

**EVALUATING THE MICROSCOPIC RECOVERY POTENTIAL OF
LOW SALINITY VISCOELASTIC POLYMER FLOOD IN OIL-WET
CARBONATE FORMATION**

BY

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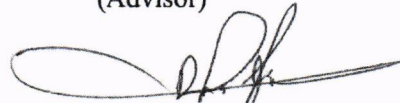
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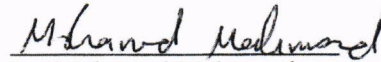
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Dedication

This thesis work is dedicated to my family, whose unwavering encouragement, support, and sacrifices have been the driving force behind and a source of guidance for me during my academic journey. I owe a debt of gratitude to my parents, ***Hager & Abdalsalam***, whose unshakable faith in my abilities has driven me to pursue my goals. To my supportive sister ***Hind***, your unwavering support has been a source of courage during trying times.

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ABSTRACT

Full Name : Moaz Abdalsalam Abdalla Dafaalla
Thesis Title : Evaluating the Microscopic Recovery Potential of Low Salinity
Viscoelastic Polymer Flood in Oil-Wet Carbonate Formation.
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Polymer flood, a variant of chemical enhanced oil recovery (EOR) is one of the most applied EOR method to enhance oil recovery factor from the matured reservoir. The conventional mechanism by which polymer flood increases the recovery factor through an enhanced sweep efficiency. Since the reporting of 20% incremental oil recovery in Daqing field by high concentrated, high Mw viscoelastic polymer flood, several researches were undertaken across the globe to study the polymer's viscoelastic influence on decreasing residual oil saturation through an enhanced microscopic displacement efficiency. Most of the previous lab-scale studies were done on sandstone reservoirs, and there were differences of opinion whether viscoelastic flood can genuinely increase the residual oil recovery at all the petro-physical, and field-conditions. Moreover, the potential of viscoelastic polymers in improving microscopic oil displacement in oil wet carbonate formations have not been investigated. Carbonate reservoirs are more complex, having oil-wet nature with a negative capillary pressure, higher heterogeneity, high salinity connate water, and reside at high temperatures. A favorable mobility ratio was adopted in this study. A series of rheological, single-phase, and multi-phase flooding experiments were done to evaluate the significance of viscoelasticity over viscosity in enhancing oil recovery under

the candidate conditions. The research revealed that, in comparison to low salinity xanthan gum solutions injection, low salinity AN-125 SH injections leads to enhanced incremental residual oil recovery in heterogenous formation with different pore sizes only at higher rates (20, 32.5 ft/day) where shear thickening was evident.

ملخص الرسالة

الاسم الكامل: معاذ عبد السلام عبد الله دفع الله.

عنوان الرسالة: تقييم إمكانية الاسترداد الموضعي لحقن البولييمر المرن للزوجة ومنخفض الملوحة في الصخور الكربونية الرطبة بالنفط.

التخصص: هندسة البترول.

تاريخ الدرجة العلمية: ديسمبر 2023

يُعد حقن البولييمر، أحد أشكال الاستخلاص المعزز للنفط كيميائيًا وأحد أكثر طرق الاستخلاص المعزز للنفط تطبيقًا لتحسين عامل استخلاص النفط من المكامن الناضبة. الآلية التقليدية التي يعمل من خلالها حقن البولييمر هي العمل على زيادة عامل الاسترداد من خلال زيادة كفاءة المسح نسبة للزوجته العالية. منذ الإبلاغ عن الحصول على 20% من الاستخلاص المحسن للنفط في حقن داتشينغ عن طريق حقن البولييمر مرن للزوجة وعالي وزن الجزيء والتركيز، تم إجراء العديد من الأبحاث في جميع أنحاء العالم لدراسة تأثير اللزوجة المرنة للبولييمر على زيادة استخلاص النفط العالق المتبقي من خلال كفاءة الإزاحة الموضعية المحسنة. تم إجراء معظم الدراسات العملية السابقة على مكامن الحجر الرملي، وكانت هناك اختلافات في الرأي حول ما إذا كان الحقن مرن للزوجة يمكن أن يزيد بالفعل من استخلاص النفط المتبقي في جميع الظروف البتروفيزيائية والمكمنية. علاوة على ذلك، لم يتم دراسة إمكانات البولييمرات ذات اللزوجة المرنة في تحسين إزاحة الزيت الموضعي في الصخور الكربونية الرطبة بالنفط. خزانات الصخور الكربونية هي أكثر تعقيدًا، فهي ذات طبيعة رطبة بالنفط مع ضغط مسامي سلبي، ومياه جوفية عالية الملوحة، وتتواجد في درجات حرارة عالية. في الآونة الأخيرة، تم تقييم حقن المياه منخفضة الملوحة لزيادة عامل الاسترجاع في أحواض النفط السعودية الكربونية. الهدف من هذه الدراسة هو تقييم قدرة بولي أكريلاميدات مسلفنة عالية الأداء التي تم تصنيعها لتحمل البيئات القاسية لمكامن الصخور الكربونية الرطبة مثل تلك الحاضنة للنفط السعودي لتحسين استخلاص النفط الموضعي في ظروف الحقن منخفضة الملوحة. وسيتم اعتماد نسبة لزوجة مفضلة بين النفط والبولييمر في هذه الدراسة. تم إجراء سلسلة من تجارب الحقن الأساسية الريولوجية أحادية الطور ومتعددة الأطوار لتوضيح أهمية اللزوجة المرنة مقابل اللزوجة في تعزيز استخلاص النفط في ظل الظروف المرشحة لفحص ما

إذا كان هناك تآزر بين الملوحة المنخفضة واللزوجة المرنة للبوليمر. كشف البحث أنه بالمقارنة مع صمغ الزانتان، أظهر SH AN-125 استخلاصًا متزايدًا للنفط بمعدلات حقن تؤدي إلى تعزيز استخلاص الزيت المتبقي في تكوين المسامية المزوجة مع أحجام المسام العالية في المعدلات العالية (20، 32.5 قدم / يوم) حيث تكون مرونة البوليمر واضحة.

