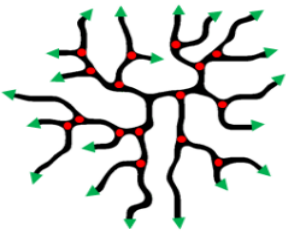
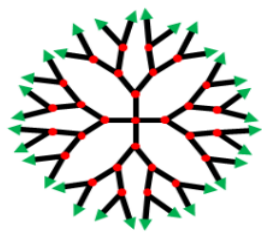
linear polymer	hyperbranched polymer	dendrimer
 linear one-step synthesis easy purification by precipitation easy scale-up dispersity ($\bar{D}$) > 1.01 DB = 0 no cavity 2 end-groups strong entanglements high viscosity	 three-dimensional, irregular one-step synthesis easy purification by precipitation easy scale-up $\bar{D}$ > 1.1 DB = 0.4-0.6 presence of cavities multiple end-groups weak entanglements low viscosity	 three-dimensional, regular multi-step synthesis purification by chromatography difficult scale-up $\bar{D}$ = 1.0 DB = 1.0 numerous cavities large number of end-groups no entanglements very low viscosity

Fig.3: The relationship of BHPs to linear polymers and dendrimers

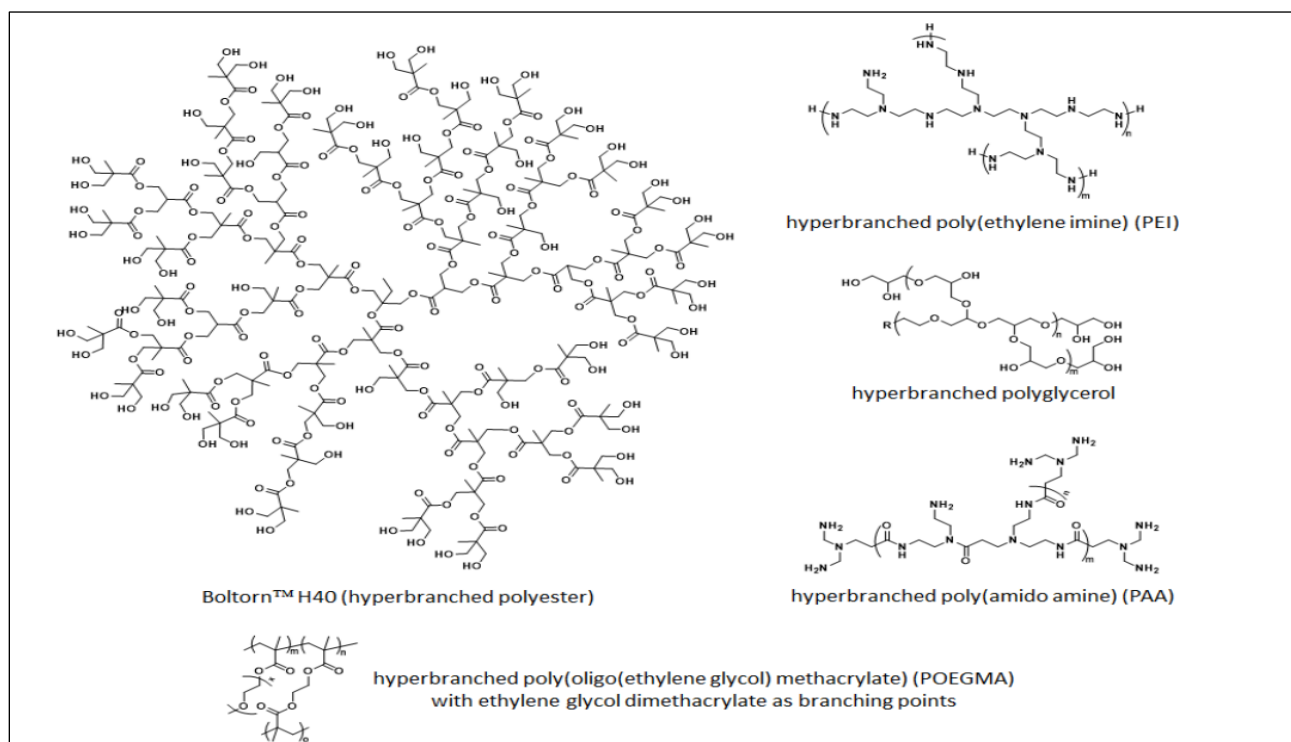


Fig.4: Hyperbranched polymers (HBPs) that are utilized most frequently in medication

delivery, [49]

Fig. 5 shows an overview of synthesized hyperbranched polymers. Compared to working with a single monomer, working with monomer pairs is more likely to result in the creation of (multi)cyclic species. This is because monomer pairs, as opposed to single monomers, possess a greater degree of stability [50].

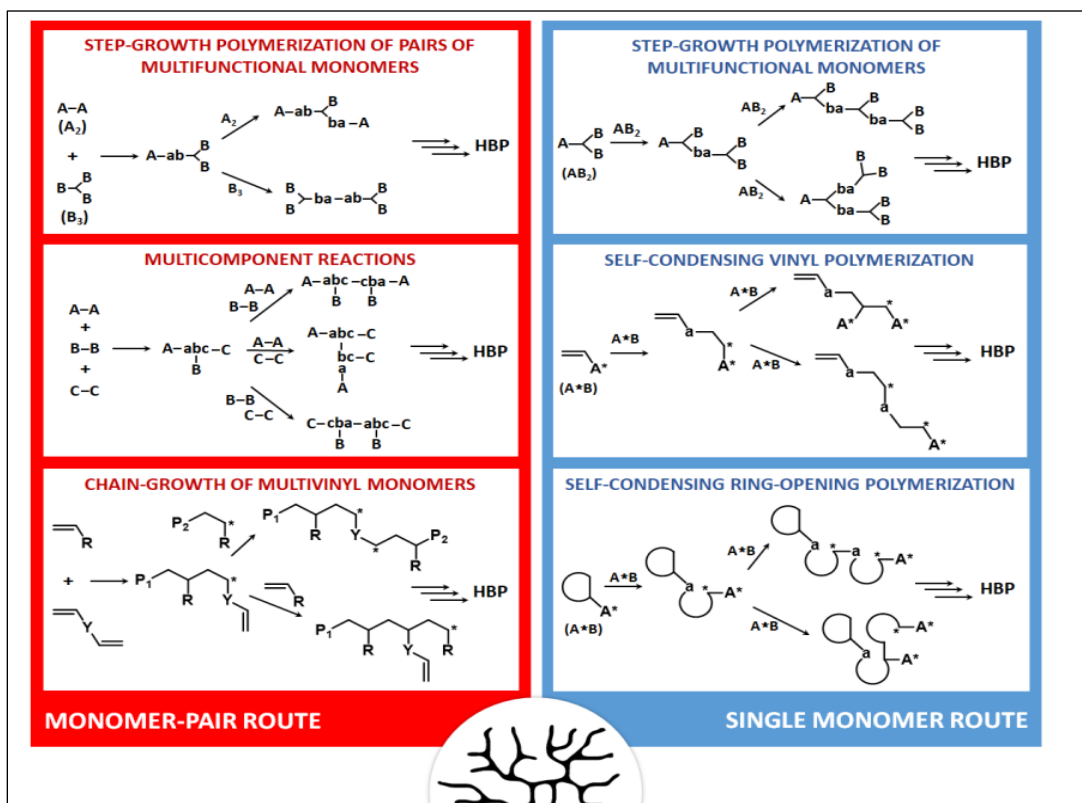


Fig.5: Principal synthesis pathways for the production of HBPs, [50]

In the innovative process of stepwise growth copolymerization, the selective reactivity of functional groups plays a crucial role in determining the choice of functional group. The initial mixture of components A_2 and B_3 leads to the formation of a gel, followed by an intriguing process of intramolecular cyclization. Gelation can be effectively

reduced through various methods, such as halting the polymerization process before it reaches the gel point, using an excessively diluted solution, or incorporating monofunctional end-capping agents. The implementation of any of these three choices promises a significant reduction in gelation [51].

When multivinyl monomers are utilized in chain-growth polymerization, one strategy for lowering the rate at which gelation occurs is to use thiols as agents for the chain transfer of free radicals. However, to produce HBPs, the thiols have to be added equally. An increase in the temperature at which polymerization occurs and an increase in the amount of multifunctional comonomer present contribute to an increase in branching [52-53]. In recent years, polymerization in dispersed media has been introduced to this process. This includes polymerizations such as suspension, emulsion, and controlled radical polymerization to produce HBPs from multifunctional monomers. A controlled radical polymerization technique known as catalytic chain transfer polymerization is used in manufacturing [54-55].

In step-growth polymerization of AB_x Monomers, we can produce highly branched polymers without forming gels, even in relatively low intramolecular reactions. This was based on the observation that such monomers contain one reactive group A. The creation of a branching point results from a reaction between the B groups of AB₂ monomers and the A groups. Those HBPs created from AB_x monomers have a greater observed dispersity but a lower computed dispersity than the other HBPs. This is the case when compared to other types of HBPs. The expectation of creating HBPs with a narrower molecular weight dispersion has prompted the development of several distinct techniques in recent years [56-57].

The process of self-condensing vinyl polymerization, also called SCVP, was first uncovered by Fréchet. He achieved this result by bringing together a group and a vinyl monomer. Including this specific group, referred to as an inner (A^*B), is feasible in the AB_2 system [58]. In order to lessen the likelihood of crosslinking reactions and gelation of reaction mixtures, radical polymerizations, in addition to cationic polymerizations and anionic polymerizations, were considered. This was done so that cationic polymerizations would no longer be the only type covered by SCVP. This was done so that the process would be more all-encompassing and successful. Because carbanions have a high rate of reactivity, it is essential to produce animals in situ that contain a vinyl group and an anionic initiator. This is because of the need to prevent carbanion formation [59]. In order to facilitate the self-condensing anionic or cationic ring-opening polymerization of cyclic epoxides, oxetanes, lactones, and phosphates, a new type of timer known as A^*B timers has been designed and developed specifically for this purpose [60]. B is a ring structure, which stands in stark contrast to A^* , which is a hydroxyl group. You can make hyperbranched polyethers useful for nucleophilic propagation by coupling the hydroxyl group from glycidol with the epoxide group of another chemical. This will result in the production of glycidol. There is a possibility that cyclization will take place within the molecule itself [61-62].

HBP's have the potential to revolutionize drug delivery. By enhancing the amount of transport to tumor tissue through drug loading achieved via various methods such as encapsulation or conjugation, and passive targeting, we can significantly increase the quantity of transport to the tumor. The interactions between pharmaceuticals and polymers not only make drugs more stable but also increase their loading capacities, enabling the

creation of more personalized drug delivery patterns. Our research has explored the possibility of covalently binding the drug to the polymer through linkers that can be modified to induce drug release, a promising avenue due to the susceptibility of non-covalent methods to the physical forces in their surroundings. HBPs are capable of conjugating a substantial pharmacological payload to their terminal functionalities, underscoring their potential in drug delivery [64-67].

Cationic polymers, with their amine functional groups that can be protonated to be either primary, secondary, or tertiary [68], are a complex yet promising area of study. A cationic polymer like PEI is often used in non-viral methods of gene delivery. However, its application is limited by cytotoxicity, posing a significant challenge. The PEI can adopt either a branching or a linear shape, adding to the complexity of its use, Fig. 6 [68].

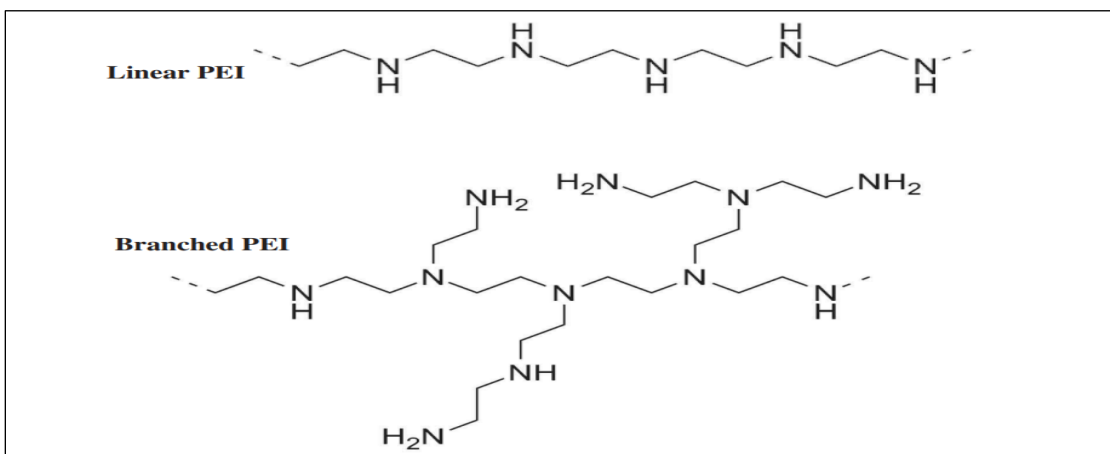


Fig.6: Linear PEI vs. Branched PEI, [68]

PEIs are polymer molecules made up of amine units that are repeated in a pattern and two aliphatic carbons. The linear PEI only contains the primary and secondary forms of amino groups, whereas the branched PEI may contain all three amino groups. In addition, LPEI is a liquid at ambient temperature, but BPEI is a solid (independent of its molecular weight). The melting point of LPEI is close to that of BPEI [69-71]. Considerable molecular weight PEI can attach to DNA in a multivalent manner, whereas a small molecular weight PEI can only form monovalent bonds [72].

Because of the secondary amine protonation throughout the backbone, the PEI chain takes on a positive charge when exposed to acidic conditions. It is essential for the polymer to exhibit weak buffer properties in order for it to be utilized as a DNA delivery agent because of its ability to absorb H^+ ions [73]. PEI offers more benefits over other cationic polymers and other non-viral vectors than it does over other non-viral vectors because of the high density of the charge that it carries and the so-called "sponge-proton effect." However, strong PEI efficacy is typically linked with considerable toxicity, which restricts its utilization in clinical settings. This is partly because PEI cannot be degraded [74-75]. PEI has grafted saccharides such as oligo-maltose, chitosan, galactose, and mannose onto it to reduce its toxicity. However, most of these alterations required either a multi-step synthesis or rigorous experimental conditions, Fig.7 [76].

Reagent(s)	Functionalized		Product(s)
	-NH ₂	-NH-	
mPEG-NCO	✓		
R = COOCH ₂ CH ₃ R = COOCH ₃ R = CN	✓		
R = disulfide hyaluronic acid R = CH ₃ , CH(R)NH ₂	✓	✓	
R = R = R =	✓	✓	
R = CH ₃ , CH ₂ CH ₃ and many more	✓	✓	
	✓	✓	
	✓	✓	
R ₁ , R ₂ = H R ₁ = CH ₃ ; R ₂ = 	✓		

Fig.7: Techniques of synthetic post-polymerization modification for the purpose of improving the biocompatibility of branched PEI, [76]

It was anticipated that neutralizing the PEI amines would improve biocompatibility. After some alteration was performed to neutralize the PEI amines, the positive charges of PEI were protected. As a result, the biocompatibility of PEI was significantly improved. This research highlights the fact that the biocompatibility of the produced neutral or negatively charged PEI derivatives was greatly improved after the neutralization of PEI amines by acylation, PEGylation, or hydroxylation [77].

Below low critical solution temperature (LCST), the aqueous polymer solution will be in a soluble hydrophilic state. Above LCST, the polymer precipitates and becomes

hydrophobic. Monomer units can influence the interaction between the water and the polymer chains, which then affect the polymer solubility [78]. There are interactive forces that result in the coil-globule transition of linear polymers. For example, hydrophobic interaction, electrostatic interaction (electric dipoles and ions), hydrogen bonding between polymer side chains and solvent, and topological interactions (entanglement, etc.) [79].

There are different types of polymer phase transition as the temperature increases. For example, we could have a clear, opaque (milky) solution or a two-phase state where the solvent and polymers are separated [80]. The type of phase transition will depend on the polymer chain hydrophobic character. The precipitation will give a solution at high temperatures and low concentrations of the polymer chain. Precipitate aggregation will occur if we use a high concentration of polymer chain at high temperatures. The hydrogen bonding between the hydrophilic group in the polymer and surrounding water will cause polymer chain elongation. As the temperature increases, the solvent quality will decrease, leading to hydrophobic polymer-polymer interactions. In the beginning, we had a balance between hydrophobic and hydrophilic interaction in aqueous polymer solution. When hydrogen bonds are formed between the polymer and the water, we have $+\Delta G$ (free energy) contribution of the solution since ΔH is negative and ΔS is negative too [81]. As the temperature increases, the hydrogen bonding gets affected, and precipitation takes. The temperature where this precipitation occurs is known as cloud point temperature when the $T(\Delta S)$ contribution is higher than ΔH [82]. We could have some clouding below LCST for copolymers with high heterogeneity (less than ideal copolymerization) [83]. There are different methods to detect LCST. For example, we can use light scattering to detect coil-to-globule transition [84]. Phase separation could be detected using

turbidimetric measurements [85]. Differential scanning calorimetry (DSC) can be used for transition heat measurement [86]. Poly(N-isopropyl acrylamide) PNIPAAm is a water-soluble thermally sensitive polymer.

We have the hydrophilic CONH_2 and the hydrophobic $\text{CH}(\text{CH}_3)_2$ groups. At a temperature below LCST, we will have strong H-bonding and the hydrophilic polymer group and, thus, good solubility. As the temperature increases, the hydrogen bonding between the carbonyl oxygen and water molecules gets weaker, and the interaction of the isopropyl chain gets better. The interaction of the hydrophobic isopropyl chain gets much more vital as the temperature increases than LCST. There will be an increase in entropy due to the release of structured water around the hydrophobic polymer part [87-88]. The relative hydrophilicity of the polymer determines the phase separation temperature [89]. The transition temperature is close to the temperature at which osmotic pressure becomes zero. It has nothing to do with cross-linking density or polymer concentration [90]. We can have two-step mechanisms for the phase separation. For example, raising the temperature above the UCST of the aqueous PNIPAAm solution causes a coil-to-globule transition followed by a phase separation [91]. There are methods to try to modify the LCST, for example, using solvents [92], surfactants [93], salts [94], or polyelectrolytes [95] in aqueous solutions. However, the most practical method to control and modify LCST is to add a co-monomer or to perform polymer chemical modification. If we add a hydrophobic co-monomer, the LCST will be decreased, while adding a hydrophilic co-monomer will increase the LCST [87]—co-monomers with ionizable groups such as tertiary amines or carboxylic acids. Hydrophobicity or hydrophilicity can be modified by changing the pH of the water [88]. If we have acidic pendant groups in the polymer, the swelling will increase

as the pH of the solution increases. If we have a weakly basic gel, it will expand if the solution pH decreases [96]. In low pH of 2-3, the carboxylic acid dissociation is inhibited due to the presence of the counter ion (H^+); thus, LCST will be lower compared to a polymer with no acrylic acid monomer [96]. For a polymer containing both the amide and carboxylic acid groups at low pH, there will be more intra and intermolecular hydrogen bonding between these two groups. Thus, the hydrophobicity of the polymer will increase, reducing the water access to the polymer. In order to overcome this and increase the cloud point temperature of the polymer, we can increase the pH. At a pH of about 4.0, we will have increased hydrophilicity from the ionized acrylic acid component. Increasing the pH will introduce strong electrostatic repulsive interactions [97].

In poor solvents, the hydrophobic interaction is more than the electrostatic interaction, and polymer-polymer interaction becomes strong, leading to gel shrinkage [90]. To maintain good polymer solubility for polymers with acrylic acid, the pH must be higher than the pK of the acid groups to ionize them to the carboxylate [90]. Another alternative is to increase the basicity of the polymer if a constant solution pH is required. We can, for example, use more extended alkyl segment monomers such as polyacrylic acid and butyl acrylic acid to increase polymer pKa and LCST, the temperature at which the phase temperature takes place. An important factor is the effect of the alkyl chain length on solubility. The hydrophobicity of the carbon chain is more significant than the hydrophilicity of the carboxylic groups, and as we increase the amount of carbon, the LCST will decrease [82]. So, increasing hydrophilic co-monomer will lead to an increase in the LCST.

Cloud points of random copolymer are higher than cloud points of homopolymer. As the acrylic acid content increases in the copolymer, the cloud point will increase due to the hydrophilic character of the acrylic acid monomer unit along the backbone. For grafted polymers, the cloud point is not influenced by the acrylic acid content [98]. As the n-alkyl chain length increases, it is anticipated that the LCST will decrease for amphiphilic copolymers. This trend was observed for C10 and C14 alkyl chains but not for C18-containing polymers. The reason for not lowering the LCST is that the alkyl chains were not exposed to water, and they formed a micellar structure instead. Not exposing this alkyl group to water means no hydrophobic contribution was made to the LCST [99].

Polymers with low polydispersity indices show a sharper LCST transition than polymers with high polydispersity indices [100]. Transition temperature is the temperature at which a sudden change of physical properties occurs, for example, phase or crystalline structure. High polymer weight polymer can show low transition temperature [94]. As the hydrophilicity of the polymer increases, we will have a weaker and broader phase transition. The polymer will be better solvated with increasing hydrophilicity, i.e., the solvent is firmly bonded, and less water release will occur in case of polymer chain collapse [83]. The cloud point will shift to a higher temperature if the charged octyl units increase in a copolymer due to increased hydrophilic character. However, charged dodecyl groups will decrease LCST due to increased hydrophobic character. Draw the structure Turbidity measurement showed that the turbidity of charged C12 was lower than charged C8. Lower LCST means lower turbidity [82]. Adding surfactant to the polymer changed the conformation by binding an anionic surfactant to cause micellar repulsion along the polymer chain, reduce intermolecular aggregation, and increase polymer solubility [101].

Adding an excessive amount beyond the saturation point of surfactant will result in micelles formation, similar to salts in lowering LCST. Also, adding too small surfactants will not enhance polymer solubility [102-103].

When we want to add polymers in a high salinity solution, the salt ion will interact with the side chain of the polar groups, such as amide or carboxyl, which will affect hydrogen bonding with water [104]. When we dissolve polymers in fresh water, we will have a hydration sheath surrounding the polymer. Adding salts will alter the hydration sheath and change the orientation of the water molecule surrounding the polymer, increasing the hydrophobic character of the polymer chains and reducing LCST. We will have different effects on LCST based on the type and concentration of the salt used [105]. In the Hofmeister Series, ions on the right-side produce (stabilizing) effect on the polymer, whereas the ions on the left side lead to a salting-out (destabilizing) effect. Cl^- and Na^+ ions are typically considered as the broad line between strongly and weakly hydrated anions and cations, respectively. Large ions are weakly hydrated and will cause large polarizability and will interact with the polymer surface. Small ions are intensely hydrated and will cause small polarizability and will interact with the hydration shell or hydration sheath. For anionic ions: Citrate³⁻ > Sulfate²⁻ > Phosphate²⁻ > F¹⁻ > Cl^{1-} > Br^{1-} > I^{1-} > NO_3^{3-} , ClO_4^- . For cationic ions: $\text{N}(\text{CH}_3)_4^{1+}$ > NH_4^{1+} > Cs^{1+} > Rb^{+1} > K^{1+} > Na^{1+} > Ca^{2+} > Mg^{2+} > Al^{3+} . The direct binding of large weakly hydrated anions to the polymer, a novel aspect of our study, is driven by a favorable change in enthalpy. This interaction, as we will demonstrate, unveils significant implications for the behavior of the polymer [106].

Weakly hydrated salts such as calcium bromide lower the Lower Critical Solution Temperature (LCST), thereby raising the surface tension between the hydrophobic

polymer component and water molecules. Strong hydrated ions weaken the hydrogen bonding between polar groups such as amide and carboxyl by polarization effect [107]. In general, increasing the phase transition temperature will reduce hydrogen bonding and thus reduce ΔH . For a solution with ions, lowering the phase transition temperature is associated with a reduction in ΔH . The reason here is the ability of ions to subtract water molecules from the polymer chain and increase the hydrophobic character and interaction, thus lowering the phase transition temperature. The abstracted water will hydrate the ions and will be associated with exothermic heat and reduction of the endothermic heat of the transition. These findings have direct implications for the design and behavior of polymers in various applications [108].

Salt with no alkyl groups lower the transition temperature. If there is a long alkyl chain, the transition temperature will increase. This was observed when using salt with C_4H_9 , C_5H_{11} alkyl groups. This was due to the hydrophilic interaction, which refers to the attraction between water and a substance, between the salt alkyl group and isopropyl group in the polymer. This interaction promoted ions attachment to the polymer part, making them behave like fixed charges on the polymer network [108].

A cross-linked hydrophilic network, also known as a hydrogel, is defined as a network of polymer chains that are hydrophilic, or water-loving. Whether they are cross-linked or not, they show a similar response to different types of salts and concentrations. A study suggested that a small amount of NaCl will result in increasing the phase transition temperature. However, the phase transition temperature will be reduced as we increase the NaCl salt concentration. For Gel polymer with fixed acrylic acid content the H^+ ions will be exchanged for the salt content which lead to further increase of free counter ions

produced by acrylic acid dissociation leading to increase in swelling pressure and viscosity. However, increasing the salt concentration will cause complete acrylic acid dissociation, reducing the ion swelling pressure and resulting viscosity [109] and [81].

Some additives, such as alcohol, weaken hydrophobic hydration, i.e., hydrocarbon interaction with the hydrogen bond surface is more favorable than that of liquid water. So, adding alcohol to water will reduce hydrophobic hydration and increase hydrophobic interaction. Using alcohol as a solvent will reduce ΔH and ΔS . Water as a solvent will result in bigger $-\Delta S$ and more significant $-\Delta H$ values. An enormous $-\Delta H$ value indicates a strong association between hydrophilic groups such as $-\text{NH}$ and $-\text{C}=\text{O}$ in the polymer and water molecule, i.e., hydrogen bonding is taking place. A sizeable absolute ΔH value shows that we have strong temperature dependence conditions. A more positive ΔS , such as the one associated with using alcohol, indicated reduced hydrogen bonding. DMSO (Dimethylsulfoxide) is an aprotic solvent. It cannot form hydrogen bonding. Therefore, the DMSO will replace hydrated water molecules and decrease transition temperature. These findings underscore the importance of solvent selection in polymer behavior and have significant implications for polymer science and materials chemistry [110].

Shale Inhibition

The process of shale swelling is a complex interplay of various mechanisms. One of these is the cationic exchange between water (cations) and the damaging clay minerals, which occurs when water comes into contact with the shale. Swelling, in this context, signifies an increase in interlayer spacing and increased thickness of individual layers. This cationic

exchange is not a straightforward process, but rather takes place through different mechanisms. The first of these is spontaneous/osmotic imbibition, which occurs when the shale has high contact with saline connate water compared to drilling fluids salinity. Osmosis, in this case, occurs by moving water molecules from the low salinity zone to the high salinity zone, resulting in shale swelling [111].

The process of shale swelling is governed by three main mechanisms, each playing a significant role. The first mechanism is hydraulic pressure differences, where the density of drilling fluids should ideally be higher than the formation pressure, and filtrate invasion is inevitable. Minimizing this invasion is desirable to enhance drilling operations and reduce shale swelling. The second mechanism is surface hydration, which occurs gradually and is much slower than the hydraulic pressure differences mechanism. Surface hydration is further divided into inter-crystalline swelling and intra-crystalline swelling, as illustrated in Fig.8 [111]. This comprehensive understanding is essential for professionals in the field of oil and gas exploration and production.

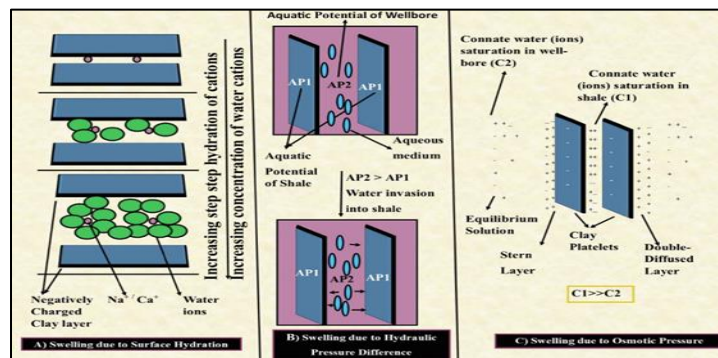


Fig.8: Types of shale swelling: (a) Crystalline swelling (b) swelling due to difference in aqueous potential (c) Swelling due to Osmotic Pressure, [111]

Surface tension measurement of clay surface can indicate shale inhibitor performance. Capillary forces or increased surface tension indicates a lack of shale inhibition. Zeta potential is a good stability indication of colloidal dispersion. The shale surface is negative and will attract the cation from water, resulting in diffused double electrical layers. If zeta potential is reduced, shale inhibitors perform successfully. Another method to characterize shale inhibitors is to conduct XRD analysis and measure spacing before and after using shale inhibition. If we see a decline in d spacing, our shale inhibition is good, as shown in Fig.9 [111]. Now, to measure the performance of shale inhibitors, we need to apply testing from the petroleum engineering domain, such as the use of a linear swell meter, shale dispersion testing, and detailed fluids testing for rheology and filtration at suitable formation conditions (temperature and pressure).

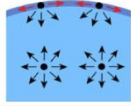
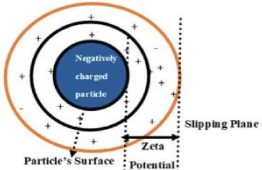
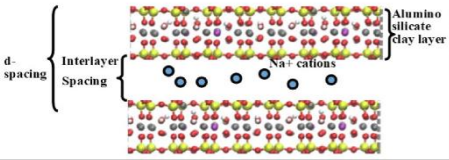
Characterization		Effect on Shale Inhibition
Surface Tension		Less surface tension → lesser capillary pressure → lesser water invasion into shale → more shale inhibition
Zeta Potential		Less zeta potential → smaller electrical double layer thickness → more shale inhibition
d-spacing		More decline in d-spacing → the more intercalation of DES between clay layer → the more expulsion of water from clay layers → more shale inhibition

Fig. 9: Characteristic mechanism of Shale Inhibition, [111]

We can perform inhibition by using mechanical or chemical inhibitors, Fig.10. The mechanical inhibitor's objective is to physically plug the pores of the shales to minimize

water invasion—for example, nanomaterials or cellulosic materials. The chemical inhibitors counteract the negative charges on the shale surface. Chemical inhibitors can perform cations exchange and form hydrogen bonding to neutralize and negate shale charges. Salts such as KCl, CaCl₂, and NH₄Cl are typical shale inhibitors. Polymers and ionic liquids form hydrogen bonding as a way of shale inhibition. For example, polymers with imine groups, amine groups, hydroxyl groups, and carboxylic groups can achieve shale inhibition [111].

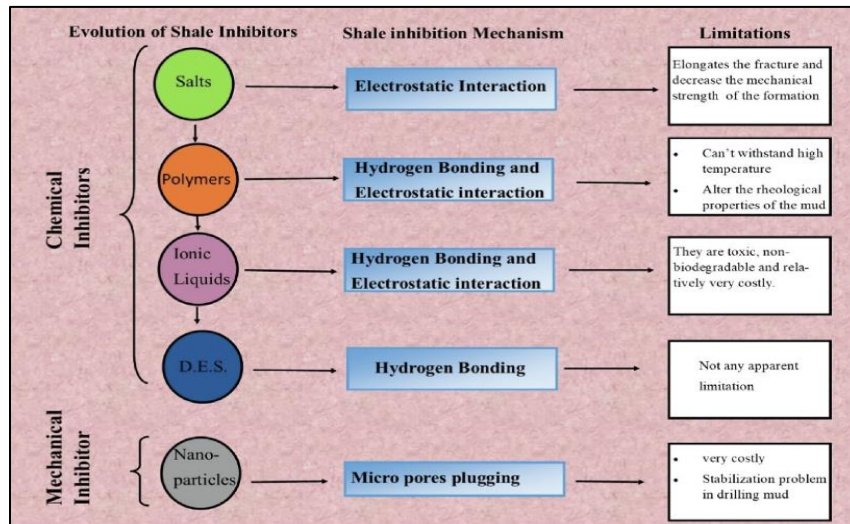


Fig.10: Evolution of Shale Inhibitors, [111]

Nanomaterials can form compact filter cakes to minimize fluid loss or water invasion. By minimizing water invasion, Nanomaterials can perform shale inhibition. Oil-based fluids show improved shale inhibition compared to water-based fluids. However, for environmental reasons, water-based drilling fluids are always preferred. Generally, shale inhibition is achieved by stabilizing negative shale charges using positive charges from

salts or by forming hydrogen bonds with polymer with lone pair atoms such as nitrogen or oxygen [112].

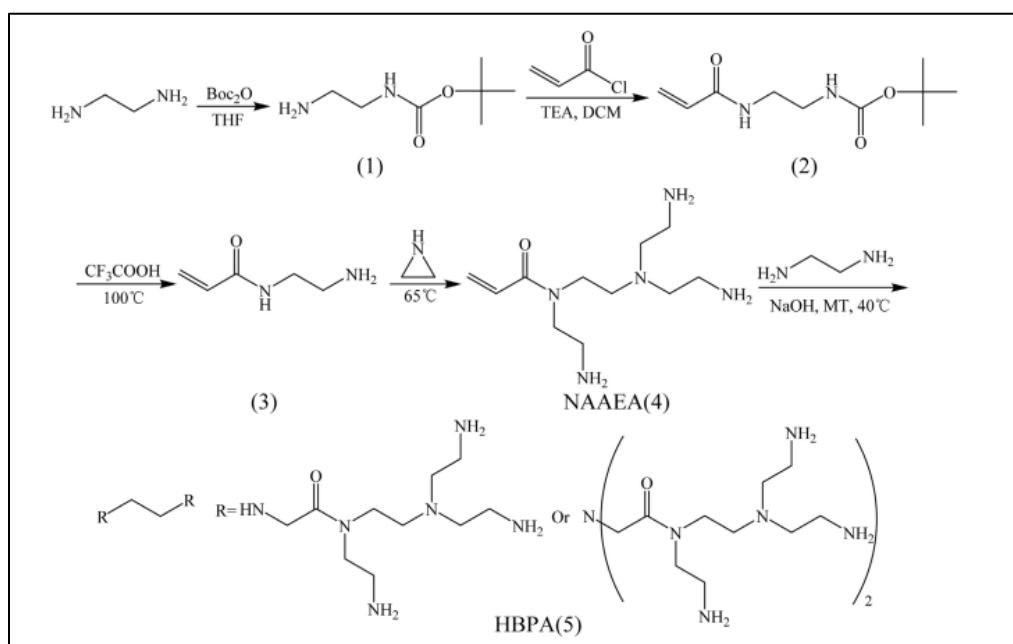
According to [113-115], there are two mechanisms. The first mechanism is due to the inhibitors coating the surface of the shales to separate it from water. The second mechanism is related to the replacement of the water between the shale clay crystal layers with inhibitors that will be adsorbed inside the crystal layer. Common shale inhibitors could be an inorganic salt, asphalts, polymers, or silicate. However, we can have issues when using some of these shale inhibitors. For example, silicate can negatively affect the drilling fluids' properties, and asphalts can be harmful to the environment. Ammonium-based shale inhibitors are prepared by acid-base reaction between secondary tertiary amine and acid. However, they are not stable at high temperatures [116-121].

KCl salt is a promising inhibitor for drilling fluids. The K^+ hydration energy and hydration radius are smaller than Na^+ and Ca^{2+} within the shale. The K^+ will enter the hexagonal oxygen ring within the clay crystal layer, replacing Na^+ and Ca^{2+} and inhibiting the shale. In some cases, K^+ can be strongly connected with the clay water, which might affect the inhibition performance [122-124]. Therefore, we must consider the optimum concentrations of KCl salts used in drilling fluids.

Ionic liquids can be used as additives in drilling fluids for shale inhibition. They interact with the electrostatic forces of clay and neutralize the charges. However, due to their toxicity and high cost, ionic liquids have limitations, especially when using imidazolium-based fluids [125-128]. Deep Eutectic solvents can be used instead of ionic liquids. Ionic liquids are a mixture that becomes solid at a temperature lower than the individual gradient's melting points. The individual gradients (hydrogen bond acceptor and

hydrogen bond donors) can bond with each other through hydrogen bonding at a specific temperature. Both ionic liquids and deep eutectic solvents have good thermal stability; however, DES is easier and cheaper to prepare than ionic liquids. DES has been used in catalysis, separating particular materials, corrosion inhibition, and hydrates inhibition [129-133]. Polymers degrade at high temperatures, so ionic liquids and nanomaterial were studied for shale inhibition to compensate for polymer limitation in high-temperature environments. However, ionic liquids or nanomaterials are expensive. Nanomaterials are complex to stabilize and require a sonification process, sometimes making them unsuitable for the industry.

Ionic liquids are expensive, non-biodegradable, toxic, and require multistep preparation, which makes them unsuitable for drilling applications. Ionic liquids interact with shale clay using electrostatic forces of attraction. For Deep Eutectic solvents, hydrogen bonding with shale is the inhibition mechanism. However, additional work will be required to understand more deep eutectic solvent inhibition mechanisms and how to optimize their synthesis using different natural salts [45]. Metal-organic framework (MOF) was utilized as a catalyst for ring opening polycondensation (ROP) of hyperbranched polyamine inhibitor with a high ratio of amine groups in a five-step synthesis containing ethylenediamine, acryloyl chloride, and aziridine, Scheme 1 [134].



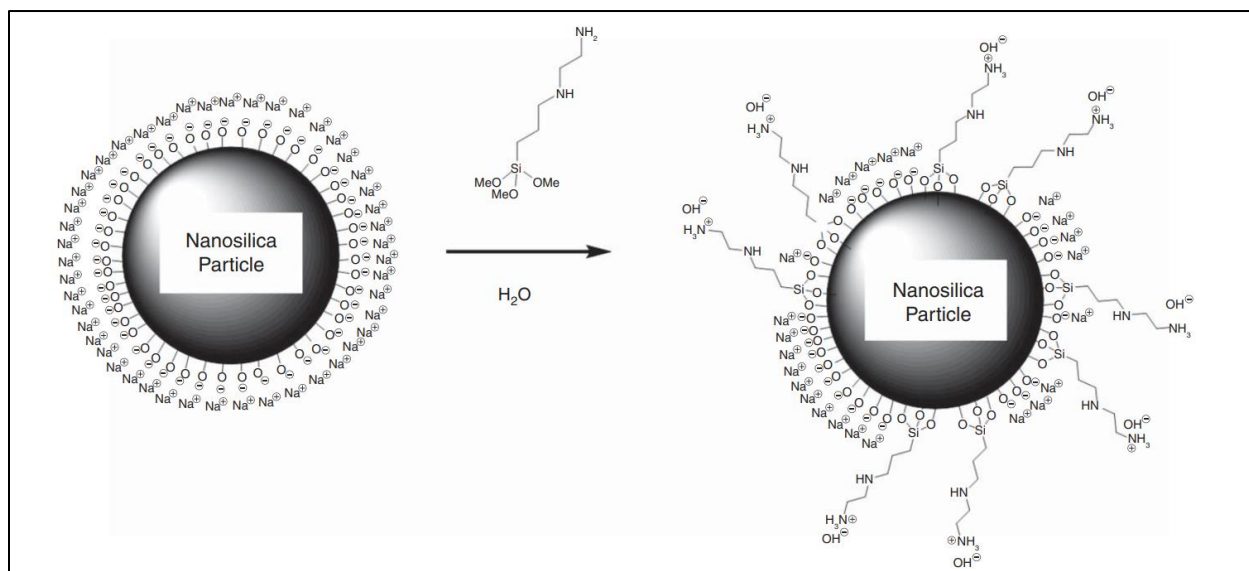
For shale inhibition, linear-chain molecular structure shale inhibitor does not result in long-term shale inhibition. They are molecules with low-density absorbing groups that got adsorbed on the surface of the electronegative clay. Downhole conditions can lead to desorption and loss of inhibition, i.e., loss of long-term shale inhibition [135-137]. On the other hand, hyperbranched polymers can introduce considerable absorbing groups at the end of the molecular chains by modification and functionalization of end groups. This more significant number of absorbing groups can increase the adsorption capacity to improve shale inhibition. The hyperbranched polymer synthesized here has primary amine, secondary amine, and amide groups that produce protonated products in highly alkaline drilling fluids, resulting in high shale inhibition due to strong adsorbability [138].

Partially hydrolyzed polyacrylamide (PHPA) combined with KCl is used for shale inhibition. PHPA can coat the shale to minimize filtrate invasion, and KCl can perform cationic exchange with shale pore water. Another shale inhibition package included KCl, silicate mud, or KCl and glycol mud. KCl is 2% required to activate these packages for good shale inhibition. Silicate mud will precipitate on the shale surface and minimize filtrate invasion [139-143]. However, there is a concern about long-term shale inhibition of silicate fluids. Also, an extremely high pH will be required for good inhibition and performance (pH 11-12.5) [144].

A polymer with both hydrophilic and hydrophobic moieties was used with ZnO nanoparticles in drilling fluids for shale inhibition, achieving a 97% recovery factor [145]. However, these water-based drilling fluids had bentonite, which could induce risks in some formations. Different linear polyamines with different chain lengths were synthesized by two-step synthesis followed by hydrolysis or reduction. The study details the synthesis of different linear polyamines (LPEI, LPPI, and LPBI) with variable spacing between the amino groups [146]. Field results showed that polymers are unstable at high temperatures and pressure due to their lack of suitable thermal, mechanical, and chemical properties. Polymers like carboxyl methyl cellulose, and XC are also unsuitable at high-temperature environments and incompatible with anionic additives [147].

Colloidal silica with 35 nm particle size was used in drilling fluid for shale inhibition against conventional KCl. A high quantity exceeding ten wt.% was required for acceptable shale inhibition [148]. Nano silica with 20 nm in 4% sea salt water-based fluid showed good tolerance against high temperature and pressure and minimized shale invasion [149]. Another study [150] showed that a high quantity of 20 nm nano silica is

required to formulate water-based fluid using four wt.%. The study mentioned that it was effective up to 77 °C only. Up to 29 wt.% was used to effectively seal Texas shale (35 um fractures) [151]. Silica with 5-100 nm was investigated with different salts. It showed good compatibility when using NaCl. However, it solidifies when using sodium hydroxide [152]. Nano silica, in general, was used in water-based fluids for shale inhibition successfully. However, nano silica does not work in oil-based fluids to minimize filtrate invasion due to a lack of proper dispersion [153]. Polyethylene glycol PEG was used to coat the nano-silica but only showed good inhibition up to 55 °C. The shale inhibition mechanisms here are physical plugging due to nano silica and hydrogen bonding from the OH group in the polyethylene glycol [154]. Nano silica modified with 2-aminoethyl-3aminopropyltrimethoxysilane (AEAPTS) showed good inhibition only when combined with calcium ions and PAC, Scheme 2 [155].



Scheme 2: Depiction of the functionalization of a nano-silica particle with a methoxy silane compound. In this case, the reagent is AEAPTS, [155]

Ethylenediamine-modified graphene was used as a shale inhibitor due to physical plugging and hydrogen bonding with EDA [156]. A study [157] mentioned that graphene nanoplatelet improved performance against different fluids, such as KCl and PHPA, nano silica, and multi-walled carbon nanotube and KCl fluids. Nano-flexible polymer can also be used as a shale inhibitor by physically plugging the shale pores [158]. Polymers that work as fluid loss additives can also improve shale inhibition; for example, a terpolymer of acrylamide-2acrylamido-2-methyl-1-propane sulfonic acid-N-vinyl-pyrrolidone (AM-AMPS-NVP) [159]. High thermal stability up to 95 °C, good shale inhibition, and compatibility in high salinity fluids were achieved using polyacrylamide-grafted-polyethylene glycol/SiO₂ nanocomposite [160]. Hydrophobic polymer-based silica nanoparticles composite with a center core showed good shale inhibition by physical plugging, hydrogen bonding, and water repulsion by styrene chain [161]. Physical plugging by acrylic resin/nano-SiO₂ (AR/SiO₂) composite provided good shale inhibition in temperatures up to 250 °C due to good adhesion of the deformable AR/SiO₂ [162].

Titanium Nitride nanoparticles were added to CMC and KCl solutions to inhibit shale by minimizing filtrate invasion [163]. Laponite nanoparticles improve fluid loss control by forming compact filter cakes, thus helping in shale inhibition [164]. Sodium stabilized nano-silica with 10-20 um particle size was functionalized with AEAPTS (2-aminoethyl-3-aminopropyltriethoxysilane). Twenty grams of the nano-silica was mixed with AEAPTS for 1 hour. The inhibition tests were done under 150 °F, and the results

showed approximately a recovery factor of approximately 94%. The duration of testing was 24 hours, and the formulation was done using seawater. Nano silica in freshwater did not achieve good inhibition. The addition of seawater indicates that the ions strengthen the effect of nano-silica. Nano silica is compatible under 150 °F against ions such as magnesium, calcium, and potassium [155].