CHAPTER 1

INTRODUCTION

1.1 Overview

Oil extraction from subsurface reservoirs often occurs through three main stages, primary, secondary, and tertiary. In the primary stage, recovery depends on reservoir's in-situ natural energy to deliver the hydrocarbon to the wellbore. Those natural energies involve fluid expansion and pressure support of nearby aquifers. The secondary recovery supports the natural energy by injecting fluids to support the pressure gradient across the reservoir, usually done through water flooding and gas injection. Waterflooding in the oil zone is classified as a secondary recovery mechanism and improves the amount of oil produced above oil recovery accomplished by the primary stage but it's generally leaves majority of oil trapped in the reservoir (Willhite & Green, 1998, Papavinasam, 2013). Tertiary recovery is the process of mobilizing capillary trapped oil and/or recovering mobile oil to increase the recovery beyond the secondary recovery levels by altering the physical rock and fluid properties. This stage in recovery often occurs late in the production phase, but in some instances, it is applied directly as the primary recovery method when the reservoir is unable to produce any oil by its own, e.g., extra-heavy oil (G. P. Willhite & Green, 1998). Residual oil pertains to the oil that is left in the porous pores of a reservoir that has been thoroughly swept by waterflood (Lake, 1989). The most likely component of residual oil

would be oil droplets that have been separated from the flow stream and are now confined because of capillary forces (G. Willhite, 1986). Oil adsorbs on the oil-wet or oil-mixed-wet surfaces of the pores and pore throats. Another type of residual oil saturation is residing oil in flow pockets at dead ends or stagnant flow pockets (Ehrenfried, 2013).

Oil remaining after waterflooding as residual or bypassed oil occurs for many reasons; oil characteristics like oil's viscosity and composition, wettability, rock heterogeneity, displacing fluid characteristics such as viscosity, surface activity, and pH, initial water saturation; when the saturation of water increases the oil will disconnect from streamflow and trapped as ganglia, flow rate, the capillary end effect and adsorption (Ehrenfried, 2013).

EOR processes are designed to minimize remaining oil caused by the aforementioned reasons. EOR operations are divided into four major categories; chemical flooding, thermal flooding, miscible flooding, and microbiological flooding (Terry, 2001). One of the significant EOR strategies that have been commonly used in some oil fields is chemically enhanced oil recovery (CEOR). 11% of EOR projects globally are done using CEOR, according to Rellegadla et al., 2017. Over 77% of these techniques use polymer flooding, while 23% use polymer in combination with surfactants (Mohsenatabar Firozjahi & Saghafi, 2020). Polymer flooding's prime target is to improve mobility control and sweep efficiency. The higher sweep efficiency achieved by lessening viscous fingering is the most important and evident mechanism of polymer flooding. After polymer flooding, permeability is reduced, making subsequent water flooding more efficient. Through disproportionate permeability reduction, the water's relative permeability experiences a greater decrease than the oil's permeability during flow (J. J. Sheng et al., 2015).

Biopolymers and synthetic polymers are the two types of polymers that are employed in EOR operations. Biopolymers are susceptible to biological disintegration despite being able to endure higher salinities and temperatures than the common synthetic polymer polyacrylamide (HPAM) (Jensen et al., 2018, Gbadamosi et al., 2019). However, due to its ease of onsite manufacture, cheaper cost, and better control over molecular weight distribution, HPAM (Hydrolyzed polyacrylamide) is preferably used for polymer flooding operations (Diab & Al-Shalabi, 2019; Kim et al., 2010). Because of this, HPAM has been applied frequently in polymer flooding field projects more than biopolymers (J. J. Sheng et al., 2015; Standnes et al., 2014). Additionally, unlike biopolymers, synthetic polymers experience viscoelastic behavior that appears as shear-thickening during flowing in porous media, where their apparent viscosities noticeably rise with the shear rate (Demin et al., 2011; Clarke et al., 2016; Azad & Trivedi, 2019, 2020). Due to their viscoelastic properties, synthetic HPAM polymers could therefore, significantly improve oil recovery at the lab-scale in sandstone formations (Hincapie et al., 2017).

Although polymer flooding is a common chemical enhanced oil recovery (CEOR) technique applied in sandstones, its application in carbonates remains limited due to the challenging conditions present in carbonates. These include mixed-to-oil wettability, low permeability, and high heterogeneity. Additionally, the effectiveness of polymer flooding in carbonates is limited by severe conditions like high temperatures that go beyond 90° C, high levels of divalent cations or hardness surpassing 1,000 ppm, and high salinity levels above 100,000 ppm (Alsofi et al., 2017b). New polymers are developed for harsh carbonate environments (Gaillard et al., 2010; M. Han et al., 2013; Levitt & Pope, 2008; Vermolen et al., 2011; Jouenne, 2020). These new polymers contain certain monomers that shield the

polymer from deterioration due to high temperatures and saline environments (Dupuis et al., 2017). The term "sulfonated polyacrylamide" or (SPAM) refers to modified synthetic polymers like 2-acrylamido-2-methyl propane sulfonate (AMPS), an anionic monomer that increases HPAM's tolerance to salinity and hardness, and acrylamide-Tertio-butyl sulfonate (ATBS), a monomer that restricts hydrolysis and thermal degradation. Another nonionic monomer that can shield HPAM against thermal hydrolysis at high temperatures is NVP, also known as N-vinyl pyrrolidone (Gaillard et al., 2010; M. Han et al., 2013; Levitt & Pope, 2008; Vermolen et al., 2011). Despite the fact that NVP, ATBS, and AMPS increase aqueous solution viscosity to provide sufficient sweep efficiency and improve thermal stability, salinity, and hardness tolerance, they are 3–10 times more expensive than standard HPAM (Gaillard et al., 2014).

Most world oil reserves are located in carbonate rocks (G. P. Willhite & Green, 1998), unlocking the viscoelastic potential of polymers in carbonate similar to the reported recovery from successful sandstone projects like Daqing would lead to more recovery on a global scale.

1.2 Problem Statement

Polymer flooding is commonly used to enhance oil recovery via an enhanced sweep. Synthetic and biopolymer polymers are used in chemical EOR projects. Synthetic polymers like hydrolyzed polyacrylamide HPAM are frequently used in sandstone formation where the salinity, divalency and temperature are relatively lesser. Carbonate reservoirs are characterized by high salinity, high divalency, temperature and oil-wet nature. A series of synthetic polymers with higher sulfonation degree were developed and some of them were tested for high salinity, high temperature applications (Seright et al., 2021). Synthetic polymers, unlike biopolymers, have flexible chains that allow them to experience elastic deformation while flowing in porous media. This gives synthetic polymers the ability to exhibit both viscous and elastic behavior depending on the time required by the chains to return to their initial shape, a property known as viscoelasticity. Studies have shown that the viscoelastic properties of polymers can have a significant impact on residual oil saturation reduction especially at higher fluxes (Erincik et al., 2018; Seright 2017 Azad and Trivedi, 2021). However, there are also contradictory findings regarding the influence viscoelastic polymers have on mobilizing trapped oil especially if it is heavy (Vermolen et al., 2017). Due to the complexity of the residual oil saturation reduction in porous media and complex nature of viscoelastic flow in porous media, it has been suggested that the influence of viscoelasticity on residual oil saturation should be investigated on a case-by-case basis (Seright, 2017). Carbonate reservoirs are not only characterized by high salinity, high temperature but also by an oil wet to mix-wet nature. Residual oil recovery becomes more complex when the wetting nature is non-water-wet. Further, carbonate reservoirs are characterized by relatively higher heterogeneity. Therefore, it becomes important to

understand the influence of stable viscoelastic polymers on residual oil recovery in oil-wet, heterogeneous carbonate conditions. Research

1.3 Objectives

The main deliverables of this proposed thesis work are to:

- 1- Evaluate the bulk rheology of SPAM polymer under reservoir temperature conditions (75 °C).
- 2- Evaluate the in-situ rheology of SPAM polymer under carbonate formation conditions to track the different in-situ flow regimes.
- 3- Compare the oil recovery potential between bio polymers with lesser non-linear viscoelasticity and viscoelastic sulfonated polymers in heterogeneous non water-wet carbonate formations at the flux-rates representing the shear thinning and shear thickening regime.

1.4 Chapters Organization

This thesis is organized into five chapters, each serving a specific purpose in addressing the research problem. The organization is per the Deanship of Graduate Studies of King Fahd University of Petroleum & Mineral guidelines.

Chapter 1. provides an overview of aspects related to oil recovery mechanisms, including residual oil saturation, chemical-enhanced oil recovery processes, and advanced polymer types. Additionally, it outlines the research problem statement, objectives, and the organization of the thesis.

Chapter 2. Commences by discussing various types of remaining oil and the factors that influence them. Subsequently, delves into the viscoelastic behavior of polymers, exploring the factors that govern this phenomenon and the methods used for its characterization. Additionally, provides an overview of significant field projects where polymers have been applied. Lastly, this section presents a comprehensive literature review on the utilization of viscoelastic polymers in laboratory studies.

Chapter 3. Outlines the research methodology starting with showing the properties of the materials utilized in this work including porous media, polymers, brine and crude oil. Details the procedure used in characterizing and screening sulfonated polymer beside a description of the core flooding setup employed in both the single and two-phase core flooding.

Chapter 4. Discusses the characterization of displacing polymers, specifically sulfonated polymer and xanthan gum, and presents the screening process results. Encompasses various rheological characterization tests conducted at different molecular weights and concentrations.

Chapter 5. Summarizes the in-situ rheology of polymers used in oil recovery flooding experiments and the oil recovery profiles of viscoelastic and viscous polymers. Clarify the viscoelasticity role in the oil recovery process for oil-wet heterogeneous reservoir conditions.

Chapter 6. Summarizes the conclusions and outlines the significant research findings with recommendations for future research works.

CHAPTER 2

LITERATURE REVIEW

2.1 Enhanced Oil Recovery

The process of extracting more oil by injecting various fluids into the reservoir to act as displacement agents is known as enhanced oil recovery, or EOR. Unlike waterflooding or secondary recovery, many definitions of EOR exclude water injection. The main objective of EOR, as detailed by Lake et al. (2014) and Sorbie (1991), is to raise the quantity of crude oil extracted and prolong the profitable lifespan of oil wells. EOR methods include gas, chemical, and thermal techniques, as illustrated in **Figure 2.1**. In the context of chemical EOR, various approaches are employed, including polymer flooding, surfactant-polymer flooding, alkaline-surfactant-polymer flooding, and the use of nanoparticles, among others. The primary goal of chemical methods is to alter fluid and/or rock characteristics, such as interfacial tension between fluids and fluid viscosity.

Conversely, the thermal method focuses on reducing the viscosity of heavy oil to facilitate its flow, making it easier to extract. The gaseous method, on the other hand, aims to eliminate interfacial tension and achieve miscibility or dissolution of the injected gas within the moving oil bank.

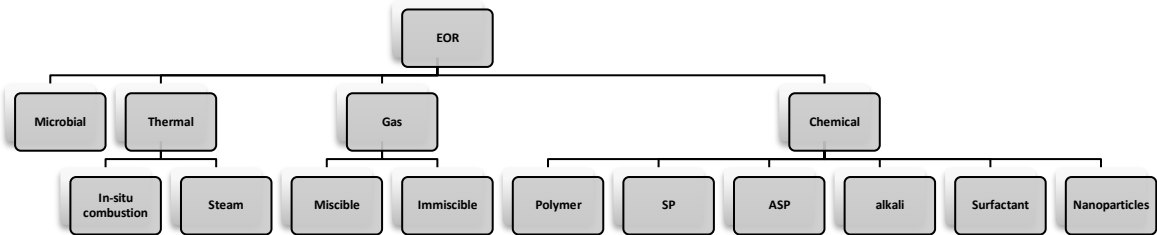


Figure 2-1 Enhanced oil recovery methods

2.2 Remaining Oil Saturation

Waterflooding is a frequently employed technique for enhancing oil recovery in reservoirs, yet a significant portion, often exceeding 60% of the initial oil reserves, remains untapped following this process (Statter and Iqbal, 2007). Oil that remains in the reservoir following primary extraction procedures is known as "residual" or "bypassed" oil. Bypassed oil is defined as the oil that remains undisturbed by a less viscous displacing fluid, such as water, especially in heterogeneous reservoirs. The amount of this unrecovered oil typically increases in scenarios where there's significant heterogeneity in the reservoir and a notable difference in mobility between the displacing fluid (water) and the oil. (Qi et al., 2017).