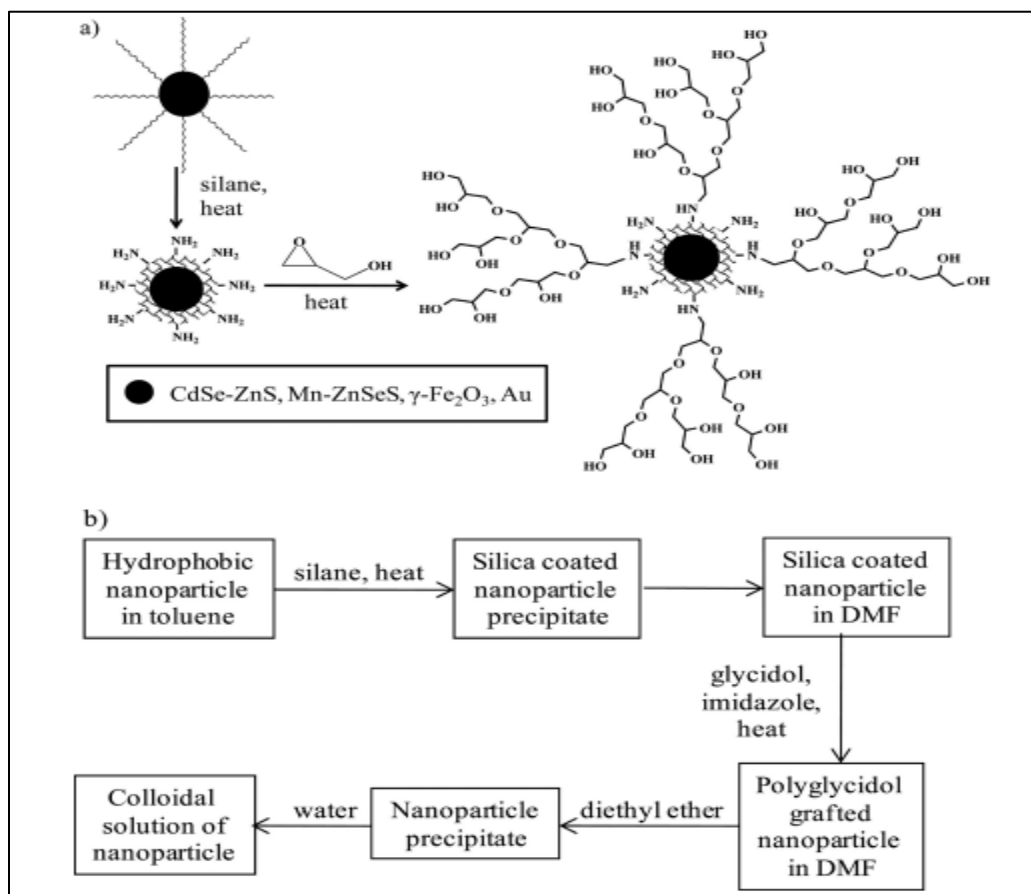
A study looked at using nano-silica particles and graphene nanoplatelets to formulate water-based fluid for improved shale inhibition. No synthesis occurred here, only the physical addition of the nanomaterials in the water-based drilling fluids. The ultrasonication step was used to reduce aggregation in both nanomaterials before utilizing them as additives. Zeta potential was used to ensure the stability of the nanofluid. The recommended value for stable nanofluid is ζ -values <-30 mV or >30 mV [165].

Nanofluids of CuO and ZnO (size <50 nm) in a xanthan gum aqueous solution as a base fluid enhanced the thermal stability of water-based fluids up to 110 °C [166]. The major drawback related to using nanomaterials in drilling fluids is cost. Before starting any projects related to synthesis, it is strongly recommended to consider the production process of nanomaterials, which is generally too expensive [167]. Aluminum oxide NPs in low concentrations improved the performance of water-based fluids at high temperatures. It outperforms the nano-silica particles and the base fluids with no nanoparticles. The conditions stated in the study were 120 °C. Plans included trying different nanoparticles at higher temperatures, up to 160 °C [168].

Nano ZnO particles were added in 0.25, 0.5, and 0.75 wt./volume percentage of Nano-ZnO mixture in water-based drilling fluids to minimize filtrate invasion. Stability tests against seawater showed acceptable results. However, the study was not done at

elevated temperatures and long distances [169]. A study investigated the effects of zinc oxide nanoparticles-acrylamide composite termed as ZnO-Am composite on rheological and shale swelling behavior of conventional WBDF. The testing condition was at 150 °C. The rheological properties were acceptable, but not the shale inhibition [170].

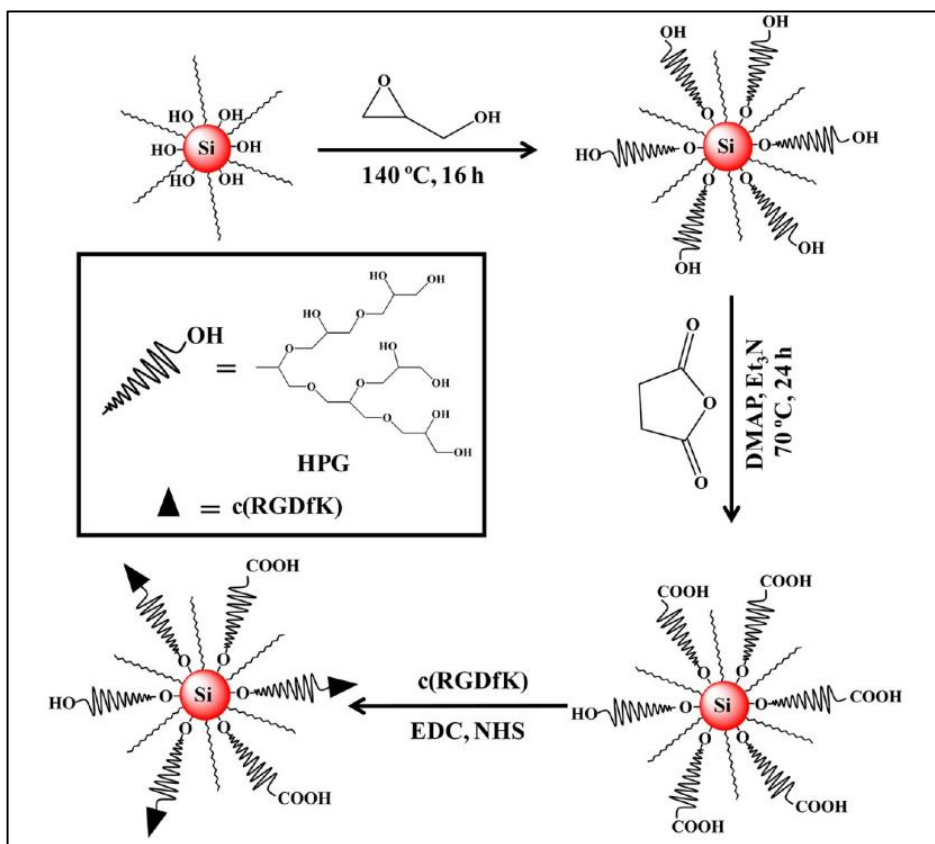
Scheme 3 shows the hyperbranched polyglycerol grafting on the surface of silica-coated nanomaterial. The first product is silica-coated nanoparticles terminated with primary amine groups. The second product is a generation of hyperbranched polyglycerol, done by the primary amine groups that will work as an initiator with glycidol monomer to start ring-opening polymerization. This study used four different nanoparticles: CdSe-ZnS-based quantum dots with red emission, Mn: ZnSeS-based quantum dots with orange emission, Magnetic Fe₂O₃ nanoparticles, and plasmonic Au nanoparticles [171].



Scheme 3: (a) Schematic representation of hyperbranched polyglycerol grafting on surface of silica-coated nanoparticles. (b) Steps for transforming hydrophobic nanoparticles into hyperbranched polyglycerol-grafted Nanoparticles, [171]

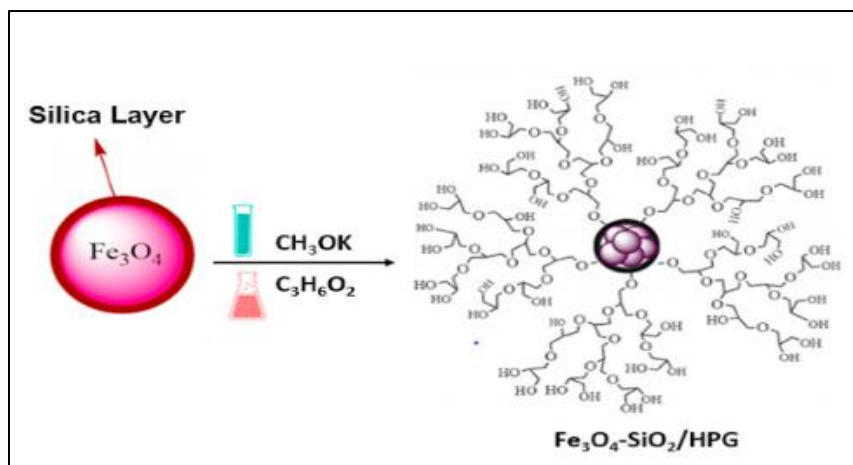
Scheme 4 shows the synthesis of Si-HPG. It is ring-opening polymerization at the hydroxyl groups terminal of the silicon nanoparticles at 140 °C and under an argon environment. Next, the hydroxyl groups terminal of the Si-HPG are reacted with succinic anhydride to produce carboxylic acid terminated silicon nanoparticles (Si-HPGCOOH) with carboxylic acid terminal groups. The last step is to utilize 1-ethyl-3-(3-dimethyl aminopropyl)- carbodiimide hydrochloride (EDC) to produce cyclic RGD peptide-

functionalized silicon nanoparticles (Si-HPG-RGD) [172]. It is ring opening polymerization at the hydroxyl groups terminal of the silicon nano particles at 140 °C and under argon environment. Next the hydroxyl groups terminal of the Si-HPG are reacted with succinic anhydride to produce carboxylic acid terminated silicon nanoparticles (Si-HPGCOOH) with carboxylic acid terminal groups. Last step is to utilize 1-ethyl-3-(3-dimethylaminopropyl)- carbodiimide hydrochloride (EDC) to produce cyclic RGD peptide functionalized silicon nanoparticles (Si-HPG-RGD) [172].



Scheme 4: Synthesis strategy of hyperbranched polyglycerol grafted fluorescent silicon nanoparticles (Si-HPG) and further functionalization with cyclic RGD peptide, [172]

Hyperbranched polyglycerol was introduced to synthesize mesoporous nanosilica particles for drug delivery. A one-pot modified sol-gel method was utilized to dop silica nanoparticles with polyglycerol [173]. Polyglycerol with amino groups was synthesized using the detailed methods in [174-175]. The amino-functionalized polyglycerol was mixed with silicon precursor, which grew nano silica when adding ammonium hydroxide. The mixture was performed overnight under slight vibration. The silica seeds have a Si-OH group that interacts with the amino group from the amino-functionalized polyglycerol by hydrogen bonding or electrostatic forces. This sol-gel hydrolysis condensation reaction resulted in amorphous nano silica coated with polyglycerol. Anti-cancer drugs can be loaded into amorphous nano silica particles and released in an acidic environment. Nano silica can exist in the body through the urinary system [174]. Nanomaterials such as Fe_3O_4 were coated with a layer of silica (Scheme 5) and then attached to hyperbranched polyglycerol. The silica expanded the stability of the nanomaterial, and the final product attached to the hyperbranched polyglycerol was used for enhanced oil recovery [176].



Scheme 5: Fe_3O_4 were coated with a layer of silica and then attached to hyperbranched polyglycerol, [176]

A study [177] aimed to improve the water-based drilling fluid properties using the TiO₂/polyacrylamide (PAM) nanocomposite to control fluid loss and increase viscosity. Polymerization of acrylamide monomer in the presence of TiO₂ nanoparticles using the solution polymerization method was conducted, as shown in Fig.11.

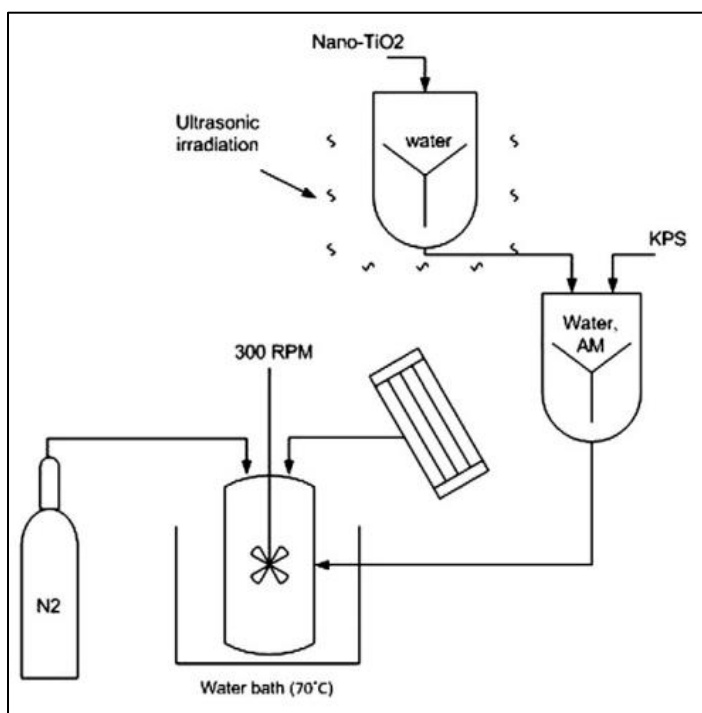
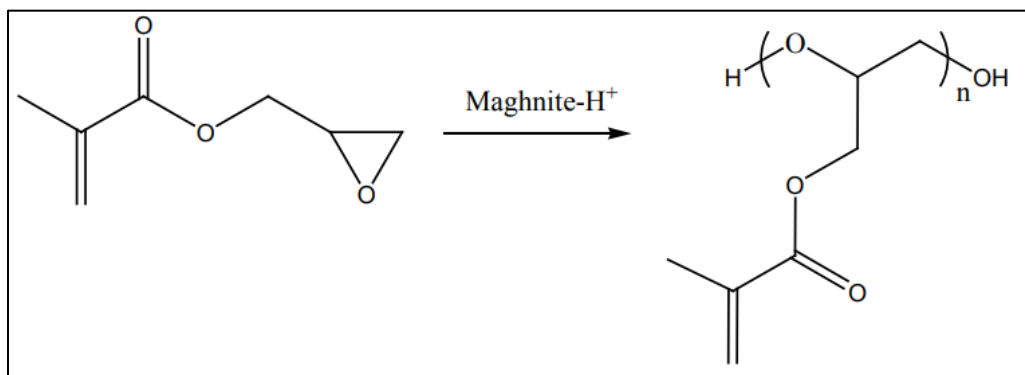


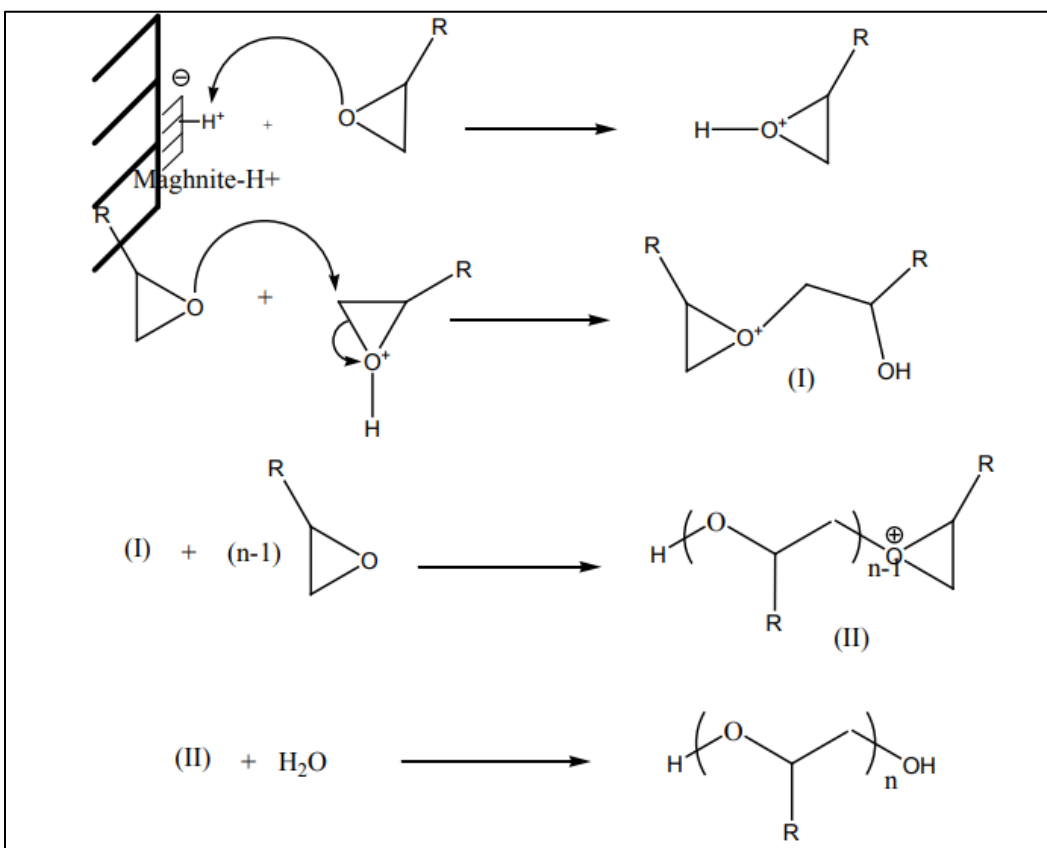
Fig.11: Schematic of the solution polymerization process, [177]

A novel hydrophobic associated polymer-based silica nanoparticle composite with core-shell structure was used to develop an additive for drilling ultra-deep wells under ultra-high temperature, ultra-high pressure, and salinity. It was prepared with Acrylamide, 2-Acrylamide2-methyl propane sulfonic acid, Maleic anhydride, Styrene, and silica nanoparticles via inverse microemulsion polymerization and sol-gel preparation and was

characterized by particle size distribution, SEM, TEM, and ESEM [178]. Maghnite- H^+ was used to initiate ring-opening glycidol methacrylate (GMA) polymerization. The effect of solvent, reaction time, and weight ratio of initiator/monomer were investigated. The result concluded that increasing the initiator leads to faster polymerization but lower polymer weight. Polymerization in solution gives higher polymer weight compared to bulk polymerization. Using a polar solvent led to slow conversion compared to non-polar solvents. The polar solvent reduced the contact between the initiator surface and the monomers. Scheme 6 shows the Ring-opening polymerization of glycidyl Methacrylate by Maghnite- H^+ , and Scheme 7 shows the proposed mechanism [179].



Scheme 6: Ring opening polymerization of glycidyl Methacrylate by Maghnite- H^+ , [179]



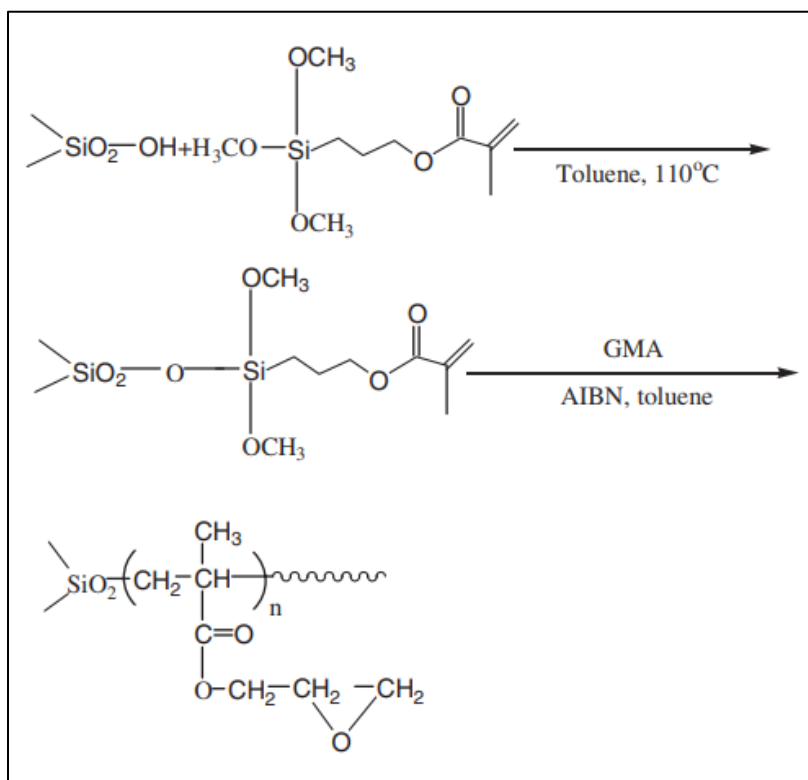
Scheme 7: Mechanism of the ring opening polymerization of Glycidyl Methacrylate catalyzed by Maghnite-H⁺, [179]

Free radical polymerization was conducted to graft polyglycidyl methacrylate onto silane-pretreated nano-SiO₂. The monomer (glycidyl methacrylate) has an unsaturated vinyl group and an epoxide functional group that can be opened by carboxyl, amino, or hydroxyl. The double bond in the monomer can be utilized to construct grafted polymers. Maleic anhydride grafted polypropylene can also be used as a compatibilizer [180].

To introduce a double bond, the OH group with nano SiO₂ was treated with silane. This is a requirement to perform free-radical graft polymerization. Silane was added in excess to the suspension of SiO₂ in 300 ml of toluene. A weight ratio of 1/30 of nano-silica

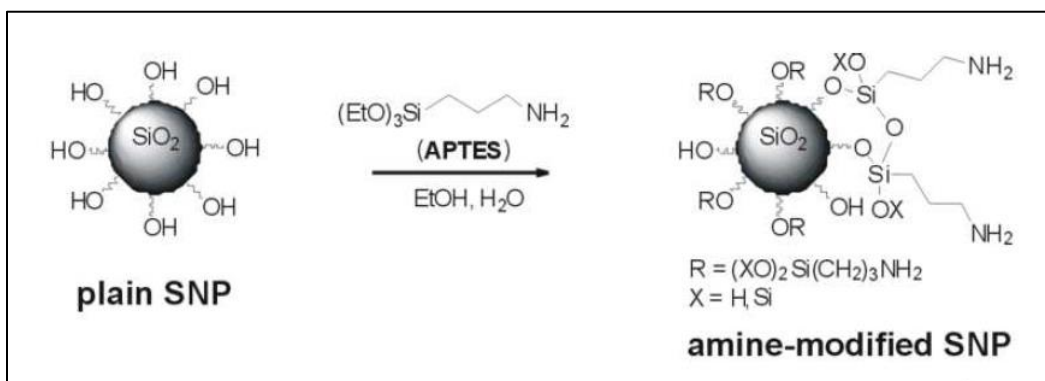
to toluene was used. The suspension solution was ultrasonically aged for 30 minutes and refluxed for 10 hours at 110 °C under nitrogen. Filtration and extraction with alcohol for 24 hours was conducted to remove excessive absorbed silane. Then, drying in an oven at 50 °C for 24 was performed. TGA was used to detect the attached silane [180].

The nano-silica treated with silane was mixed with toluene and sonicated for 30 minutes. Then, the initiator AIBN was added into the reactor under a specific temperature and N₂. 5 minutes later, the monomer was added to the reactor, and the reaction lasted for several hours, Scheme 8. The final grafted polymer was precipitated by pouring a large amount of methanol. The precipitated products were filtered and washed several times with methanol to ensure the removal of residual monomer. Acetone separated grafted SiO-poly glycidyl methacrylate and the generated homopolymerized poly glycidyl methacrylate. The SiO-poly glycidyl methacrylate was then dried at 50 °C. TGA was used to estimate the grafting percentage [180].



Scheme 8: Surface grafting of PGMA onto nano-SiO₂, [180]

Amine-modified silica nanoparticles were synthesized by adding 4.8 grams of nano-silica in H₂O and performing dilution with 100 ml of ethanol/H₂O in a 1:1 ratio, followed by the slow addition of 5 ml (20 mmol) of aminopropyltriethoxy silane (APTES), Scheme 9. Silane oligomer was observed by stirring the suspension solution for three days. Then, the solution was washed with ethanol and centrifuged at 6000 rpm for 20-40 minutes to remove impurities. Ethanol was used to keep the final product [181].



Scheme 9: Synthesis of amine-modified SNP, [181]

Hybrid polymers can have inorganic nanoscale building blocks, for example, nanotubes, layered silicates (e.g., montmorillonite, saponite), nanoparticles of metals (e.g., Au, Ag), metal oxides (e.g., TiO_2 , Al_2O_3). For years, Silica nanoparticles SiO_2 have been a significant and attractive material for academia and industry. Silica/polymer composite has also been discussed in many publications [182]. The polymer component can be introduced as (i) a precursor such as a monomer or an oligomer, (ii) a linear polymer solution or emulsion state), or (iii) a physical polymer network such as semicrystalline linear polymer or chemically, such as thermosets or elastomers. Precursors such as TEOS or (ii) nanoparticles can be introduced as the mineral component [183].

Generally, three methods exist to synthesize polymer/silica nanocomposites (Fig.12). The first method is blending or mixing silica nanomaterials into the polymer. The second method is sol-gel synthesis, which is done during the presence of a polymer or polymerization of the monomer(s). The third method involves the first dispersion of the nano-silica in the monomer(s), then polymerization occurs. Colloids are considered a category of nanocomposites [182].

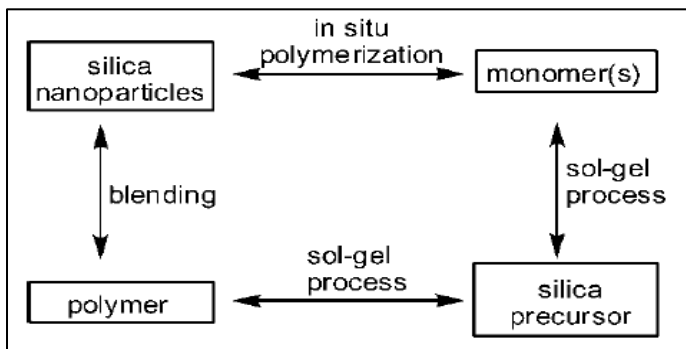


Fig.12: The three general approaches to prepare polymer/silica nanocomposites, [182]

Typically, a hybrid term is used when the sol-gel process forms the inorganic component in situ. Some publications do not distinguish between hybrid and nanocomposites [184]. Silica nanoparticles are typically used with polymers added to the blending and conducting in situ polymerization synthesis. However, silica precursors are used differently by utilizing the sol-gel process. Examples of silica precursors are silicon alkoxides, TEOS and TMOS, PHPS, water glass sodium silicate, and silicic acid. Sometimes, we used alkoxy silane mixtures with polymers as silica precursors in sol-gel synthesis.

Hydrolysis of a TEOS diluted solution in ethanol at high pH produces monodisperse spherical silica particles. This hydrolysis can also be controlled in an inverse microemulsion. Nano silica is available commercially, either as powder or colloid. There are two ways to synthesize the powder form, either by the fuming method or the precipitation method. The precipitation method requires treating silicates with mineral

acids and obtaining hydrated silica particles to be precipitated later. This method is not expected to produce silica nanocomposite since we have more Si-OH groups, which makes the silica easier to agglomerate than the fumed method. The fumed method produces silica in a large, smooth, nonporous surface area, which leads to more vital polymer interaction. Fume silica is white and produced by hydrolyzing SiCl_4 in a flame of hydrogen-oxygen, as shown below in this reaction. The colloidal silica spheres are commonly used in a solution with alcohol or water as a dispersing medium [185-186].

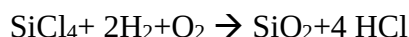


Fig.13 shows a schematic illustration of three types of surfaces of silanol and aggregate formation between fumed silica particles through hydrogen bonding among the silanol groups. The interaction shown in Fig.14 leading to aggregate formation can result from non-strong interaction between polymer and nano-silica [187-188]. The dispersion of nanomaterials, such as nano silica, is a requirement for the properties of the synthesized hybrid system. We may use chemical or physical modification to control interfacial interaction between the polymer and the nanomaterial to achieve good dispersion. There are different methods to increase the compatibility between polymers (hydrophobic) and nano silica (hydrophilic). The most known method is to modify the surface of the nano-silica either by physical or chemical method to increase its dispersion into the polymer matrix [189-190]. a schematic illustration of three types of surfaces silanol and aggregate formation between fumed silica particles through hydrogen bonding among the silanol groups. The interaction shown in Fig.14 leading to aggregate formation can be the result of non-strong interaction between polymer and nano silica [187-188]. Dispersion of nano

materials for example nano silica is a requirement for good properties of the synthesized hybrid system. To achieve good dispersion, we may use chemical modification or physical modification to control interfacial interaction between the polymer and the nano material. There are different methods to increase the compatibility between polymers (hydrophobic) and nano silica (hydrophilic). The most known method is to modify the surface of the nano silica either by physical or chemical method to increase its dispersion into the polymer matrix [189-190].

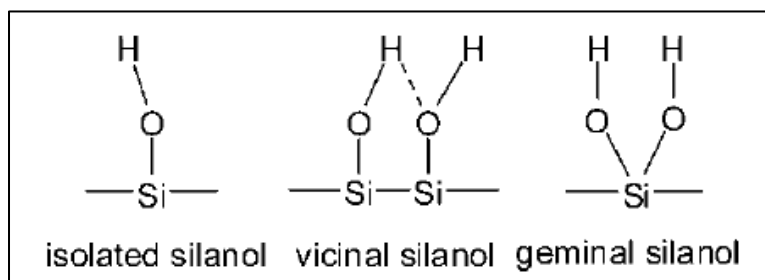


Fig.13: Illustrations of three types of surfaces Silanol, [187]

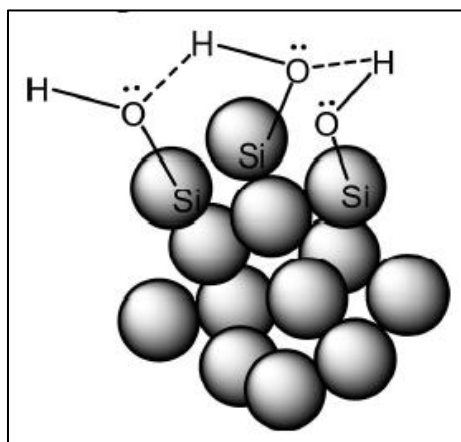


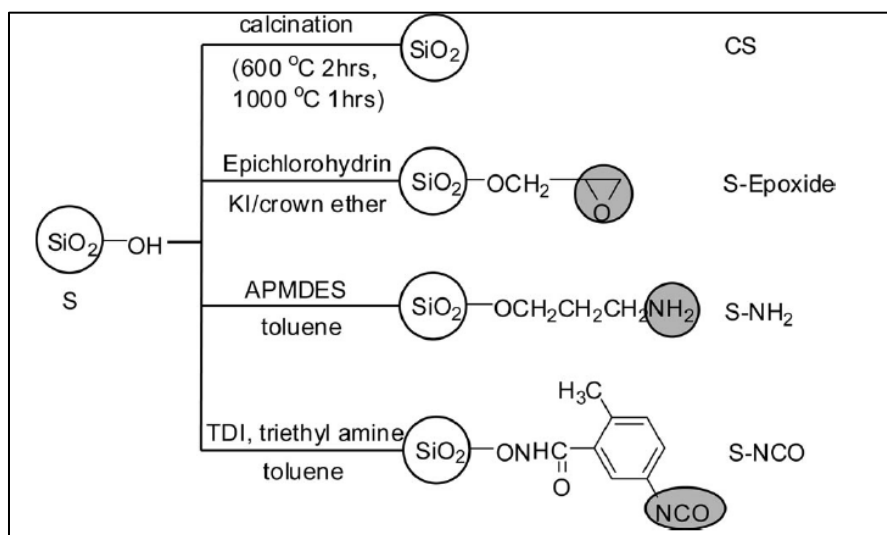
Fig.14: Schematic of aggregate formation between adjacent fumed silica particles through hydrogen bonding among the Silanol groups, [188]

Chemical interaction can be used to modify nano-silica surfaces. We can use either modifier agents or by grafting polymers. Silane coupling is a joint modifier agent. Silane generally has an organofunctional group and a hydrolyzable group. We can present Silane as RSiX , where X is the hydrolyzable end that reacts with the hydroxyl group on the SiO_2 surface, such as ethoxy, methoxy, or chloro. The R is an alkyl chain that reacts with the polymer. Table 1 shows examples of Silane groups for nano-silica surface modification [191-192].

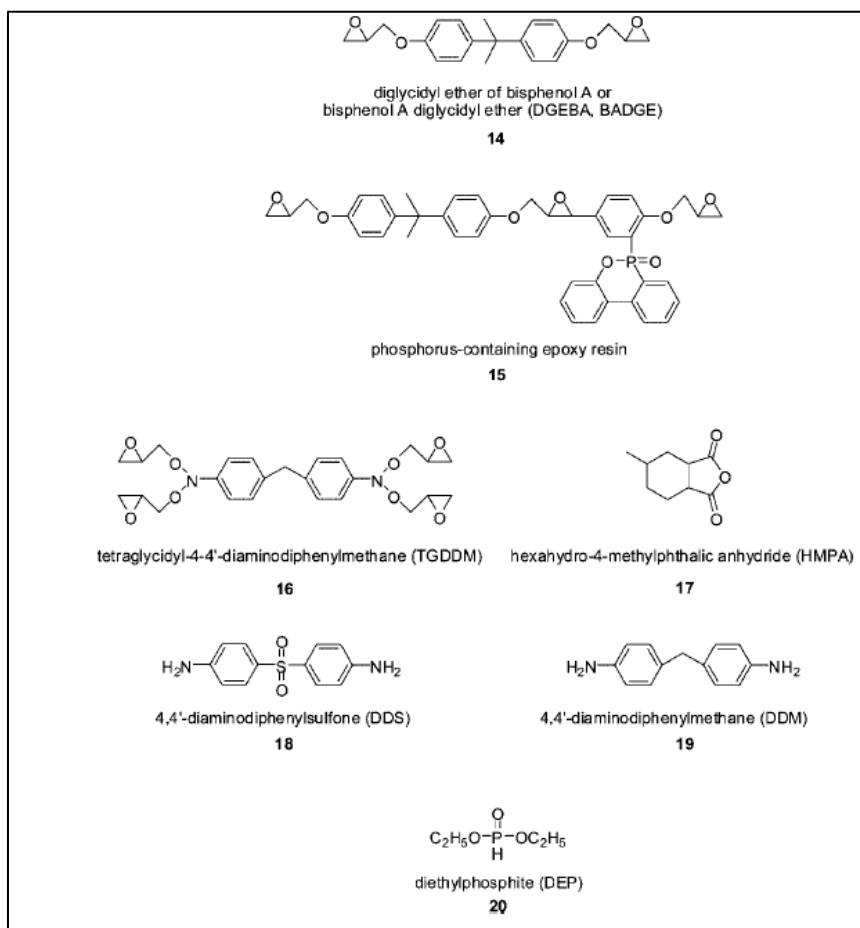
Table 1: Typical Silane Coupling Agents Used for Surface Modification of Silica Nanoparticles, [191-192]

abbreviation	name	chemical struture
APMDES	aminopropyl methyldiethoxysilane	$\text{H}_2\text{N}(\text{CH}_2)_3(\text{CH}_3)\text{Si}(\text{OC}_2\text{H}_5)_2$
APMDMOS	(3-acryloxypropyl)methyldimethoxysilane	$\text{CH}_2=\text{CHCOO}(\text{CH}_2)_3(\text{CH}_3)\text{Si}(\text{OCH}_3)_2$
APTES (APTS, APTEOS, APTTEOS)	3-aminopropyltriethoxysilane	$\text{H}_2\text{N}(\text{CH}_2)_3\text{Si}(\text{OC}_2\text{H}_5)_3$
APTMS (APTMOS, APTMOS)	3-aminopropyltrimethoxysilane	$\text{H}_2\text{N}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$
APTMS (APTMOS)	(3-acryloxypropyl)trimethoxysilane	$\text{CH}_2=\text{CHCOO}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$
APTMS (APTMOS)	aminophenyltrimethoxysilane	$\text{H}_2\text{NPhSi}(\text{OCH}_3)_3$
TESPT	bis(triethoxysilyl)propyl tetrasulfane	$(\text{C}_2\text{H}_5\text{O})_3\text{Si}(\text{CH}_2)_3\text{S}_4(\text{CH}_2)_3\text{Si}(\text{OC}_2\text{H}_5)_3$
DDS	dimethyldichlorosilane	$(\text{CH}_3)_2\text{SiCl}_2$
GPS (GPTS, GOTMS, GPTMOS, KH560)	3-glycidyloxypropyltrimethoxysilane, 3-glycidyloxypropyltrimethoxysilane	$\text{CH}_2(\text{O})\text{CHCH}_2\text{O}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$
ICPTES	3-isocyanatopropyltriethoxysilane	$\text{OCN}(\text{CH}_2)_3\text{Si}(\text{OC}_2\text{H}_5)_3$
MMS	methacryloxymethyltriethoxysilane	$\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_2\text{Si}(\text{OC}_2\text{H}_5)_3$
MPS (MPTMS, MPTS, MAMSE, MATMS, MSMA, TPM, MEMO, KH570)	methacrylic acid 3-(trimethoxysilyl) propyl ester, 3-(trimethoxysilyl)propyl methacrylate, 3-methacryloxypropyltrimethoxysilane	$\text{CH}_2=\text{C}(\text{CH}_3)\text{COO}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$
MPTES	methacryloxypropyltriethoxysilane	$\text{CH}_2=\text{C}(\text{CH}_3)\text{COO}(\text{CH}_2)_3\text{Si}(\text{OC}_2\text{H}_5)_3$
MPTS	mercaptopropyl triethoxysilane	$\text{SH}(\text{CH}_2)_3\text{Si}(\text{OC}_2\text{H}_5)_3$
MTES	methyltriethoxysilane	$\text{CH}_3\text{Si}(\text{OC}_2\text{H}_5)_3$
PTMS	phenyltriethoxysilane	$\text{PhSi}(\text{OCH}_3)_3$
VTES	vinyltriethoxysilane	$\text{CH}_2=\text{CHSi}(\text{OC}_2\text{H}_5)_3$
VTMS	vinyltrimethoxysilane	$\text{CH}_2=\text{CHSi}(\text{OCH}_3)_3$

Epichlorohydrin can also be used to chemical modify the surface of nano silica [193]. To enhance mechanical properties of epoxy resin for molding compounds, silica particle was added. Typically, the nano silica is added first to the epoxy resin then curing agent is added. Schemes 10, 11 and Table 2 show potential epoxy resin and their curing additives. Silica nanocomposite were added into epoxy resin up to 70% without adding silane modifiers. Nano silica effect was also investigated as a curing agent for the epoxy resins. Nano silica showed high reactivity toward epoxy resin at mild conditions. Addition of MgCl_2 showed counter action effect against the curing agent and reduced its activation energy [194].



Scheme 10: The surface modification of silica, [194]

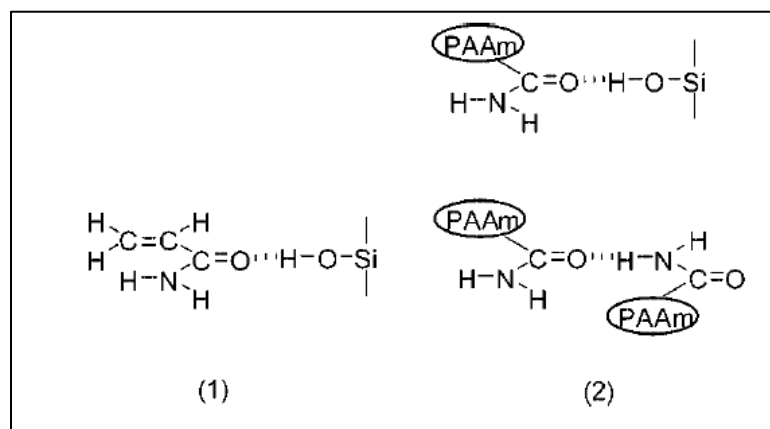


Scheme 11: Typical epoxy resins and hardeners used for the preparation of epoxy/SiO₂ nanocomposites, [194]

Table 2: Examples of Preparation of Epoxy/SiO₂ Nanocomposites by in Situ Polymerization, [194]

epoxy resin type	hardeners	SiO ₂
DGEBA	Z	400 nm, functionalized particles
bisphenol A	DDS	9 nm, PAAM-grafted
DGEBA	aromatic hardener	15 nm
DGEBA	HMPA	100 nm
DGEBA	aliphatic polyamine	~330 or ~75 nm
DGEBA	piperidine	15–50 nm, surface-modified
DGEBA	HMPA	20 nm
DGEBA	DDA	
DGEBA, P-containing epoxy	DDM, DEP	dispersed in MIBK, 10–20 nm
DGEBA	SiO ₂	dispersed in MIBK, 10–20 nm
TGDDM	DDS	dispersed in isopropanol, 10–15 nm
DGEBA	polyamide-amine	

Generally, there are two main approaches either grafting to method that is done by chemically attaching polymers to surface of nano silica or in situ monomer polymerization or grafting from method. Nano silica could be physically modified either by adding surfactants or polymers. The polar group of surfactants will be adsorbed to the silica surface by electrostatic interaction. CTAB can be used to improve interaction between silica and polymer. Stearic acid can also improve dispersion and adhesion between polymer and nano-silica [195-201]. PVA has hydroxyl groups in the repeating units, which can potentially form a strong interaction with the silanol group in the nano-silica. A composite of 30 wt.% nano silica in PVA has produced a matrix with a three-dimensional network [202]. Polymers with amide groups, such as PA, PAAM, and PU, are suitable to prepare hybrid polymers due to the NH₂CO group, which can easily form hydrogen bonding with the silanol groups, scheme 12 [203-204].



Scheme 12: The tentative modes of hydrogen bonding in the monomer (structure 1) and polymer (structure 2), [203]

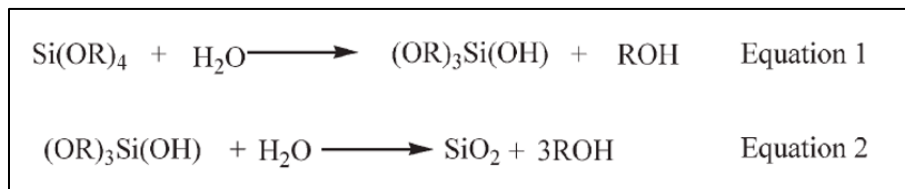
Some factors can affect the grafting process, for example, contamination from non-grafted polymer, the difficulty separating grafted chains from non-grafted ones, and prevention of further grafting due to substantial hindrance between grafted polymer chains. The "grafting-from" technique is also called surface-initiated polymerization. Polymerization starts from initiators on mineral surfaces, producing "hairy nanoparticles" or "polymer brushes." Different polymerization was conducted utilizing the "grafting-from" techniques such as free radical polymerization, living anionic polymerization, living cationic polymerization, ring-opening polymerization, and others. The most common one is controlled radical polymerization, including its three categories: atom transfer radical polymerization (ATRP), free-radical polymerization, reversible radical addition, fragmentation, and transfer (RAFT) polymerization [205].

Inorganic material surfaces can be functionalized with polymer by chemical modifiers for covalent bonding formation or physically by utilizing sticky segments in the synthesis, leading to non-covalent bonding. Non-covalent bonding utilizing the physical method is based on adsorption, which is reversible, which makes it an unfavored method of synthesis. Covalent grafting synthesis is the recommended method for a stable interfacial result. Covalent grafting synthesis can be divided into "grafting from" and "grafting-to." The grafting-to-synthesis is achieved by reacting the macromolecule with the suitable surface group. However, we can have low grafting densities due to the steric effect of reactive previously attached polymers [206].

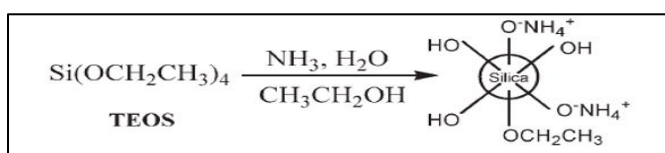
The "grafting-from" synthesis can solve the abovementioned issue for the "grafting-to" method. In the "grafting-to," an initiator is used to modify the particles' surface, and then polymerization is performed. The steric barrier in the "grafting-from" synthesis by the grafted chains will not block further monomers from initiation sites, resulting in higher grafting density than in the "grafting-to" synthesis. The "grafting-from" synthesis, also known as surface initiation polymerization, can be achieved by different polymerization mechanisms [207-208].

Many inorganic materials could be used for inorganic-organic hybrid materials. The most common ones are the silica-polymer hybrid materials due to their wide use and ease of synthesis. Nano silica has been used to manufacture paints, rubber, plastics, and other essential products. Coated silica particles are used for stationary chromatography phases, heterogenous catalysts, sensors, and aerospace [209-213]. In a solvent of alcohol, water, and ammonia as a catalyst, hydrolysis and condensation of tetraethyl orthosilicate (TEOS) takes place to produce TEOS monomer, as shown in Scheme 13. Electrostatic

repulsion from ammonia ions in solution stabilizes the produced nano-silica, Scheme 14 [214-217].

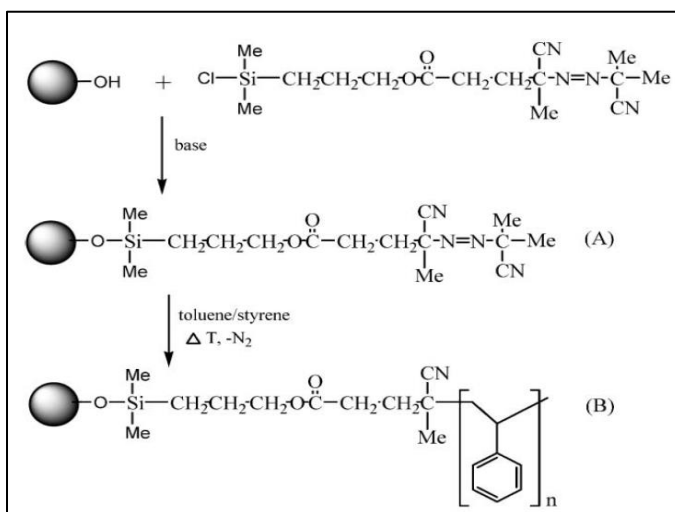


Scheme 13: Synthesis of silica particles, [214]



Scheme 14: Stabilization of the silica particles, [215]

Due to the hydroxy groups on the surface of the silica particles, we can attach organic compounds to act as initiators for required polymerization synthesis. An azo initiator was grafted onto a particle on a flat silica surface to initiate radical chain polymerization of styrene, Scheme 15 [218-219]. Table 5 shows previously investigated monomers, common coupling agents, or chemical modifiers [220-223]



Scheme 15: An azo initiator was grafted onto a particle on flat silica surface to initiate radical chain polymerization of styrene, [218-219]

Table 5: Previous investigated monomers and common coupling agent or chemical modifiers, [220-223]

Coupling reagent	Polymer
3-Methacryloxypropyl trimethoxysilane (MPS)	PS, PMAA, PS- <i>co</i> -PBuA,
Methacryloxy methyltriethoxysilane (MMS)	PS
Oleic acid	PS

The immobilization of polyglycidol onto solid substrates and the subsequent production of polymer coatings has received only a small amount of scientific attention, even though polyglycidol, in both its linear and branching architectural forms, possesses unique qualities. Grafting-to and grafting-from are the two primary methods that are utilized for attaching polyglycidol with flat surfaces or nanoparticles, respectively (Fig.15). Both approaches result in the formation of covalent bonds between the polymer and the support, which is necessary for the formation of a stable layer. In preparing surfaces with linear or branched polyglycidol, the grafting-to procedure was given the majority of the attention [224-228].