2.2.1 Bypassed Oil

There are at least two ways that caused bypassed oil, in situations with heterogeneous permeability, higher permeability channels might enable water to advance faster, potentially leaving sections of oil stranded. Once enough channels form around a

lower permeability area, the pressure gradient through this area decreases, rendering the viscous forces inadequate for further invasion and oil mobilization in that section. In cases where the oil is more viscous, its reduced relative mobility promotes the formation of unstable water fingers advancing into channels. When these fingers break through or merge, the resulting swept flow paths can leave nearby oil sections stranded. The greater the heterogeneity or oil viscosity, the higher the likelihood of oil being bypassed. Viscous oils, in particular, may interact with even minor heterogeneities to remain immobile under water flooding.

2.2.2 Residual Oil

Lake, in "Enhanced Oil Recovery, 1989," describes residual oil as the "oil left in a permeable medium that has been extensively swept by water." Based on this definition, residual oil is typically composed of:

1. Oil adhered to the surfaces of pores and pore throats that are oil-wet or mixed-wet.
2. Oil droplets that have broken off from the streamflow and become trapped by capillary forces (Willhite, 1986).
3. Oil situated in inaccessible pore volumes or dead-ends.

The wettability of the medium, the pore structure, and fluid interactions like interfacial tension (IFT) all play a role in the trapping of oil droplets in a porous environment like a reservoir (Green and Willhite, 1998). In scenarios with small sized pore openings, capillary forces, which oppose the viscous forces generated by fluid movement, play a pivotal role in trapping oil droplets. The nature of these forces is influenced by the varying velocities and viscosities of the fluids, impacting the pressure gradient profile within the medium. Capillary forces are more significant in smaller pores and with higher IFT. Moreover,

capillary pressure, indicating the contrast between wetting and non-wetting phases, is influenced by factors such as pore size, contact angle, and IFT.

2.3 Mobility ratio and capillary forces

The mobility ratio and the capillary number—two crucial variables for estimating oil saturation levels following waterflood and polymer flood procedures are examined in detail in the subsequent sections.

2.3.1 Fluids Mobility Ratio

The ratio of the fluid's mobility that is causing the displacement to the fluid's mobility that is being displaced is known as the "mobility ratio" (M). The displacement fluid in this study is light oil, and the displacing fluids are water and a polymer solution. The following is the equation that can be used to calculate the end-point mobility ratio (M):

$$M = \frac{K_{rw}\mu_o}{k_{ro}\mu_w} \dots\dots\dots (2.1)$$

Where (k_{rw}) is the relative permeability of displacing water, (k_{ro}) is the relative permeability of displaced oil, (μ_o) is the viscosity of displaced oil, (μ_w) is the viscosity of displacing fluid e.g. water. When the mobility ratio is favorable (below 1), it indicates a stable displacement process that improves both the efficiency of the sweep and the recovery of oil. while a mobility ratio that is not favorable can lead to an unstable displacement, characterized by the development of viscous fingering. This instability can result in oil being bypassed or left un-swept.

2.3.2 Rock Capillary Forces

Capillary number is the ratio between viscous force and capillary force and it is denoted by (N_c). The capillary number can be illustrated through the following model:

$$N_c = \frac{u \mu_w}{\sigma}$$

In this model, N_c denotes the capillary number, u represents the interstitial injection rate, μ_w is the viscosity of the displacing fluid, and σ signifies the interfacial tension between the displaced and displacing fluid. Gas and surfactant-based EOR methods aim to minimize trapped oil. Experiments show that residual oil saturation stays nearly constant at low capillary numbers (N_c), but significantly drops above a certain threshold ($\sim 10^{-4}$ to 10^{-6}), as depicted in the capillary number desaturation curve (CDC) in **Figure 2.2**. This curve, which varies with rock type, is vital for EOR strategy development. In typical waterflood operations, the capillary number usually remains less than a critical threshold. To effectively reduce residual oil saturation, it needs to be increased significantly. This can be achieved by raising the pressure gradient which is not practical or lowering the oil-water interfacial tension. While viscous polymers can increase the pressure gradient, their capillary numbers usually remain below the CDC's critical point in reservoirs. Research on viscoelastic polymers suggests they can also decrease residual oil saturation, an effect not captured by the traditional viscosity value in the N_c formula. It is recommended to use pore scale extensional viscosity instead (Azad and Trivedi, 2019).

In laboratory core flood experiments, which can span from a few inches to several feet, the core's end interfaces with a medium where capillary pressure is zero. For a steady state to be maintained, the capillary pressure inside the core must match this zero-external pressure. This leads to the accumulation of the wetting phase at the core's end, a phenomenon observed in laboratory settings but not typically in real reservoirs. The extent of this capillary end effect is influenced by factors such as the flux rate, the core length, and the viscosity of the displacing fluid. According to Rapport and Leas (1953), when the Rapport-Leas number, calculated as $Lv\mu_w$ where 'v' is the interstitial Darcy velocity, exceeds ~ 3.5 centipoise centimeters squared per minute, the impact of capillary end effects is generally minimal.