In this method, a polymer that has already been synthesized and contains a functional group somewhere along the polymer chain reacts with complementary functional groups placed on the substrate. The reactive function, such as triethoxysilyl, amine, or thiol, was inserted at the chain-end of the polymer in the instance of linear polyglycidol. The interaction of the outer hydroxyl groups of hyperbranched or dendritic polyglycidols with a molecule that introduced a reactive function, such as thiol, amine, or triethoxysilyl, was often the method that was used to modify the polyglycidols. When using a polymer that has low molar mass dispersity, the grafting-to approach produces polymer layers that are generally homogeneous. Because the polymer chains already attached to the support can screen out some of the reactive sites on the support, achieving a high grafting density can be challenging. In most cases, one can obtain fragile layers [229].

In addition to this name, the grafting-from approach is known as surface-initiated polymerization (SIP). Initiation of polymerization occurs as a result of the initiator being connected to the substrate in this process. In most cases, radical polymerizations are

utilized to modify grafted-from polymers; cationic and anionic polymerizations may also be utilized. When using this procedure, you will end up with a surface made of functional polymer brushes that have a greater thickness and a higher density than those produced by the grafting-to method. However, this method is complex to implement technically, and the resulting polymer brushes are often highly heterogeneous in composition. In polyglycidol-based surfaces, the grafting-from technique was utilized in the works that involved the immobilization of linear and hyperbranched polyglycidol on two-dimensional materials [229].

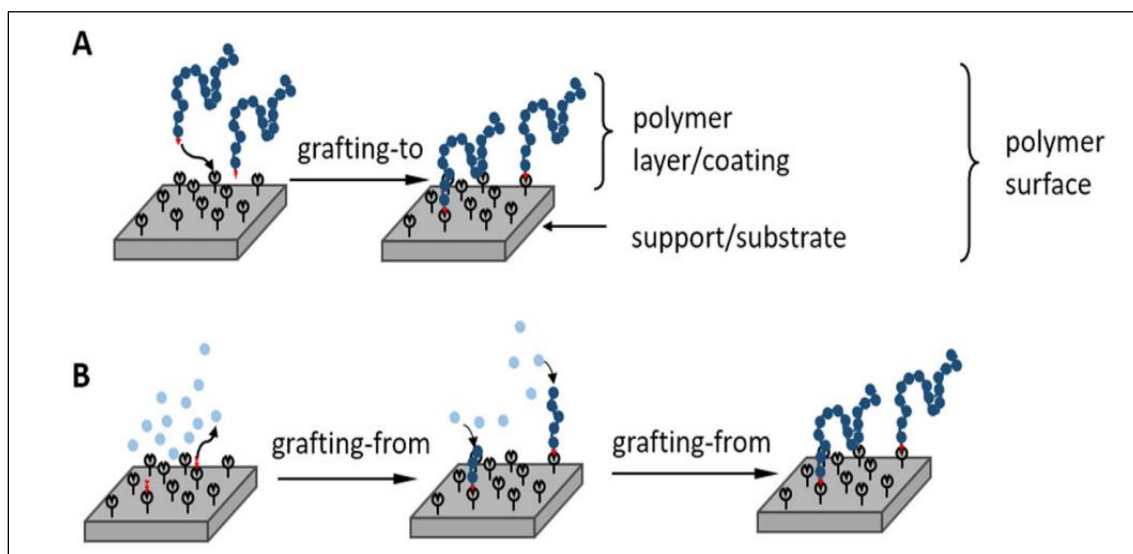


Fig.15: The plan for the formation of covalent bonds between a polymer and a solid support by means of the (A) grafting-to and (B) grafting-from approaches, [229]

CHAPTER 3

RESEARCH OBJECTIVES

3.1 Problem Statement

Oil-based drilling fluids can be used because they show good performance at high temperatures, excellent inhibition for water-sensitive shales, and a high rate of penetration. However, oil-based drilling fluids are known to be toxic to the environment, and there is always a high cost associated with them and required disposal techniques. In addition, oil-based fluids can damage the elastomeric parts of downhole drilling tools.

3.2 Thesis Objectives

The objective of this dissertation can be summarized as follows:

- To synthesis different hyperbranched polymers and hyperbranched hybrid polymers with suitable functionalities for water-based drilling fluids to replace oil-based fluids
- To formulate water-based drilling fluids using synthesized hyperbranched polymers and hyperbranched hybrid polymers
- Conduct performance testing for viscosity at 300 °F (149 °C) and optimize formulations as needed
- Conduct performance testing for shale inhibition and optimize formulations as needed

3.3 Thesis Milestones

Task 1 – Synthesis of Various Modified Hyperbranched PEI Polymers

I will synthesize a range of modified branched PEI for trial testing in water-based drilling fluid formulations. The performance (rheology and viscosity) and stability of the formulated drilling fluids, incorporating the synthesized modified branched PEI, will guide our decision-making process in selecting the most suitable conditions (initiator/monomer ratio, acidic vs. basic media). The proposed general molecular structures of branched PEI, depicted in Figs. 16-17.

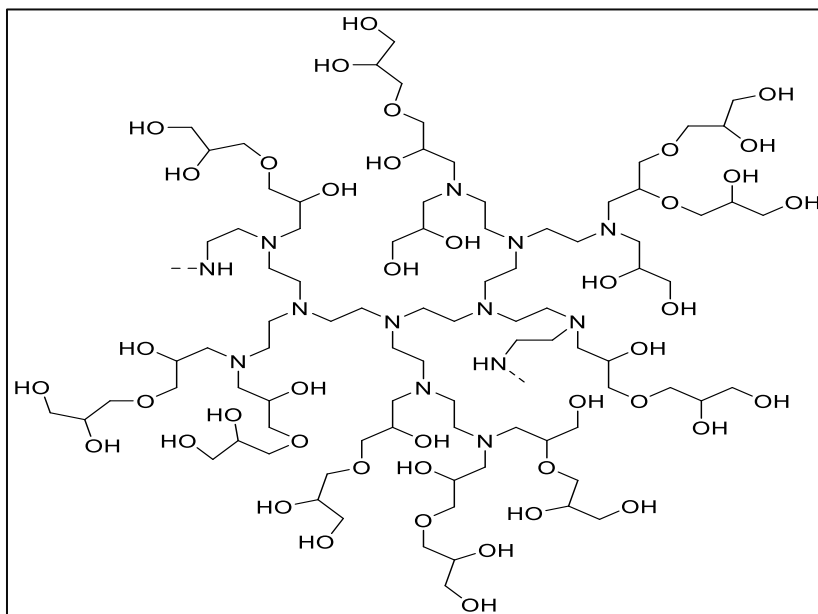


Fig. 16: Polyglycidol substituted PEI

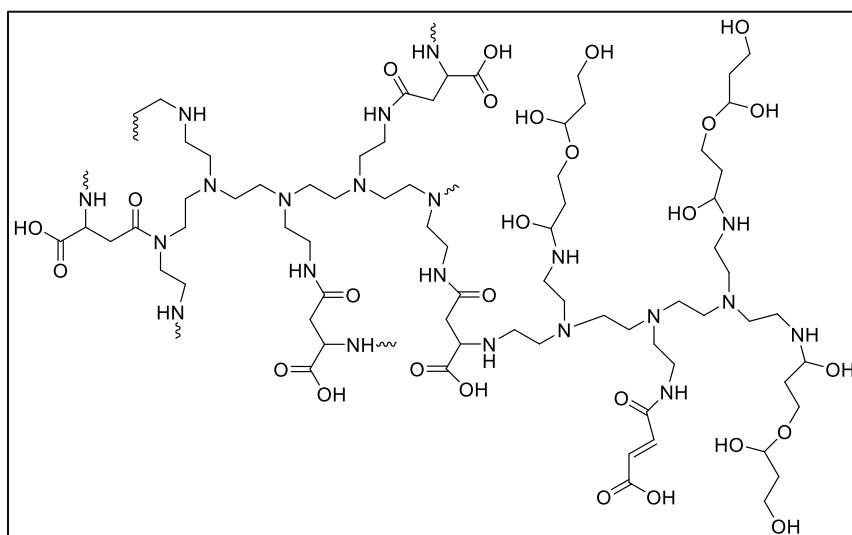


Fig. 17: Maleic anhydride crosslinked hyperbranched PEI

Task 2 – Synthesis of Hybrid Organic-Inorganic Particles for Oil/Gas

Here, we propose inorganic nanoparticles and polymeric ligands (multifunctional polymeric ligands or hyperbranched polymers) based hybrid nanocomposites to act as “nano-shale-fillers” to gate the micro-cracks in rock/shale surface at the same time minimizing the contact of water with shale surface by adjusting the hydrophobic moieties in the corona. We will synthesize nanoparticles with different compositions, morphologies, and dimensions. The nanoparticles will be functionalized using targeted polymeric ligands, Fig. 18. These inorganic-organic hybrid nanocomposites will be employed to enhance their ability to reduce water/shale surface interaction and micro-cracks gating by adjusting the ratio of hydrophobic chains and surface anchoring groups.

The inorganic core will play a dual role: (i) will offer a high surface area to help increase the high density of surface ligands, and (ii) being inorganic will enhance the mechanical properties of nano-shale fillers. The polymeric ligand on the surface of

nanoparticles will offer a suitable functional group to selectively bind to the shale surface and enhance hydrophobicity to minimize the direct contact of water with the shale surface.

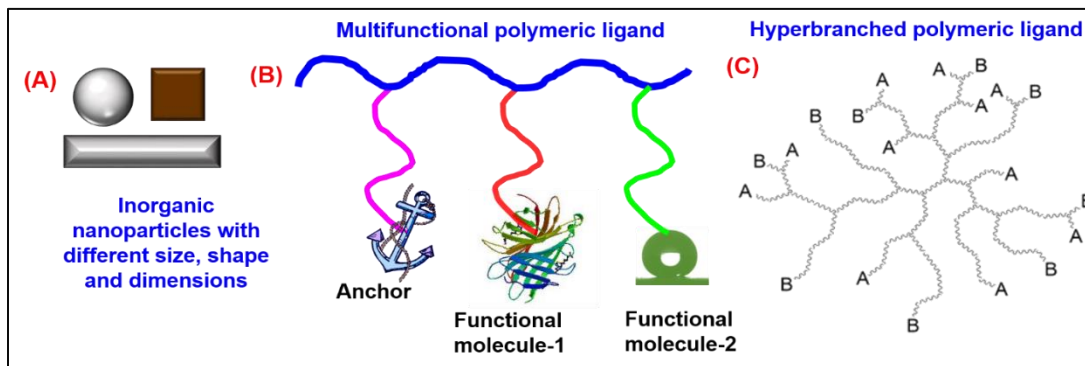


Fig.18: Schematic representation of different building blocks; (A) inorganic nanoparticles, (B) multifunctional polymeric ligands and (C) hyperbranched polymer-based surface ligands.

Task 3 – Characterization

We will use NMR mainly and other analytical methods to characterize the synthesized branched PEI and other additives to relate the branching degree to the performance in water-based drilling fluids. Analytical methods will also characterize the synthesized inorganic nanomaterials and polymeric ligands.

Task 4 –Fresh Water Based Drilling Fluids Performance Testing

We will conduct standard and API tests that are accepted by the industry to prepare and characterize drilling fluids. The tests that are covered here are fluids preparation, density and rheology measurements, API and HT/HP filtration and thermal stability tests.

Task 5 – Contamination and Salts Compatibility Testing

We will investigate the stability and tolerance of the synthesized branched polymers against contamination and different types of salts at different concentrations.

CHAPTER 4

SYNTHESIS OF VARIOUS MODIFIED HYPERBRACHED PEI POLYMERS

We have conducted a meticulous synthesis of various modified branched PEI, which are now ready to be trial-tested in water-based drilling fluid formulations. The performance (rheology and viscosity) and stability of the formulated drilling fluids, meticulously designed around the synthesized modified branched PEI, will provide robust support for our decision on selecting suitable conditions (initiator/monomer ratio, acidic vs. primary media). Table 1 presents the polymer synthesized in terms of initiator and glycidol details, a testament to the precision and thoroughness of our research. Our objective was to identify the optimum initiator-to-monomer ratio, a task we approached with utmost care and attention.

Table 3: Polymer synthesized in terms of initiator and glycidol details

Polymer #	60K PEI as Macro initiator, grams	Glycidol as Monomer, grams	PEI: Glycidol Weight Ratio
1	4	20	1:5
2	10	20	1:2
3	4	60	1:15
4	60	15	4:1
5	15	15	1:1

Materials

Additional synthesis was performed using different chemicals. This section details the polymers based on their code (AY).

Polymer AY1001A

- 300 ml N-Methylpyrrolidone (NMP) solvent
- 10 grams of 800 g/mole PEI
- 6.8 grams maleic anhydride (MA)
- 80 ml of Triethylamine (TEA)
- 100 ml of DI water

We first measured 10 grams of 800 gram/mole PEI and solubilized it in 150 ml NMP solvent. We then added 80 ml of TEA. TEA is a strong base, and it can completely deprotonate carboxylic acids. We then measured 6.8 grams of MA solubilized 100 ml NMP solvent and slowly added it to the PEI and TEA reaction mixture. Some precipitation was observed, so we added DI water to the reaction. MA was getting attacked by amines so fast

that it generated a hydrophobic salt. The addition of the DI water accelerated the ring opening of MA. An orange color and excess heat indicated the ring opening of MA. The reaction was done at 50 °C for five days. We are adding 10 ml of DI every day to ensure the completion of the MA ring opening. The reaction was completed due to the observed increase in solution viscosity. We have taken 2/3 of the solution and performed dialysis. Potassium hydroxide was added to the dialysis step. The polymer was transferred later for drying.

Polymer AY1001B

- 300 ml N-Methylpyrrolidone (NMP) solvent
- 10 grams of 800 g/mole PEI
- 6.8 grams maleic anhydride (MA)
- 80 ml of Triethylamine (TEA)
- 100 ml of DI water
- 30 ml glycidol

We have taken 1/3 of the polymer AY1001A solution and added 30 ml of glycidol. We want to see if the Polymer AY1001A also worked as an initiator for glycidol ring opening and observe any added benefit in drilling fluids. A potassium hydroxide solution was added to the dialysis step. The polymer was transferred later for drying.

Polymer AY1002

Monomer Design

- 10.5 ml Diethanol Amine
- 10.5 grams Maleic anhydride

- 200 ml NMP solvent
- 20 ml TEA

In this step of the reaction, we designed and synthesized our monomer using NMP solvent and TEA. We conducted the reaction at 50 °C over night.

Initiator Design

- 30 grams of 60K PEI
- 50 ml of DI water
- 50 ml NMP solvent

We added the mixed initiator solution to the monomer solution at 50 °C and let the reaction occur until it became slightly viscous. A potassium hydroxide solution was added to the dialysis step. The polymer was transferred later for drying.

Polymer AY1003

- 33 grams 10 K PEI
- 400 ml DI
- 3.0 grams Maleic anhydride
- 40 ml Triethanol amine
- 20 ml glycidol

MA was added step-wise over 2 hours. Triethanol amine helps in the solubility of MA in solution. Triethanol amine was added twice in 20 ml intervals. The reaction was kept for days at 50 °C until a viscosity increase was observed. A potassium hydroxide solution was added to the dialysis step. The polymer was transferred later for drying.

Polymer AY1004 & AY1005

- 33 grams 10 K PEI
- 400 ml DI
- 6.0 grams Maleic anhydride
- 160 ml Triethanol amine

MA was added step-wise over 4 hours. Triethanol amine helps in the solubility of MA in solution. Triethanol amine was added in two intervals. The first interval was 20 ml in the middle of the MA addition. The second interval was 140 ml at the end. The reaction was kept for days at 50 °C until a viscosity increase was observed. 10 ml DI of water was added daily to the reaction mixture. A potassium hydroxide solution was added to the dialysis step. We added KOH to ensure that the carboxylic acid of MA is in salt form in the final polymer. The polymer was transferred later for drying. In polymer AY1005, the same procedure was repeated, but we added triethanol amine in steps as we added MA in steps to compare the performance and validate the synthesis.

Polymer AY1006

- 10 ml ARC Control
- 300 ml DI
- 30 ml glycidol

The ARC control is a mixture of polyamines that are manufactured locally. We wanted to use it as an initiator for glycidol ring opening. We kept the reaction for seven days at 50 C. We added KOH, which was unnecessary since we have no carboxylic acid

and the polyamine is a base. KOH was added only at the dialysis stage. The polymer was transferred for drying.

Polymer AY1007

- 10 ml ARC Control
- 300 ml NMP solvent
- 30 ml glycidol

In polymer AY1007, we have repeated AY1006 exactly but changed the solvent type from DI water to NMP solvent.

Polymer AY1008&AY1009

- 10 ml ARC Control
- 300 ml DI water or 300 ml NMP solvent
- 30 ml C12-C14-alkylglycidyl ether (oxirane, mono[(C12-14-Alkyloxy)methyl] derivatives

In polymer AY1008, we wanted to see if we could form a polymer by using ARC control as our initiator for the ring opening of the epoxy resin. The difference between AY1008 and AY1009 was the type of solvent.

Polymer AY1010

- 10 grams of 10K PEI
- 300 ml DI water
- 30 ml C12-C14-alkylglycidyl ether (oxirane, mono[(C12-14-Alkyloxy)methyl] derivatives

In polymer AY1010, we wanted to see if we could form a polymer by using PEI as our initiator for the ring opening of the epoxy resin. No KOH was added here at the dialysis stage. The polymer was transferred for drying.

Polymer AY1011

- 10 grams of 60K PEI
- 200 ml DI water
- 0.25 Dopamine
- 11.3 ml glycidol

This is a reference polymer to compare against hybrid polymers synthesized using different nanomaterials. We wanted to see the effect on shale inhibition and the high-temperature drilling fluids testing.

Polymer AY1012

Monomer Design

- 5 ml Diethanol Amine
- 6.6 grams Maleic anhydride
- 50 ml NMP solvent
- 10.836 ml TEA

The reaction was kept for three days at 30 °C. Then, 50% of the monomer solution was mixed with 50 ml DI water and purged with Argon for more than 1 hour to remove the oxygen content from the solution. 0.0911 grams of potassium persulfate (K₂S₂O₈) initiator was added under an argon environment, and the free radical polymerization was conducted

at 55 °C. The initiator was dissolved, and the reaction was kept for 2 days. KOH was added only at the dialysis stage. The polymer was transferred for drying.

Polymer AY1013

Monomer Design

- 5 ml Diethanol Amine
- 6.6 grams Maleic anhydride
- 50 ml NMP solvent
- 10.836 ml TEA

The reaction was kept for three days. The first-day reaction was kept at 40°C, then the temperature was raised to 80°C for two days. Then, 50% of the monomer solution was mixed with 50 ml NMP solvent and purged with argon for more than 1 hour to remove oxygen content from the solution. 0.0911 grams of potassium persulfate ($K_2S_2O_8$) initiator was added under an argon environment, and the free radical polymerization was conducted at 100 °C. The initiator was dissolved, and the reaction was kept for two days. KOH was added only at the dialysis stage. The polymer was transferred for drying.

Polymer AY1014

Monomer Design

- 5 ml Diethanol Amine
- 6.6 grams Maleic anhydride
- 50 ml NMP solvent
- 10.836 ml TEA

The reaction was kept for three days. The first-day reaction was kept at 40°C, then the temperature was raised to 80°C for two days. Then, 50% of the monomer solution was mixed with 50 ml DMSO solvent and purged with argon for more than 1 hour to remove oxygen content from the solution. 0.02762 grams of Azobisisobutyronitrile (AIBN) initiator was added under an argon environment, and the free radical polymerization was conducted at 100 °C. The initiator was dissolved, and the reaction was kept for two days. KOH was added only at the dialysis stage. The polymer was transferred for drying.

Polymer AY1015

- 10 grams of 10K PEI
- 300 ml DI water
- 2 grams or 2.247 ml of C12-C14-alkylglycidyl ether (oxirane, mono[(C12-14-Alkyloxy)methyl] derivatives

Polymer AY1017

- 10 grams of 10K PEI
- 300 ml DI water
- 0.2 grams or 0.22 ml of C12-C14-alkylglycidyl ether (oxirane, mono[(C12-14-Alkyloxy)methyl] derivatives

Polymer AY1018

- 10 grams of 10K PEI
- 300 ml DI water
- 0.25 ml of C12-C14-alkylglycidyl ether (oxirane, mono[(C12-14-Alkyloxy)methyl] derivatives

Polymer AY1019

- 10 grams of 10K PEI
- 300 ml DI water
- 0.025 ml of C12-C14-alkylglycidyl ether (oxirane, mono[(C12-14-Alkyloxy)methyl] derivatives)

In the above polymers, we wanted to see if we could form a polymer by using PEI as our initiator for the ring opening of the epoxy resin. Similar to AY1010 but with lower concentrations of the epoxy resin. No KOH was added here at the dialysis stage since PEI is basic. However, we have divided the final polymer solutions into two parts. We added HCl acid in one part to compare the performance of drilling fluids later. Both polymer solutions, acidic and basic, were transferred for drying.

Polymer AY1020

- 1 grams of 600 PEI
- 50 ml DI water
- 50 ml glycidol

In the above polymers, we wanted to confirm that we performed polymerization in DI water solvent where the proton transfer termination mechanism was accessible. Only a tiny amount of low polymer weight initiated the glycol monomer ring opening

Polymer AY1021

- 2 grams of 600 PEI
- 50 ml NMP solvent
- 50 ml glycidol

A small amount of low polymer weight was used as an initiator for the glycol monomer ring opening. The difference between polymer AY1020 and AY1021 is in the solvent type. We want to compare the difference in performance and yield between DI and NMP as solvents.

Polymer AY1022

- 2 grams of 60K PEI
- 100 ml NMP solvent
- 100 ml glycidol

Polymer AY1023

- 2 grams of 60K PEI
- 100 ml NMP solvent
- 100 ml glycidol

To initiate the glycol monomer ring opening, a small amount of higher polymer weights of 60 K PEI and 10 K PEI was used. We wanted to compare the performance and yield of a higher polymer weight of 60 K gram/mole and 10 K gram/mole PEI against 600 grams/mole.

Polymer AY1024

- 350 ml DI water
- 0.30 gram of XC polymer (Xanthan Gum)
- 50 ml glycidol
- 0.1 gram KOH

A small amount of XC polymer was added to DI water. The solubility of the XC polymer was not complete, which was evident in the cloudy color of the solution. The objective of this synthesis was to modify the XC polymer by trying to use it as an initiator for the ring opening of the glycidol monomer. The XC polymer has OH, which could be used as an initiator but would require high temperature, which could break down the backbone of the XC polymer. Another more suitable approach was to add KOH to deprotonate the OH group in the XC polymer to make it suitable for ring opening the glycidol. The reaction was kept for days at 50 °C.

Polymer AY1025

- 350 ml DI water
- 0.30 gram of XC polymer (Xanthan Gum)
- 0.1 gram KOH
- 1 gram of maleic anhydride polymer dissolved in 50 ml DMF solvent (Dimethyl formamide)
- 0.5 gram of KOH

A small amount of XC polymer was added to DI water. The solubility of the XC polymer was not complete, which was evident in the cloudy color of the solution, even after heating it at 80 °C for two days. Next, we dissolved 1 gram of MA polymer in 50 ml DMF solvent by sonication for 5 minutes. The MA solution was added slowly into the reaction mixture of XC polymer. The solution color became light blue. The pH was four after adding the MA polymer solution for one day. A reduction of the neutral pH to 4

indicates the ring opening of MA by the deprotonated XC polymer. An additional amount of 0.5 grams of KOH was added to raise the pH to 8, and the temperature was raised to 80 °C for one day to ensure a complete ring opening of the MA polymer. This system aimed to synthesize the XC modification by using it as an initiator for the ring opening of the MA anhydride mixture solution, which was apparent in color, indicating the XC polymer's complete solubility. Temperature was reduced to 50 °C, and the reaction resumed for a few days. KOH was used to deprotonate the OH group in the XC polymer, making it suitable for ring opening the MA polymer. The solution became yellow, which indicated the complete ring opening of the MA polymer. The reaction was stopped, and the polymer was transferred for drying.

Polymer AY1026

- 350 ml DI water
- 0.30 gram of XC polymer (Xanthan Gum)
- 0.6 gram KOH
- 1 gram of maleic anhydride polymer dissolved in 50 ml DMF solvent (Dimethyl formamide)
- 50 ml glycidol

A small amount of XC polymer was added to DI water, and the pH was measured to be 7. After adding 0.6 grams of KOH, the pH was recorded to be 12. Next, we dissolved 1 gram of MA polymer in 50 ml DMF solvent by sonication for 5 minutes. The MA solution was added slowly into the reaction mixture of XC polymer. The solution color became light blue. The reaction was run at 80 C for two days, and the pH was measured at 9. After that,

glycidol was added at intervals of 10 ml per day at 50 °C, and pH was measured at 9-10. The objective of this synthesis was to use the modified XC -MA polymer as an initiator for glycidol ring opening. The solution became yellow, indicating the complete ring opening of the MA polymer. The reaction was stopped, and the polymer was transferred for drying.

Polymer AY1027

- 350 ml DI water
- 0.30 gram of XC polymer (Xanthan Gum)
- 0.6 gram KOH
- 50 ml glycidol
- 1 gram of maleic anhydride polymer dissolved in 50 ml DMF solvent (Dimethyl formamide)

A small amount of XC polymer was added to DI water, and the pH was measured to be 7. After adding 0.6 grams of KOH, the pH was recorded to be 12. Next, we added 50 ml glycidol at 50 C and ran the reaction for one day. The pH was measured at 12. Then, we dissolved 1 gram of MA polymer in 50 ml DMF solvent by sonication for 5 minutes. The MA solution was added slowly into the reaction mixture of XC polymer. The solution color became light blue. The reaction was run at 50 °C for one day, and the pH was measured to be 9, but the solution was clear in color. We then increased the temperature to 80 °C and kept the reaction for three more days. The objective here was to use the XC-glycidol mixture to initiate the ring opening of the MA polymer. The solution became yellow, which indicated the complete ring opening of the MA polymer. The reaction was stopped, and the polymer was transferred for drying.

CHAPTER 5

SYNTHESIS OF HYBRID HYPERBRACHED

POLYMERS WITH SUITABLE FUNCTIONALITIES

Materials

Many hybrid polymers were synthesized using different chemicals and materials. This section will detail hybrid polymers based on their code (AYN). PEI 10 K and 60 K were used to synthesize the hybrid polymers. Figs. 19 and 20 show their DSC-TGA.

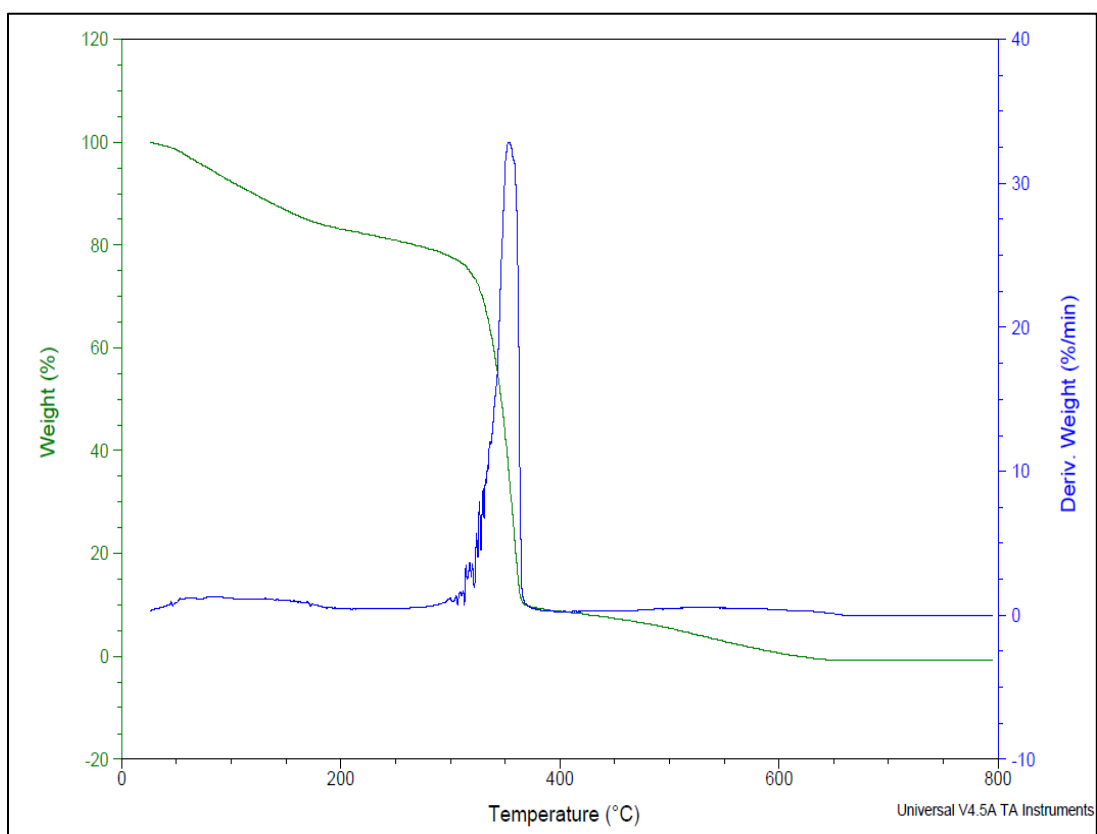


Fig19: DSC-TGA of 10 K PEI

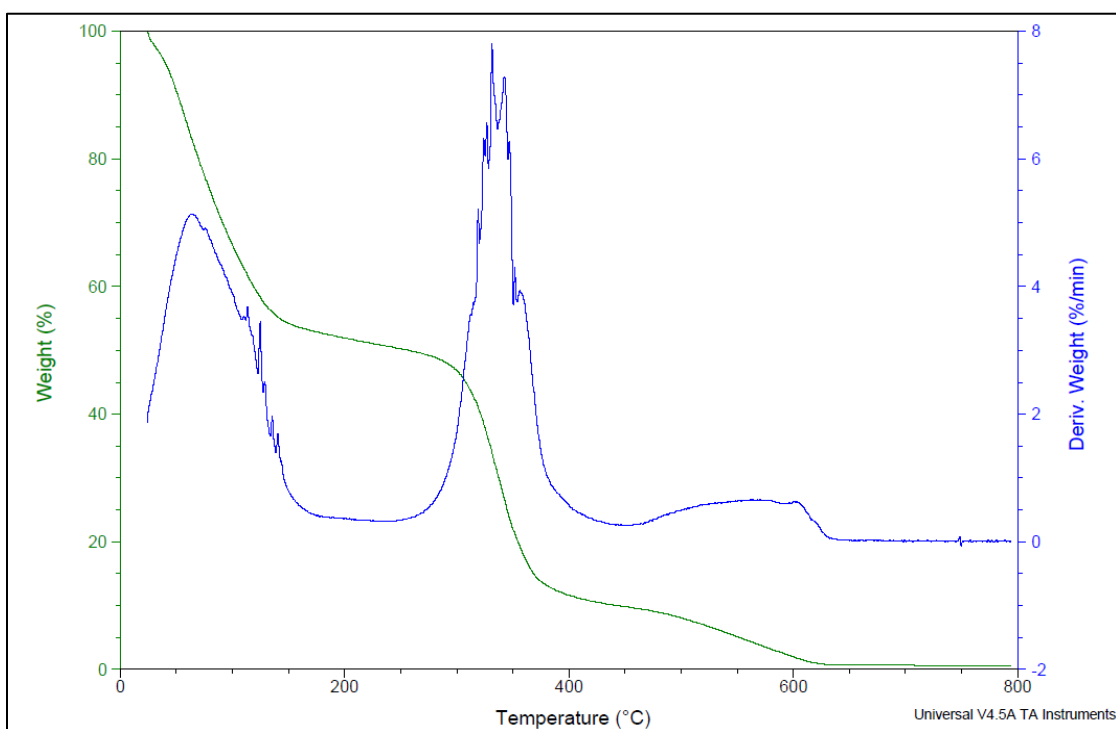


Fig20: DSC-TGA of 60 K PEI

Hybrid polymer AYN1001

- 300 ml DI water
- 5 ml post functionalized nano silica (Levasil CS40-222)
- 5 ml glycidol
- 30 grams of 60K PEI
- 10 ml glycidol

There was a severe separation of the nano-silica out of the polymer solution, so the polymerization reaction was stopped. The reaction was done at 50 °C.

Hybrid polymer AYN1002

- 10 ml post functionalized nano silica (Levasil CS40-222)
- 200 ml of NMP (N-Methyl-2-pyrrolidone 99%) solvent
- 10 ml of glycidol

We heated the aqueous nano-silica in the NMP for 3 hours at 100 °C to remove all the water within the nano-silica solution. Then, we added the glycidol and kept the reaction overnight at 100 °C. The nanomaterials separated severely. The nano-silica did not act as an initiator for the ring opening of the glycidol. Fig. 21 shows the DSC-TGA.

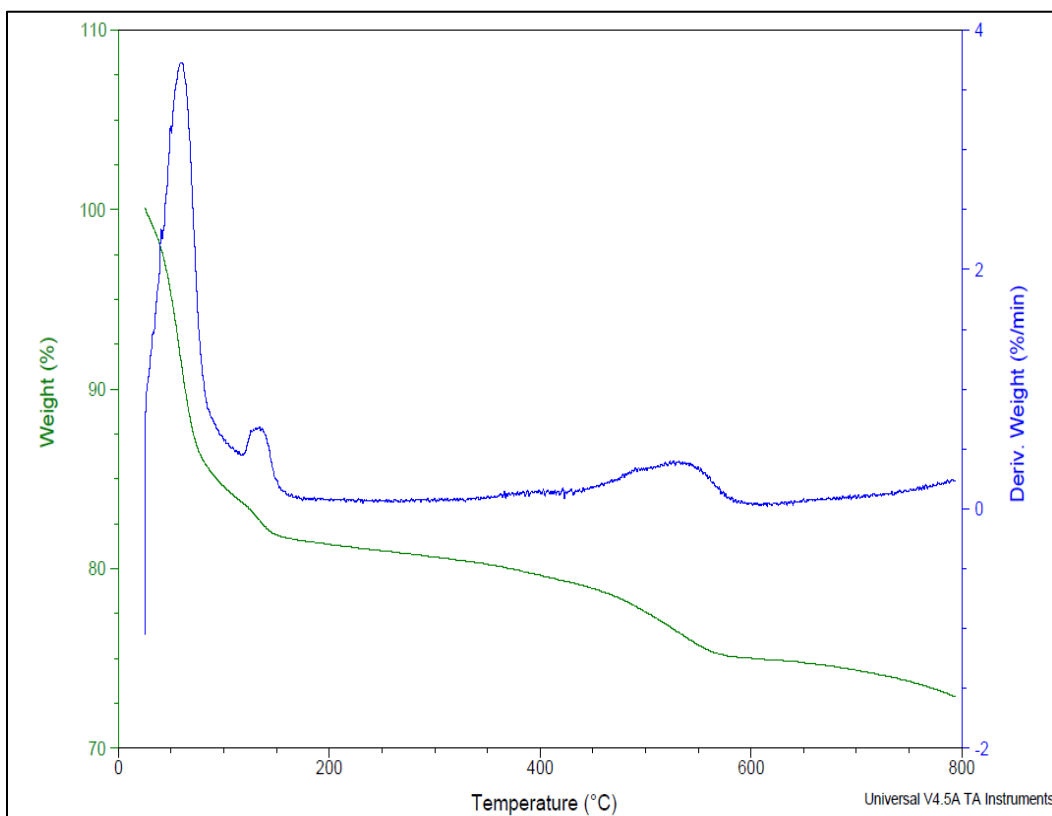


Fig.21: DSC-TGA of AYN-1002

Hybrid polymer AYN1003

- 10 ml post functionalized nano silica (Levasil CS40-222)
- 200 ml of NMP (N-Methyl-2-pyrrolidone 99%) solvent
- 1.0 gram of sodium methoxide
- 10 ml of glycidol

Despite our careful execution of the experimental procedure, we encountered an unexpected outcome. After heating the aqueous nano-silica in the NMP for 3 hours at 100 °C to remove all the water within the nano-silica solution, we introduced a strong base of sodium methoxide and allowed it to mix for 15 minutes. We then added the glycidol and

left the reaction to proceed overnight at 100 °C. However, we were confronted with a severe phase separation of the nano-silica materials. It was evident that the addition of the strong base did not facilitate the formation of the hybrid polymer and ring opening of the glycidol, as we had anticipated.

Hybrid polymer AYN1004

- 200 ml of NMP (N-Methyl-2-pyrrolidone 99%) solvent
- 50 ml post functionalized nano silica (Levasil CS40-222)
- 50 ml of glycidol

We heated the aqueous nano-silica in the NMP for 3 hours at 110 °C to remove all the water within the nano-silica solution. We then lowered it to 100 °C to add the glycidol in intervals over four days (20, 10, 10, and 10 ml). We kept the reaction running over five days at 100 °C. Unfortunately, there was a severe phase separation of the nano-silica materials, as depicted in Fig.23. This finding is significant as it indicates a potential limitation in the use of nano-silica. The nano-silica did not act as an initiator for the ring opening of the glycidol, which further adds to the importance of our research. Fig.24 shows the DSC-TGA of AYN-1004.



Fig.23: There was a sever phase separation of the nano silica materials AYN1004

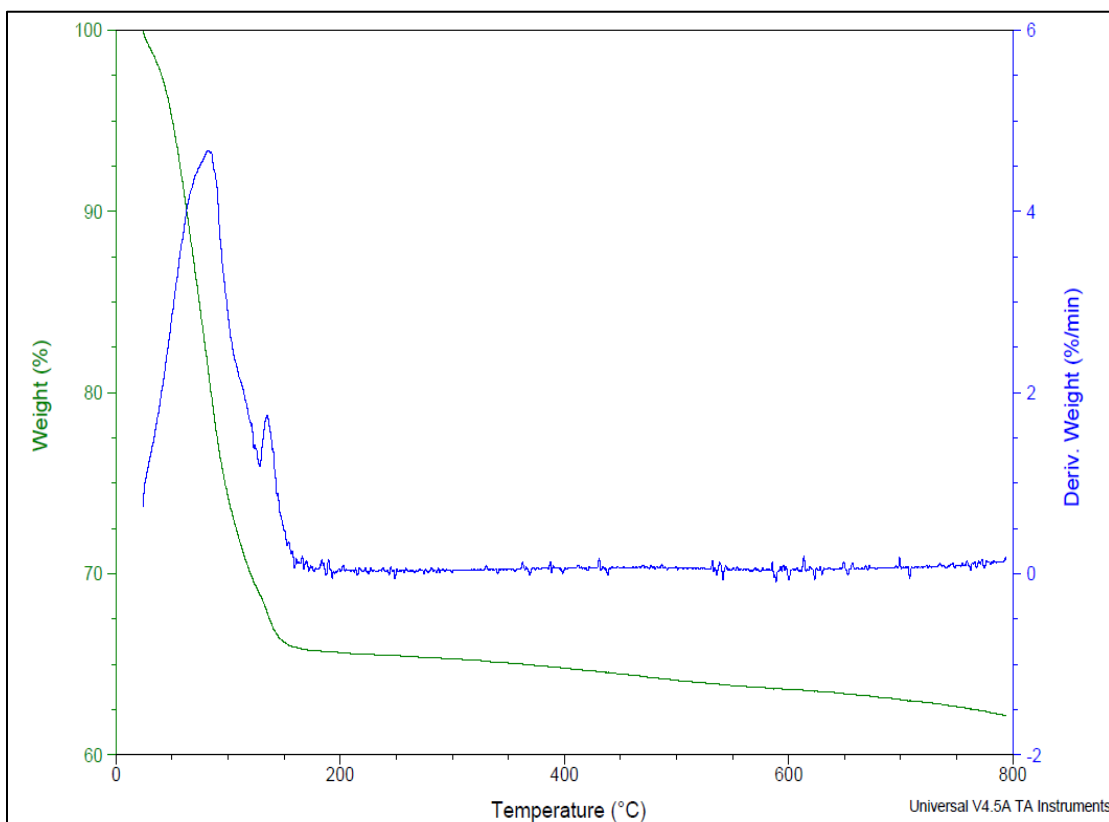


Fig.24: DSC-TGA of AYN1004

Hybrid polymer AYN1005

- 4.8 grams or 10 ml of post functionalized nano silica (Levasil CS40-222)
- 100 ml of ethanol
- 5 ml of (3-Aminopropyl)triethoxysilane (APTES)
- 200 ml of NMP (N-Methyl-2-pyrrolidone 99%) solvent
- 10 ml of glycidol

Following a systematic approach, 4.8 grams of nano silica or 10 ml of the post-functionalized nano silica solution was diluted in 100 ml of ethanol. In a step-by-step manner, 5 ml of the APTES was drop-wise added to the silica suspension solution. The

mixture gradually evolved to a suspension of silane oligomers. After a carefully timed three days of stirring, we added 200 ml of NMP solvent and heated it to 110 C to evaporate ethanol and water for 24 hours. Then, add the glycidol. The outcome was coated nano silica particles after complete drying, as illustrated in Fig.25. Fig.26 presents the DSC-TGA of AYN-1005.



Fig.25: AYN1005 before and after complete drying

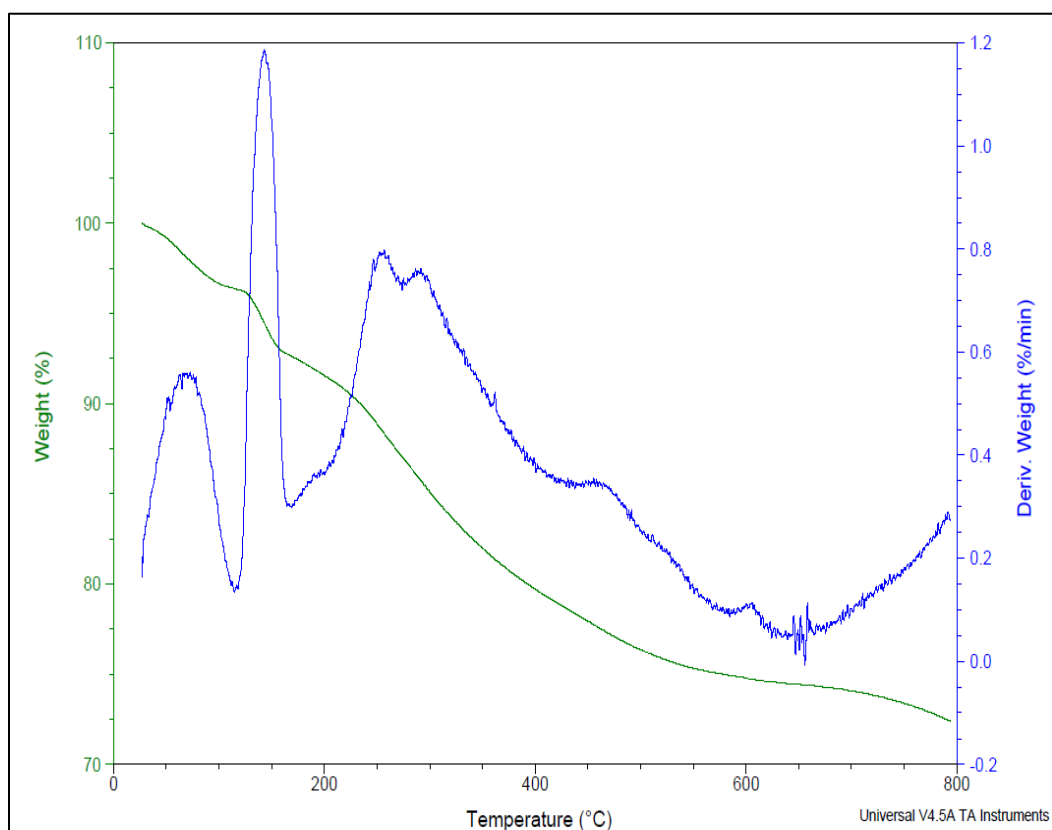


Fig.26: DSC-TGA of AYN-1005

Hybrid polymer AYN1006

- 10 grams of 10K PEI
- 200 ml DI water
- 1 gram of Dopamine
- 11.35 ml glycidol
- 10 ml of post functionalized nano silica (Levasil CS40-222)

For AYN 1006, we have utilized Dopamine (4-(2-aminoethyl) benzene-1,2-diol) as a chemical modifier for the hybrid polymer, a significant advancement in materials science and polymer chemistry. The PEI was first appropriately dissolved in DI water at 50 °C, and then 1 gram of Dopamine was added. The reaction was kept overnight at 50 °C. Next, glycidol was added slowly to the reaction mixture, and the reaction was kept for two days at 50 °C. Next, 10 ml of aqueous nano silica (Levasil CS40-222) was added slowly at a high mixing speed, and the reaction was kept for an additional day at 50 °C. After that, we conducted dialysis using 14,000 dialysis bags in mildly acidic water for 4 hours before taking the polymer solution for drying. We have kept a minimum of 10% liquid volume in the final hybrid polymer, Fig.27. Taking the hybrid polymer to complete drying will result in a composite that was not soluble in water, as shown in Fig.28.



Fig.27: AYN1006 hybrid polymer not completely dried



Fig.28: Complete drying of hybrid polymer leads to composite that has little solubility in

water

Hybrid polymer AYN1007

- 10 grams of 10K PEI
- 200 ml DI water
- 0.25 gram of Dopamine
- 11.35 ml glycidol
- 10 ml of post functionalized nano silica (Levasil CS40-222)

For AYN 1007, the procedure was followed for AYN 1006, except the amount of Dopamine was reduced from 1 gram to 0.25 gram to see if we would have an excellent hybrid polymer for our intended application. Fig.29 shows the DSC-TGA of AYN-1007.

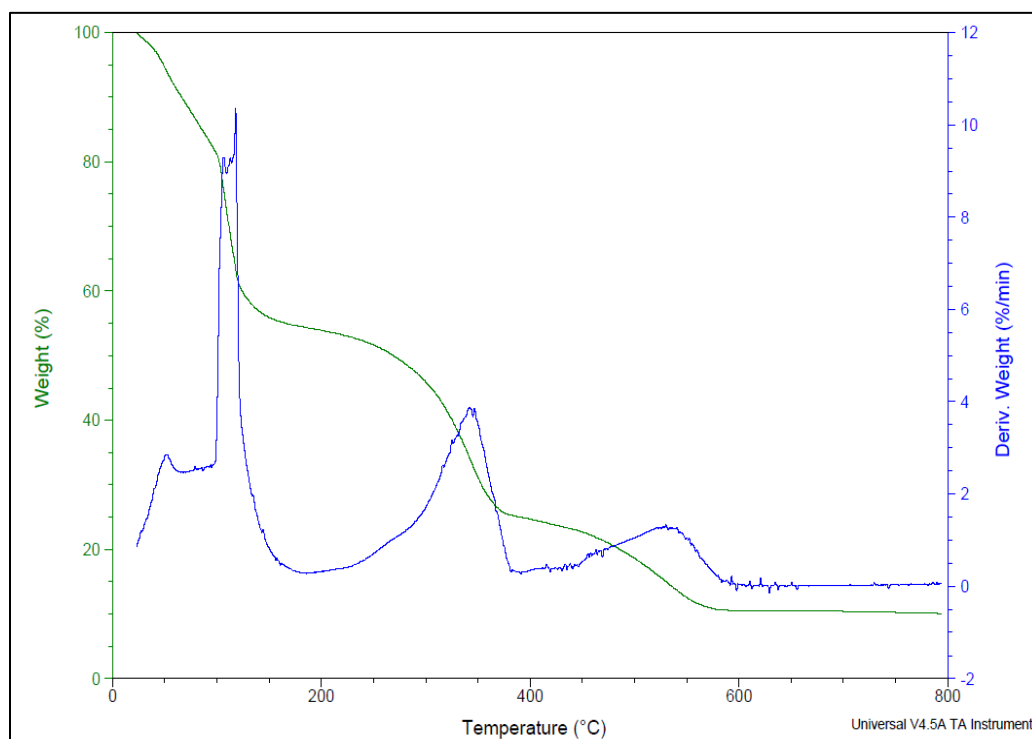


Fig.29: DSC-TGA of AYN-1007

Hybrid polymer AYN1008

- 10 grams of 60K PEI
- 200 ml DI water
- 0.25 gram of Dopamine
- 11.35 ml glycidol
- 10 ml of post functionalized nano silica (Levasil CS40-222)

For AYN 1008, the procedure was followed as before for the hybrid polymer. This time, we have used a higher polymer weight of PEI 60K instead of 10K to assess the performance of shale inhibition compared to 10K PEI. Fig.27 shows the DSC-TGA of AYN-1008.

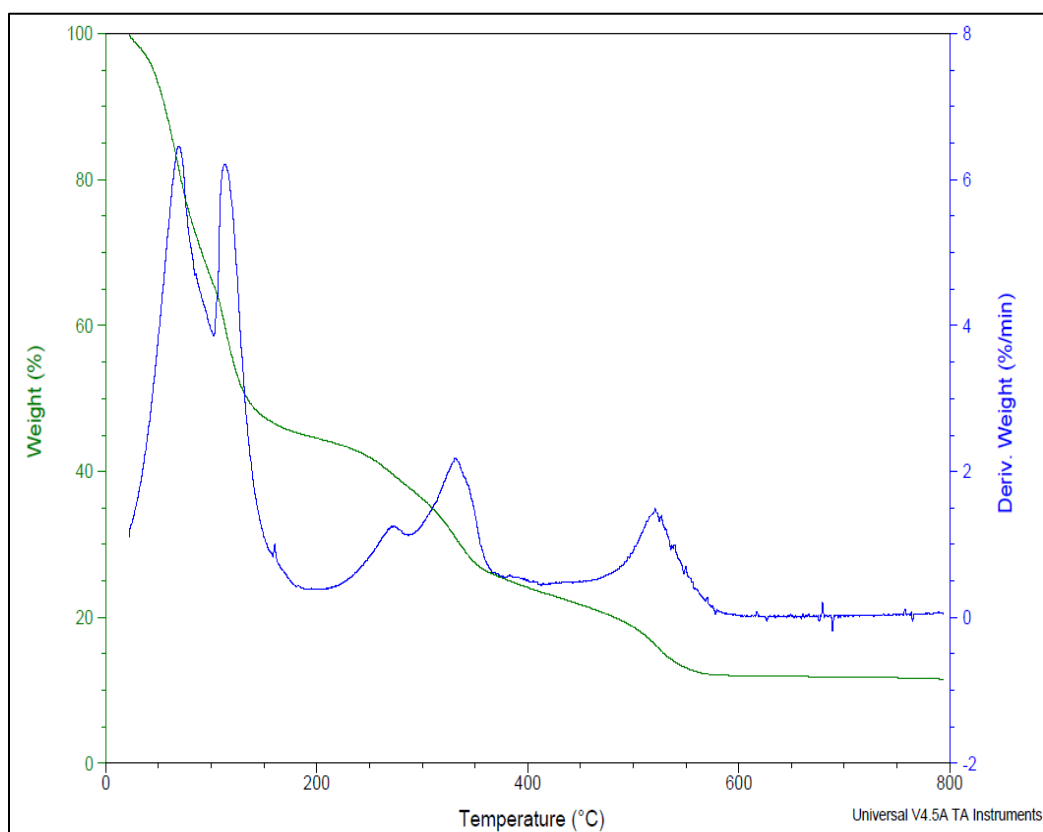


Fig.30: DSC-TGA of AYN-1008

Hybrid polymer AYN1009

- 10 grams of 60K PEI
- 200 ml DI water
- 0.25 gram of Dopamine
- 11.35 ml glycidol
- 2.5 ml of Titanium (IV) Isopropoxide

For AYN 1009, the procedure was followed as before for the hybrid polymer. This time, we have used a higher polymer weight of PEI 60K and a new nanomaterial. The nanomaterial is Titanium dioxide from titanium (iv) isopropoxide. Fig. 31 shows the DSC-TGA of Titanium (IV) Isopropoxide, a crucial step in our research. 2.5 ml of titanium (iv) isopropoxide was added slowly at high-speed mixing. A silver-white aggregate was observed during addition. The reaction was kept overnight at 50 C. After that, we conducted dialysis using 14,000 dialysis bags in mildly acidic water for 4 hours before taking the polymer solution for drying, a process that led to significant results.

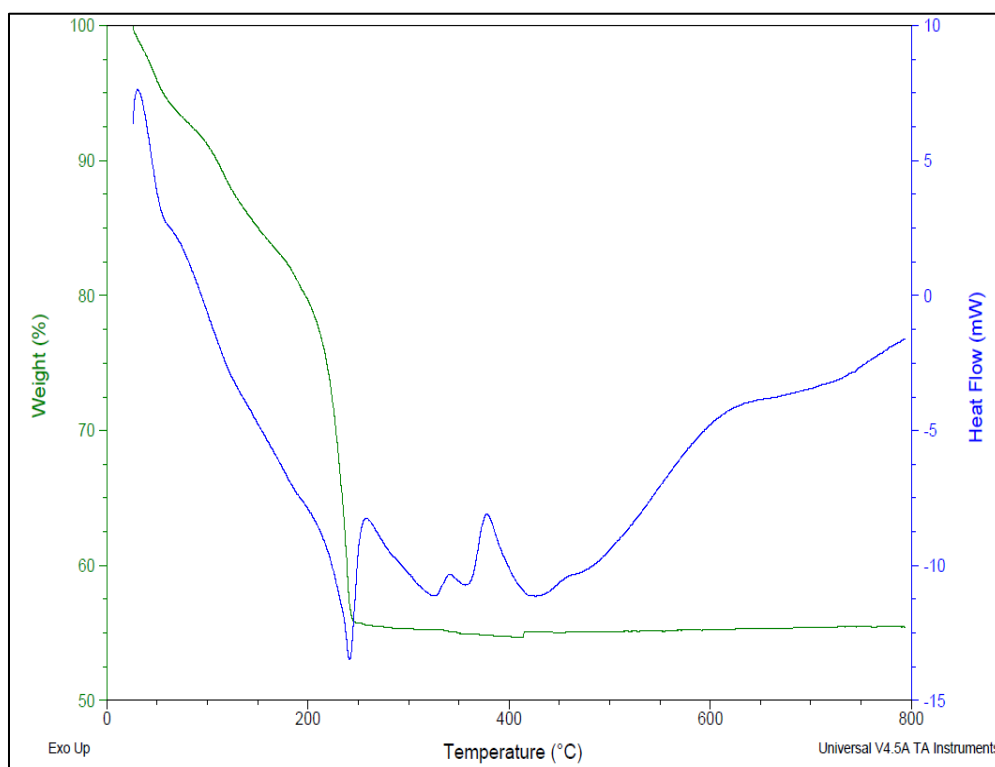


Fig.31: DSC-TGA of Titanium (IV) Isopropoxide

Hybrid polymer AYN1010

- 10 grams of 10K PEI
- 200 ml DI water
- 0.25 gram of Dopamine
- 11.35 ml glycidol
- 2.5 ml of in-situ Titanium (IV) Isopropoxide

Hybrid polymer AYN1011

- 10 grams of 60K PEI
- 200 ml DI water
- 0.25 gram of Dopamine
- 11.35 ml glycidol
- 1.00 ml of Titanium (IV) Isopropoxide

Hybrid polymer AYN1012

- 10 grams of 10K PEI
- 200 ml DI water
- 0.25 gram of Dopamine
- 11.35 ml glycidol
- 1.0 ml of Titanium (IV) Isopropoxide

AYN 1011 is similar to AYN 1009 but with a minor nanomaterial concentration. AYN 1012 is similar to AYN 1010 but with a minor nanomaterial concentration. To see the effect on shale inhibition, we used 1.0 ml of titanium (IV) isopropoxide instead of 2.5 ml. Fig. 32 shows DSC-TGA of AYN-1011, and Fig. 33 shows DSC-TGA of AYN-1012.

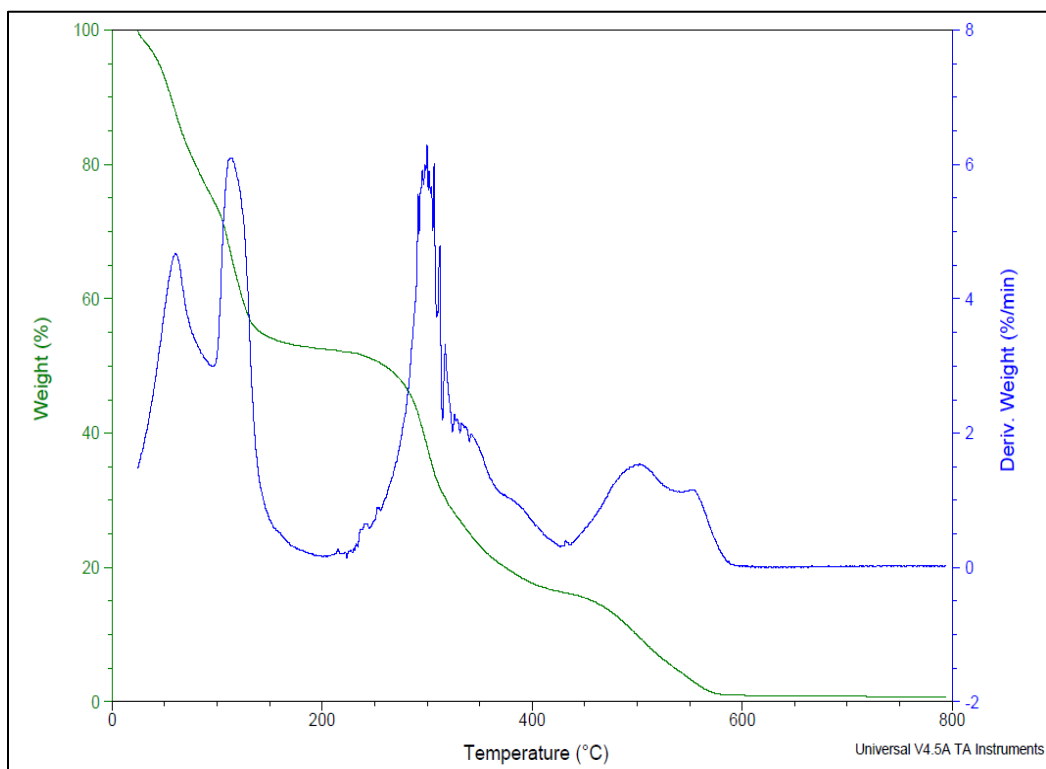


Fig. 32: DSC-TGA of AYN-1011

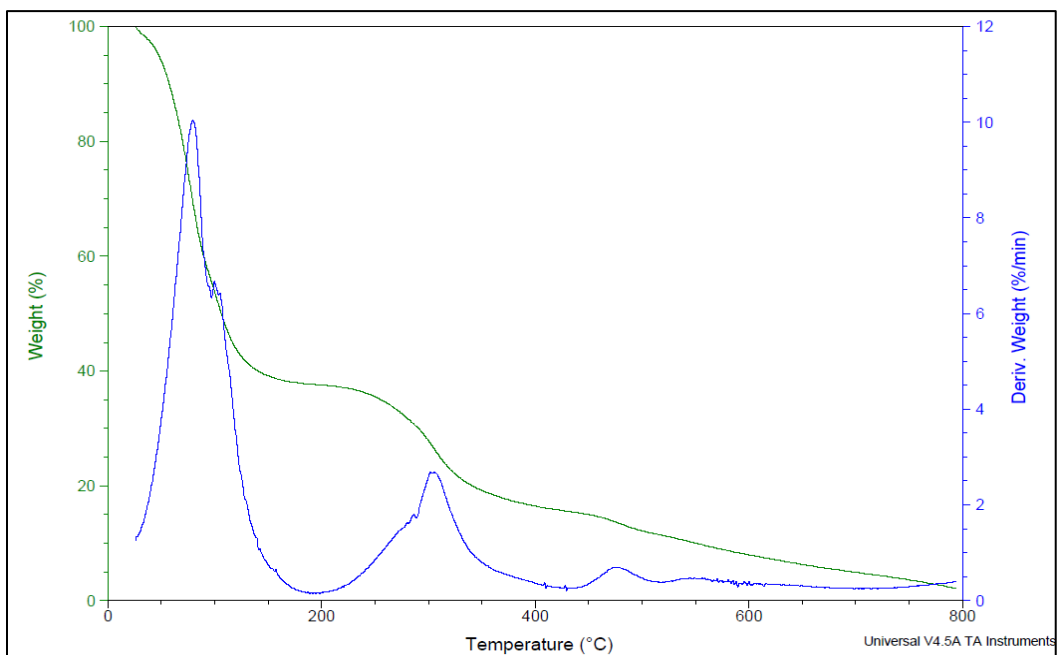


Fig. 33: DSC-TGA of AYN-1012

Hybrid polymer AYN1013

- 10 grams of 10K PEI
- 200 ml DI water
- 0.25 gram of Dopamine
- 11.35 ml glycidol
- 10 ml of post functionalized nano silica (Levasto F50P)

Hybrid polymer AYN1014

- 10 grams of 10K PEI
- 200 ml DI water
- 0.25 gram of Dopamine
- 11.35 ml glycidol
- 10 ml of post functionalized nano silica (Levasil CC301)

Hybrid polymer AYN1015

- 10 grams of 10K PEI
- 200 ml DI water
- 0.25 gram of Dopamine
- 11.35 ml glycidol
- 10 ml of post functionalized nano silica (Levasil CC401)

AYN 1013, AYN 1014, and AYN 1015 hybrid polymers were synthesized with different post-functionalized nano silica solutions. Table 4 compares the four different types of aqueous nano silica solutions. Figs. 34-37 shows the SEM of each type of nano silica. They were all coated with an organic layer, which explains its good suspension in liquid forms. Figs. 38-42 shows the DSC-TGA for the different post-functionalized nano silica types used in this synthesis. Figs. 43-47 show DSC-TGA of synthesized hybrid polymers AYN-1013 to AYN-1015 under different acidic and basic dialysis conditions.

Table 4: Comparisons among the 4 different types of aqueous nano silica solutions

post functionalized nano silica solutions	pH	Viscosity, cp @ 20 °C	SiO ₂ , %
nano silica (Levasil CS40-222)	9.7	18.7	40.3
nano silica (Levasto F50P)	10	30	15.1
nano silica (Levasil CC301)	6.9	4.4	28.1
nano silica (Levasil CC401)	6.3	5	36.5

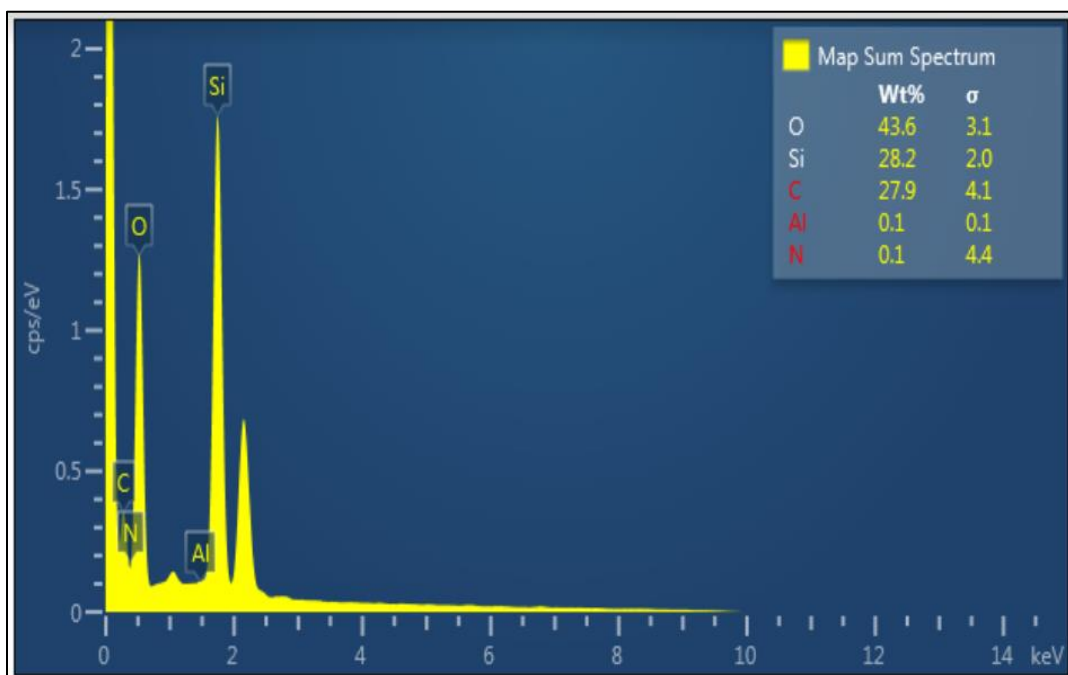


Fig. 34: SEM of post functionalized nano silica (Levasil CS40-222)

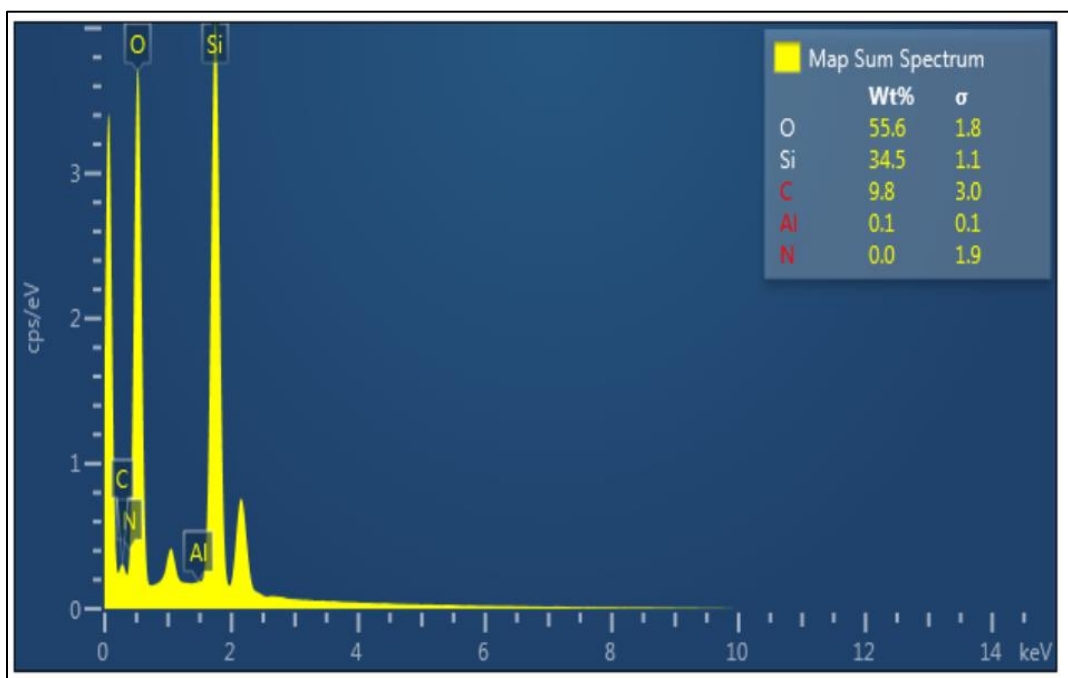


Fig. 35: SEM of post functionalized nano silica (Levasto F50P)

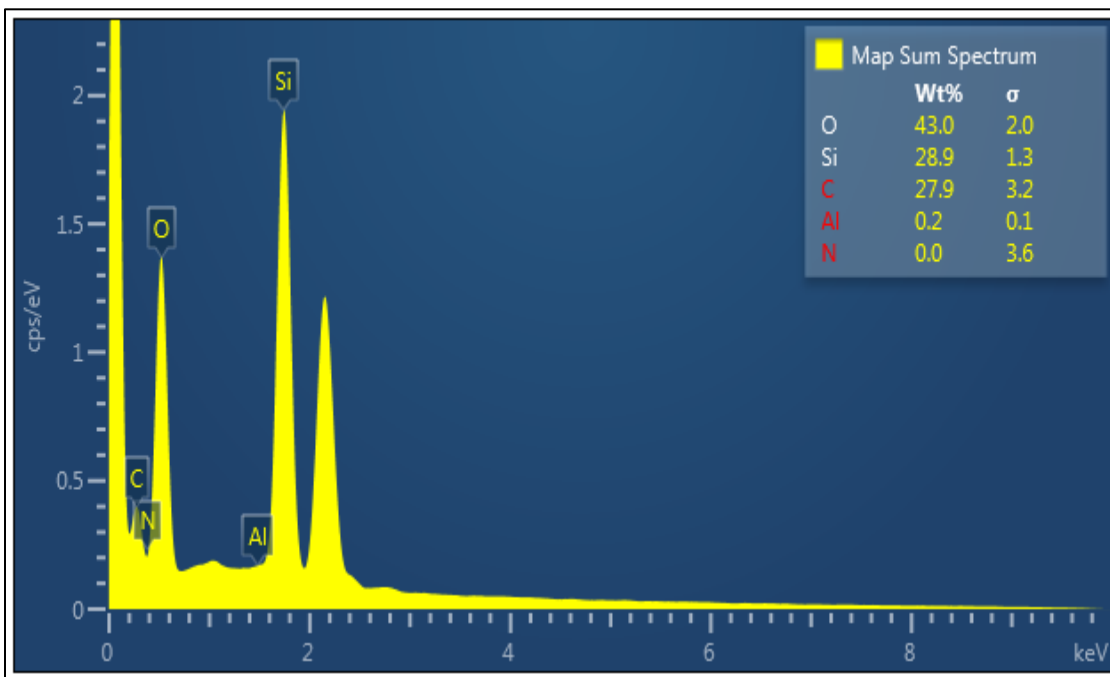


Fig. 36: SEM of post functionalized nano silica (Levasil CC301)

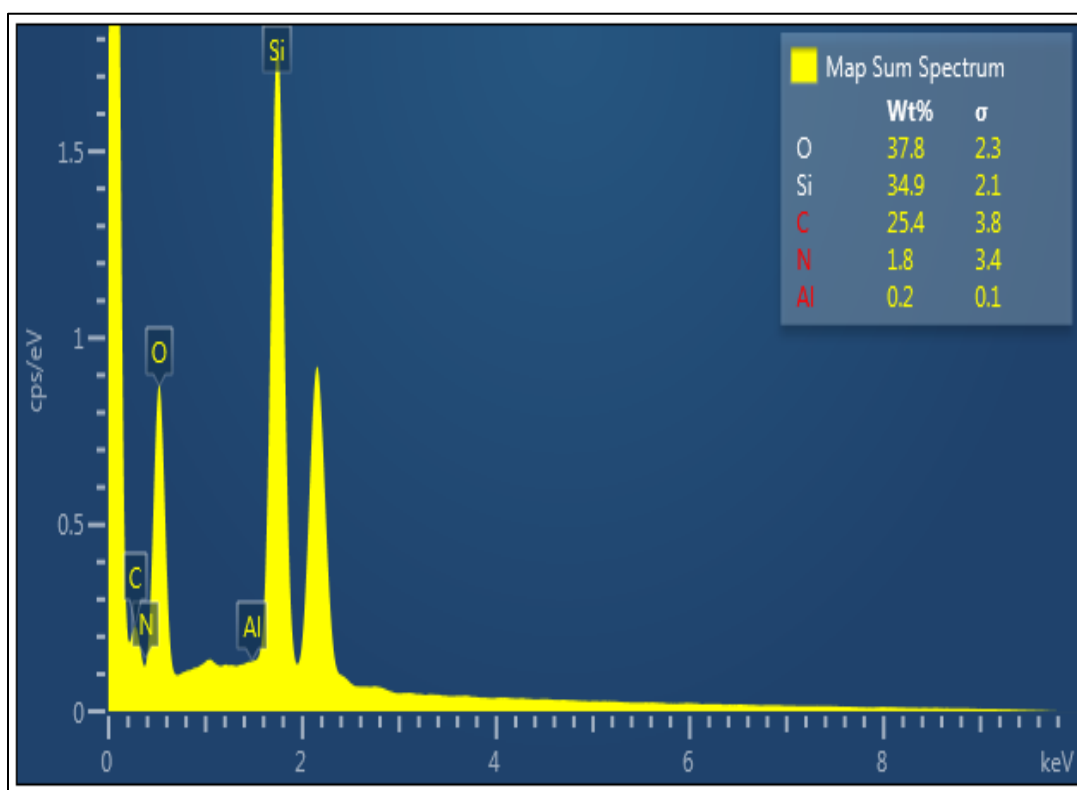


Fig. 37: SEM of post functionalized nano silica (Levasil CC401)

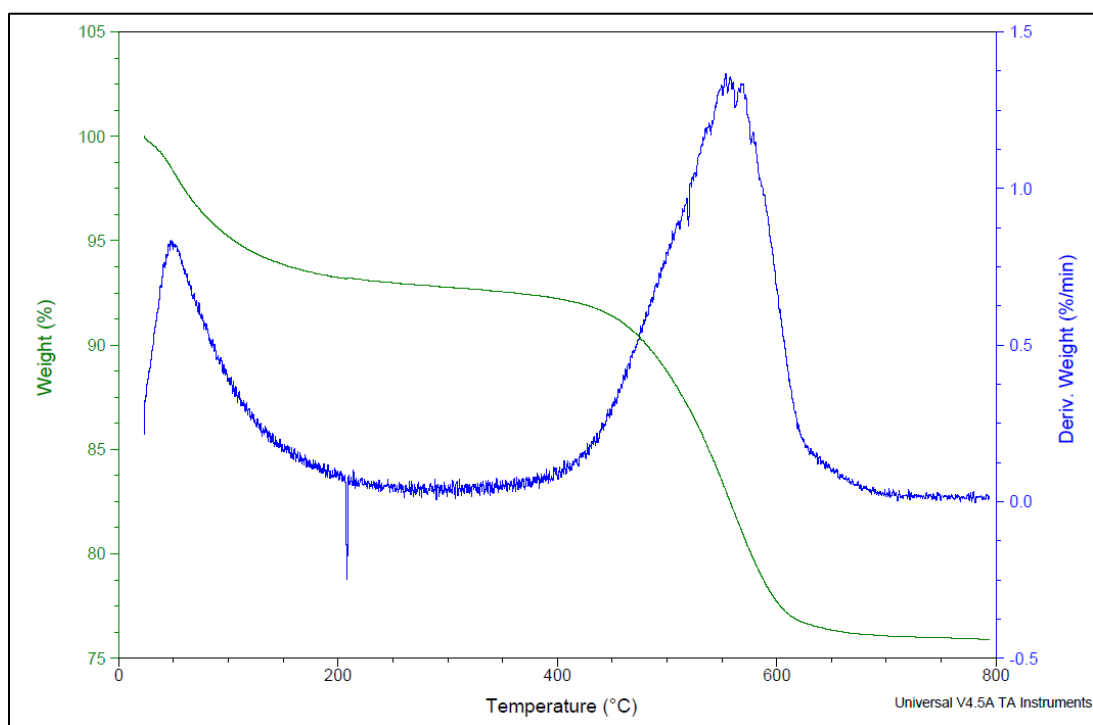


Fig. 38: DSC-TGA of post functionalized nano silica (Levasil CS40-222)

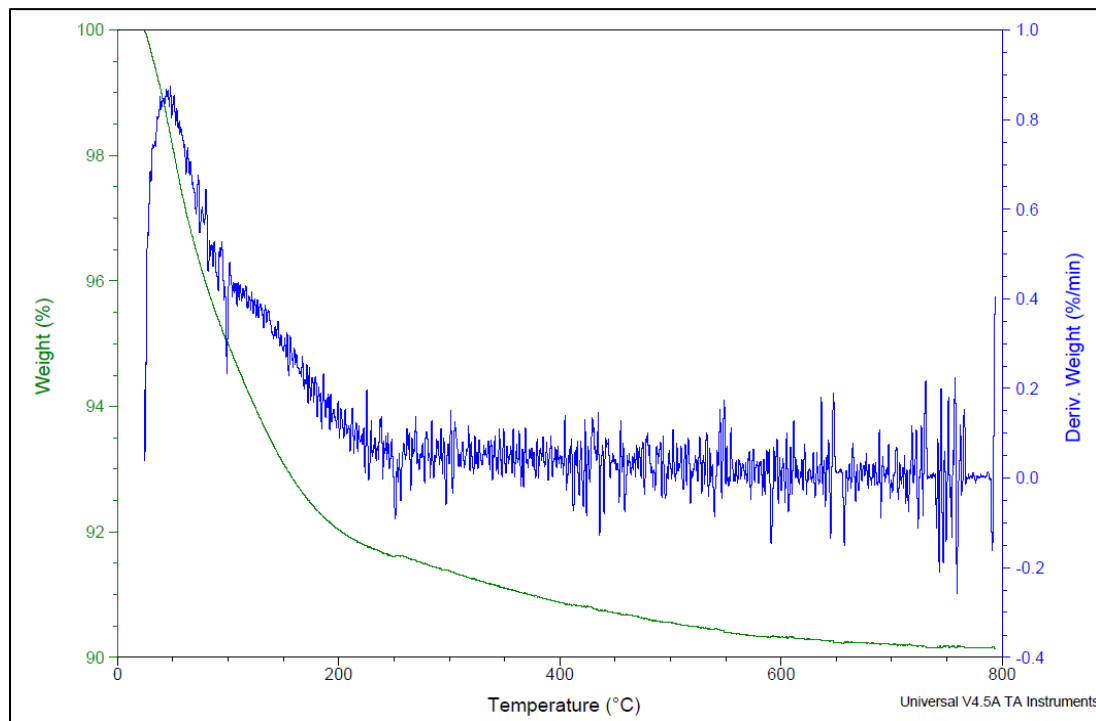


Fig. 39: DSC-TGA of post functionalized nano silica (Levasto F50P)

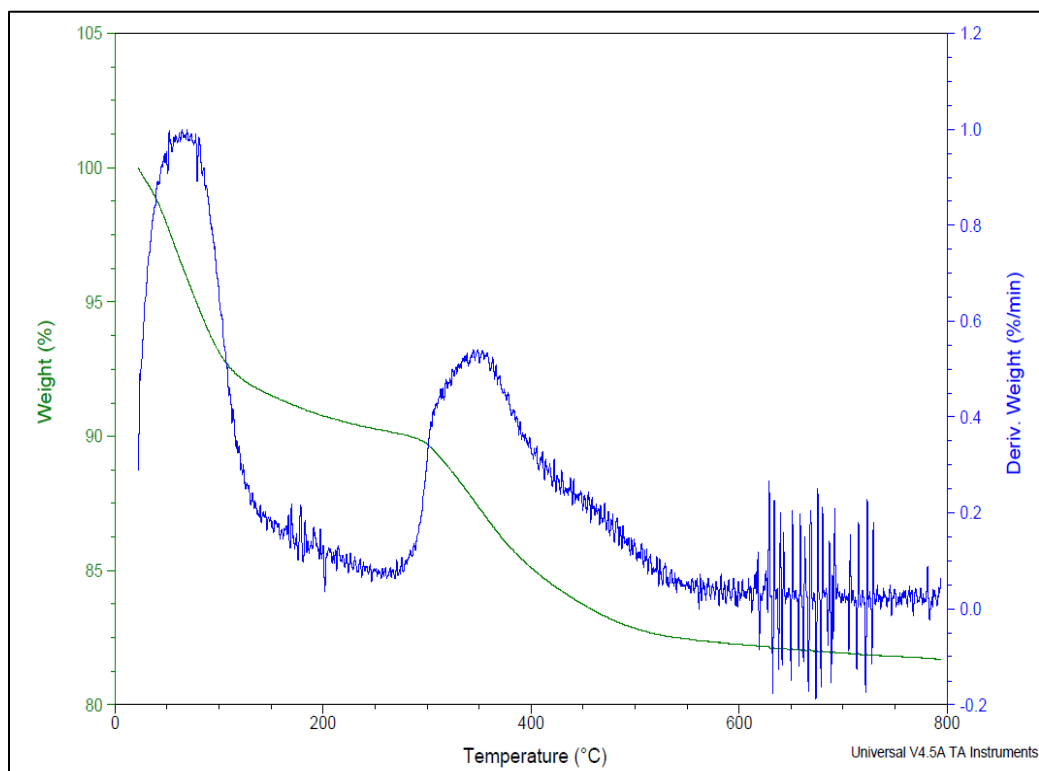


Fig. 40: DSC-TGA of post functionalized nano silica (Levasil CC301)

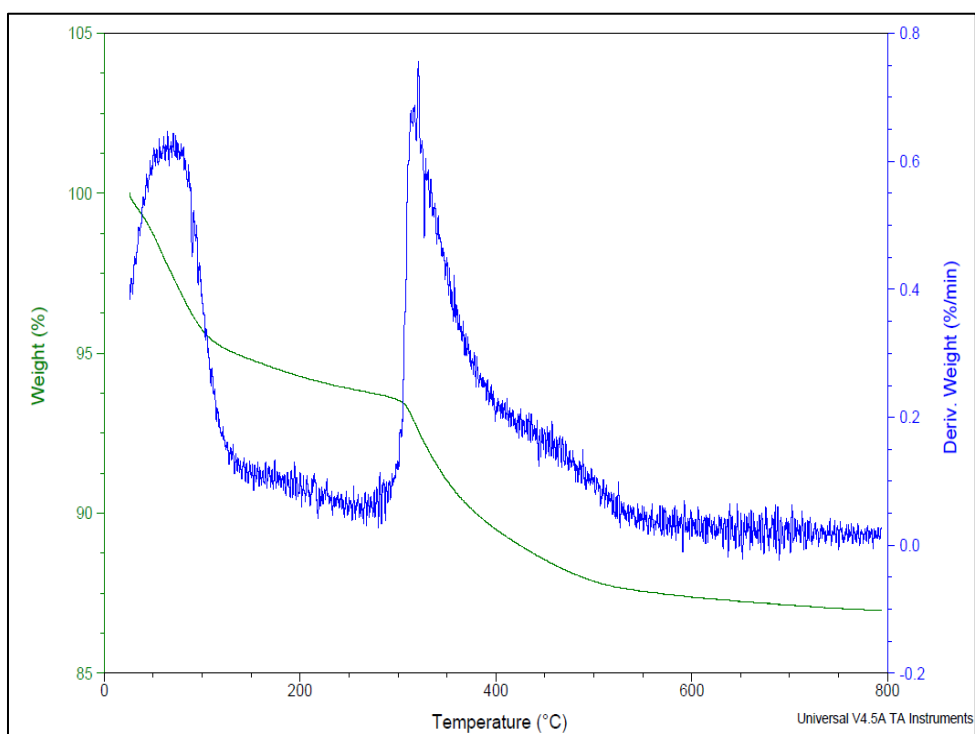


Fig. 41: DSC-TGA of post functionalized nano silica (Levasil CC401)

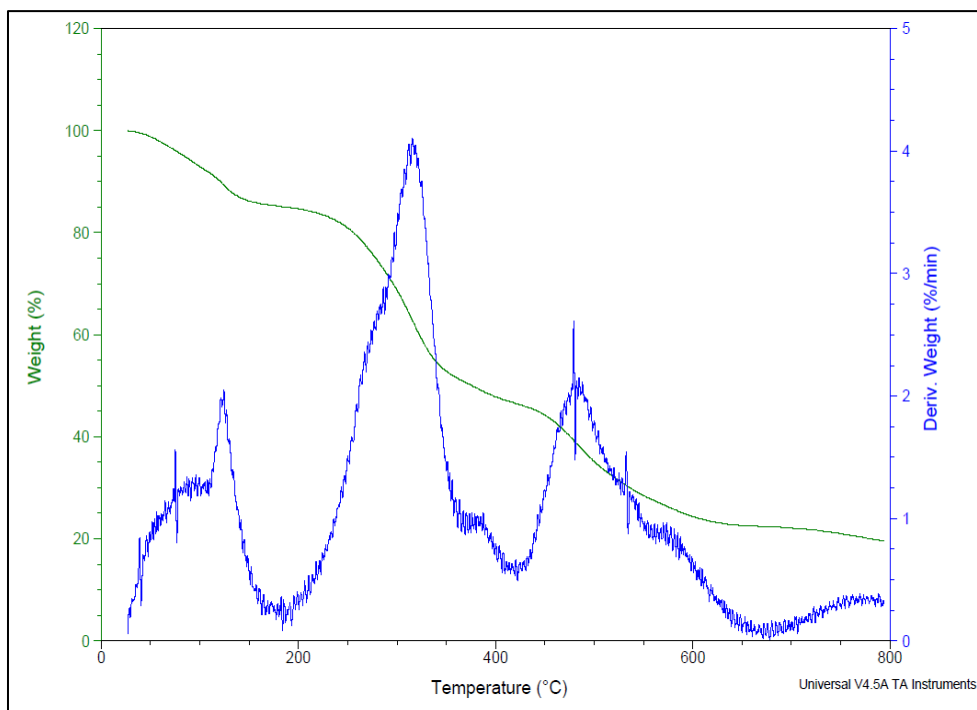


Fig. 42: DSC-TGA of AYN-1013 A

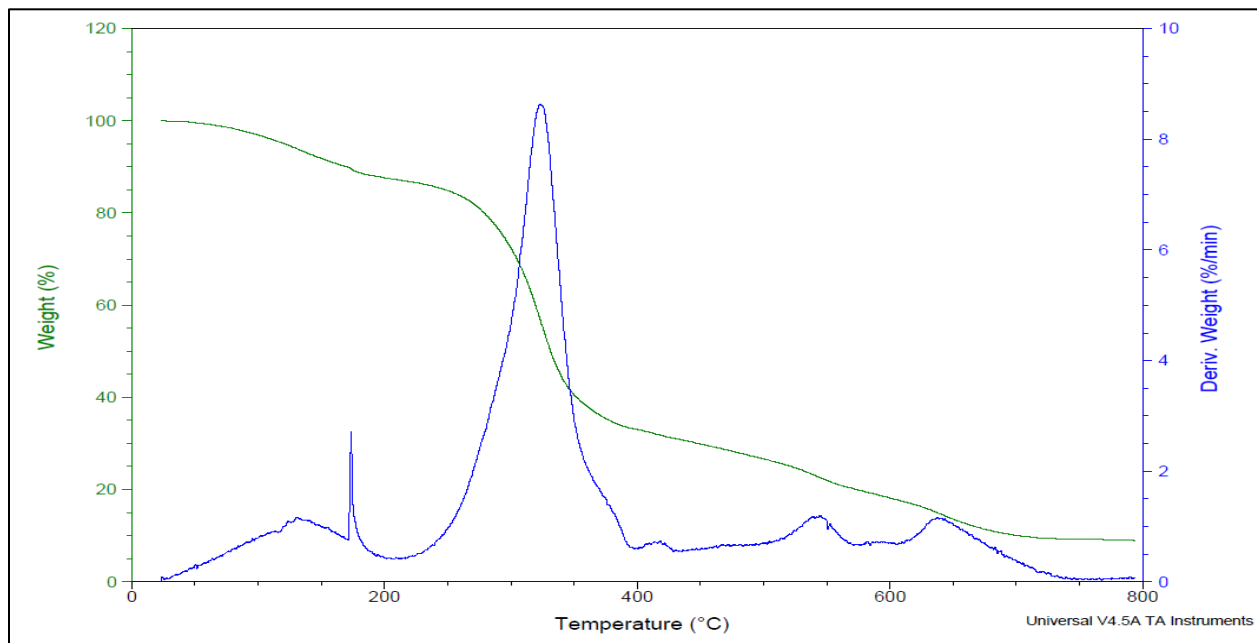


Fig. 43: DSC-TGA of AYN-1013 B

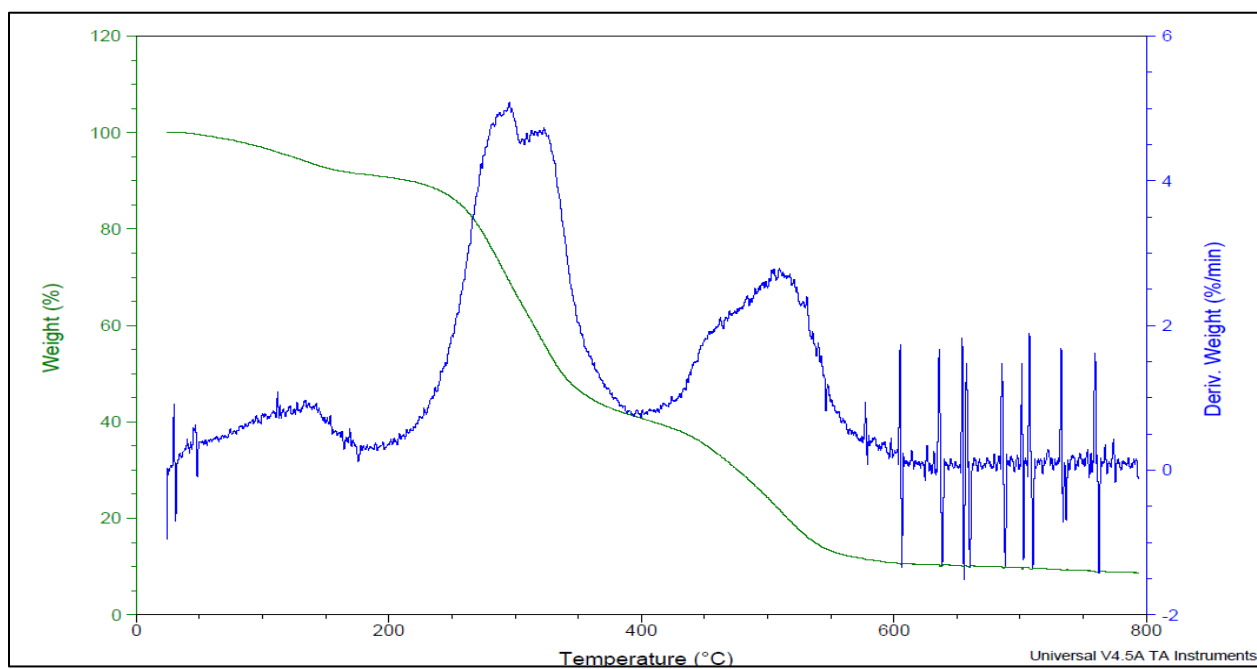


Fig. 44: DSC-TGA of AYN-1014 A

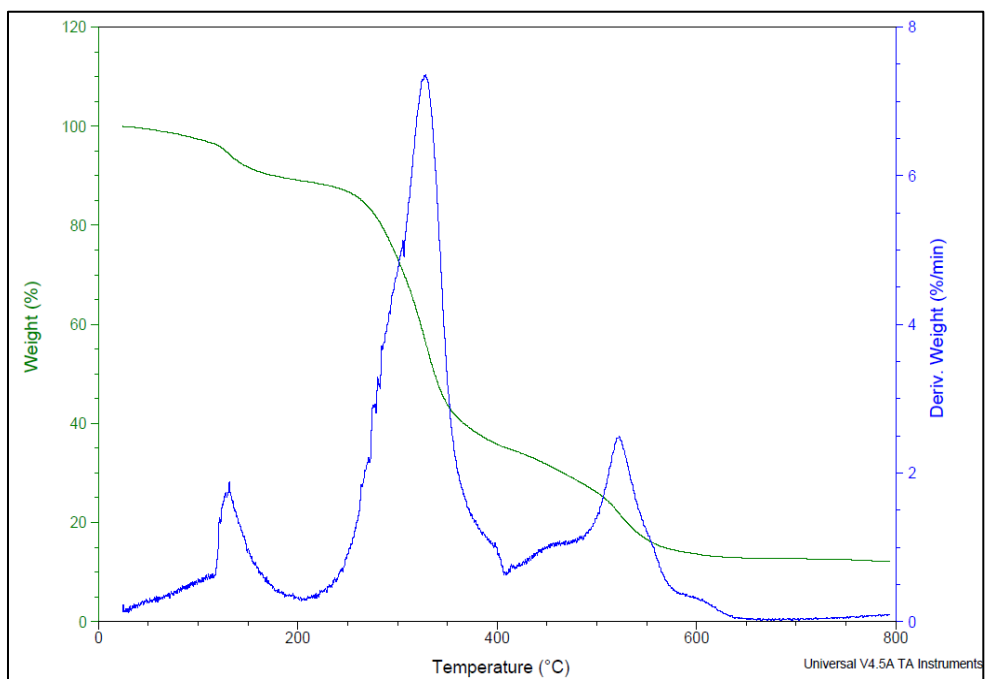


Fig. 45: DSC-TGA of AYN-1014 B

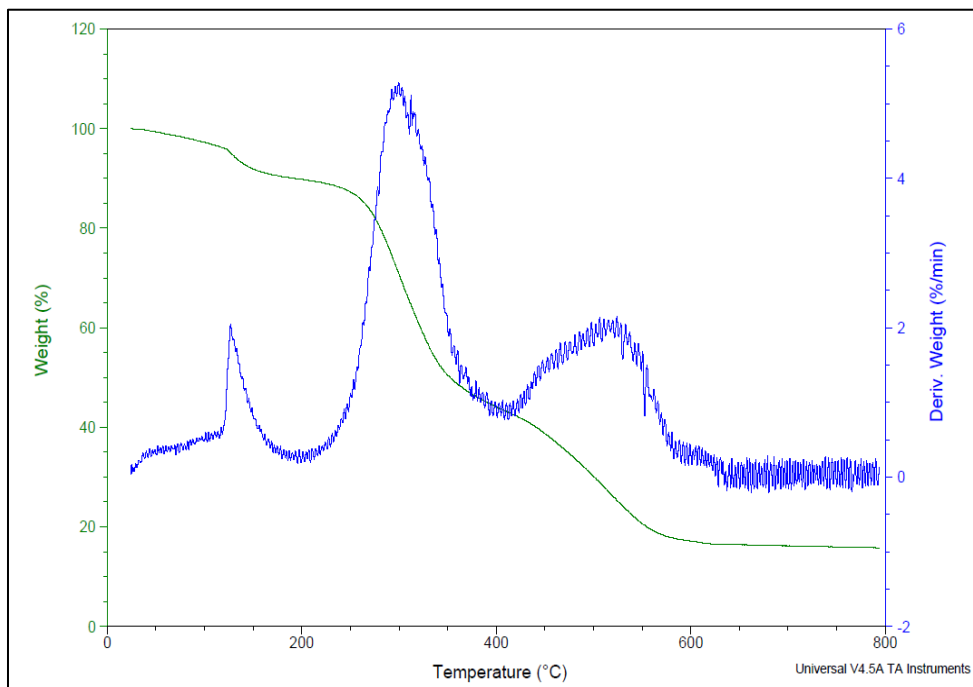


Fig 46: DSC-TGA of AYN-1015 A

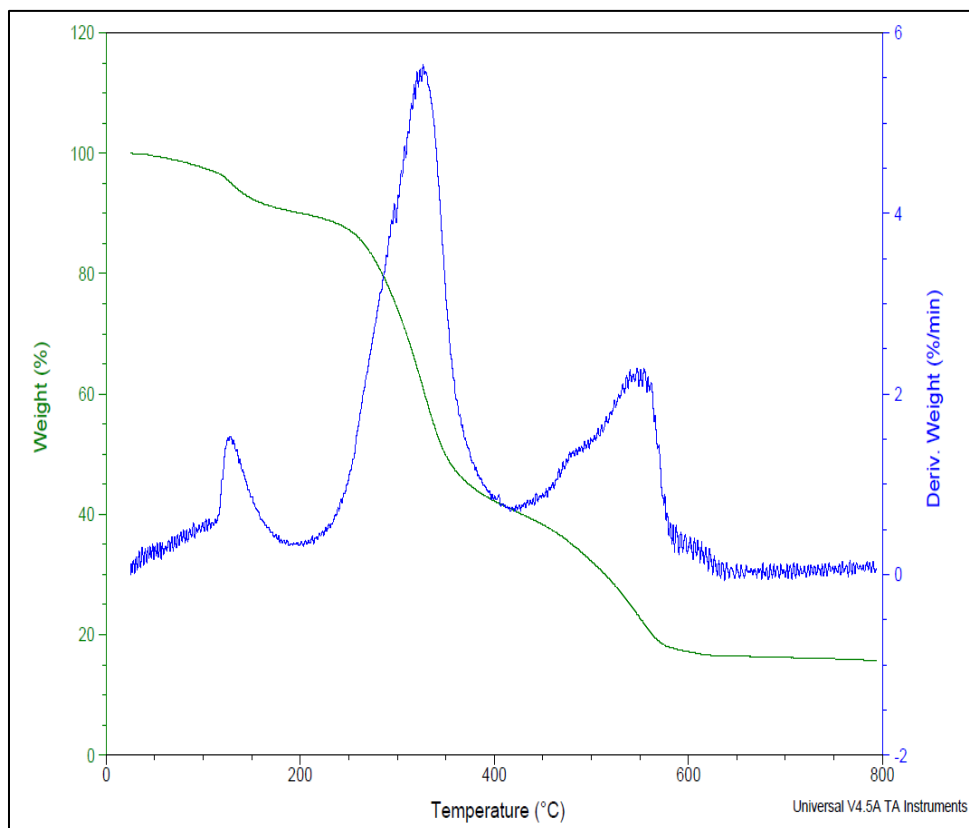


Fig. 47: DSC-TGA of AYN-1015 B

Hybrid polymer AYN1015

- 10 grams of 10K PEI
- 200 ml DI water
- 0.25 gram of Dopamine
- 11.35 ml glycidol
- 10 ml of post functionalized TiO₂