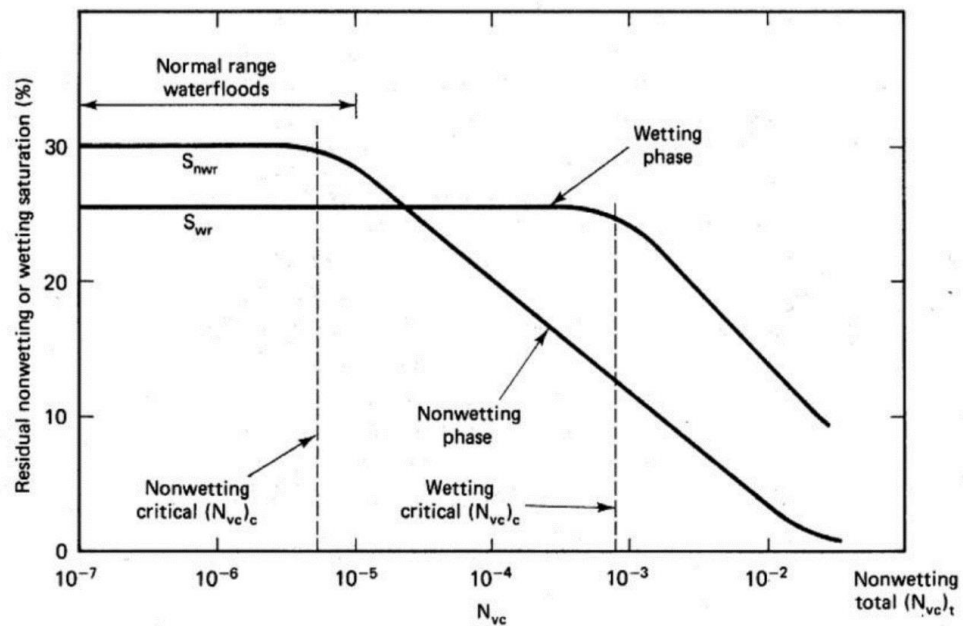


Figure 2-2 Typical CDC desaturation curves for oil/water wet systems (from Lake et al., 2014)

2.4 Polymer Viscoelasticity and Deborah Number

Viscoelastic polymers display behaviors of both shear thickening and shear thinning. Shear thinning is predominant in regimes of shear flow, whereas shear thickening

dominates in extensional or elongational flow regimes, as noted by Sochi in 2010. The polymer flow in porous media is complex; as a result of its tortuous nature, a combination of shear and extensional flow occurs in porous media, increasing the apparent viscosity of the polymer and generating the dilatant effect. This thickening behavior is potent under pure extensional flow but only develops itself in pure shear flow at extremely high shear rates. As flow rates rise, the frequency of deformation reaches a point where the polymer lacks sufficient time to revert to its original shape after disturbance. This leads to elastic strain, a type of deformation that results in a significant increase in pressure drop and induces shear-thickening in the polymer, as described by Delshad et al. (2008) and Tahir et al. (2017).

One way to evaluate the elasticity of polymers is through Deborah number, which is defined as the ratio of relaxation time to its resident time, indicating elastic to viscous behavior ratio (Bird et al., 1987; Macosko, 1994). A large Deborah number means high elastic behavior like in solids materials while low indicates viscous behavior like in fluids (Sorbie, 1991). According to Marshall & Metzner 1967, When the fluid instantly reacts to its current state of deformation without "remembering" its previous configurations, the viscoelastic effect becomes negligible, particularly for small Deborah numbers (De). Additionally, viscoelastic materials begin to exhibit solid-like properties as De approaches a critical value. They also highlighted that crucial Deborah levels around 0.05 are where the fluid's significant impact on pressure decrease is initially felt. But there is contrasting reports on the De threshold, (Heemskerk et al., 1984) found that at a crucial Deborah number of around one, polymer chains started to stretch and show thickening. Associative polymer and HPAM were subjected to an extensional rheological evaluation by Azad et al

2018, which characterized the onset of viscoelastic behavior to Deborah numbers of 0.132 and 0.156, respectively. The impact of viscoelastic polymers on incremental oil recovery during polymer flooding in sandstone cores was also studied by Qi, (2018). De has been used to quantify the viscoelastic effect on Sor reduction during polymer flooding (Ehrenfried, 2013; Koh et al., 2015; Qi et al., 2018; Azad et al., 2018). There is a wide range of De being reported during polymer flood application. This contrast in the reported De is due to the definition of relaxation time and observation time employed (Azad & Trivedi, 2019). When polymer chains return to their original shape after being deformed, it's called relaxation time. When a polymer solution experiences rapid deformation, and its residence time matches its relaxation time, it is considered to exhibit greater viscoelastic properties. Newtonian fluid has a relaxation time of zero, while a solid with Hookean elastic properties has an infinite linear relaxation time. Relaxation time varies based on the flow regime employed for its measurement. For instance, in a shear flow field, the dynamic frequency sweep test yields the oscillatory relaxation time. Two models are commonly used for estimating this time: The Rouse model (Rouse Jr, 1953) and the elastic and viscous moduli cross-over method (Castelletto et al., 2004). For an accurate understanding of polymer flow in porous media, measuring the relaxation time in a regime that is either shear-free or extensional is advisable. The capillary breakup extensional rheometer is used to ascertain the extensional relaxation time. In this method, a polymer sample is placed between two plates. When the top plate is rapidly separated from the bottom, the change in filament diameter is measured. Time-based plots of filament diameter are created and fitted to the upper-convected Maxwell model, with regression analysis used to determine the

extensional relaxation time (Azad & Trivedi, 2019). Additionally, Qi (2018) offers a comprehensive overview of various methods for estimating polymer relaxation time.

The duration for which the fluid stays in the pore is known as the residential or observation time, inversely related to the velocity gradient, as noted by Wilton & Torabi (2013). The method chosen to calculate the deformation rate significantly affects the range of the Deborah number that marks the onset of viscoelastic behavior (Azad & Trivedi, 2019). Various researchers, such as Koh et al. (2018), Lotfollahi et al. (2016), Masuda et al. (1992), and Qi et al. (2017), have employed the shear rate in their calculation of observation time, whereas others like Azad et al. (2018a), Haas & Durst (1982), Heemskerk et al. (1984), and Hirasaki & Pope (1974) have utilized the strain rate. Given that the denominator in strain rate calculation includes a larger coefficient compared to that in shear rate calculation, the Deborah number estimated using strain rate will be lower than that calculated using shear rate (Azad & Trivedi, 2019).