The post-functionalized TiO_2 was obtained by slowly adding 5 ml of titanium (IV) isopropoxide dropwise in a mixture of 100 ml DI water and 10 ml acetic acid at 23 °C. The acetic acid will stabilize the surface of the nanomaterial to prevent it from overgrowth. I kept the solution mixing for three days and then for a week until it became white-bluish. Performed sonication for 30 minutes and then performed dialysis in slightly acidic water for 1 hour. The primary objective was to synthesize a hybrid polymer utilizing post-functionalized TiO_2 and compare it against the in-situ TiO_2 hybrid polymers. The previous hybrid polymers utilizing Titanium (IV) Isopropoxide led to the in-situ TiO_2 hybrid polymers. Fig. 48 shows the DSC-TGA of post-functionalized TiO_2 , and Fig. 49 shows the DSC-TGA of the synthesized hybrid polymer, providing a clear comparison between the two.

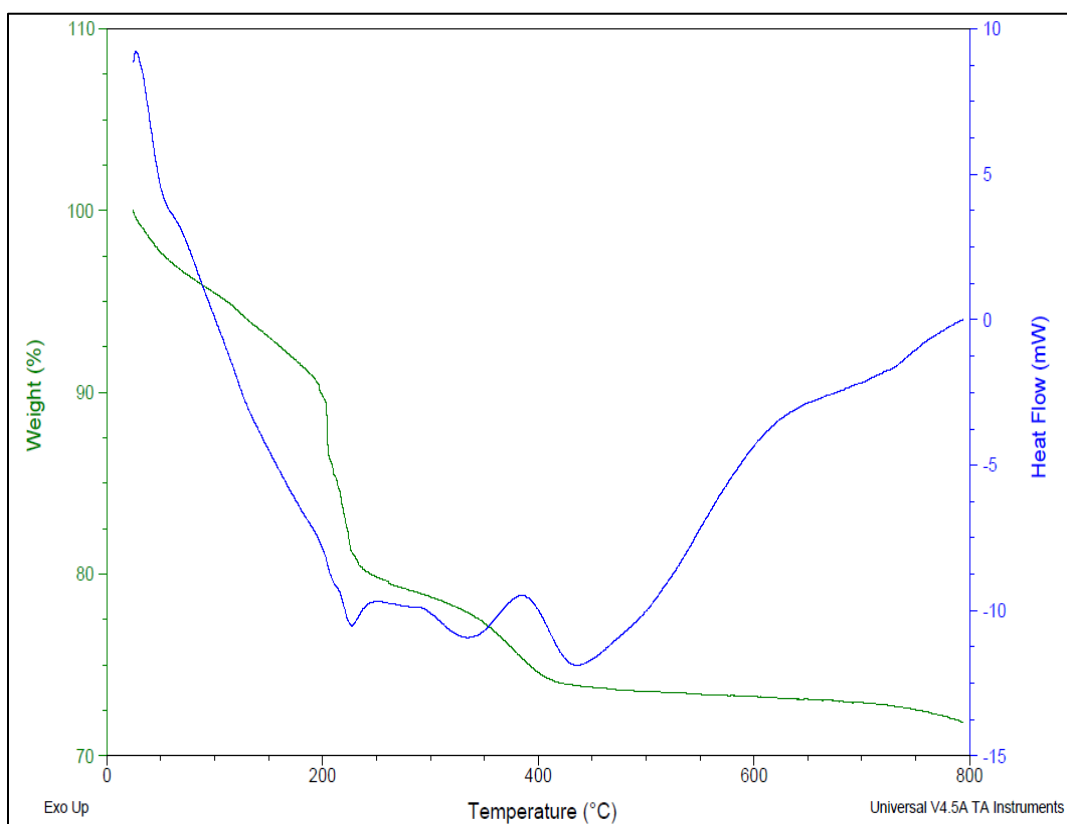


Fig. 48: DSC-TGA of post functionalized TiO_2

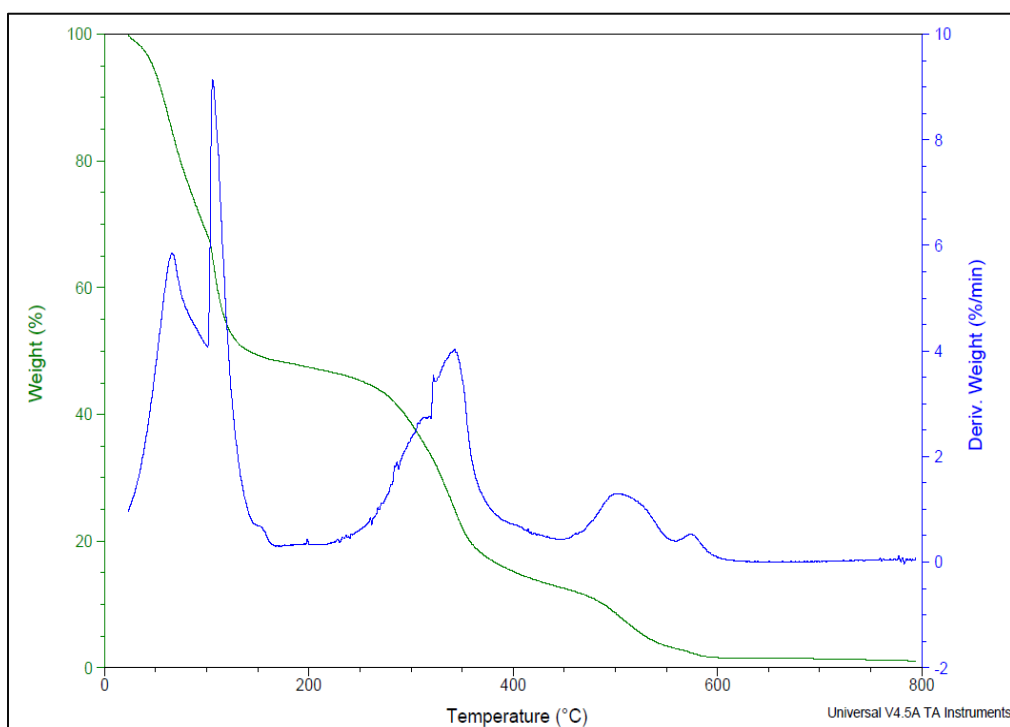


Fig. 49: DSC-TGA of AYN-1015

Hybrid polymer AYN1016

- 10 grams of 10K PEI
- 200 ml DI water
- 0.25 gram of Dopamine
- 11.35 ml glycidol
- 25 ml of post functionalized TiO₂

Hybrid polymer AYN1017

- 10 grams of 10K PEI

- 200 ml DI water
- 0.25 gram of Dopamine
- 11.35 ml glycidol
- 35 ml of post functionalized TiO₂

Hybrid polymer AYN1018

- 10 grams of 10K PEI
- 200 ml DI water
- 0.25 gram of Dopamine
- 11.35 ml glycidol
- 50 ml of post functionalized TiO₂

We have synthesized hybrid polymers utilizing different concentrations of the post-functionalized TiO₂ to assess the effect of the nanomaterial's dispersion and performance on shale inhibition.

Hybrid polymer AYN1019

- 2 grams of 60K PEI
- 200 ml DI water
- 0.25 gram of Dopamine
- 15 ml glycidol
- 1 ml of in-situ TiO₂

The synthesis of the previous hybrid polymers was based on terminal polymerization with approximately a 1:2 initiator-to-monomer ratio. The branching peak should be shown around 80 ppm. Using a 1:15 initiator-to-monomer ratio showed branched peaks around 80 ppm (Fig. 50). So, for AYN1019, we have successfully synthesized a branched hybrid polymer with a 1:15 initiator-to-monomer ratio utilizing in-situ TiO₂ nanomaterial. This successful synthesis process allows us to compare the effect of branching on the suspension of the nanomaterials and the effect of shale inhibition, with confidence in the results.

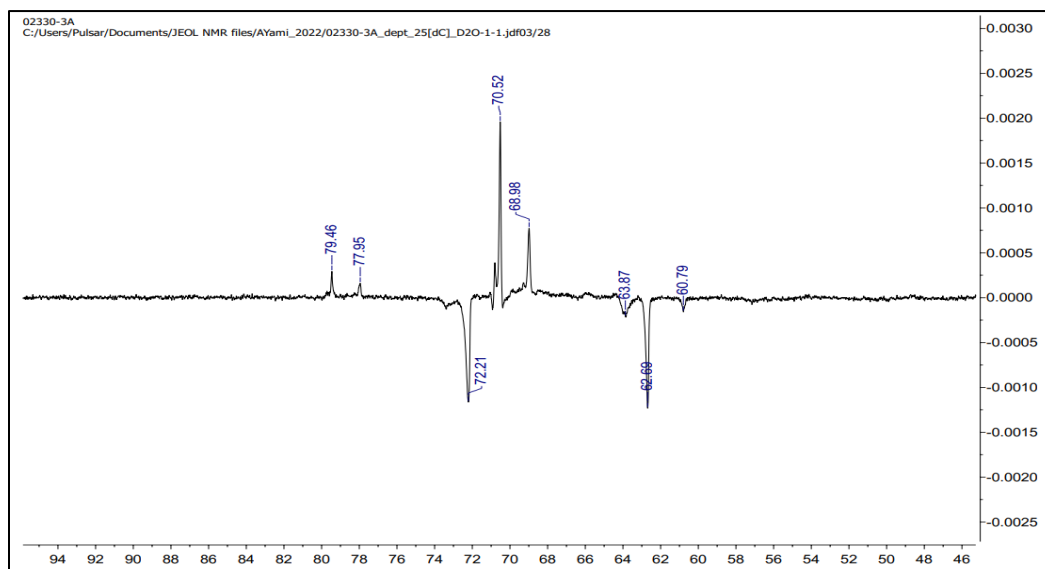


Fig. 50: ¹³C NMR of synthesized polymer 3 (ratio 1:15 PEI to Glycidol)

Hybrid polymer AYN1020

- 2 grams of 60K PEI
- 200 ml DI water

- 0.25 gram of Dopamine
- 15 ml glycidol
- 35 ml of post functionalized TiO₂

We used post-functionalized TiO₂ on the branched polymer to produce hybrid AYN1020.

Hybrid polymer AYN1021

- 30 grams of 60K PEI
- 200 ml DI water
- 15 ml glycidol
- 0.25 gram of Dopamine
- 1 ml of in-situ TiO₂

Hybrid polymer AYN1024

- 30 grams of 60K PEI
- 200 ml DI water
- 15 ml glycidol
- 0.25 gram of Dopamine
- 35 ml of post functionalized TiO₂

Here, we first did polymerization and then attached the in-situ nanomaterial to observe the effect of the nanomaterial settling and shale inhibition performance. A terminal polymer was synthesized using a 1:1 ratio of initiator to monomer ratio, Fig. 51. The nanomaterial was in-situ TiO₂ in hybrid polymer AYN1021 and post-functionalized TiO₂ in hybrid polymer AYN1024.

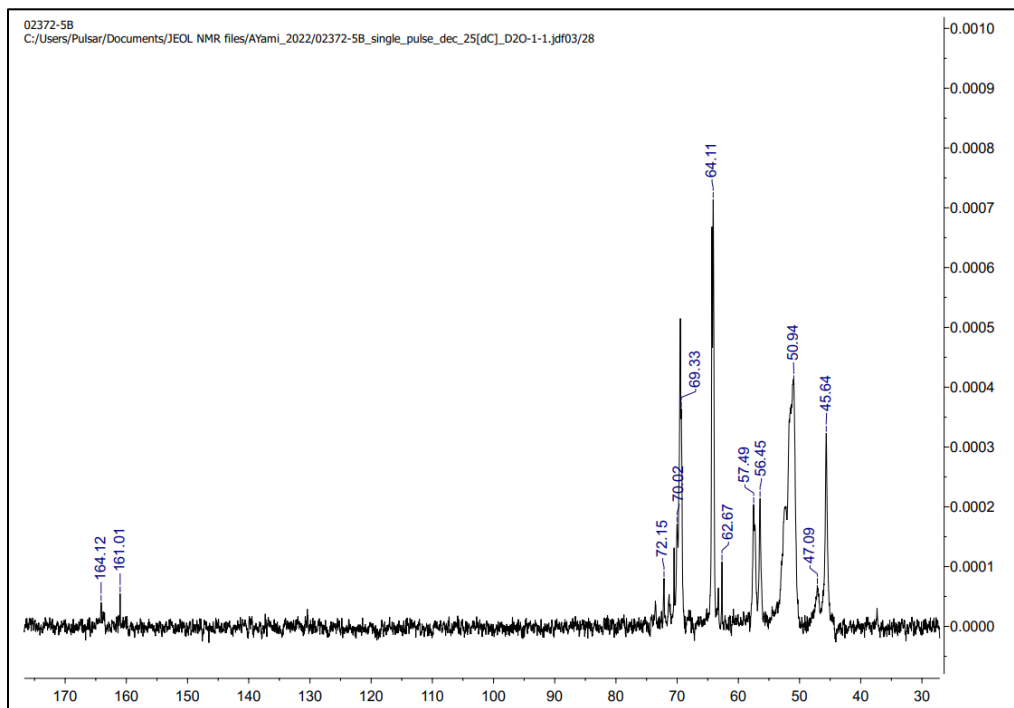


Fig. 51: ^{13}C NMR of synthesized polymer (ratio of 1:1 PEI to Glycidol)

Hybrid polymer AYN1022

- 30 grams of 10K PEI
- 400 ml DI water
- 0.25 gram of Dopamine
- 3 grams of maleic anhydride
- 1 ml of in-situ TiO_2

Hybrid polymer AYN1023

- 30 grams of 10K PEI

- 400 ml DI water
- 0.25 gram of Dopamine
- 3 grams of maleic anhydride
- 10 ml of post functionalized nano silica (Levasil CS40-222)

Hybrid polymer AYN1026

- 30 grams of 10K PEI
- 400 ml DI water
- 0.25 gram of Dopamine
- 3 grams of maleic anhydride
- 35 ml of post functionalized TiO₂

Here, we have synthesized a hybrid polymer using maleic anhydride monomer instead of glycidol. We used post-functionalized nano silica in AYN1023, post-functionalized TiO₂ in AYN1026, and in-situ TiO₂ in AYN1022.

Hybrid polymer AYN1025

- 30 grams of 10K PEI
- 400 ml DI water
- 0.25 gram of Dopamine
- 35 ml of post functionalized TiO₂

Hybrid polymer AYN1027

- 30 grams of 10K PEI

- 400 ml DI water
- 0.25 gram of Dopamine
- 1 ml of in-situ TiO₂

We have synthesized a hybrid polymer without using monomers (glycidol or maleic anhydride). The nanomaterial was post-functionalized TiO₂ in hybrid AYN1025 and in-situ TiO₂ in hybrid polymer AYN1027. We wanted to see the nanomaterial's behavior and the result of shale inhibition.

Hybrid polymer AYN1028

- 10 grams of 10K PEI
- 200 ml DI water
- 0.25 gram of Dopamine
- 11.35 ml glycidol
- 1 ml of in-situ nano silica (using tetraethoxysilane, TEOS)

Hybrid polymer AYN1029

- 10 grams of 10K PEI
- 200 ml DI water
- 0.25 gram of Dopamine
- 11.35 ml glycidol
- 10 ml of in-situ nano silica (using tetraethoxysilane, TEOS)

Hybrid polymer AYN1031

- 10 grams of 10K PEI
- 200 ml DI water

- 0.25 gram of Dopamine
- 11.35 ml glycidol
- 20 ml of in-situ nano silica (using tetraethoxysilane, TEOS)

In AYN1028, AYN1029, and AYN1031 hybrid polymers, we synthesized in-situ nano silica using different concentrations of TEOS (1 ml, 10 ml, and 20 ml) to see their effect on shale inhibition.

Hybrid polymer AYN1030

- 10 grams of 10K PEI
- 200 ml DI water
- 1 gram of Dopamine
- 11.35 ml glycidol
- 10 ml of post functionalized nano silica (Levasil CS40-222)
- Surfactant (CTAB)

In hybrid AYN1030, we have added a surfactant to the synthesized hybrid polymer to observe its effect on the nanomaterial suspension.

CHAPTER 6

PERFORMANC TESTING

This chapter summarizes the performance testing for water-based drilling fluid formulations at 300 °F (149 °C), which includes viscosity and shale inhibition. The industry accepts standard and API tests (Fig. 52) to prepare and characterize drilling fluids. The tests covered here are fluid preparation, density and rheology measurements, API and HT/HP filtration, and thermal stability tests.

Drilling Fluids Preparation

In this study, the duration of mixing of each additive will be 20 minutes. A Hamilton mixer will be used to prepare the samples. Drilling fluids will be mixed using the Multimixer Model 9B with 9B29X impellers. The average speeds of the impellers were 11300 rpm. Metal containers used for mixing slurries were according to the descriptions furnished in the API RP. Density measurement and rheological properties follow API RP13 standards [230]. The rheology of the fluid is characterized by two key parameters-plastic viscosity (PV) and yield point (YP). The YP and PV are parameters from the Bingham Plastic rheology (BP) model, which play a significant role in understanding the fluid's behavior. The YP is determined by extrapolating the BP model to a zero-shear rate; it represents the stress required to move the fluid. The YP indicates the cuttings carrying capacity of the

fluid through the annulus. The PV represents the viscosity of a fluid when extrapolated to an infinite shear rate, expressed in units of centipoise (cP). The PV indicates the type and concentration of the solids in the drilling fluid; a low PV is preferred.

API and HT/HP Filtration

Pressure can be applied with either gas or liquid. In the HT/HP filtration test, 4.5-cm diameter filter paper will be used at 300 °F and 600 psi [230].



Fig. 52: Thermal Stability (Aging Test)

Many drilling fluid components degrade at high temperatures. An aging at high-temperature test can evaluate drilling fluids due to such drilling operations. The drilling fluid sample is placed in an aging cell constructed from suitable metals to expose it to

elevated temperatures. Dynamic aging should be performed in rolling or rotating ovens capable of achieving and safely maintaining temperatures for at least 16 hours [230].

Contamination and Salts Compatibility Testing

We will investigate the stability and tolerance of the synthesized branched polymers against contamination and different types of salts at different concentrations.

Long Term Shale Inhibition Testing

Petroleum engineering has established a standard method to test the inhibition performance of drilling fluids, such as the dispersion and swelling tests. This test is acceptable when drilling at full circulation conditions. However, a new process needs to be developed to simulate the inhibition of shale when drilling with total losses [231].

Due to the presence of severe losses, there is a need to use an inhibitive drilling fluid that lasts long enough till we complete drilling the severe loss circulation zone. Once we hit the complete loss circulation zone and cannot establish circulation we need to switch to water as our drilling fluid to save costs on chemicals. We must ensure that the upper previously drilled entire circulation zone maintains its inhibition. Otherwise, that shale section will react with water, resulting in stuck pipes or wellbore instability.

A study [232] introduced a procedure for testing long-term shale inhibition. Since we are switching to water once we hit losses and continue drilling, exposure of inhibited shales to water must be tested in the lab. The procedure is detailed as follow below:

The testing procedure (Fig. 53) is composed of the following three stages:

1. The first stage is the conventional dispersion test used to assess the shale inhibition potential of different drilling fluid systems.

It consists of the following steps.

a. Prepare 350 ml inhibitive mud for each of the selected mud systems using standard test equipment and procedure.

b. Prepare 2-4 mm shale cuttings using shale cores or outcrop shales.

c. Add 20 g of shale cuttings and 350 cc inhibitive drilling fluid into the hot roll cell. Screw the cap tightly and then place the cell on the roller of the hot roll oven and roll for 16 hours.

d. After 16 hours, remove the cell from the hot roll oven and then pour the cell content into a 500-micron sieve.

e. Wash the content of the sieve with mildly running water to remove all shale pieces smaller than 500 microns.

2. The second stage is to dry the cuttings in an oven at 105 °C for 24 hours. Weigh the dried shale and record the dry weight.

3. The third stage of the test is the inhibition durability assessment test, which evaluates the longevity or durability of inhibition by conducting a variable time re-dispersion test using the already inhibited shale cuttings recovered from the previous stages. In this stage, water is used as a representative of the most aggressive reactive fluid to assess the durability of shale-cutting inhibition. Water was also used to represent fresh or sea water that is usually used to drill a severe loss zone below a reactive shale formation.

a. Pour 350 cc fresh water into the hot roll cell again to represent a highly reactive fluid environment.

b. Place 5 gm dried shale cuttings that were recovered after the first stage dispersion test into the freshwater of the hot roll cell.

c. Place the cell in the rolling oven and roll for different periods.

d. After rolling for the pre-determined period (2 hr., four hr., six hr., etc.), pour the contents into a 500-micron sieve and wash using mildly running water to remove all particles below 500 microns.

e. Measure the weight after drying at 105 °C for 24 hours and then plot the mass recovered as a function of rolling time.

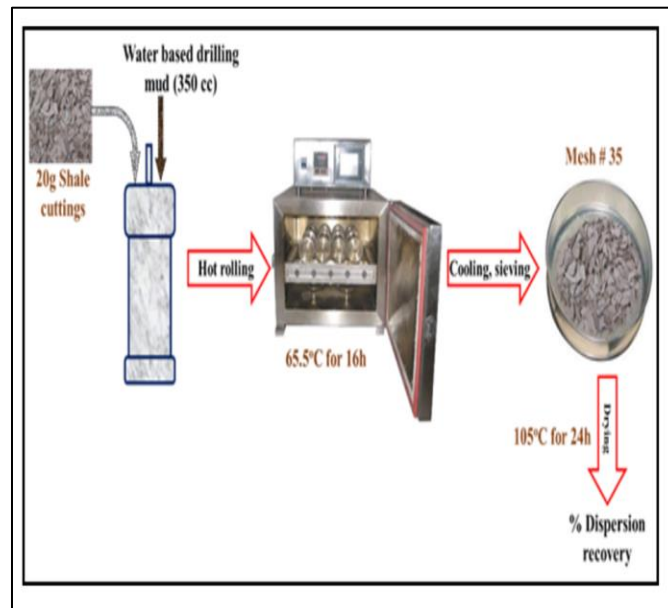


Fig.53: Testing apparatus for shale inhibition, [232]

CHAPTER 7

RESULTS AND DISCUSSION

Our pursuit to replace oil-based drilling fluids with more efficient alternatives has led us to focus on three crucial objectives. The first is to develop polymers that can withstand high-temperature environments, the second is to minimize environmental impact, and the third is to ensure acceptable shale inhibition. We have successfully synthesized families of hyperbranched and hybrid polymers that not only meet these objectives but also synergize with conventional polymers, significantly enhancing temperature stability and shale inhibition.

Our research involved three major experimental phases, each contributing to the development of water-based drilling fluids as a viable alternative to oil-based ones. The first phase focused on polymer synthesis and characterization, utilizing a solution ring opening polymerization set-up. The second phase involved formulation and performance testing, specifically at a temperature of 300 °F. The third and final phase was dedicated to shale inhibition performance testing and formulation optimization, as required.

In our synthesis process, we chose branched PEI as our macroinitiator for several reasons. Its interaction with conventional polymers used in drilling operations, such as XC polymer and HPAM, through acid-base reactions leads to electrostatic solid interaction and ionic bond formation. Additionally, it can interact with PEI via a transamidation mechanism, resulting in cross-linking and enhanced viscosity. This interaction also leads

to elevated hydrogen bonding, a crucial factor for water solubility and shale inhibition. The use of branched PEI allows us to grow a higher number of functional groups, including degradable ones like glycidol and Maleic anhydride, enhancing the versatility of our synthesized polymers, Fig.54.

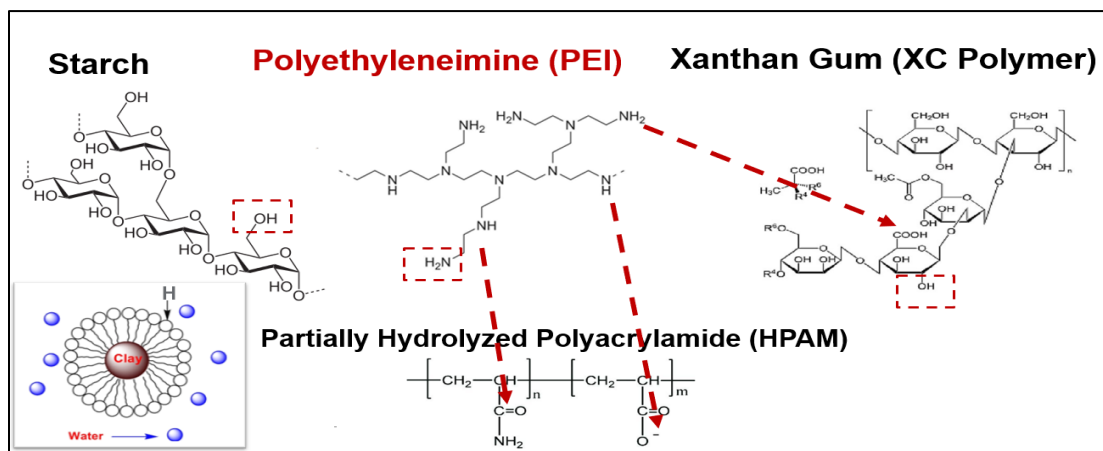


Fig.54: Interaction of PEI with conventional polymers

Our choice of PEI as the macro-initiator is a testament to our innovative approach. The mechanism we employ is a form of ring-opening multibranching polymerization (ROMP), with the cyclic monomer being Glycidol. We are pushing the boundaries of polymer modification by introducing an additional layer of non-toxic polymer to the PEI. This modification not only enhances the polymer's density of functional groups but also facilitates cross-linking with ease.

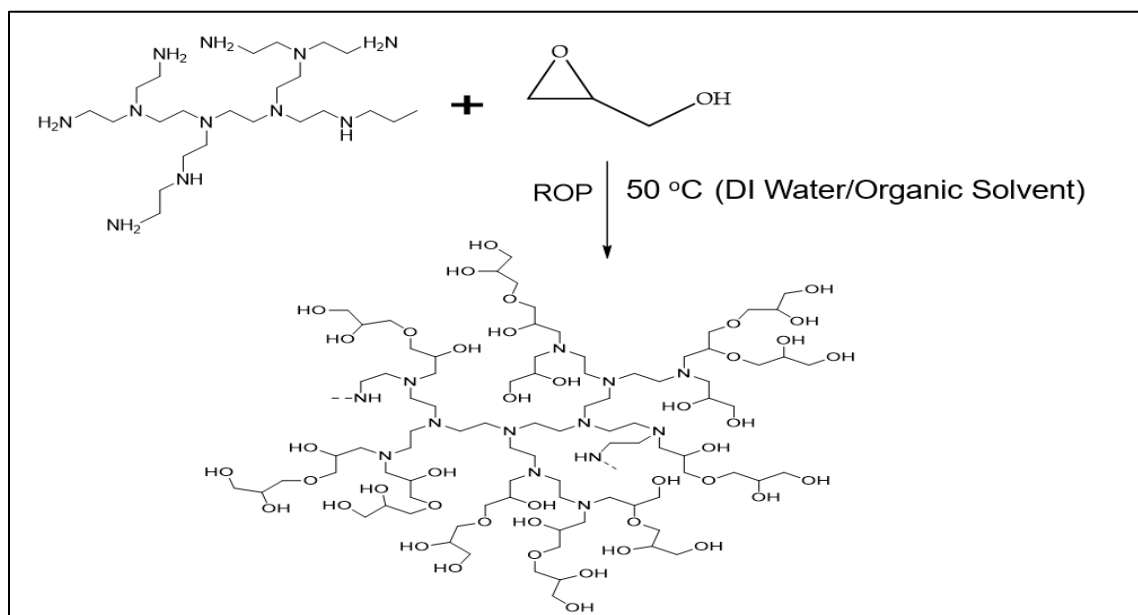
Fig. 55 provides a visual representation of the sequential steps involved in the synthesis of modified branched polymers. We initiate the process by dissolving PEI in water, followed by the gradual addition of Glycidol into the mixture. The reaction is allowed to proceed at a temperature of 50 C for seven days. Subsequently, we introduce

HCl acid to a portion of the polymer and subject it to filtration using 14,000 dialysis bags for seven days, effectively removing unreacted monomers and low molecular weight polymers. The final step involves air-drying the sample to eliminate excess water from the polymer. For the basic condition, we repeat the previous steps, omitting the addition of HCl acid before dialysis.

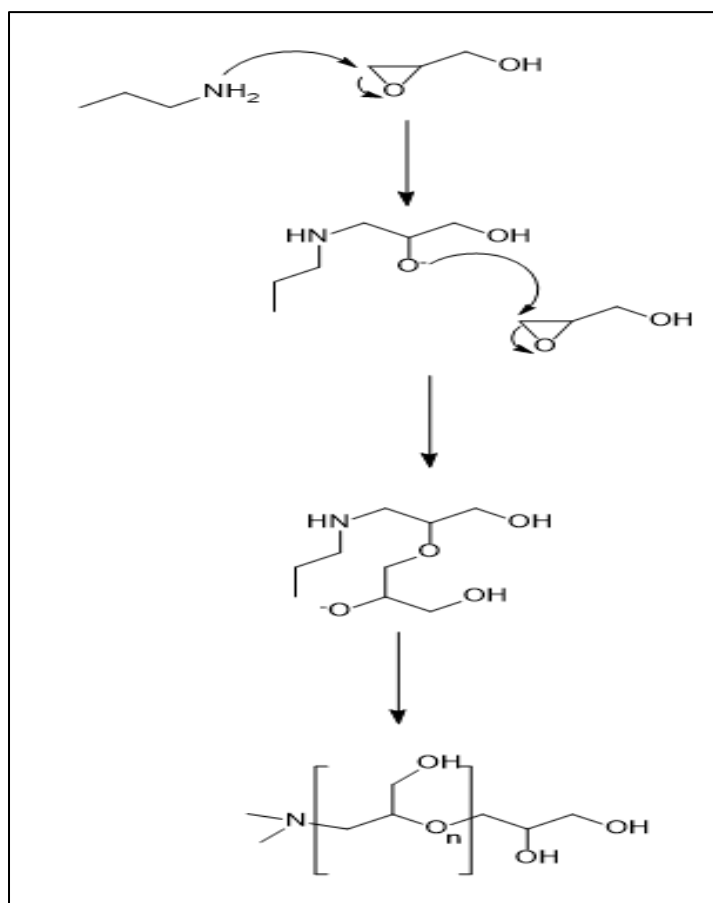


Fig.55: Synthesis of hyperbranched polymers

My first scheme of reaction utilizes branched PEI as a macroinitiator, and glycidol as the cyclic monomer, Schemes 16-17. Different ratios were used to find the optimum PEI: glycidol weight ratio (Table). The polymerization mechanism is anionic ring-opening polymerization.



Scheme 16: Ring Opening Polymerization



Scheme 17: Anionic ring opening polymerization mechanism

Table. 5: Synthesis of hyperbranched polymers (PEI: Glycidol weight ratio)

Polymer #	60K PEI as Macro initiator, grams	Glycidol as Monomer, grams	PEI: Glycidol Weight Ratio
1	4	20	1:5
2	10	20	1:2
3	4	60	1:15
4	60	15	4:1
5	15	15	1:1

We obtained a ^1H -NMR spectrum of Glycidol in D_2O ; the significant peaks show the glycidol, Fig.56. ^1H -NMR of Glycidol in D_2O showed one peak, Fig.57. Fig.58 shows the spectra for one of the synthesized polymers. Region 1 corresponds to the methylene protons ($-\text{CH}_2-$) of PEI, and region 2 represents the methylene and methine protons ($-\text{CH}(\text{OH})-$) of the glycidol unit.

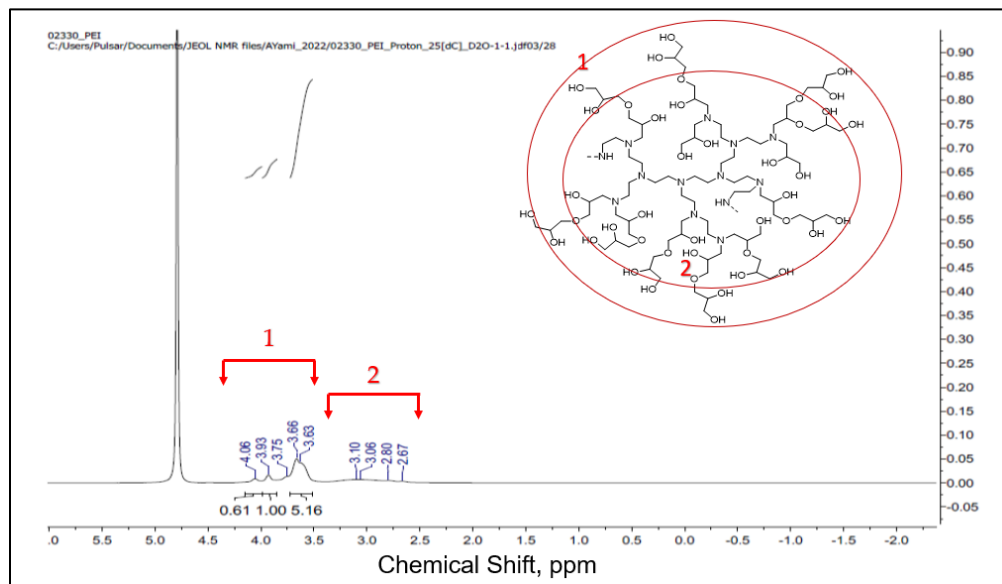


Fig.58: ^1H NMR analysis of the synthesized hyperbranched polymer

We have also conducted ^{13}C NMR on selected synthesized polymers to confirm the presence of branching subunits in the polyglycerol layer in the synthesized polymers. Fig. 59 shows that the region of PEI is between 36-58, and the peaks above 60 are due to the glycidol unit. However, there are no dendritic branching subunits since no peak is presented around 80 ppm. So, we have glycidol on the surface of the PEI, but mainly as linear and terminal subunits. Another indication is the high viscosity we have seen with this polymer. ^{13}C NMR for same polymer but under basic conditions similar type of linear poly glycidol coating the PEI, Fig. 60. We have noticed here that we have higher peak shifts as the ratio of PEI/glycidol decrease from 4 to 1 (Fig. 61). At the 1:15 PEI: Glycidol weight ratio, we have seen a branching peak around 80 ppm (Figs. 62& 63), which confirms the presence of dendritic branching. This ratio was chosen based on previous studies and

Fig.59: ^{13}C NMR of synthesized polymer 4 A (Ratio of 4:1 PEI to Glycidol)

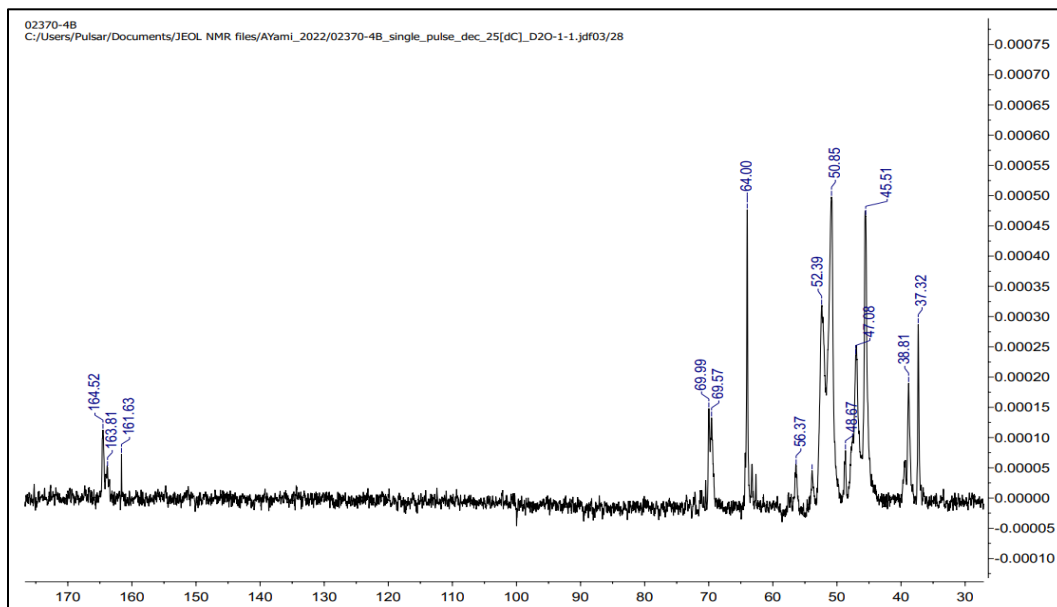


Fig.60: ^{13}C NMR of synthesized polymer 4 B (ratio of 4:1 PEI to Glycidol)

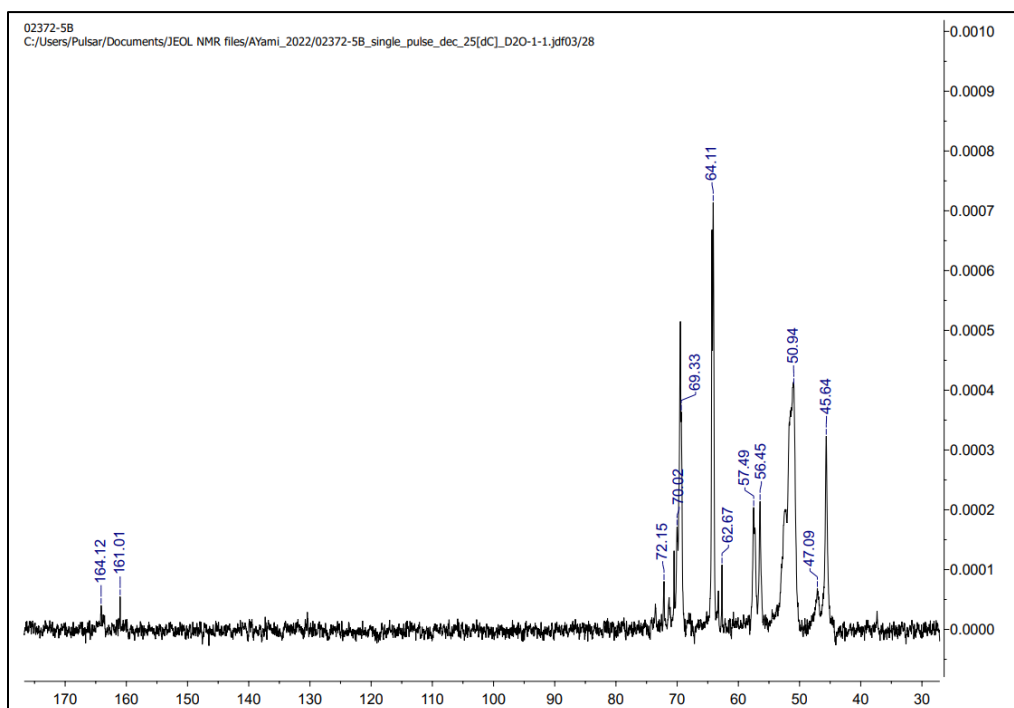


Fig.61: ^{13}C NMR of synthesized polymer 5 (ratio of 1:1 PEI to Glycidol)

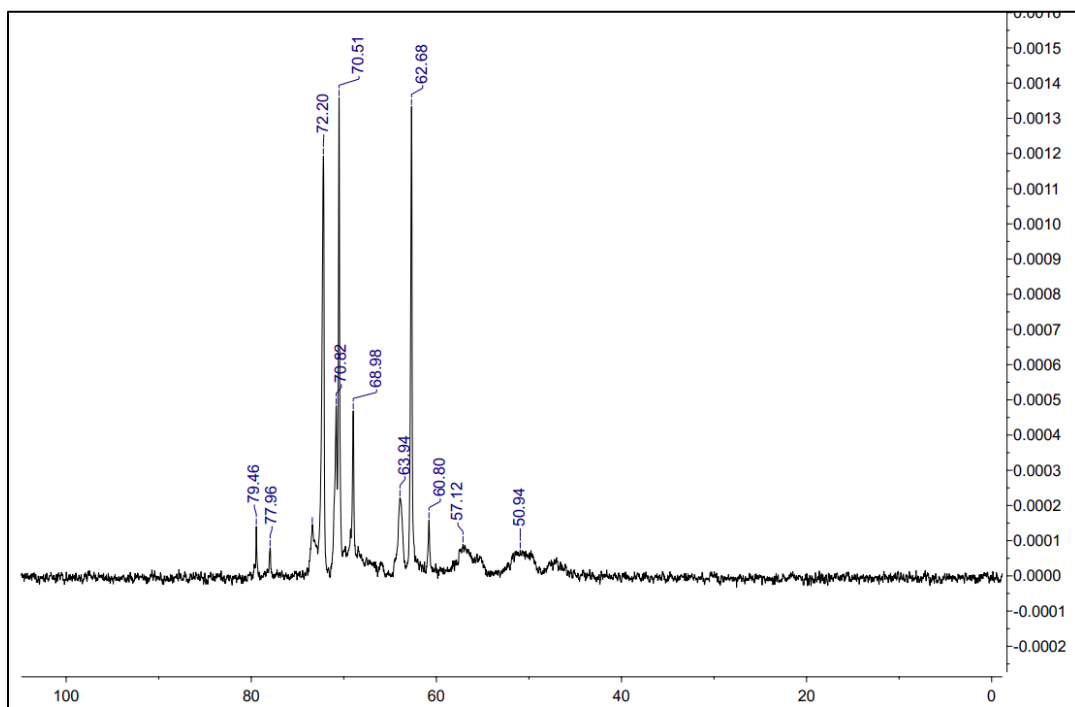


Fig.62: ¹³C NMR of synthesized polymer 3 (ratio 1:15 PEI to Glycidol)

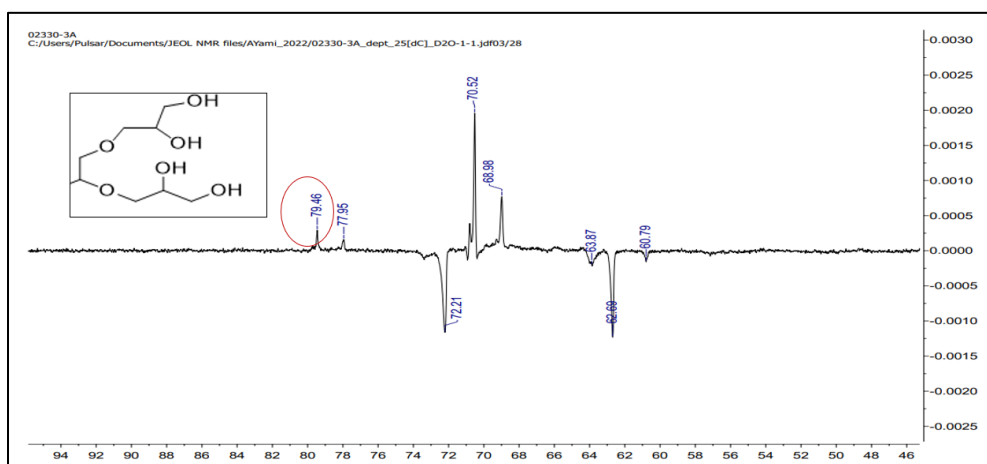


Fig.63: ^{13}C NMR of synthesized polymer 3 (ratio1:15 PEI to Glycidol)

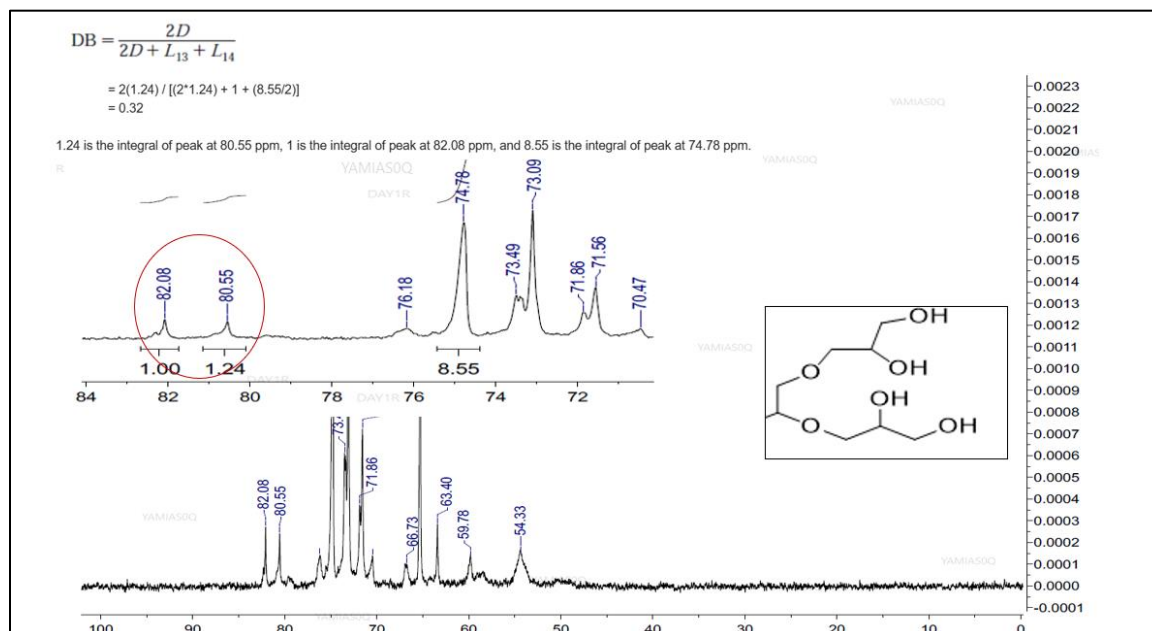


Fig.64: ^{13}C NMR of synthesized polymer 3 (ratio1:30 PEI to Glycidol)

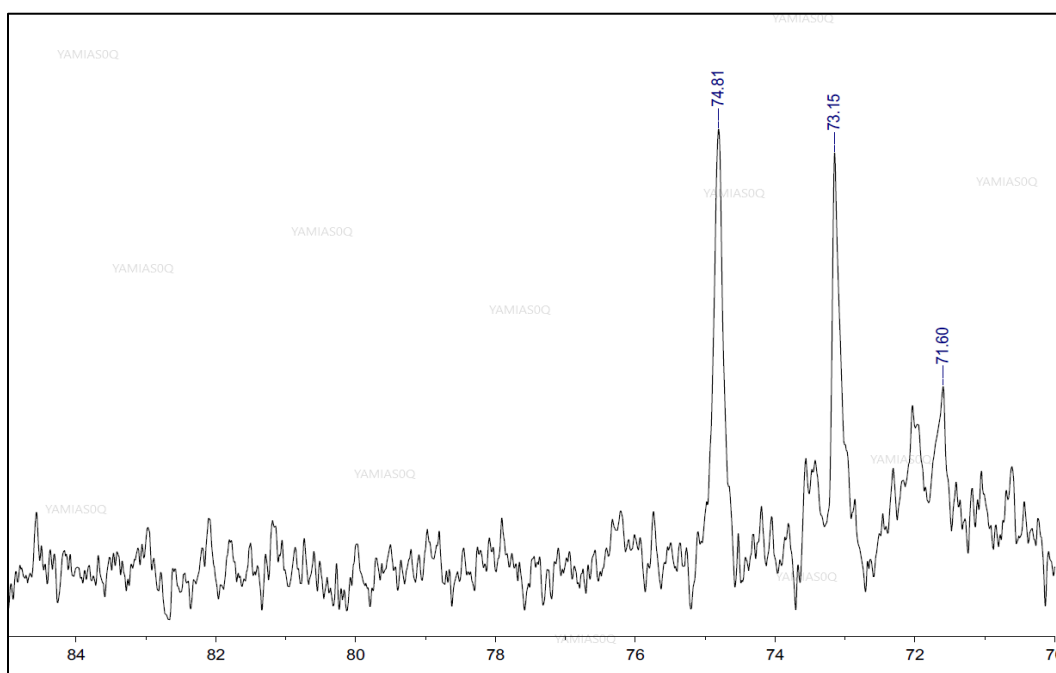


Fig.65: ^{13}C NMR of synthesized polymer 3 (ratio 1:30 Linear PEI to Glycidol)

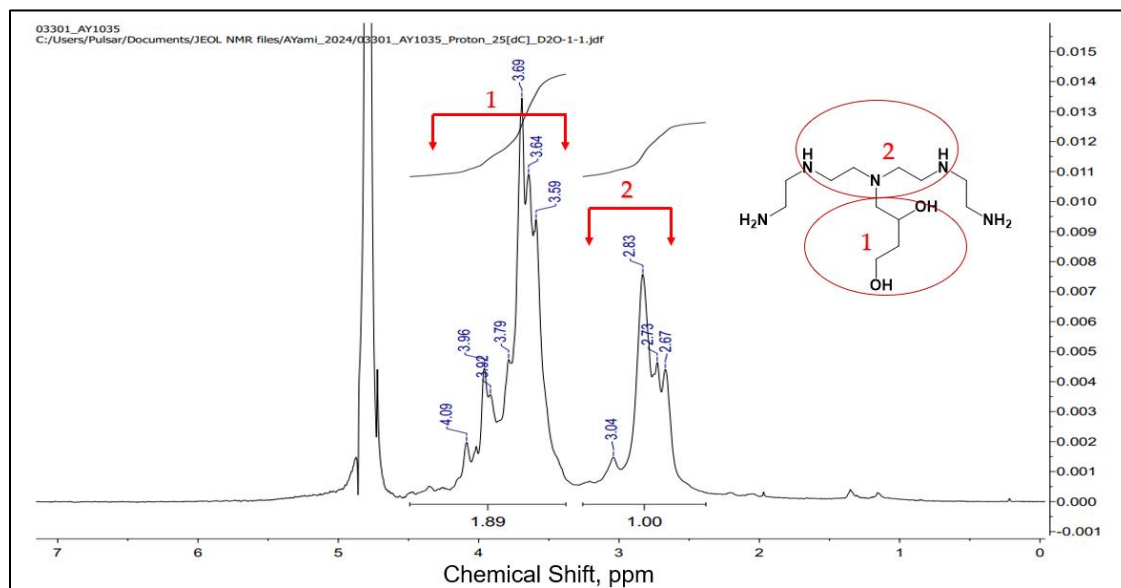


Fig.66: ^1H NMR Analysis of Synthesized Polymer (1:30 Linear PEI to Glycidol Weight Ratio)

Standard and API tests were conducted to prepare and characterize drilling fluids, which were accepted by the industry. The tests covered here are fluids preparation, density, rheology measurements, API and HT/HP filtration, and thermal stability tests. Table 6 shows the formulation we used in this study, where we used the synthesized polymer as an additive. Non-modified PEI with a molecular weight of 10,000 g/mol was used as an additive in the formulation, but it did not work due to solids settling and phase separation after exposing the fluids to 300 F for 16 hours, Fig. 67. PEI with 60,000 g/mol. We have seen an increase in viscosity when using a higher molecular weight of PEI (60,000 g/mol). Adding HPAM to the formulation with the 60,000 g/mol PEI has also resulted in higher viscosity. So, we decided to use 60,000 g/mol as our macro-initiator for the synthesis work, Fig.68.

Table 6: Formulation utilizing hyperbranched polymer and HPAM

Additive	Mixing time, min	Amount, grams
Water		287
Soda Ash	5	0.23
Starch	20 (adding slowly)	5
XC polymer	20 (adding slowly)	1.5

Caustic Soda	5	0.12
HPAM	20 (adding slowly)	3
Synthesized Polymer	20 (adding slowly)	3
Barite	5	234
Sodium Sulfite	5	0.5



Fig.67: Characterization of drilling fluids

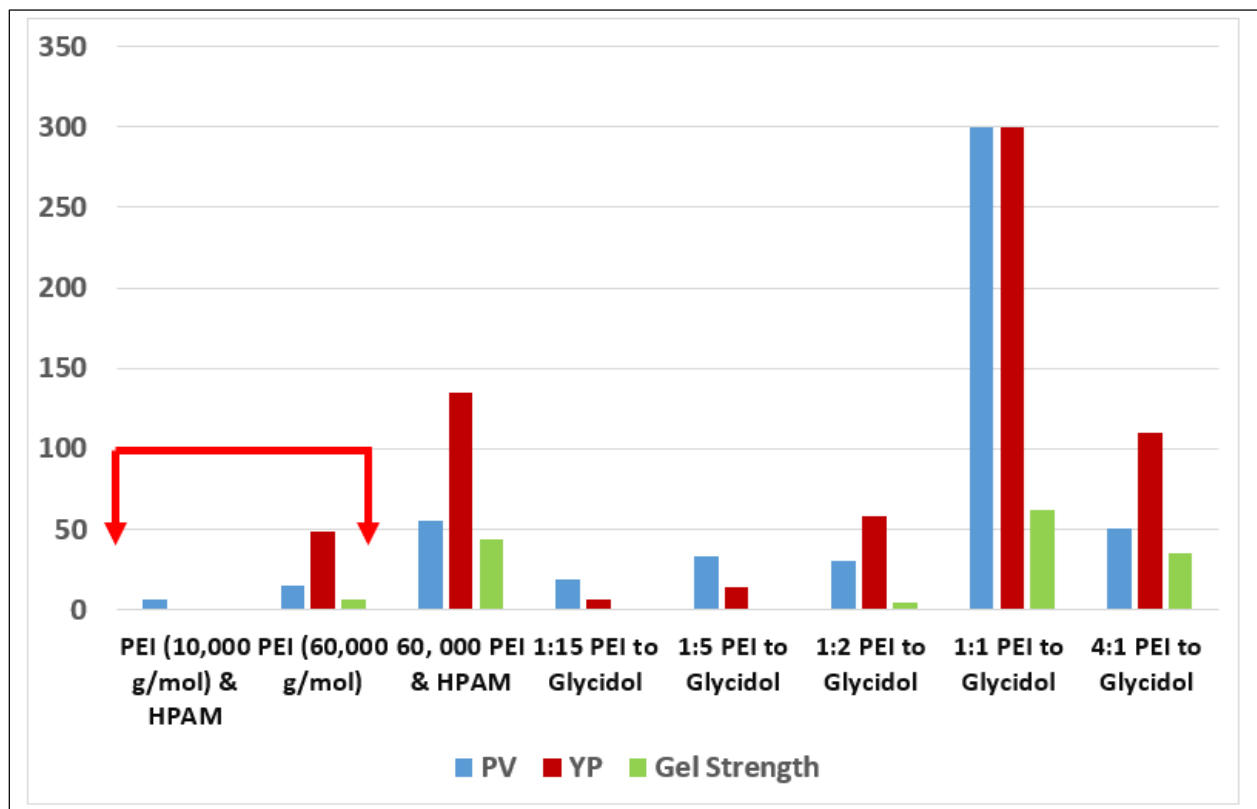


Fig.68: Non-modified PEI after aging at 300 °F

Fig. 69 shows synthesized polymer 1 with a ratio of 1:5 PEI to Glycidol BHR and AHR at 300°F. The dashed lines show the typical values used in drilling operations. Plastic viscosity is the property that allows us to suspend cutting in static conditions. The yield point is the property that allows us to carry the cutting under dynamic mode while drilling. Too low a Gel strength value means we will have settling. Too high gel strength means we need high pumping pressure to pump the drilling fluid. For any fluid to work, it has to meet all the requirements for these measurements. So, the modified polymer with a ratio of 1:5 PEI to glycidol did not meet the requirements.

Fig. 70 shows synthesized polymer 2 with a Ratio of 1:2 PEI to Glycidol BHR and

AHR at 300°F. For this polymer, we can see better performance for 2B. The yield point exceeds the recommended values after aging at 300 °F. Fig. 71 shows the synthesized polymer 3 with a Ratio of 1:15 PEI to Glycidol BHR and AHR at 300 °F. Here, this is the smallest PEI ratio to Glycidol. After aging at 300 °F, no good results were observed for gel strength or yield point.

Fig. 72 shows synthesized polymer 4 with a Ratio of 4:1 PEI to Glycidol BHR and AHR at 300 °F. Like polymer 2, the polymers modified under primary conditions showed higher viscosity than acidic ones. Fig. 73 shows synthesized polymer 5 with a Ratio of 1:1 PEI to Glycidol BHR and AHR at 300 °F. Comparing polymer 5 and polymer 4, where we have fixed the glycidol amount and varied the PEI, showed us that the optimum ratio of PEI to Glycidol is 1.

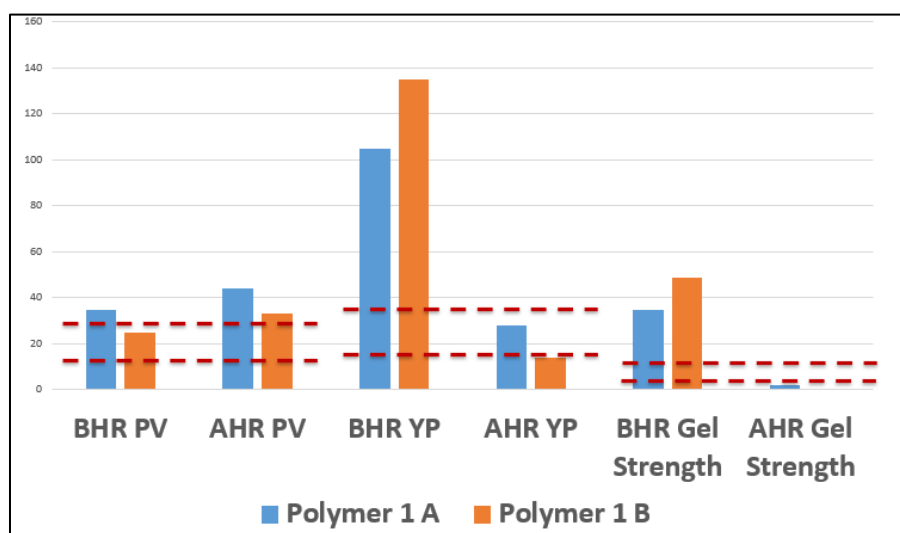


Fig.69: Synthesized polymer 1 with ratio of 1:5 PEI to glycidol BHR and AHR at 300 °F

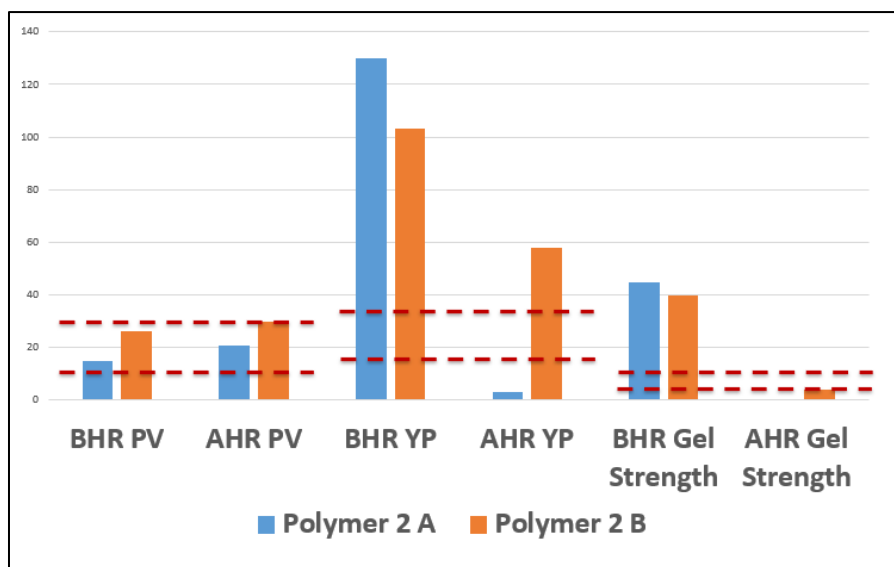


Fig.70: Synthesized polymer 2 with ratio of 1:2 PEI to glycidol BHR and AHR at 300 °F

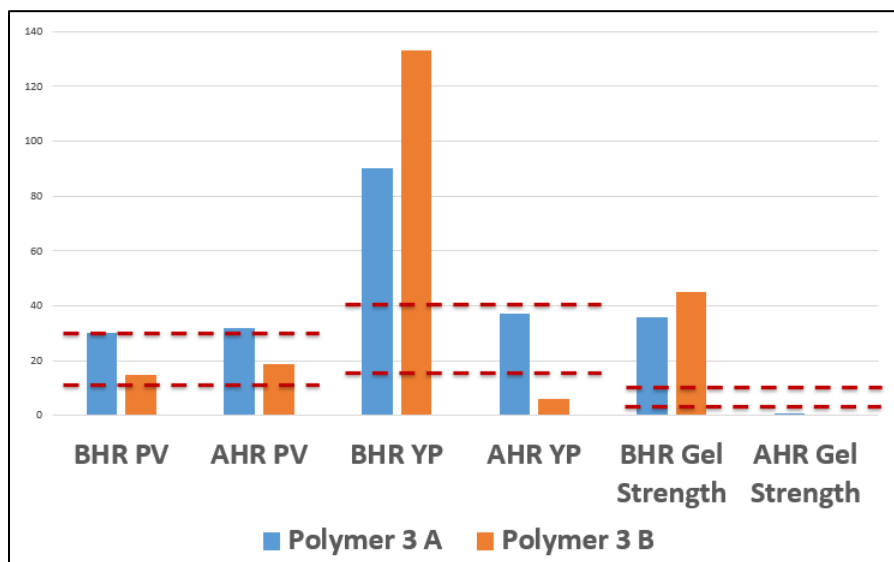


Fig.71: Synthesized polymer 3 with ratio of 1:15 PEI to glycidol BHR and AHR at 300

°F

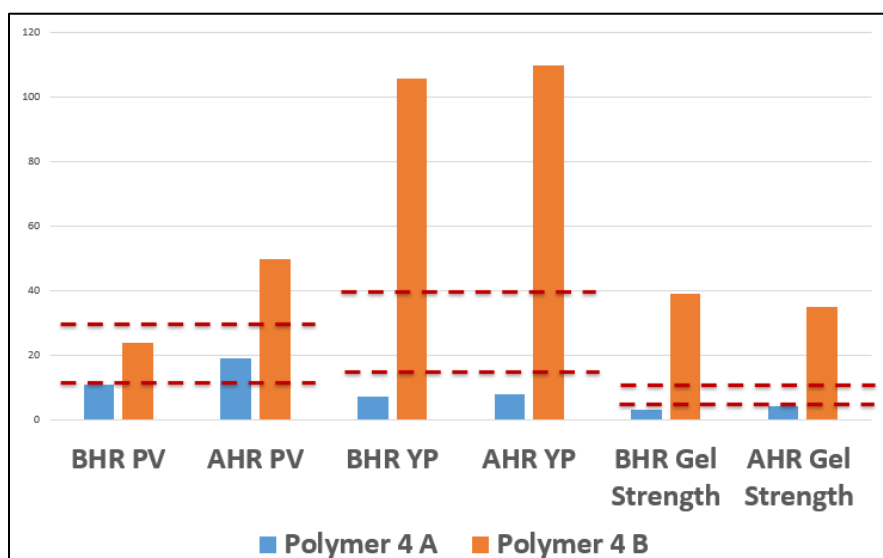


Fig.72: Synthesized polymer 4 with Ratio of 4:1 PEI to glycidol BHR and AHR at 300 °F

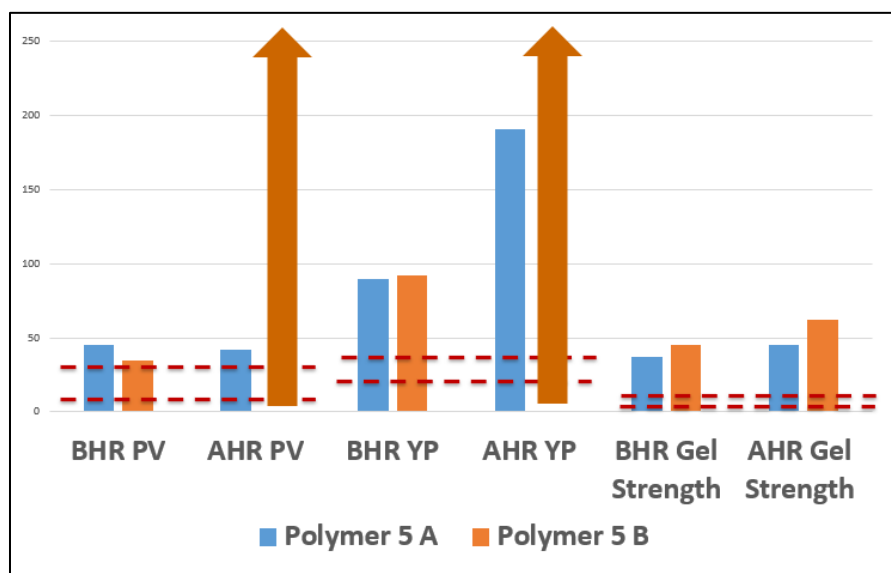


Fig.73: Synthesized polymer 5 with ratio of 1:1 PEI to glycidol BHR and AHR at 300 °F

Fig. 74 compares the rheology for all five synthesized polymers under basic conditions. We can see that the optimum point is at a ratio of 1:1 PEI to glycidol, which is

in primary condition. We have carried out a ^{13}C NMR analysis on selected synthesized polymers to see if we have achieved branching in the polyglycerol layer of the synthesized polymers. We know that higher branching means lower viscosity. The same trend applies to the acidic condition (Fig.75), where we have obtained the highest viscosity when using the ratio of 1:1 PEI to glycidol. However, we can observe that we always get the highest viscosity under basic conditions. The reason for lower viscosity under acidic conditions is that when we add HCl, the salt anion here will make the core of the PEI denser, which can restrict its movement to form hydrogen bonding or get cross-linked with the HPAM.

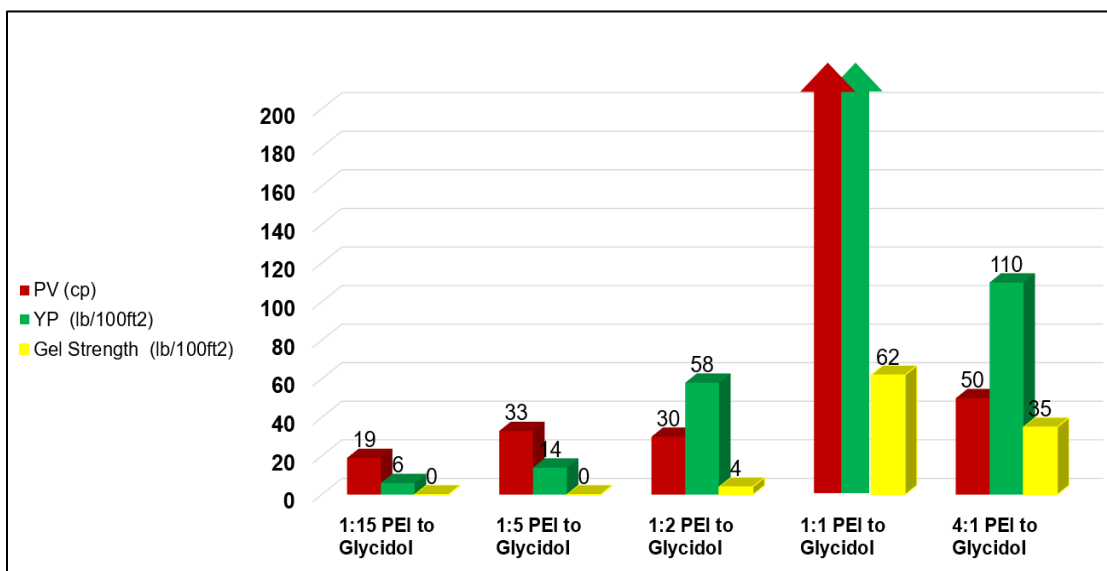


Fig.74: Ratio of PEI to glycidol Vs. performance (basic conditions)

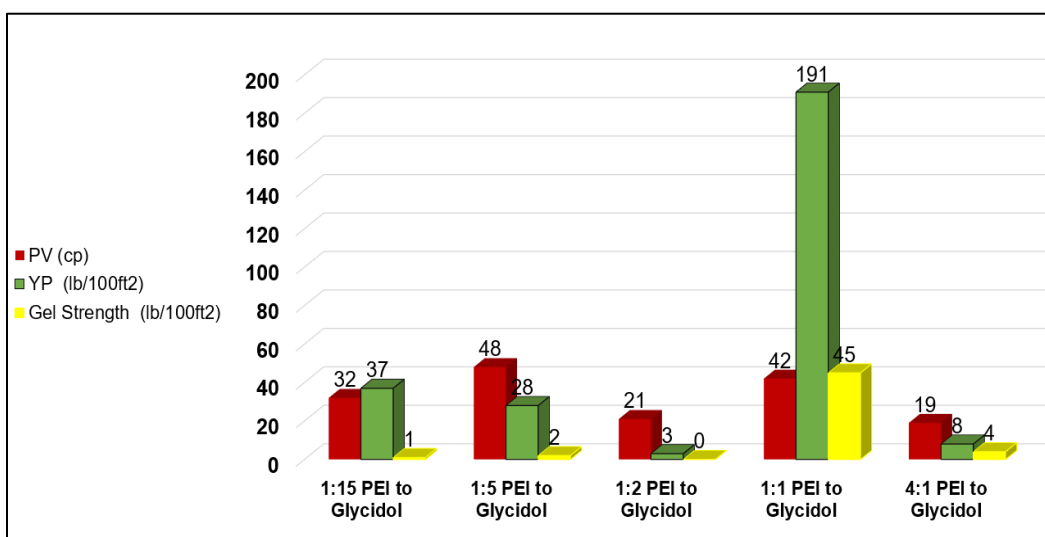


Fig.75: Ratio of PEI to glycidol Vs. performance (acidic conditions)

Table 7 shows a typical formulation that is being used to check tolerance for any polymer against salinity. We have tested all the synthesized modified PEIs and non-modified PEIs. All have shown phase separation after aging for 16 hours at 300 °F, Fig.76. It is a challenging task to have polymers that can withstand high temperature degradation and high salinity effect. So far, the modified PEI have shown good results in fresh water formulations at high temperatures. We have tried to optimized the formulations by replacing barite with Mn_3O_4 . Both are used to increase density; however, we have observed no phase separation when using Mn_3O_4 due to its small particle size and spherical shape which improves its suspension, Fig. 77. However, there was solids accumulation which prevented us from taking the measurements. Testing against $CaCl_2$ (Fig 78) and KCl (Fig. 79) showed no phase separation. Testing against $CaBr_2$ (Fig.80) showed phase separation.

Table 7: Branched polymers tolerance against salts

Additive	Mixing time, min	Amount
CaCl ₂ , 84 pcf (338,478 ppm)		42 ml
CaBr ₂ , 90 pcf (416,540 ppm)	5	262 ml
Starch	20 minutes (adding slowly)	5
XC Polymer	20 minutes (adding slowly)	1.5 grams
Synthesized Polymer	5	3 ml
HPAM	20 minutes (adding slowly)	3 grams
Barite (BaSO ₄)	20 minutes (adding slowly)	140 grams
lime	5	2.5 gram
Sodium Sulfite	5	1 gram
CaCO ₃ fine	5	15 grams
CaCO ₃ medium	5	15 grams
Revdust	5	30 grams



Fig.76: Hyperbranched polymers in high salt formulations show phase separation after aging at 300 °F



Fig.77: Hyperbranched polymers utilizing Mn_3O_4 in high salt formulations show no phase separation after aging at 300 °F

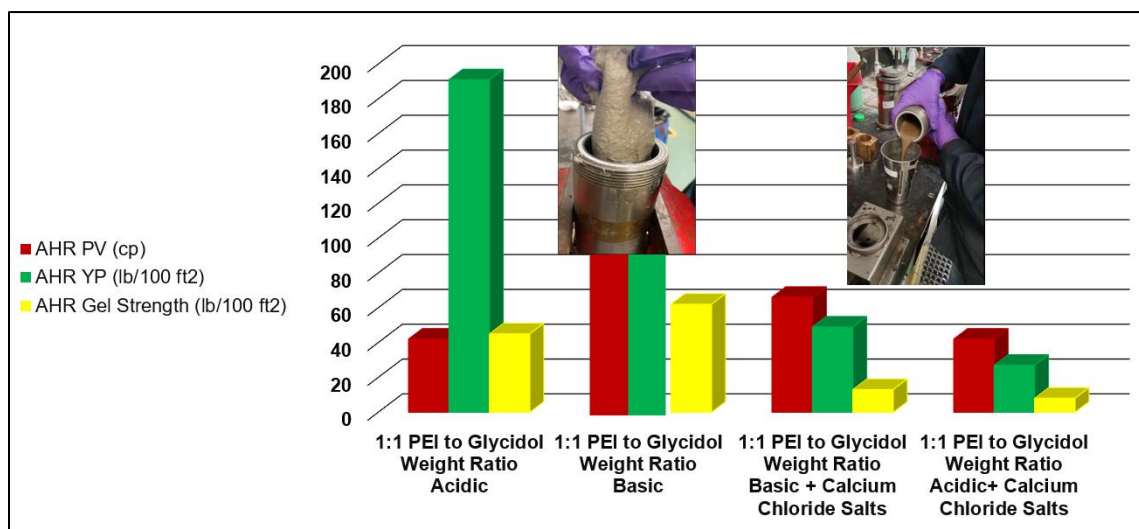


Fig.78: Hyperbranched polymers utilizing Barite in high CaCl_2 formulations show no phase separation after aging at 300 °F

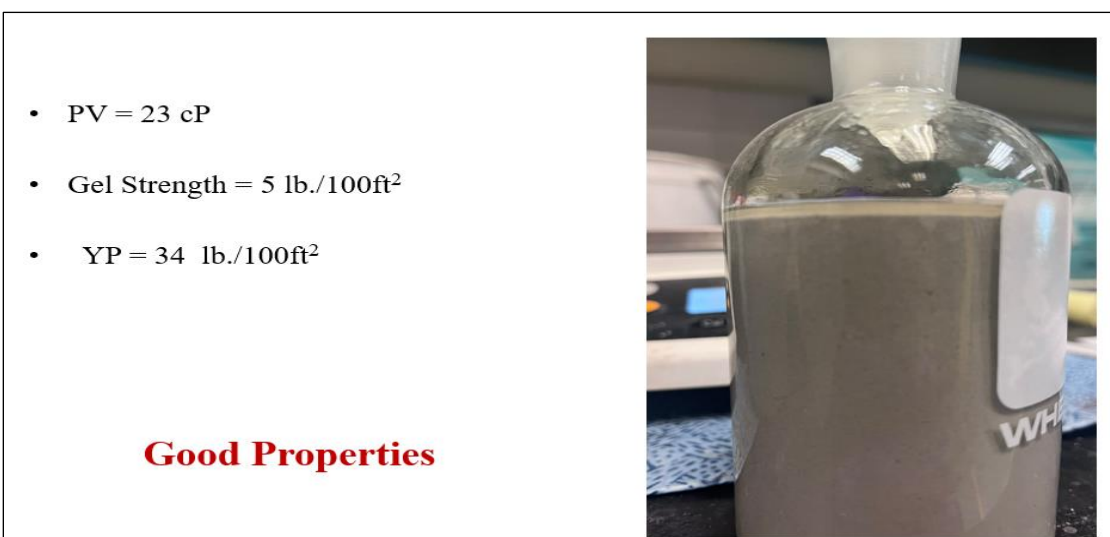
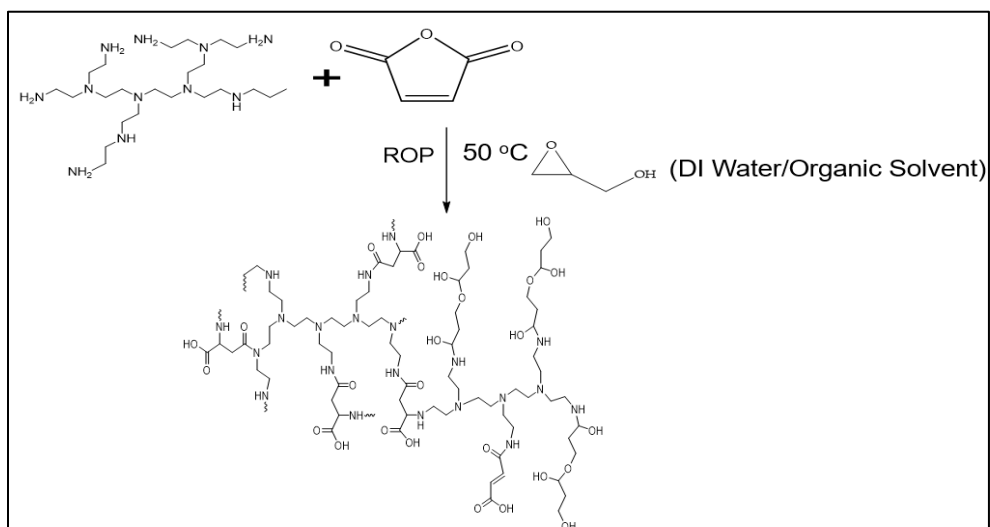


Fig.79: Hyperbranched polymers utilizing Barite in high KCl formulations show no phase separation after aging at 300 °F

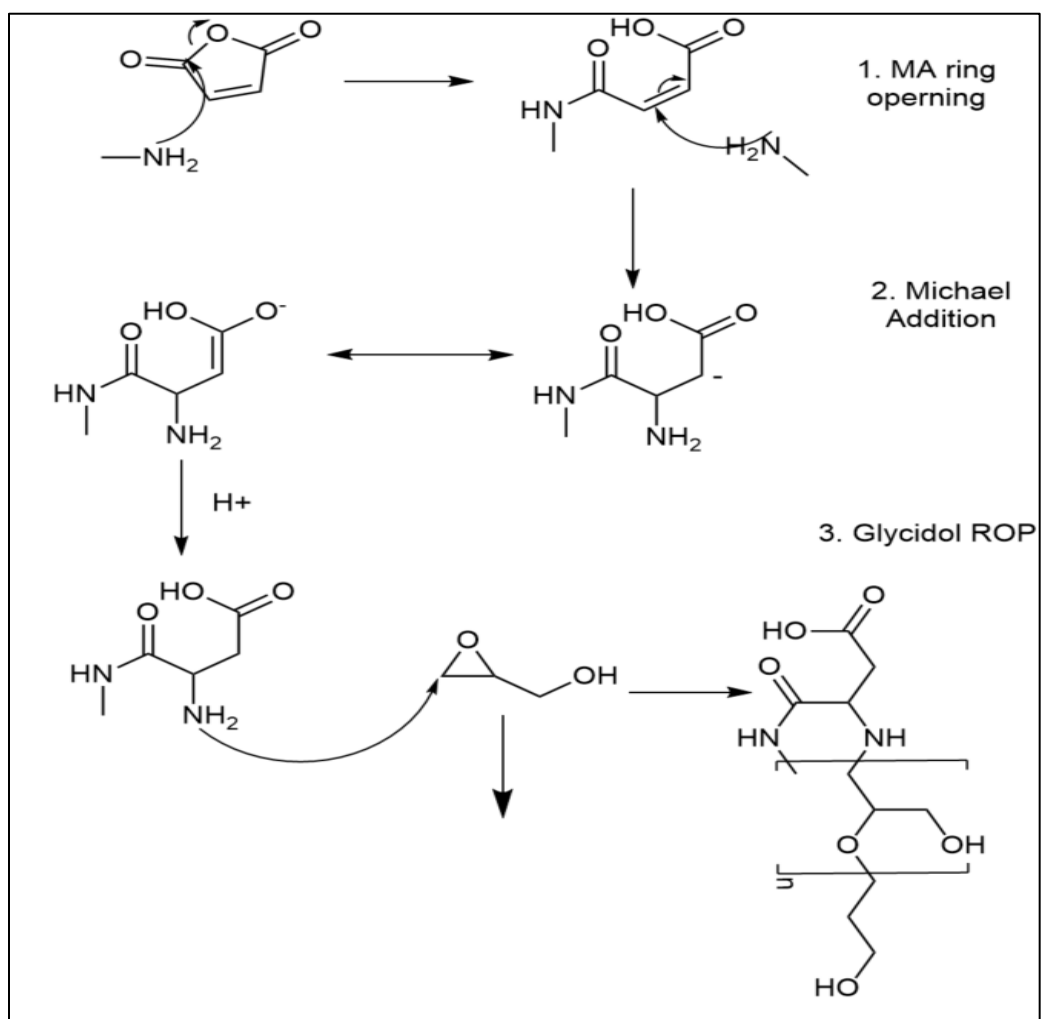


Fig.80: Hyperbranched polymers utilizing Barite in high CaBr_2 formulations show no phase separation after aging at 300 °F

We are now moving to the second family of polymers utilizing Maleic Anhydride, Scheme 18. There are three mechanism steps here. The first is the ring opening of Malick anhydride, the second step is Micheal addition, and the third and final step is the polymerization by anion ring opening of glycidol monomer, Scheme 19. The ^1H NMR (Fig. 81) provides a clear view of the glycidol and PEI region, as previously indicated in the synthesis. Additionally, a small peak at 5.9 ppm is observed, indicating the successful reaction of the majority of the double bond due to Micheal's reaction.



Scheme 18: Maleic Anhydride Cross Linking Scheme



Scheme 19: Maleic anhydride cross linking reaction mechanisms

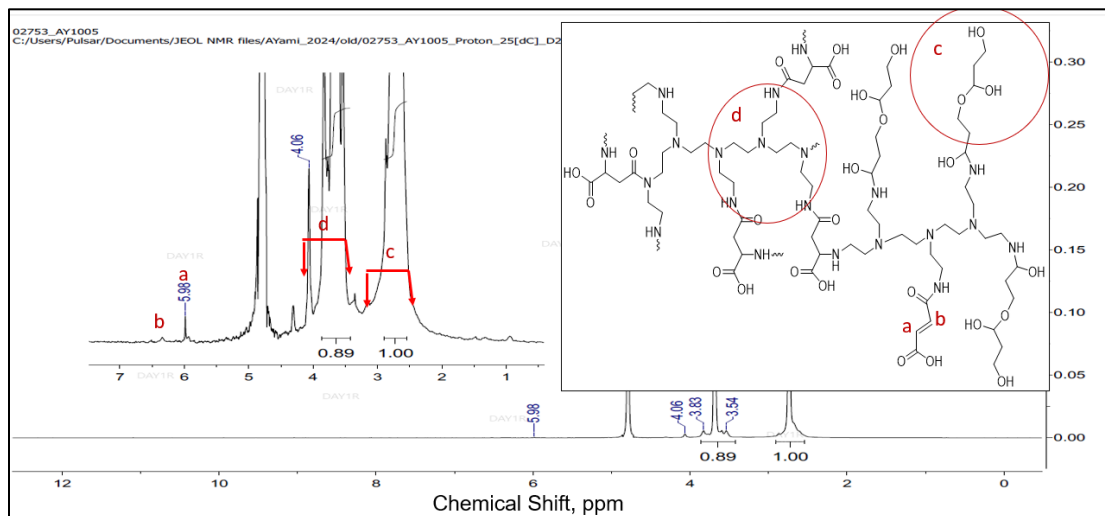


Fig. 81: Maleic anhydride crosslinked hyperbranched PEI

Our study's findings have direct implications for the industry. We have designed and tested over 60 different formulations and iterations, using synthesized branched and hyperbranched polymers. These polymers have been successfully used to formulate water-based drilling fluids, a promising alternative to oil-based fluids. The development of optimum concentrations using these innovative polymers has shown excellent resistance in high-temperature environments. Our findings emphasize the practical need for specific polymers and concentrations for achieving acceptable viscosity measurements, Fig. 82.