2.5 Polymer Field Application

One of the main EOR methods used in oil fields is chemical-enhanced oil recovery (CEOR). According to studies on EOR, CEOR is used for 11% of all EOR projects worldwide. More than 77% of these techniques include flooding with polymers (Rellegadla et al., 2017). Many successful polymer projects have been carried out over the past decades, most of them are conducted in sandstone. **Table 2-1** encapsulates key projects of polymer flooding from various countries such as the USA, UAE, China, UK, Angola, Canada, and Austria, executed in diverse formations. Notably, China has undertaken numerous commercial polymers flooding ventures, achieving an average additional oil recovery of around 9%, as reported by J. Sheng in 2013. Nevertheless, Daqing Oil Field executed the

first comprehensive commercial polymer flooding application, which is considered the largest polymer application in history so far (Guo et al., 2022), achieving around 20% incremental oil recovery harnessing high molecular weight and concentration of viscoelastic polymers. However, polymer application in carbonate rock didn't achieve such high oil recovery as in sandstones counterpart (Han, 2013; Azad & Sultan, 2014).

The reason for the lack of successful polymer field applications in carbonates under challenging conditions is attributed to factors such as natural fissures facilitating channeling, degradation of polymers, mixed-to-oil wettability, limited permeability due to high heterogeneity, and extreme conditions of high temperature, salinity, and hardness. Thus, there are no reported instances of successful polymer field applications in carbonates under difficult circumstances (Rachapudi et al., 2020).

A polymer flooding project recently employed ATBS-rich polymers in Abu Dhabi carbonate formation (S. Masalmeh et al., 2019). There have been no reports on the potential for oil recovery yet, but Rachapudi et al. (2020) state that the single-well injectivity test in this reservoir showed that new polymers performed well in terms of injectivity and viscosity at 2500 ppm.

Table 2-1 Major polymer field application projects worldwide

Field	country	Formation type	Avg Temp. °C	FM water salinity ppm	Polymer type	Incremental oil recovery
Kalamkas (Sagyndikov et al., 2022)	Kazakhstan	Sandstone	43	10,000	HPAM (15 Mda 1800ppm)	9%
Marmul (Al-Saadi et al., 2012)	Oman	Sandstone	46	7,000	HPAM 1000 ppm	59% overall
Bhagyam (Shankar et al., 2018)	India	Sandstone	70	9,500	HPAM (17-25 Mda 2200ppm)	N/A
Matzen (Zechner et al., 2015)	Austria	Sandstone	50	20,000	HPAM 2000 PPM	N/A
East Bodo (J. Sheng, 2013)	Canada	Sandstone	50	28,000	HPAM 1500 ppm	N/A
Captain (Poulsen et al., 2018)	UK	Sandstone	30	14,000	HPAM 2500 ppm	16%
Xiaermen (J. Sheng, 2013)	China	Sandstone	50	2,100	HPAM 1200	10%
Daqing (Guo et al., 2021; Wang et al., 2000)	China	Sandstone	45	8,200	HPAM 2250 ppm	20%
Shengli (Guo et al., 2021)	China	Sandstone	71	5,900	HPAM 1500 ppm	20.6%
<i>Pelican Lake</i> (Delamaide et al 2014)	Canada	Sandstone	17	N/A	HPAM 3000 ppm	25%
Dalia (Morel et al., 2015)	Angola	Sandstone	50	120,000	HPAM 900 ppm	7%
West Coyote (Shuler et al., 1987)	USA	Sandstone	57	12,000	HPAM 2000 ppm	17%
Vacuum (Hovendick, 1989)	USA	Dolomite	38	169,000	HPAM 50 ppm	1%
Eliasville Caddo (Weiss, 1992)	USA	Limestone	46	165,000	HPAM 1500 ppm	4%
Abu Dhabi Field (S. K. Masalmeh et al., 2014)	UAE	Limestone	120	200,000	HPAM 2500 ppm	N/A

2.6 Viscoelasticity and displacement efficiency- literature review

Schneider & Owens, (1982) presented a study titled "Steady-State Measurements of Relative Permeability for Polymer/Oil Systems". This study was the first to use polymer flooding in oil wet formation, the study aimed to boost oil recovery in waterflooded viscous oil reservoirs by testing six polyacrylamide polymers on 18 cores with permeabilities from 50 to 1200 md. Conducted in both oil-wet and water-wet environments, the research found that polymers consistently reduced water relative permeability while variably impacting oil permeability. In water-wet systems, polymer injection was benign or beneficial to oil permeability and significantly reduced water permeability. In oil-wet systems, polymers affected both oil and water permeabilities, but effects on oil permeability varied. Overall, the study suggests that polymer injections can enhance oil recovery by altering water permeability in different wettability systems.

Masuda et al., (1992) investigated the influence of viscoelastic polymer solutions on enhanced oil recovery (EOR) through 1D simulation models. The study incorporates elastic viscosity, using experimental data from 1D flooding experiments on glass-bead-packed cores. The viscoelastic model demonstrates better prediction accuracy for oil recovery and breakthrough times, highlighting the importance of the viscoelastic effect in polymer solutions. The study notes that polymer solutions exhibit pseudoplastic behavior in tube flow but display significant viscoelastic effects in porous media, particularly at high shear rates. Experiments using different white mineral oils and a partially hydrolyzed polyacrylamide (HPAM) polymer solution confirm the crucial role of viscoelasticity in improving oil recovery, especially at high flooding velocities. Observations on pressure drops and oil production reveal discrepancies between experimental data and model predictions, attributed to the dilution of injected polymer solution due to adsorption and dispersion, not considered in the viscoelastic model.