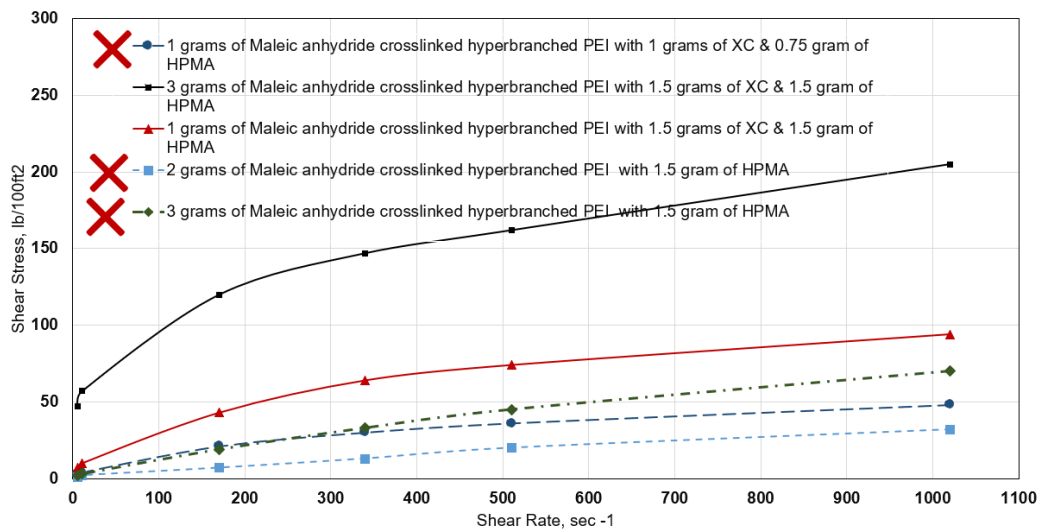


Fig. 82: Performance testing of Maleic anhydride crosslinked hyperbranched PEI in water-based drilling fluids

Shale Dispersion

Our successful development of a high-performance polymer water-based drilling fluid, capable of withstanding high-temperature conditions and being environmentally friendly, brings us to the final requirement for replacing oil-based drilling fluids—good shale inhibition. To understand this requirement, we conducted a shale characterization study. A recovery factor above 90% is considered acceptable for drilling applications. We have collected representative shales from typical formations that are drilled with oil-based fluids. The first shale is from the Qusaiba Formation, and the second is from the Sudair Formation, Fig. 83. The Qusaiba Shale formation, also known as the Silurian “hot” shale, is a significant part of our study. It was formed in the Paleozoic about 440 mya in shallow marine environments under anoxic water conditions. It serves as one of the primary source

rocks of Paleozoic hydrocarbons [233]. Fig. 84 describes the clay type in the Qusaiba shale specimens obtained using X-ray diffraction (a typical diffractogram from a sample at 35 m deep). The predominant clay types in the Qusaiba formation are highly variable and include kaolinite of between 6 to 80%, muscovite of 1 to 37%, and antigorite (serpentine group) of 0 to 56%. Fig. 85 describes the clay type in the Sudair shale specimens obtained using X-ray diffraction (seen in a typical diffractogram from a sample at 13.1 m deep). It also displays core pictures (compressed vertical scale-blue gaps show non-photographed intervals) and concentrations of different minerals with depth: illite, muscovite, quartz, and dolomite. The predominant clay types in the Sudair formation are highly variable and include 0.5 to 83% illite and muscovite of approximately 5 to 86%.

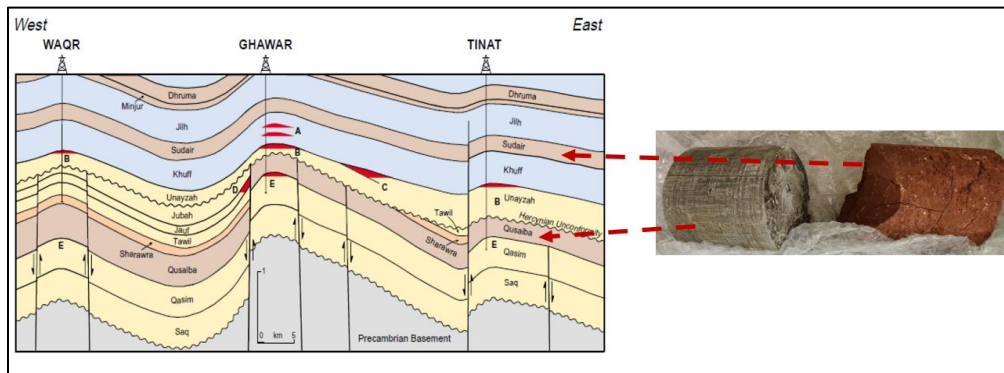


Fig. 83: Selected shales for performance testing

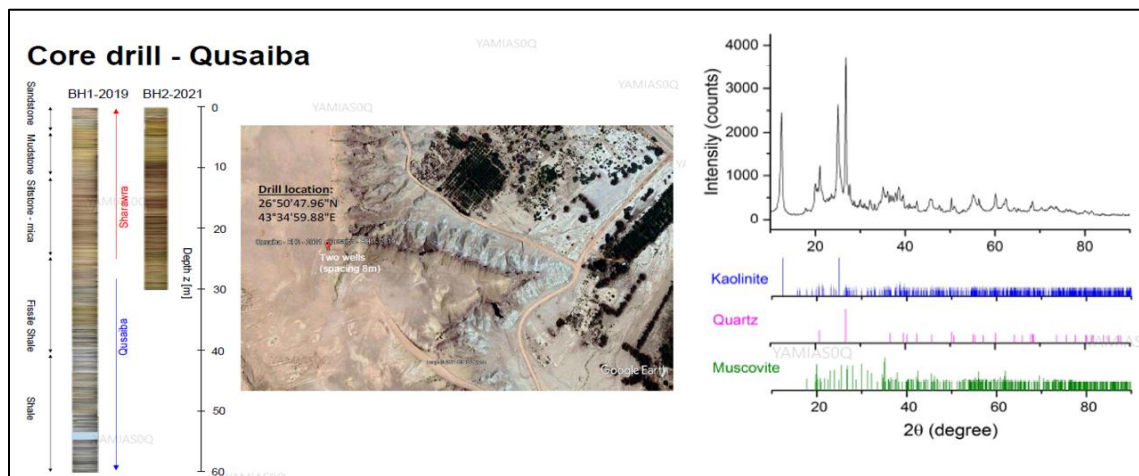


Fig. 84: Qusaiba formation composition

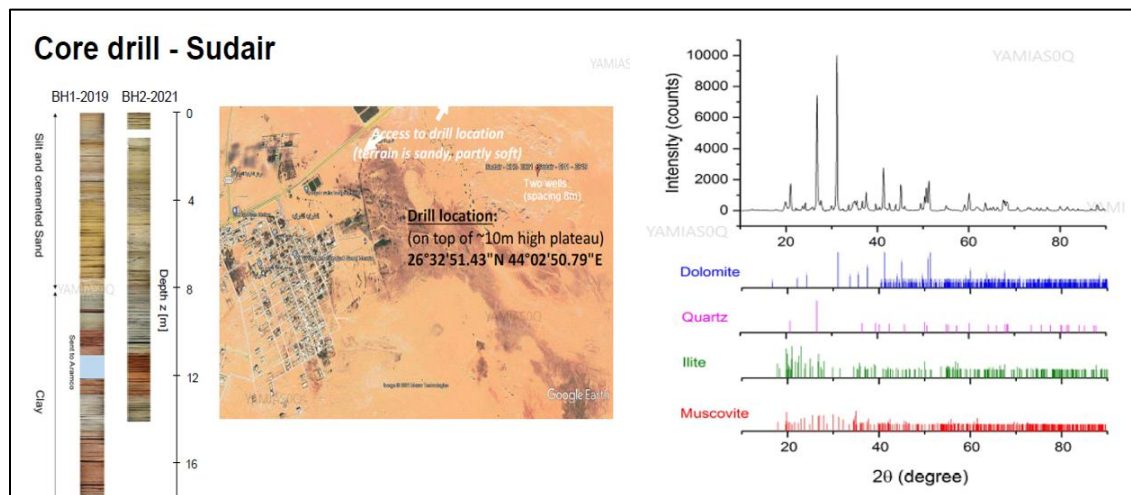


Fig. 85: Sudair formation composition

Kaolinite is a clay mineral with the chemical formula $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$. Illite dominance, a condition where illite, a type of clay mineral having the chemical formula $[(\text{K}, \text{H}_3\text{O})(\text{Al}, \text{Mg}, \text{Fe})_2(\text{Si}, \text{Al})_4\text{O}_{10}[(\text{OH})_2, (\text{H}_2\text{O})]]$, absorbs more water compared to kaolinite, has significant implications for soil properties. This dominance decreases cohesion, strength, friction angle, and safety factor and increases natural moisture content, void ratio, and wet density [234], Fig. 86. The presence of potassium ions between the Illite layers weakens the bonding between the Illite layers. Salts generally have more water affinity, so more water absorbed by Sudair Illite due to the presence of the potassium ion will even weaken the bonding between the layers and cause the shale to disperse more than Qusaiba Kaolinite. An ion exchange mechanism is not an option here since the potassium is fitted between the layers rather than on the surface. Figs. 87-88 shows the Qusaiba composition and Sudair composition.

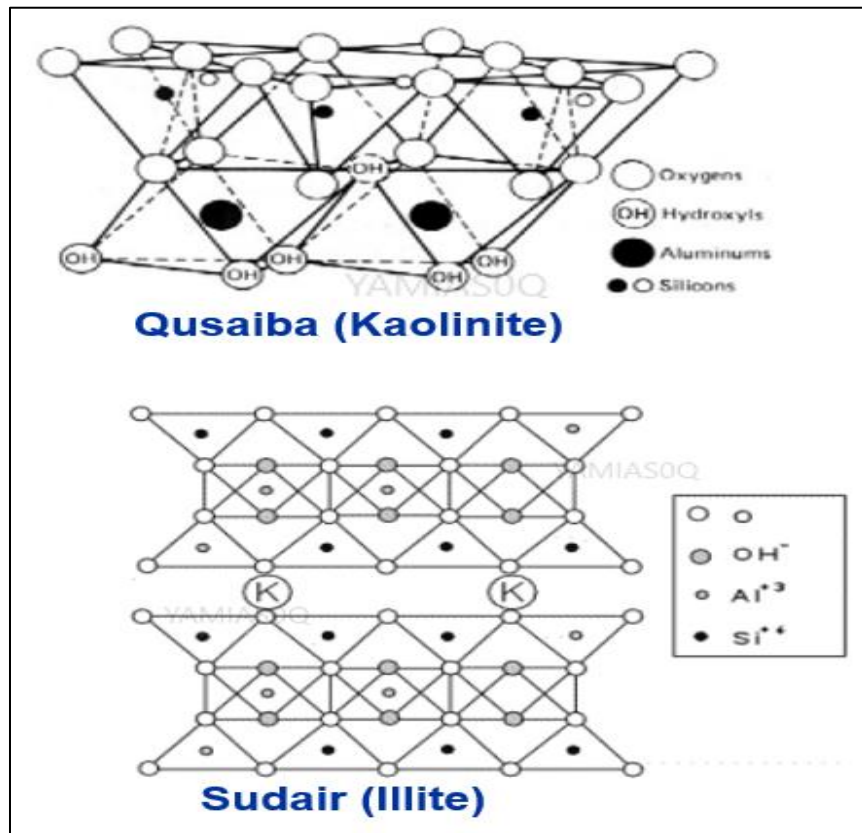


Fig. 86: Qusaiba and Sudair clay composition

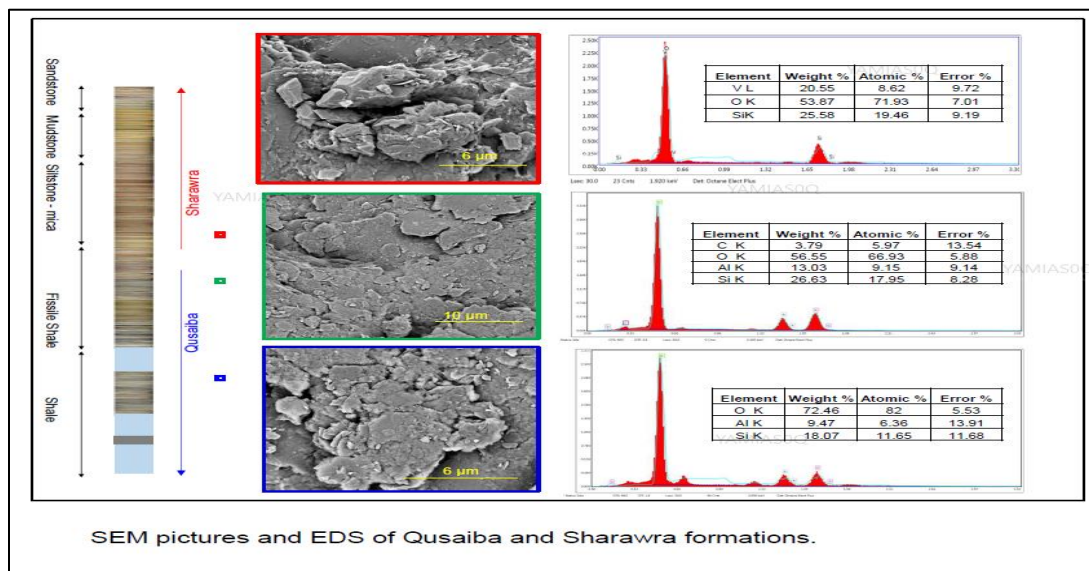


Fig. 87: Qusaiba chemical composition

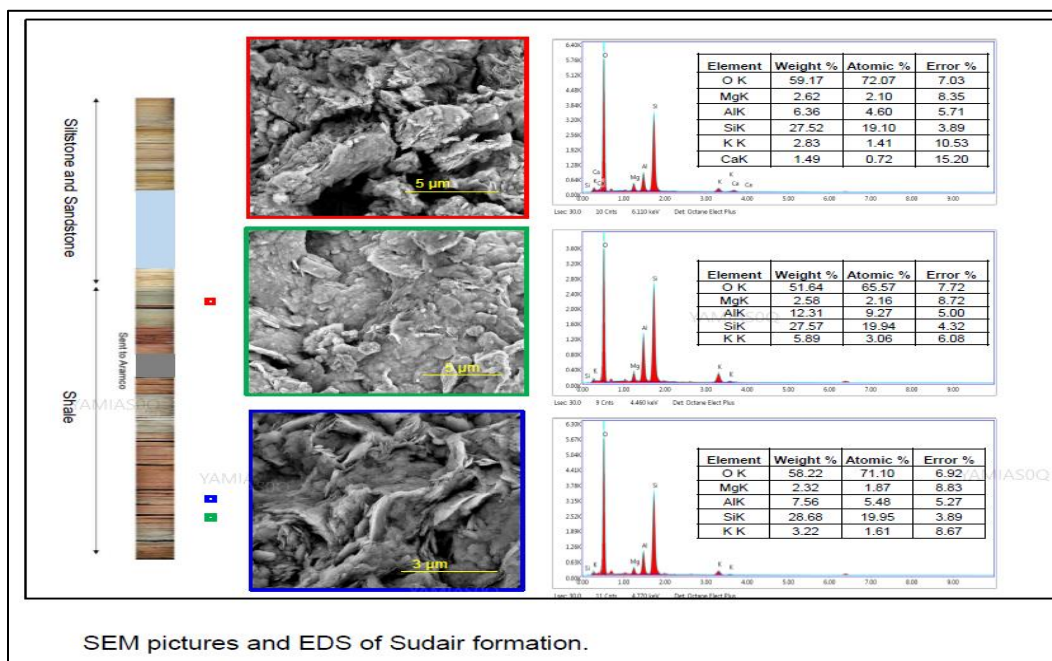


Fig. 88: Sudair chemical composition

It takes 3-4 days to complete drilling a section. A low recovery factor in a few hours means that the inhibition was lost due to water drilling and that we need to find a better

shale inhibitor to show a longer-term recovery factor. The procedure detailed in this study was followed to compare the performance of the synthesized hybrid polymers against Qusaiba shale. As discussed in the shale characterization section, severe shale loss and low recovery factors are expected when testing against Sudair shale due to higher reactivity. The differences in reactivity between both formations might be due to differences in mineral composition and clay type, with illite (the predominant clay in the Sudair formation) more reactive than kaolinite (the predominant clay in Qusaiba).

Our findings from the short- and long-term inhibition testing, conducted for both Qusaiba and Sudair using typical oil-based drilling fluids, have practical implications, Fig. 89. As expected, a 100% recovery factor was achieved for both. However, when long-term shale inhibition is conducted in water instead of oil-based drilling fluids, the recovery factor is dramatically reduced, especially in the Sudair formation. This is due to the presence of potassium salt in the Illite clay in Sudair. The long-term shale inhibition in water is a practical simulation of water use in case of hitting losses while drilling, highlighting the importance of our research in real-world drilling operations.

In the absence of a shale inhibitor, we observed a recovery rate of less than 70%, a figure that falls below the acceptable threshold for drilling operations. However, our synthesized polymer delivered impressive results, surpassing 90% in short-term recovery and maintaining a commendable 80% in long-term recovery factor. This performance outshines typical oil-based drilling fluids, underscoring the polymer's crucial role in drilling shale formations with a high potential for losses. The success of our synthesized polymer can be attributed to the hydrogen bonding from the amines and the high polymer

weight of the branched PEI, which effectively seal the shale formation and prevent invasion, Fig.90

Unsurprisingly, Sudair presented a more formidable challenge (Fig. 91), with all the polymers struggling to match their performance in Qusaiba. The SEM images (Fig. 92), both before and after the shale dispersion testing, vividly illustrate the sealing capability of the synthesized branched polymer, effectively coating the shale and minimizing water invasion.

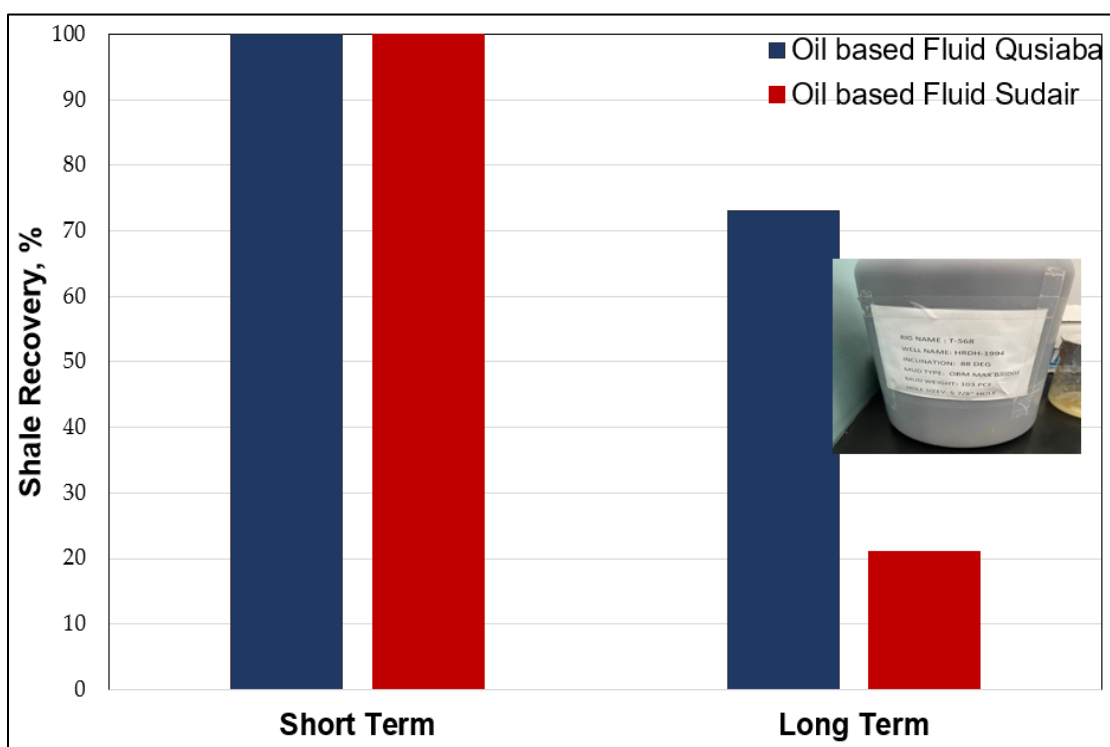


Fig. 89: Long- and Short-Term Shale Inhibitions using typical oil-based drilling fluids

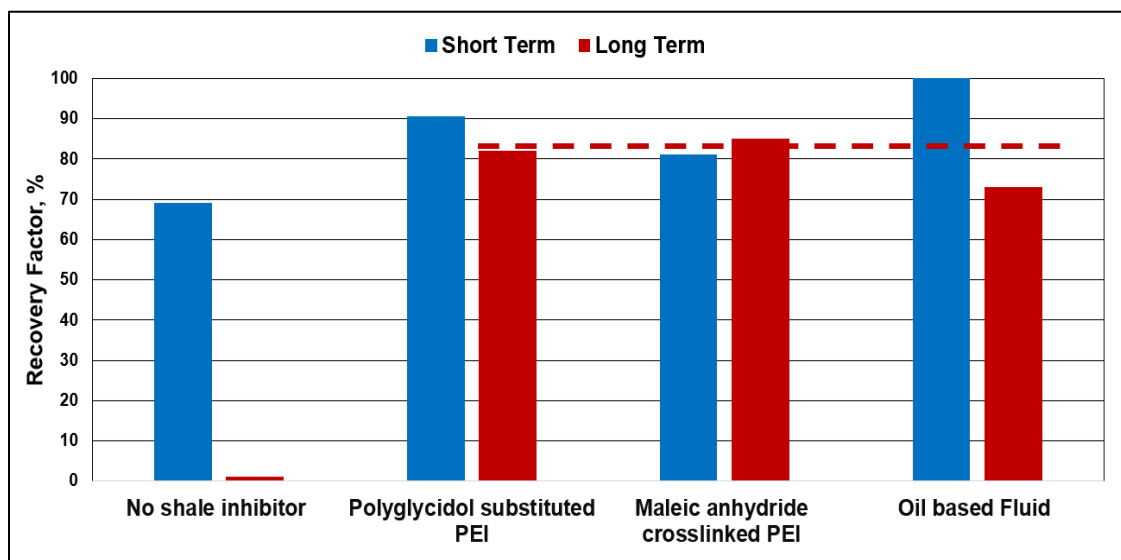


Fig. 90: Polymers Water Based Fluids' Qusaiba Shale inhibition

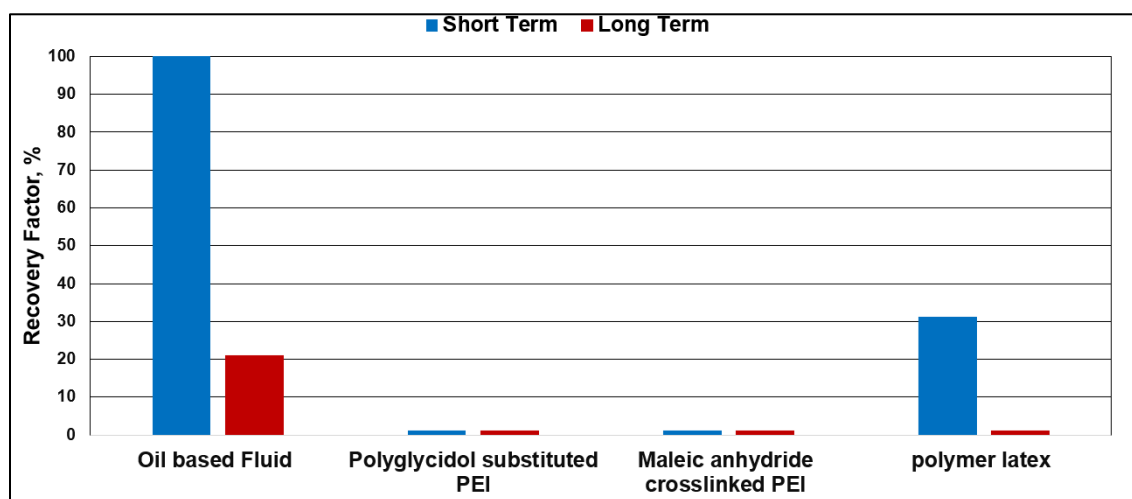


Fig. 91: Polymers Water Based Fluids' Sudair Shale inhibition

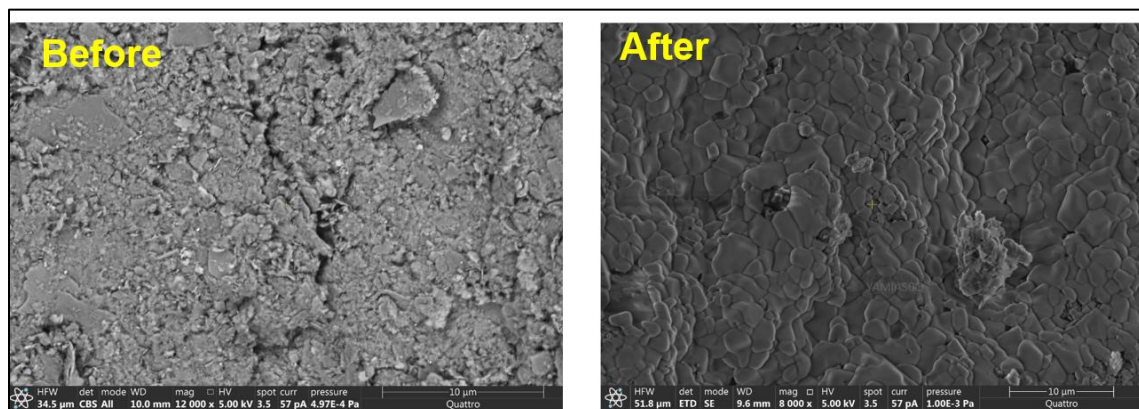
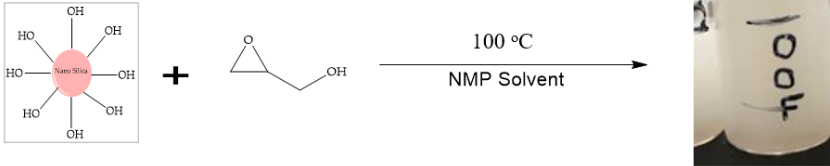


Fig. 92: SEM images of Shale Inhibition

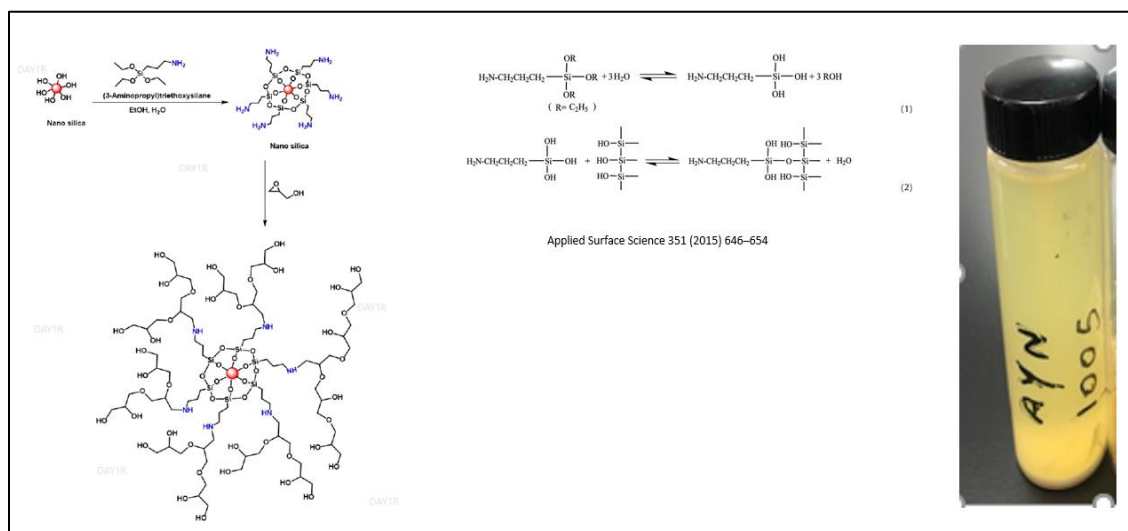
So, we still need to provide good inhibition for Sudair formation and want to see if higher shale inhibition can also be provided to Qusaiba, so we switched our strategy to hybrid polymers that are cost-effective and environmentally friendly. We select nano silica and nano titanium dioxide for our next synthesis phase. We started first to see if we could use the hydroxyl group of the silica as an initiator to open up the glycidol ring. The results showed that we could not get the dispersity required, as shown in Scheme 20. After that, we conducted surface modification of the post-functionalized nano silica using APTES. The hydrolyzed APTES will condense the hydroxyl group from the nano-silica surface and bind with it [235]. Having an amino group in the APTES can help us in the ring-opening polymerization of the glycidol since Amines are stronger nucleophiles than the hydroxyl groups. The dispersion of the hybrid polymer was improved, Scheme 21. However, the performance testing for shale inhibition was unacceptable for Qusaiba shale. Dispersion

testing also was not acceptable for the post-functionalized nano silica when used in water-based drilling formulation, Fig. 93.

Hybrid polymer	Macro Initiator	Monomer	Nano Material
1	Post Functionalized Nano Silica	Glycidol	Nano Silica
2	Amine Group Surface Functionalized Nano Silica by APTES (Aminopropyltriethoxysilane)	Glycidol	Nano Silica



Scheme 20: Hyperbranched nano silica hybrid polymers synthesized by post functionalized nano silica as macro initiator



Scheme 21: Hyperbranched nano silica hybrid polymers synthesized by modified post functionalized nano silica as macro initiator

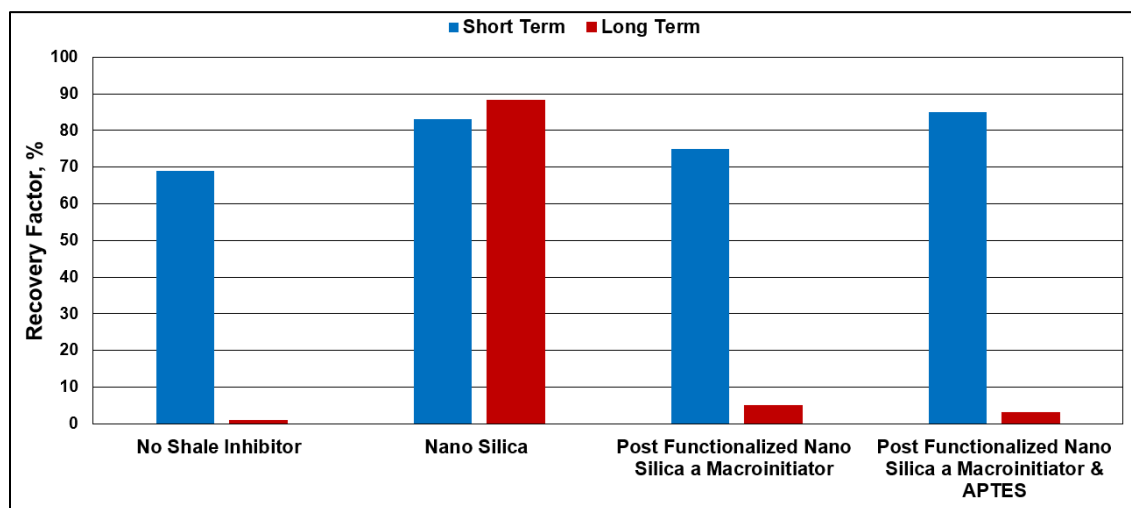


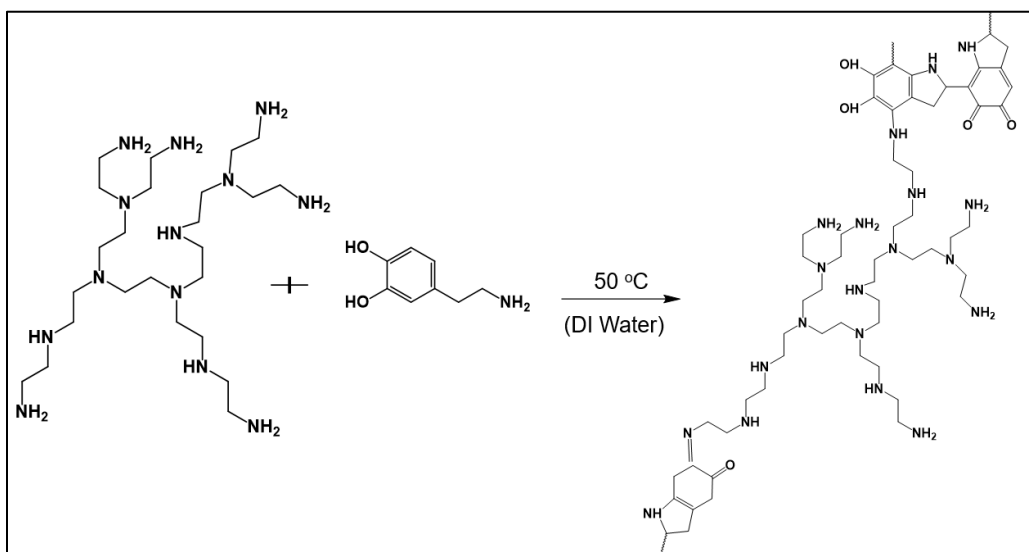
Fig. 93: Hybrid Polymers Water Based Fluids' Qusaiba Shale Inhibition

Next, we delved into the literature and discovered that Dopamine is the most effective anchor group. Dopamine's versatility lies in its ability to bind to various surfaces, including silica and titanium. It also interacts with the shales due to the presence of aluminum silicate layers. Dopamine's strong hydrogen bonding properties further enhance shale inhibition. Table 8 presents a selection of hybrid polymers and hybrid hyperbranched polymers. We used PEI as a macroinitiator in these syntheses, glycidol as our monomer, and Maleic Anhydride as a cross-linker in some of the synthesized polymers. Dopamine served as the anchor group, and we also incorporated different nanomaterials, namely Nano Silica and Titanium Dioxide. The incorporation of these nanomaterials adds an intriguing dimension to our research. In the case of Titanium Dioxide, I conducted both situ and post-functionalization synthesis. Post-functionalized TiO_2 refers to the nanomaterial being prepared separately from the polymerization step, while in situ functionalization involves preparing the nanomaterial using a precursor during the synthesis of the polymerization solution.

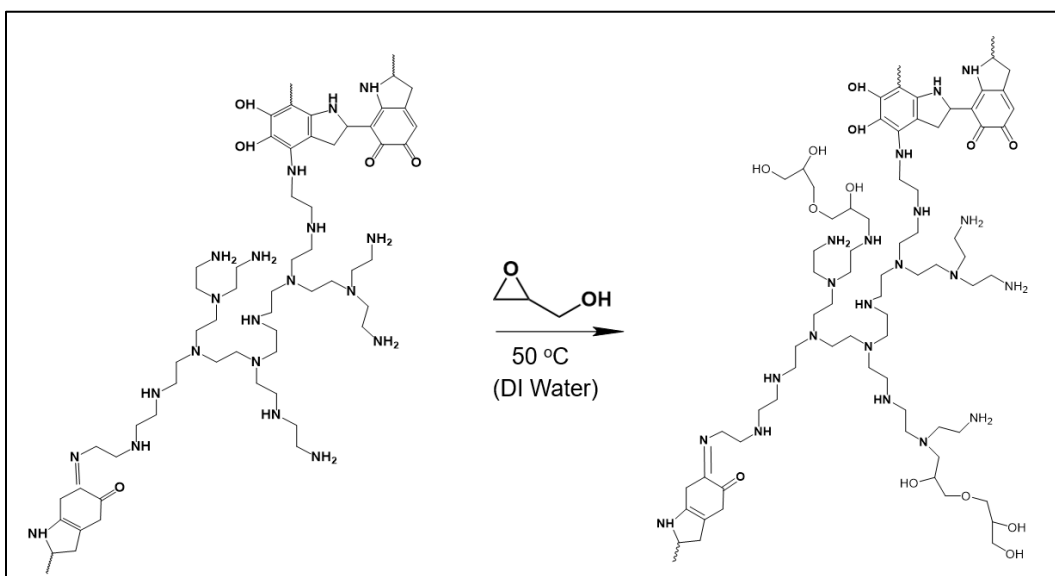
Table 8: Hybrid Hyperbranched polymers synthesis

Hybrid Polymer	Macroinitiator	Monomer	Anchor Group	Nano Material
1	PEI	Glycidol	Dopamine	Nano Silica
2	PEI	Glycidol	Dopamine	TiO ₂ (<i>post</i> Functionalization)
3	PEI	Glycidol	Dopamine	TiO ₂ (<i>in situ</i> Functionalization)
4	PEI	Glycidol (Maleic Anhydride Cross Linker)	Dopamine	Nano Silica
5	PEI	Glycidol (Maleic Anhydride Cross Linker)	Dopamine	TiO ₂ (<i>in situ</i> Functionalization)

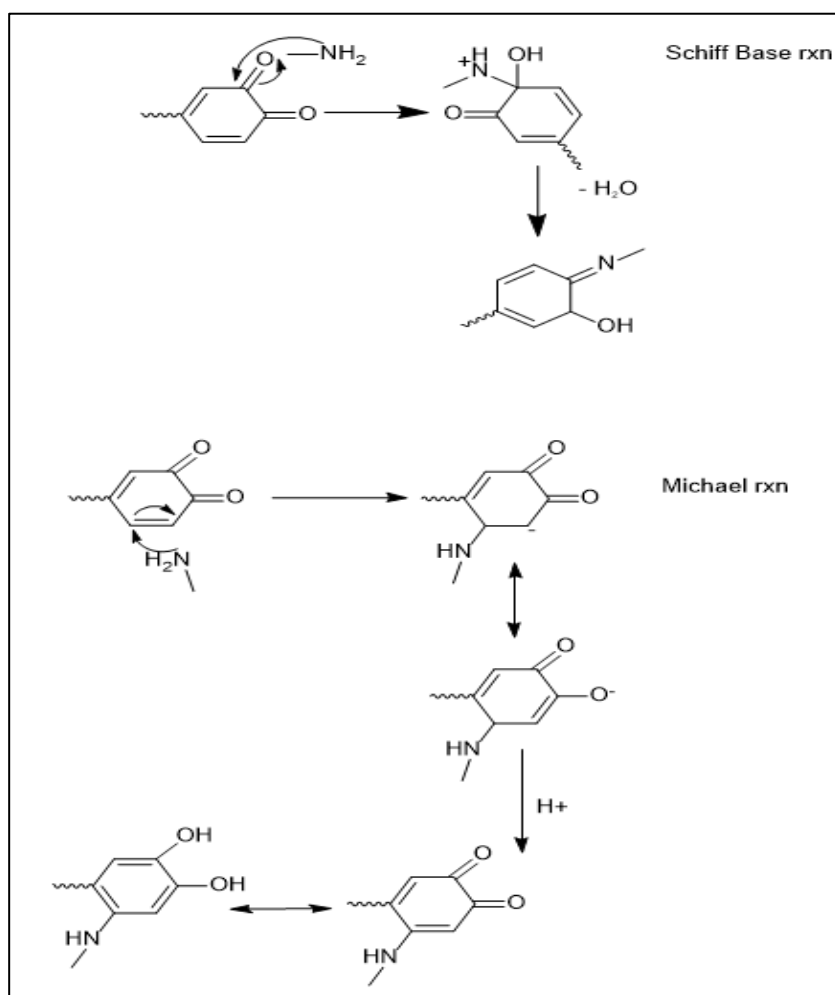
The use of Dopamine as an anchor group is illustrated in the following schemes. We have multiple steps in this synthesis. First is the oxidization of Dopamine due to the high pH of the PEI. This oxidation will convert Dopamine from its enol form to keto form. Next, we have a mixture of mechanisms, namely the Micheal and Schiff base reactions, between the Dopamine and the PEI. We also have the anionic ring-opening polymerization of the glycidol monomer, Schemes 22-24. The last step in this synthesis is the addition of the nanomaterial, Schemes 25-26. If the nanomaterial is nano-silica, the Dopamine will bind to its surface by condensation of the OH group on the nano-silica surface. If the nanomaterial is titanium oxide, the binding will be due to the chelation of the TiO₂ by Dopamine. The TiO₂ surface is under-coordinated so that the Dopamine will attach to the TiO₂ surface. A dark black conversion indicates this interaction.



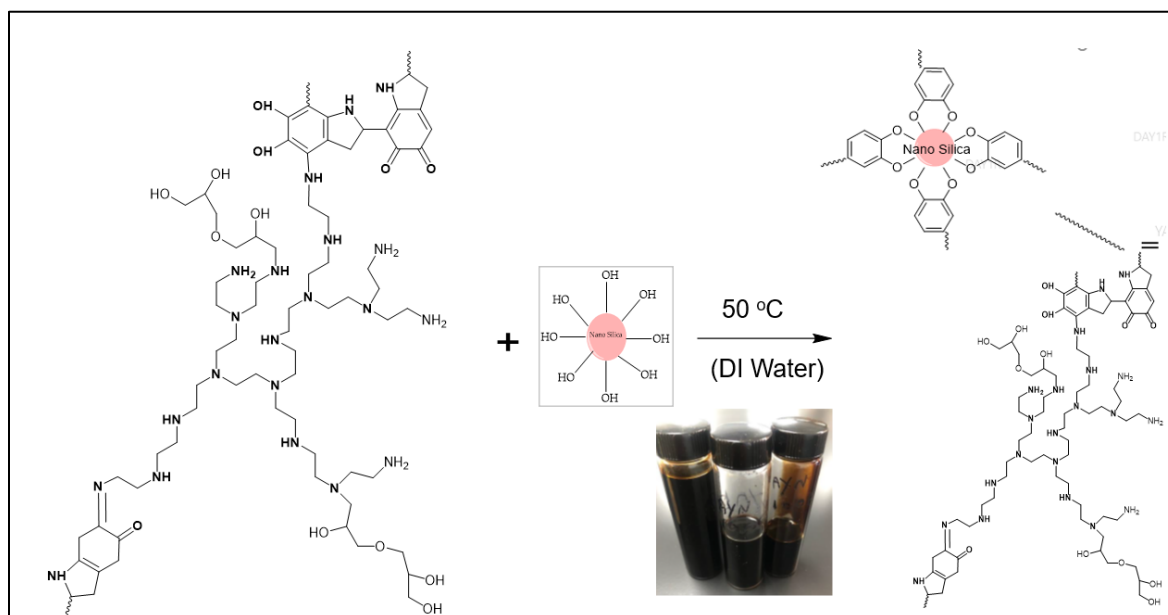
Scheme 22: Dopamine reaction with PEI



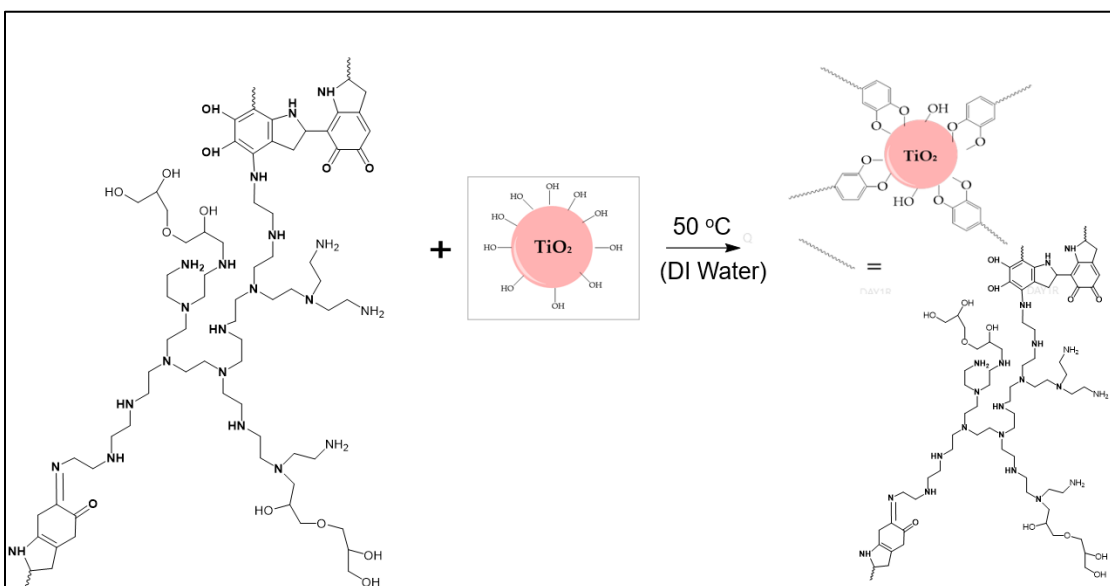
Scheme 23: Anionic ring-opening polymerization of the glycidol monomer



Scheme 24: mechanisms of Dopamine reaction with PEI and Glycidol



Scheme 25: last step of synthesis addition of nano silica



Scheme 26: last step of synthesis addition of TiO_2

¹H NMR of the synthesized hybrid hyperbranched polymer indicated the PEI region, glycidol region, and the aliphatic and aromatic parts of the Dopamine anchor group, Fig. 94 The peaks assignment is in agreement with the literature review [236]. The shale inhibition of the hybrid polymer utilizing nano-silica has shown excellent shale inhibition with more than 90% recovery factor and about 95 long-term recovery factors. These recovery factors indicate the percentage of the original shale properties that are retained after the inhibition process, with higher values suggesting better performance. The dopamine gave above 80% short shale recovery factor, which shows its benefit as an anchor group. Importantly, the synthesized hybrid polymer continues to outperform the oil-based fluids, a significant finding when tested on representative Qusaiba shales, as shown in Figs. 95-96. This reaffirms the hybrid polymer's potential in the shale inhibition field. For Sudair it was more challenging for our synthesized polymers to provide effective inhibition for the reasons above, 97.