Han et al., (1995) studied the influence of the viscoelastic properties of hydrolyzed polyacrylamide (HPAM) solutions in enhancing oil recovery through core flooding tests and mathematical modeling. The research explores how the viscoelastic effects of HPAM solutions can improve displacement efficiency in oil recovery. It examines the properties of HPAM, including Darcy flux rate, salinity, hydrolyzation degree, and core permeability. The study identifies two critical velocities: a second critical or critical transit velocity (V_{cr}) where HPAM solution changes from pseudoplastic to dilatant behavior, and a first critical velocity (V_{ce}). These velocities are key in determining the rheology of HPAM in porous environments and its impact on oil recovery. The paper discusses experiments conducted to understand the impact of injection rates on displacement efficiency. These tests show that oil displacement efficiency by 1000 ppm HPAM is higher than that by water flooding. The highest IOR of 20% is achieved when the displacing velocity approaches V_{cr} .

Wang et al., (2000) investigated the effectiveness of viscous-elastic polymers in enhancing oil recovery from cores. The study shows that these polymers reduce various types of microscale residual oil including films on rock surfaces and oil in capillary forces-retained pores. The elastic nature of polymers influences velocity distribution and exerts a "pulling effect". Lab results show that viscoelastic polymer impact micro-scale recovery by over 6% OOIP. Field results from Daqing Oil Field support these findings, showing an incremental oil recovery of over 13% OOIP, which is not solely explained by increased volumetric sweep efficiency, highlighting the potential of viscous-elastic polymers to significantly improve microscale displacement efficiency and increase oil recovery.

Delshad et al., (2008) focused on the viscoelastic properties of polymer solutions and their impact on enhancing efficiency in polymer flooding for oil recovery. It presents evidence that the viscoelastic nature of high MW partially hydrolyzed polyacrylamide (HPAM) yield maximum oil recovery factor of 80%. To evaluate how the viscoelastic properties of these polymers improve

reservoir sweep efficiency, rheological measurements and core-flood experiments were carried out. Very high molecular weight HPAM demonstrates pronounced elastic behavior, aiding in displacing residual oil after extensive water flooding. The study highlights that the viscoelasticity and shear-thickening behavior of HPAM solutions effectively displace bypassed oil in heterogeneous reservoirs. It acknowledges challenges such as high-pressure drops and mechanical degradation at the injection well when using shear-thickening polymers.

Urbissinova et al., (2010) investigated the impact of polymer-based fluid elasticity on microscopic sweep efficiency in enhanced oil recovery (EOR). Two polymer solutions with similar shear viscosity but differing elastic properties, both composed of various polyethylene oxide (PEO) grades, were examined. The research utilized a specially designed core holder for radial flow simulation, injecting polymer solutions through a sandpack saturated with mineral oil. Results revealed that adjusting the molecular weight distribution (MW) of the polymer solution, while maintaining constant shear viscosity and polymer concentration, significantly improved sweep efficiency. Higher elasticity in the polymer solution led to increased resistance to flow through porous media, enhancing sweep efficiency and reducing residual oil saturation. The findings underscore the importance of elastic properties in polymer solutions for EOR, suggesting that optimizing MW can enhance oil recovery by achieving better sweep efficacy and lower residual oil saturation under conditions mimicking actual field operations.

Meybodi et al., (2011) investigated the influence of pore structure and wettability on the efficacy of polymer flooding for enhanced oil recovery (EOR). Identifying polymer flooding as effective in heterogeneous oil reservoirs with high water cuts, the research underscores the importance of a comprehensive pre-implementation analysis, considering polymer solution rheology and its interaction with the porous medium. Emphasizing the crucial role of reservoir wettability and pore structure in displacement efficiency in EOR, the paper cites prior research revealing different effects of residual oil on polymer adsorption based on porous medium wettability. In oil-wet mediums, residual oil reduces polymer adsorption, while the opposite occurs in water-wet

mediums. The study employs five two-dimensional glass micromodels to explore the effects of pore structure and wettability on microscopic and macroscopic polymer flooding behavior. Conducting fifteen experiments, it observes slight shifts in oil recovery values but consistent overall trends, successfully replicating flow patterns and confirming result repeatability. Microscopic analysis reveals distinctive displacement mechanisms based on medium wettability, with water-wet mediums exhibiting complete microscopic pore-to-pore oil sweeping, oil-wet mediums lacking a thick connate-water film, and mixed-wet mediums displaying complex flow behaviors, leading to partial sweeping and emulsion formation.

Shiran et al., (2013) studied the impact of the initial wetting state of reservoir rocks on the efficacy of polymer flooding. The study highlighting the lack of data pertaining to the effect of wettability on oil recovery within polymer flooding scenarios. Dynamic flooding experiments were conducted utilizing low salinity polymer and polymer particles (HPAM 300 ppm) across various initial water saturation states. The experiments were conducted using homogeneous, low-permeability Berea and high-permeability (105 mD) Bentheimer sandstone cores. The purpose was to assess how wettability influences the efficiency of polymer flooding. Results from these studies reveal that the displacement efficiency in low salinity polymer flooding largely depends on the initial wettability state of the porous media. In more water-wet systems, higher resistance and residual resistance factors were observed, resulting in limited or no additional oil recovery. Conversely, intermediate-wet systems exhibited lower resistance factors and promising additional oil recovery, with a notable up to 56% decrease in waterflood oil residual saturation. The incremental oil recovery in these instances is attributed to the synergistic effects of low salinity brine and polymer injection, effectively mobilizing oil during the flooding process.

Vermolen et al., (2014) delved into the application of polymer flooding in high-salinity and high-temperature environments, concentrating on ter-polymers based on polyacrylamide. The objective is to broaden the scope of polymer flooding, particularly in demanding conditions like those found in the high-temperature, high-salinity carbonate reservoirs of the Middle East. The study evaluated

the thermal stability of various commercially available polymers, including co- and ter-polymers based on partially hydrolyzed polyacrylamide (HPAM), at 120°C in assorted brine solutions. These polymers were modified with 2-Acrylamido-2-Methylpropane Sulfonate (AMPS) and/or n-Vinyl Pyrrolidone (n-VP) monomers to enhance their tolerance to divalent ions and resistance to hydrolysis at elevated temperatures. Additionally, the research explored how these ter-polymers adsorb onto carbonate core materials, taking into account the polymer type and pH level. A significant finding was that the addition of n-VP to polymer solutions ensures their stability at 120°C in high-salinity brines containing divalent ions. The most effective ter-polymer demonstrated stability for over 180 days, suggesting a promising expansion of polymer flooding applications in challenging environments.