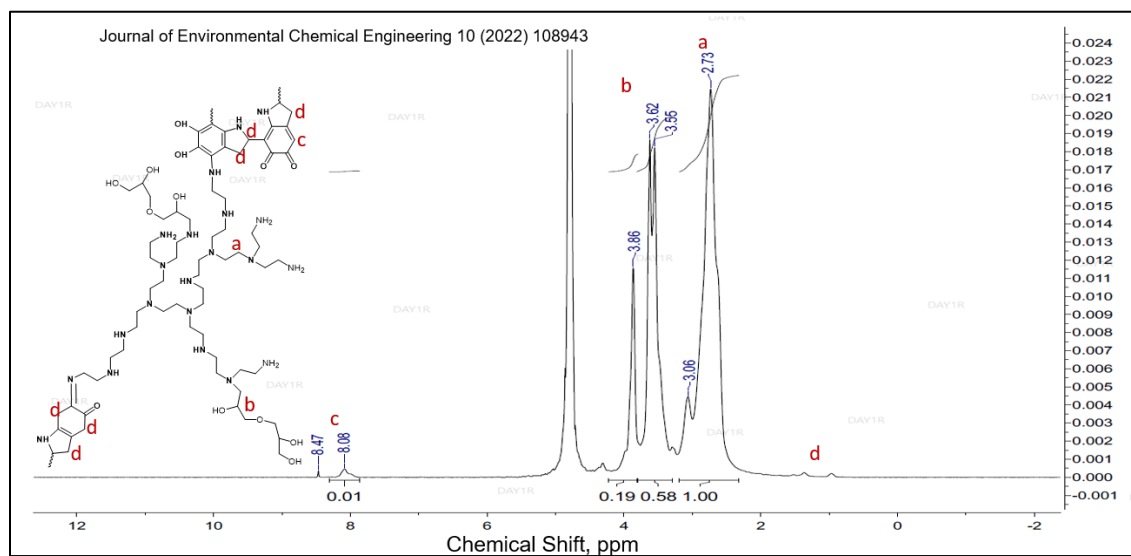


Fig. 94: ^1H NMR for hybrid hyperbranched polymer using Dopamine as an anchor group

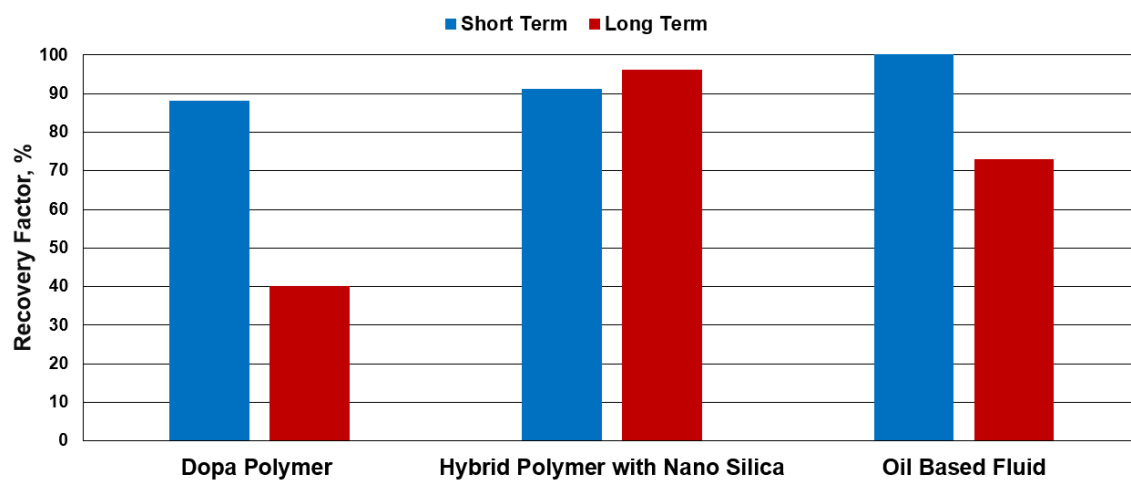


Fig. 95: Hybrid Polymer with Nano Silica and Dopamine as an Anchor Group for Qusaiba Shale inhibition

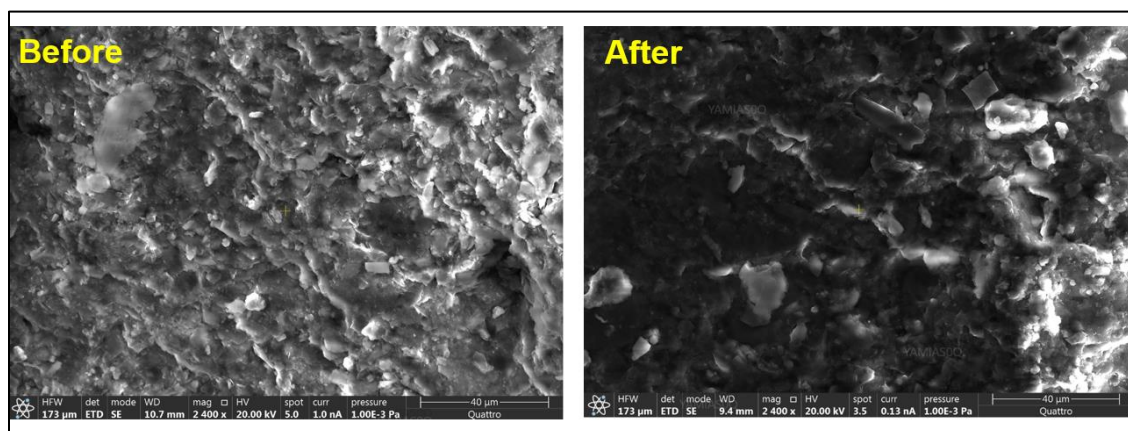


Fig. 96: SEM images for Hybrid Polymer with Nano Silica and Dopamine as an Anchor Group for Qusaiba Shale inhibition

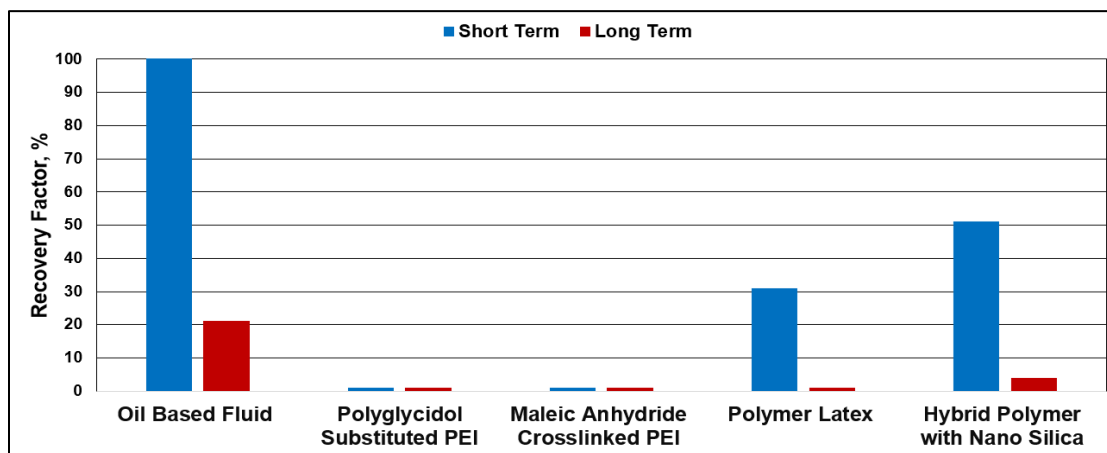


Fig. 97: Hybrid Polymer with Nano Silica and Dopamine as an Anchor Group for Sudair Shale inhibition

The hybrid polymer and hybrid hyperbranched polymer, particularly when utilizing TiO_2 , demonstrated exceptional performance in inhibiting Qusaiba shale. All the synthesized polymers in this study outperformed oil-based drilling fluids in the case of Qusaiba shales, Figs.98-99 . For Sudair, the most promising outcome was achieved with TiO_2 , boasting a recovery factor of 66% (Fig. 100). SEM images clearly show the nanomaterials effectively sealing the shale pores. This underscores the mechanism of shale inhibition, where the hybrid hyperbranched polymers, in conjunction with the nanomaterials and Dopamine, play a crucial role. Importantly, the hydrogen bonding facilitated by the PEI and the Dopamine significantly contributes to the shale inhibition, a finding of utmost significance, Figs. 101-104.

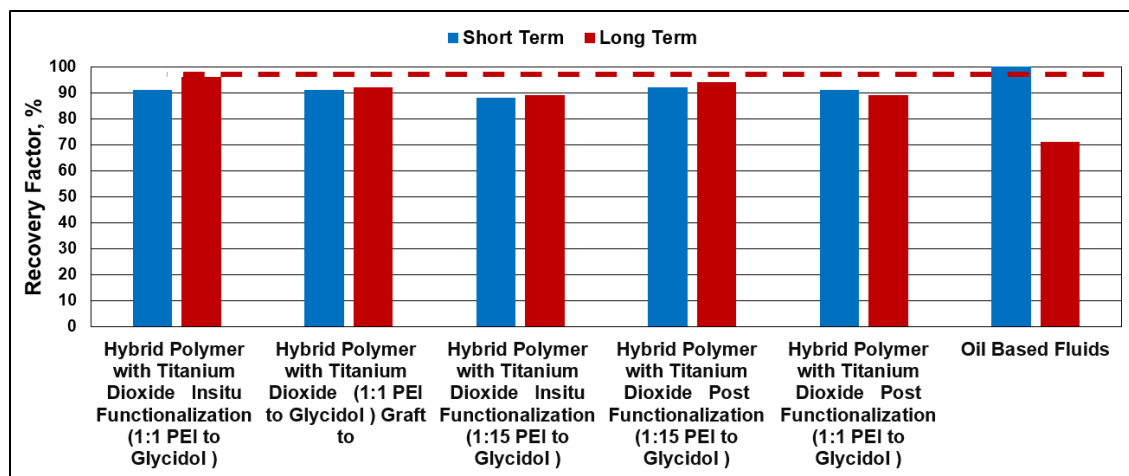


Fig. 98: Hybrid Polymer with Titanium Dioxide and Dopamine as an Anchor Group for Qusaiba Shale inhibition

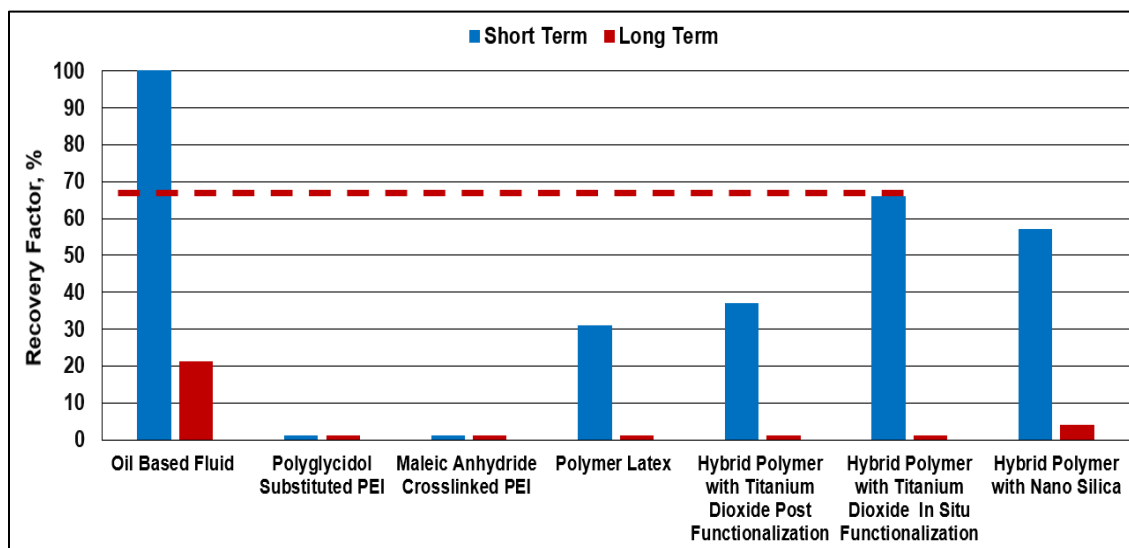


Fig. 99: Hybrid polymer with Nano Materials and Dopamine as an Anchor Group for Qusiba Shale Inhibition

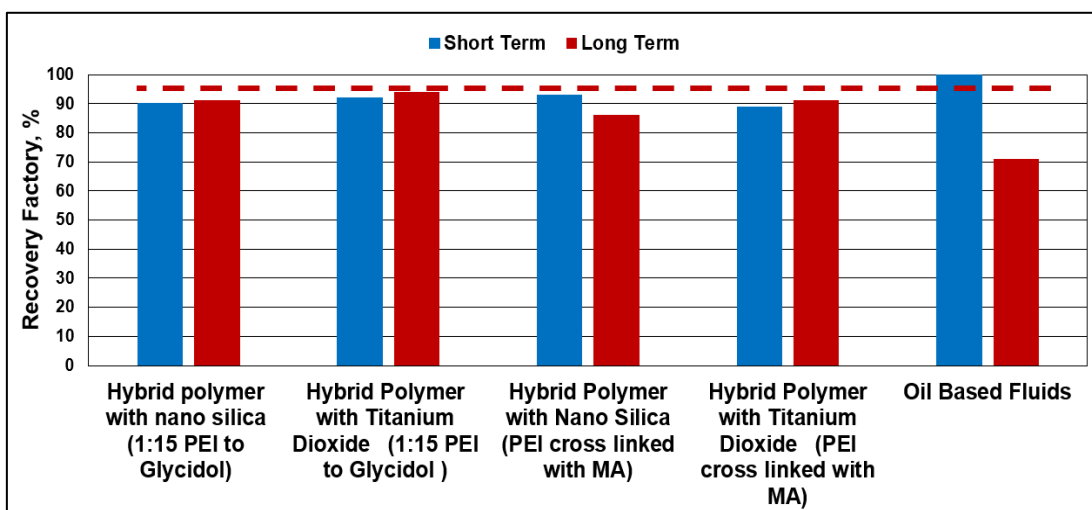


Fig. 100: Hybrid Polymer with Nano Materials and Dopamine as an Anchor Group for Sudair Shale Inhibition

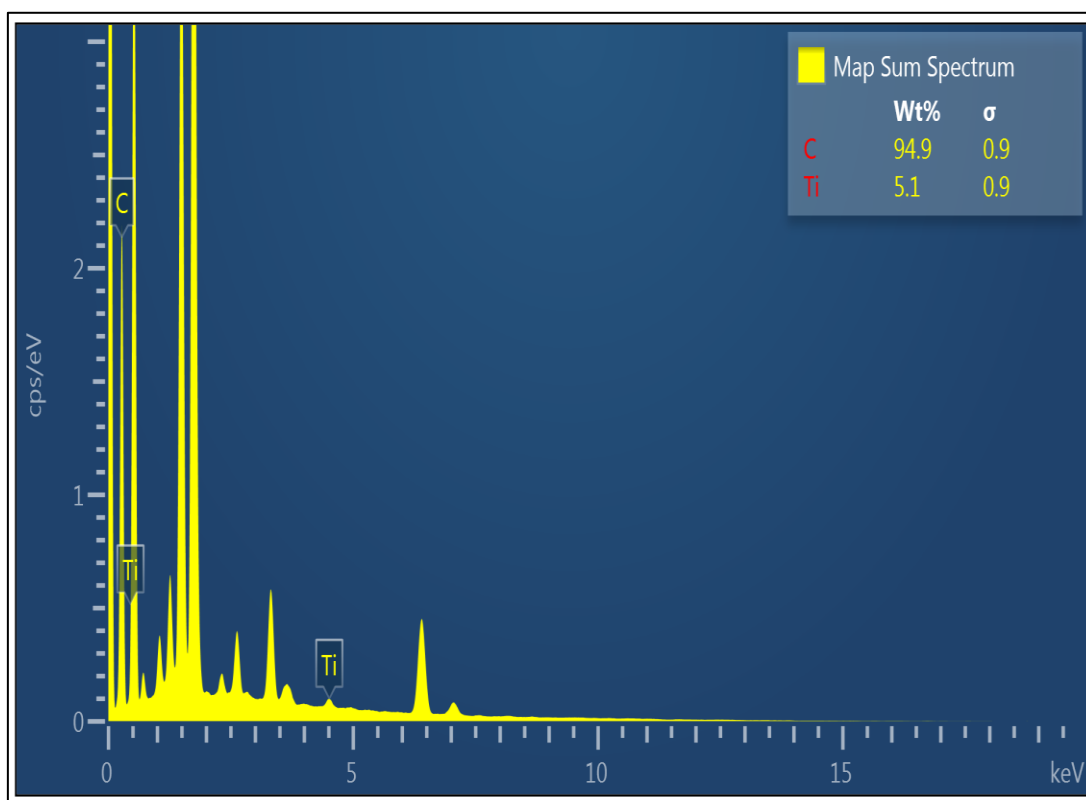


Fig. 101: Hybrid Polymer with Titanium Dioxide in Situ Functionalization and Dopamine as an Anchor Group for Qusaiba Shale Inhibition

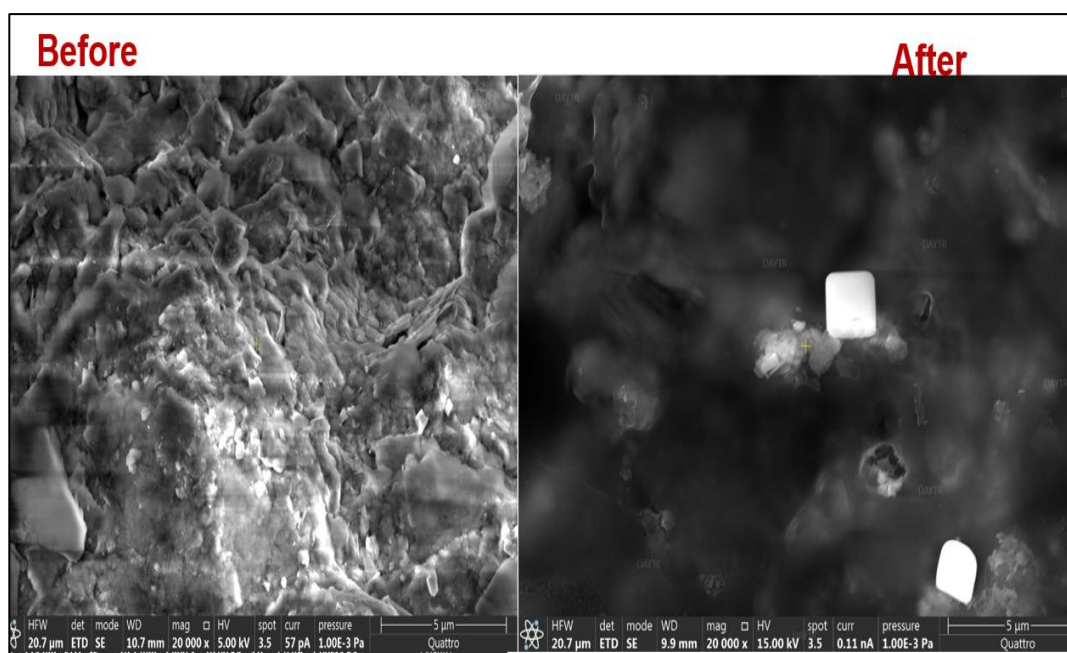


Fig. 102: Hybrid Polymer with Titanium Dioxide in Situ Functionalization and Dopamine as an Anchor Group for Qusaiba Shale Inhibition

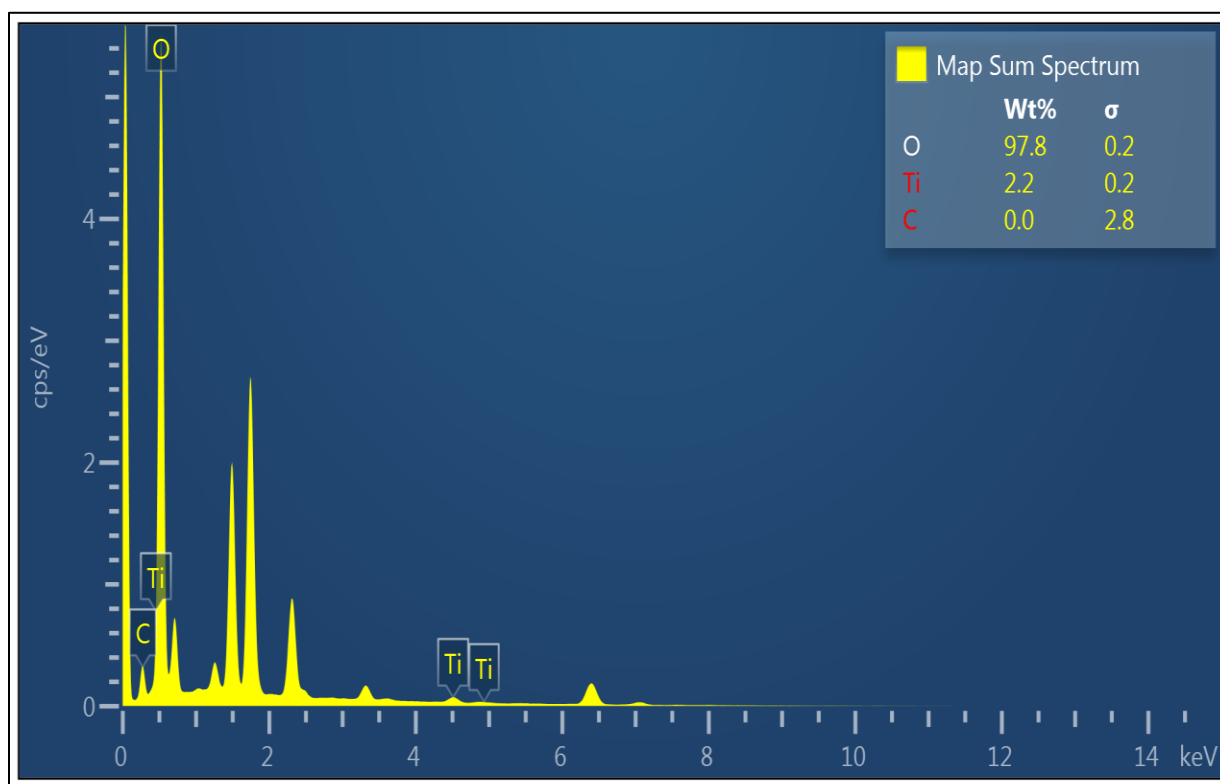


Fig. 103: Hybrid Hyperbranched Polymer with Titanium Dioxide Post Functionalization and Dopamine as an Anchor Group for Qusaiba Shale Inhibition (1:15 PEI to Glycidol)

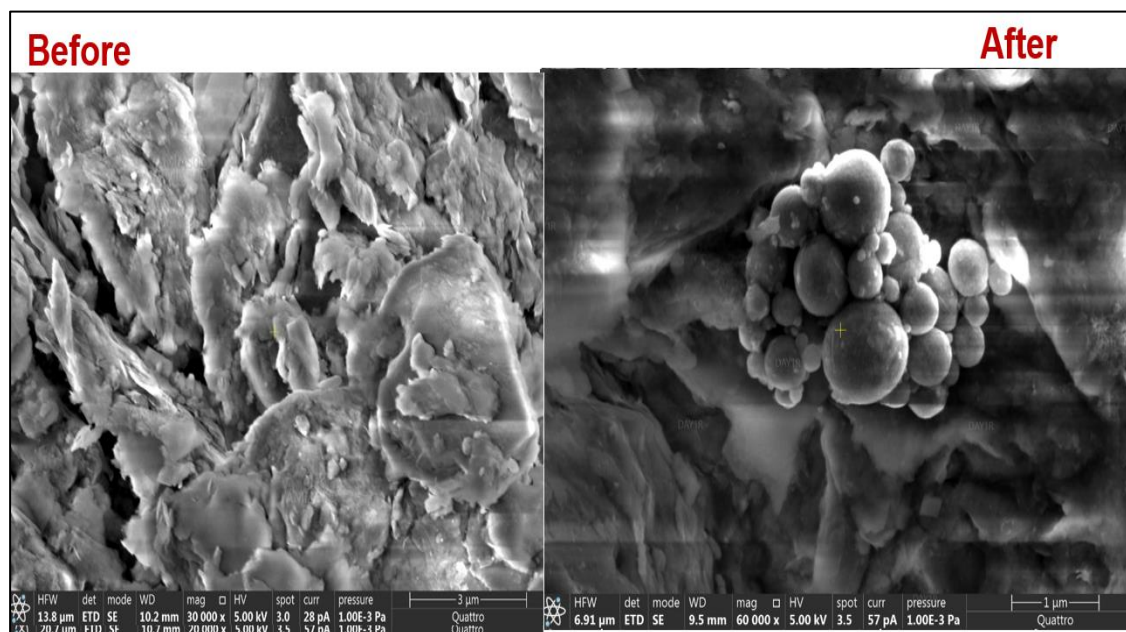


Fig. 104: Hybrid Hyperbranched Polymer with Titanium Dioxide Post Functionalization and Dopamine as an Anchor Group for Qusaiba Shale Inhibition (1:15 PEI to Glycidol)

With the successful achievement of the three requirements to replace oil-based drilling fluids for Qusaiba, we were presented with two viable options: either to employ a combination of hyperbranched polymer for viscosity and another hybrid hyperbranched polymer for shale inhibition, or to subject the hybrid hyperbranched polymer to comprehensive testing for all the requirements (viscosity and shale inhibition). The hybrid hyperbranched polymers, synthesized with utmost precision in this study, were then

formulated in water-based drilling fluids and rigorously tested at high-temperature environments, producing excellent results. The viscosity obtained was more than sufficient for effective drilling application, even after the fluid was exposed to 300 F, Fig. 105 and Table 9. The practicality of these formulations is underscored by the fact that they were finalized after several meticulous attempts.

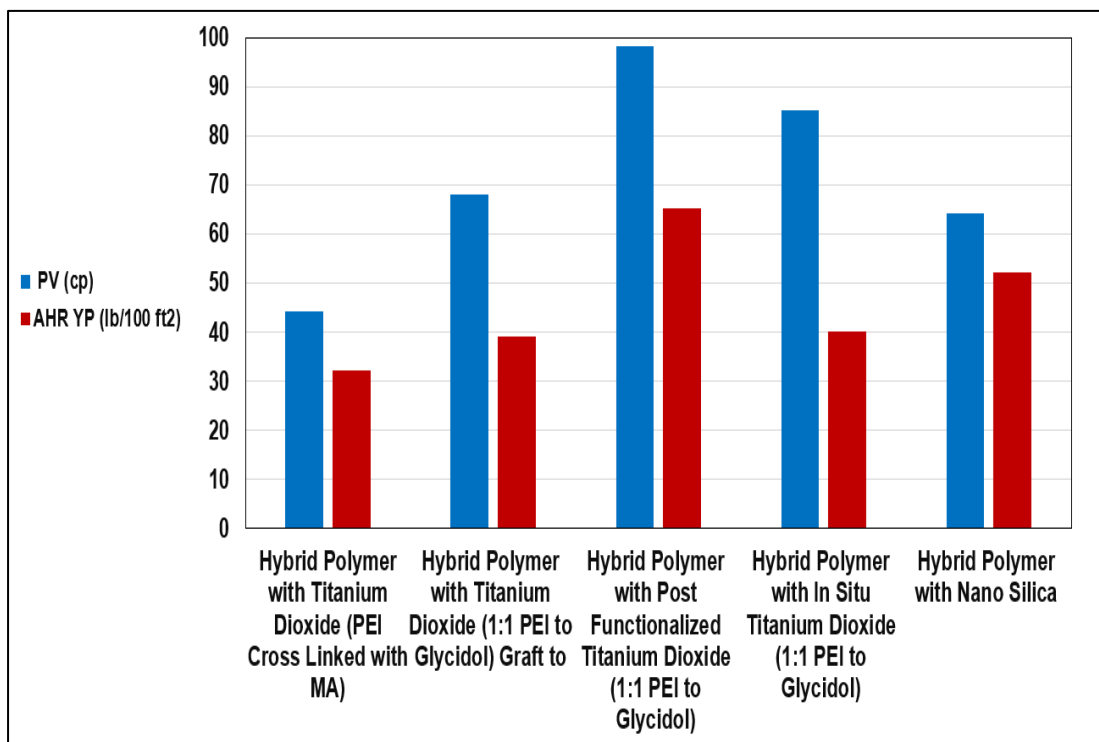


Fig. 105: Performance Measurements for Synthesized Hybrid Polymers

Table 9: Recommended Formulations with Synthesized Polymers

Additive	Mixing time, min	Amount, grams
Water		287
Na_2CO_3	5	0.23
Starch	20	5
XC polymer	20	1.5
NaOH	5	0.12
HPAM	20	3
Salt (NaCl , KCl , or CaCl_2)	5	as density required
Synthesized Hybrid polymer	20	3
Barite or Mn_3O_4	5	as density required
Sodium Sulfite	5	0.5

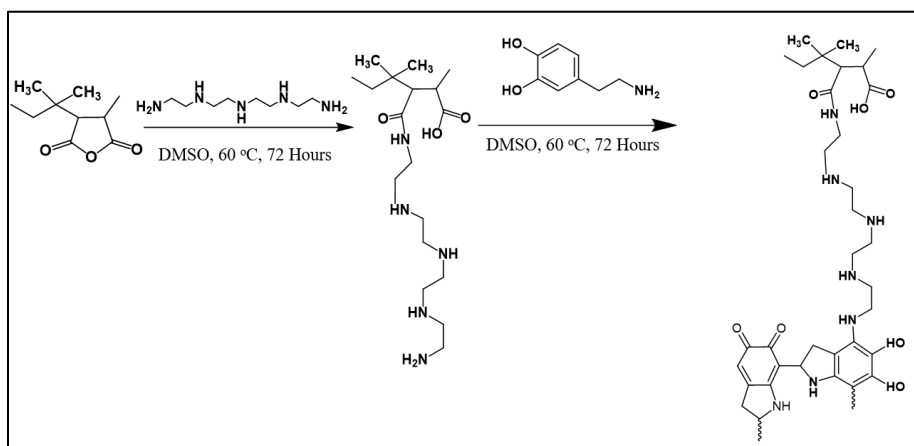
CHAPTER 8

CONCLUSIONS AND RECOMMENDATIONS

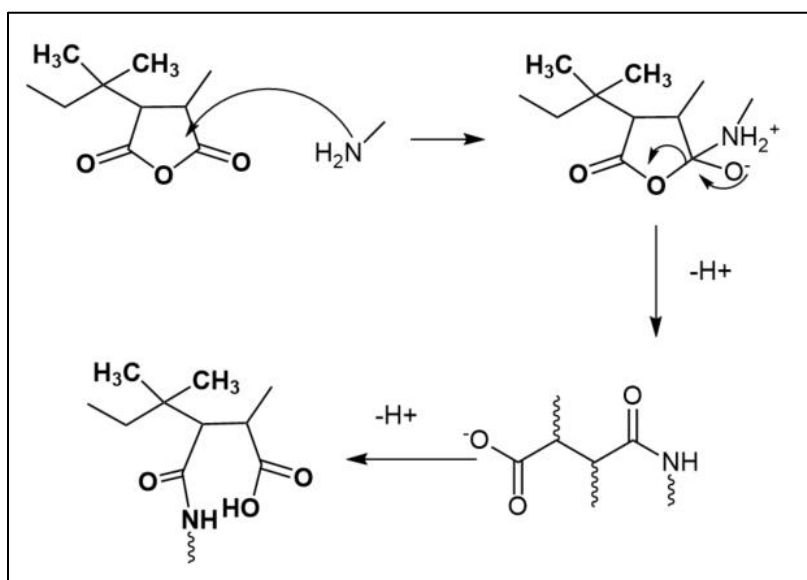
- Different hyperbranched polymers and hyperbranched hybrid polymers with suitable functionalities were synthesized for water-based drilling fluids to replace oil-based fluids
- Formulation for water-based drilling fluids using synthesized hyperbranched polymers and hybrid polymers was essential to the study.
- The synthesized hyperbranched polymers have shown high viscosities in freshwater
- The use of salts such as CaCl_2 KCl has shown improved performance due to viscosity reduction by the salt shielding effect
- Hybrid polymers and hybrid branched polymers based on Nano silica, and TiO_2 showed acceptable results for both short- and long-term inhibition for Qusaiba Shales, with more than 90% long-term shale inhibition
- Hybrid polymer provided good stability in a high-temperature environment
- For Qusaiba formation, we can switch to water-based drilling fluids utilizing the synthesized and hybrid polymers discussed in this study.

In the final leg of our study, we explored the feasibility of conducting new research on the effect of hydrophobic and hydrophilic alteration on shale inhibition. To this end, we

utilized Maleic anhydride polymer, a substance known for its lack of water solubility, in an amidation reaction to be grafted with different amines. This amidation reaction, a key step in our research, aims to introduce a hydrophilic component into the hydrophobic polymer and test for shale inhibition. The reaction is visually represented in the following schemes 27-28. While the long-term recovery factor did not yield the desired results, we achieved remarkable success in the short-term recovery factor. The pinnacle was reached with a score of 96 when post-functionalized TiO_2 was employed in the amidation synthesis for the hybrid polymer, Table10. As we progress from synthesizing hyperbranched polymers to hybrid polymers and then to hybrid hyperbranched polymers, the next phase of our research holds immense promise in the realm of Hydrophilic/Hydrophobic Hybrid Hyperbranched Polymers, Fig.106.



Scheme 26: Poly (Isobutylene-alt-Maleic Acid-Graft-Amine)



Scheme 27: Poly(Isobutylene-alt-Maleic Acid-Graft-Amine) mechanism

Table 10: Poly(Isobutylene-alt-Maleic Acid-Graft-Amine)

Hybrid polymer	Graft to	Qusaiba Shale inhibition Recovery Factor, %	
		Short	Long
1	Methyl Amine	81	51
2	Ethylenediamine	93	58
3	Tetraethylenepentaamine	91	35
4	Acid-Graft-Tetraethylenepentaamine) and Dopamine as an Anchor Group TiO ₂ (Post Functionalization)	96	69

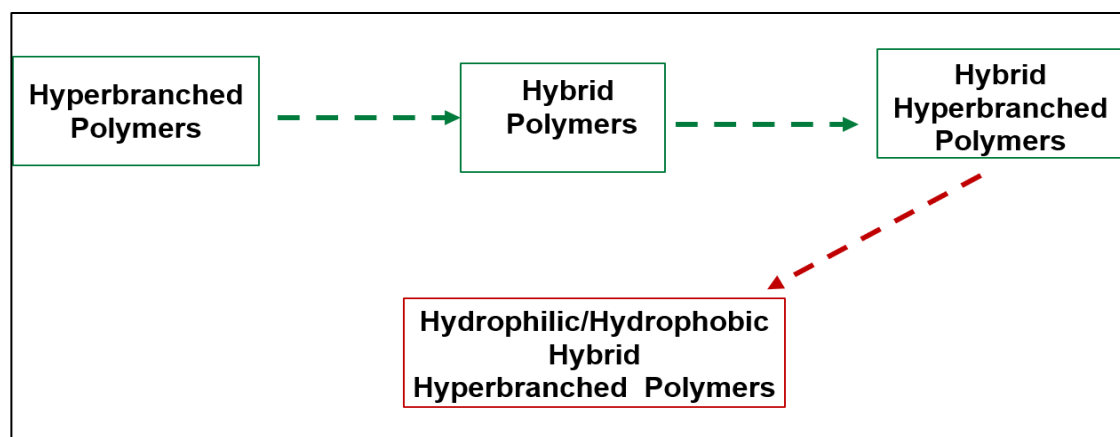


Fig. 106: Polymers synthesis research outlook

APPENDIX A: REFERENCES

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APPENDIX B: Vitae

Abdullah S. Al-Yami

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ACADEMIC QUALIFICATIONS:

2024 - Ph.D. (Hon.) **Chemistry**, King Fahd University of Petroleum and Minerals, Dhahran, Saudi Arabia. Thesis entitled: “Design, Synthesis and Characterization of Hyperbranched Polymers and Hybrid Organic-Inorganic Particles for Oil/Gas Drilling Applications.” Objective here is to replace oil-based drilling fluids with water-based fluids, several patents are being filed and publications are being prepared.

2012 - Ph.D. (Hon.) **Petroleum Engineering**, Texas A&M University, College Station, Texas, USA. Thesis entitled: “Development of Drilling Expert System Using Bayesian Network.” First effort done in the industry to develop advisory systems and link to real time operations. Nine patents granted and 12 publications.

2007 - M.Sc. (Hon.) **Petroleum Engineering**, King Fahd University of Petroleum and Minerals, Dhahran, Saudi Arabia. Thesis entitled: Development of Manganese Tetroxide Water Based Drill-In Fluids.” 2 patents granted, 4 publications, and the fluids are used intensively in daily operations in different fields in Saudi Arabia.

1998 - B.Sc. (Hon.) **Chemistry**, Florida Institute of Technology, Melbourne, Florida, USA.

AWARDS

- 2023 EXPEC ARC Research Development Program Committee Member Award
- 2022 Drilling and Workover Award for drilling automation effort
- 2020 EXPEC ARC Effective Mentorship Award
- 2017 **CEO** Saudi ARAMCO Excellence Award
- 2017 the Saudi Arabian Board of Engineering Award
- 2016 **CEO** Saudi ARAMCO Excellence Award

- 2016 Highly Recommended Ranking for the ICV Strategy of the Year for Oil and Gas Middle East for effort in Drilling Products Utilizing Local Resources Strategy
- Acted as vice chair for Saudi Arabia SPE Technical Program
- Saudi ARAMCO, EXPEC ARC for Effective Publication Award, 2012
- SPE Outstanding Technical Editor (Drilling and Completion Journal) Award, 2008
- Saudi ARAMCO, Research and Development Center Innovation Award, 2007
- Saudi ARAMCO, Research and Development Center Field Technical Support Award, 2006

GRANTED AND FILED PATENTS

- Total patents granted and filed is **323**.
 - **152** patents granted in the area of drilling fluids, cementing, automation, methods, and chemicals.
 - **171** patents filed to be granted by 2024-2026.
- Developed patents and solutions for different aspects related to drilling and workover, chemicals and fluids.

<https://ppubs.uspto.gov/pubwebapp/static/pages/ppubsbasic.html>

PUBLICATIONS

- A **book** entitled: “Underbalanced Drilling: Limits and Extremes”
 - By Gulf Publishing Company 2012,
 - By Elsevier Science and Technology 2013
- Authored more than **184** publications in different aspects related to drilling and workover, chemicals and fluids.

<https://scholar.google.com/citations?hl=ar&user=YtLTzugAAAAJ>

PROFESSIONAL EXPERIENCE

June 2023 to August 2023: EXPEC Advanced Research Center, Drilling Technology Team, Saudi ARAMCO

- Contacting D&WO for candidate well selections for multiple deployments and new developments.
- Continue leading researchers and lab tech. to achieve KPI and come up with new development that is aligned with our stake holder expectations.
- Establishing synthetic lab in terms of chemicals and plans
- Conducting polymer synthesis experiments for high performance water-based drilling fluids to replace oil-based fluids
- Developed cement free solution for primary cementing
- Synthesized polymer for HEC replacement in completion fluids

- Developed new generation of organoclay free oil-based fluids utilizing new polymer latex.
- Developed new generations of red mud cement composites.
- Continue development of ARC-ASH cement composites.
- Presented to D&WO local polymer latex for water based and oil-based drilling fluids development to mitigate differential stuck pipes. Worked on securing multiple candidate wells in unconventional wells.
- Continued collaboration with GRCs in deployments execution plans and developments.
- Continue development of new solutions in the area of drilling fluids and cementing using local petrochemicals. Examples are polyethylene glycol in packer fluids to replace oil-based fluid and water-based fluids to mitigate TCA issues.
- Lead the 1st off-bottom liner installed without lower packers in the world. This was possible by using pure resin in the primary isolation instead of conventional cement. Patent filed in the development and the operation.
- Secure candidate wells on developed chemicals such as retarders and dispersants.
- Continue filing patents and publications

June 2012 to September 2022: EXPEC ARC Drilling Technology Team

1. Oilfield Chemistry Applied Research

- Developed several products utilizing local resources. Below are selected examples of the development. All developments are protected by patents for potential commercialization:
 - ARC Resin Technology to unlock many gas and oil wells potential to produce. The technology is commercialized to TAQA Service Company
 - Linear alpha olefin as environmentally friendly base oil for drilling fluids were designed and formulated.
 - Shale stabilizers.
 - Lubricants.
 - Rheology modifier.
 - Loss circulation materials.
 - Mud thinners.
 - Development of local bentonite for water-based drilling fluids and cementing applications
 - Development of retarders for cementing.
 - Development of dispersants for cementing
 - Development of polymer latex (different chemistries) for use in water-based fluids, oil-based fluids, and cementing.

2. Drilling Fluids Applied Research

- Introduce Manganese tetroxide water-based fluids in to gas drilling operations. The fluids are used on daily bases and were considered a key enabler for some field's development such as KRSN field drilling operations. The fluid was used intensively

in MPD (managed pressure drilling) operations. Objective of this work is to reduce barite sagging in non-reservoir sections.

- Developed and introduce new generations of organo clay free oil-based fluids that were used to mitigate differential stuck pipes and reduce formation damage. More than 100 field applications were executed using this patented formulation. No differential stuck pipes were resulted and production rate was much higher than offset wells drilled with conventional oil-based fluids.
- Lead the field execution of local shale inhibitor in water-based fluids in an area that is usually drilled with oil-based fluid due to high shale content.
- Developed new water-based fluids for minimum formation damage without the need of using acids to remove filter cake.
- Developed polymer latex based on polyvinyl acetate for water-based drilling fluids and oil-based drilling fluids to mitigate different stuck pipes.
- Developed polymer latex based on styrene butadiene for water-based drilling fluids and oil-based drilling fluids to mitigate differential stuck pipes. It can also provide shale inhibition by plugging mechanism.
- Developed new solution for long term shale inhibition to simulate drilling through loss circulation zones below shale formation.
- Provide technical support when needed to drilling engineers

3. Curing Losses Applied Research

- Developed different Resins based solutions that can be pumped through BHA that is compatible with fluids for sever losses.
- Developed different cement LCM solutions that can be pumped through open ended drill pipe for sever losses
- Developed different Nano silica LCM solutions for partial losses
- Developed new solutions to mitigate losses during cementing such as LCM in spacers and innovative low-density cements.
- Provide technical support when needed to drilling engineers

4. Automation Applied Research

- Co-Established automation FA in 2015
- Developed the following in-house models and executed them in real time environment
 - Real time ECD calculation using real time drilling fluids measurements
 - Real time back pressure calculation for managed pressure drilling utilizing real time drilling fluids measurement
 - Real time kick detector with 100% positive-positive indicator
 - Executed cement jobs real time in collaboration with Schlumberger service company.
 - Updated advisory systems for cementing and drilling fluids.
- Co-developed the following in-house models and executed them in real time environment

- Real time mud window determination in collaboration with geomechanics expert
- Several Real time hole cleaning indicators for different types of drilling fluids and for different hole sections.

5. Cementing and Zonal Isolation Applied Research

- Established cementing FA in 2012
- Developed low density cement that is competitive with service company products with enhanced properties for single stage cementing in oil and gas wells.
- Investigated Cement failure in long lines in the Red Sea
- Developed high density cement formulation for gas wells (HP Jilh formation)
- Developed self -healing cements and executed in different fields
- Developed durable type of cement and executed in different fields
- Have co-written cementing best practices as requested by D&WO
- Were asked by D&WO to investigate several failures. Identified reason for failure and came up with the corrective method of testing and execution.
- Developed innovative solutions for remedial that unlock many oil and gas wells including chemicals and execution methods.
- Developed many solutions to enhance primary cementing and improve wellbore integrity.
- Presented Saudi ARAMCO in committees with other GCC companies in the area of cementing and best practices.
- Assist in service company products evaluation
- Participate in workshops for shared projects with Schlumberger, Halliburton and Baker Hughes.
- Provide technical support when needed to drilling engineers

6. Self-Development

- Started PhD program part time on 2019 in the area of Organic Chemistry (polymer synthesis and characterization).
- Learned a lot from interaction with stake holders and service companies and Saudi ARAMCO global centers.
- Learned a lot from interaction with team members (scientists and technicians) and still learning.

August 2008 to June 2012: Texas A&M University, College Station, Texas, USA

- 1st PhD from Saudi ARAMCO in PETE Engineering (Drilling Engineering)
- Coauthored a book entitled: “Underbalanced Drilling: Limits and Extremes” By Gulf Publishing Company April 2012, Elsevier Science and Technology has also published this book in 2013.
- Introduced Bayesian Intelligence to develop drilling expert systems in the industry (9 granted patents).

January 2007 to August 2008: EXPEC ARC Drilling Technology Team, Saudi ARAMCO

- Completed my Ms. Degree in Petroleum Engineering as a part time student by taking evening classes at King Fahd University of Petroleum and Minerals.
- Conducted 40 field application for low density cements to eliminate multistage tools.
- Established drilling fluids FA

January 2005 to December 2006: Research and Development Center, Saudi ARAMCO

- Provided Technical support to drilling and completion operations in the area of drilling fluids and cementing.
- Developed new lost circulation materials, (patents granted)
- Developed a kick cement plug to save time while side tracking in hard strong formation, (patent granted).
- Introduced swelling packers to Saudi Arabia fields after lab investigation.
- Introduced low density cement to Saudi Arabia fields after lab investigation.

January 2004 to January 2005: Drilling Engineer Drilling and Work over Organization, Saudi ARAMCO

- Have written drilling programs for oil wells
- Have written work over programs for oil wells
- Provide technical support to drilling and work over rigs foremen.
- Was involved in every drilling engineering aspect such as following up with rig operations, communication with service companies, communication with reservoir management and labs, and KPIs.
- Was assigned to one drilling rig and several work over rigs (offshore and onshore)

January 2003 to January 2004: Tools Pusher/ Assistant Rig Foreman Drilling and Work over Organization, Saudi ARAMCO

- Handled with rig crew all drilling activities on the rig floor
- Handled with rig crew all drilling activities on the floor such as rig move and rig maintenance.
- Handled with rig crew all other operations such as cementing, acidizing, stuck pipe release, well control practices, etc.
- Assist the foreman in calculation such as cement calculation; kill sheet calculation and BHA designs.
- Worked on 3 Saudi ARAMCO rigs (2 drilling and one workover)

January 1999 to January 2003: Lab Scientist Research and Development Center, Saudi ARAMCO

- Provided Technical support to drilling and completion operations in the area of drilling fluids and cementing.
- Conduct products evaluations
- Conduct quality control studies

- Conduct several troubles shooting and investigations.

PROFESSIONAL MEMBERSHIP AND ACTIVITIES

- 2014 Vice Chair of Saudi Arabia SPE section (Technical Program)
- International Association of Drilling Contractors
- Chaired many sessions in SPE conferences.
- Technical Editor for SPE Drilling and Completion Journal
- Technical Editor for Arabian Journal for Science and Engineering (AJSE)
- Technical Editor for American Association of Mechanical Engineering (ASME)
- Technical Editor (in progress) for Arabian Journal of Chemistry Elsevier
- Member with American Chemical Society