Koh et al., (2018) explored the impact of hydrolyzed polyacrylamide (HPAM) polymers on oil recovery, specifically focusing on their role in reducing residual oil saturation (ROS). The research is focused on comprehending and forecasting the rheology of HPAM (Hydrolyzed Polyacrylamide) polymers and their impact on Residual Oil Saturation (ROS). It concludes that polymer floods, particularly with viscous oils, recover significantly more oil compared to waterfloods, resulting in up to a 24% lower oil saturation after polymer floods. This reduction in ROS is attributed to the viscoelasticity of polymer solutions, correlated with the Deborah number. The experiments used three types of polymers with varying molecular weights under typical field conditions. Nine polymer flood experiments were conducted, considering different porous media, brine permeabilities, oil viscosities, temperatures, polymer types, concentrations, capillary numbers, and equivalent shear rates. The reduction in ROS due to polymer flooding is primarily linked to the viscoelastic properties of the polymer solutions, with other factors such as polymer viscosity, initial oil saturation, core wettability, brine composition, and core heterogeneity also influencing ROS. The study concludes that polymer flooding is effective in reducing ROS, with the magnitude of reduction dependent on factors like polymer type, formation characteristics, and experimental

conditions, making it a viable method for enhancing oil recovery, especially in the case of viscous oils and specific formations characteristic.

Howe et al., (2015) investigated the behavior of viscoelastic polymer solutions, specifically high molecular weight partially hydrolyzed polyacrylamides (HPAM), in porous media with a focus on enhanced oil recovery (EOR). Highlighting their significance in water-flooding processes, the study notes that high molecular weight solutions recover more oil than conventional models predict. The experiments, conducted in rock cores and microfluidic networks, revealed elastic turbulence within fluid flow in cores at higher apparent velocities. Utilizing cylindrical rock plugs from the Bentheimer formation, known for consistent properties, the study observed apparent flow thickening at a critical deformation rate, contrasting with standard rheometry. This thickening was attributed to additional dissipative elastic turbulence mechanisms in porous media flows. Visual evidence showcased laminar-to-turbulent flow transitions with increasing rates. The study underscores elastic turbulence's role in altering flow characteristics, enhancing oil recovery efficiency beyond conventional predictions.

Clarke et al., (2016) studied how improved oil recovery is affected by viscoelastic properties. His research emphasizes the significance of viscoelastic polymers in augmenting oil extraction, surpassing the results attainable through traditional viscous polymer flooding methods. The research used two types of polymers: 6000 ppm Hydrolyzed Polyacrylamide (HPAM), a synthetic polymer, and 640 ppm xanthan, a polysaccharide. HPAM, in particular, was chosen for its flexible random-coil conformation in solution, which is significant for its viscoelastic properties. Experiments were conducted using a synthetic brine. Rheological and single-phase flow experiments were also performed to assess the flow behavior of these solution. The study demonstrates that using viscoelastic polymers

with different elastic degree in flooding solutions reduce residual oil saturation due to changes in the steady-state flow profile and enhancements in oil stripping and thread formation. They report a sustained doubling of recovery enhancement compared to conventional viscous-polymer flooding (4% and 11% IOR due to xanthan and HPAM respectively). The article proposes that the improved efficiency in displacement is due to a phenomenon termed elastic turbulence. This mechanism, not previously identified in enhanced Oil Recovery (EOR) processes, has been shown to occur at flux rates of 1 ft/day (interstitial velocity).

Qi et al., (2017) presented research article titled "Decreasing Residual Oil Saturation in Sandstone Cores Through the Application of Viscoelastic Polymers" which investigates the effects of hydrolyzed polyacrylamide (HPAM) on lowering the residual oil saturation (ROS) in Bentheimer sandstone formations. The study, focusing on these homogeneous and permeable sandstones, aims to examine mechanisms and conditions for enhanced oil recovery. Through constant-pressure-drop experiments, the research observes a 5% reduction in S_{or} during HPAM floods with notable elasticity (Deborah number, N_{De} , values between 0.6 and 25). Low elasticity ($N_{De} < 0.6$) shows less impact, but increased flow rates ($N_{De} > 25$) achieve an additional 10% reduction in residual oil. The study underscores the importance of polymer elasticity, influenced by concentration, and salinity in improving oil recovery in specific rock formations.

Erincik et al., (2018) investigated the effects of hydrolyzed polyacrylamide (HPAM) polymer solutions in diminishing the residual oil saturation (ROS) within Bentheimer sandstone cores, a key factor in improving Enhanced Oil Recovery (EOR) through polymer flooding techniques. Six core flood experiments were conducted, evaluating the influence

of HPAM's viscoelasticity on ROS. The experiments, involving oil, brine, glycerin, and polymer solutions with varying salinities, aimed to assess the conditions under which viscoelastic polymers, like HPAM, can effectively reduce ROS. The study highlights the intricate relationship between HPAM solution viscosity and various factors, including shear rate, molecular weight, hydrolysis degree, concentration, brine composition, and temperature. Employing nearly uniform Bentheimer sandstone cores, the experiments yielded surprising outcomes, demonstrating a decrease in residual oil saturation to 0.08 following the second high salinity polymer flood at 4 ft/day. This occurred despite the absence of a reduction in interfacial tension (IFT) and while keeping the capillary numbers below the critical threshold. However, there may be other factors that might have influenced the reported higher residual oil recovery in Erincik's experiments. For more details refer to (Erincik et al., 2018).

Ming Li et al., (2017) concentrated on applying magnetic resonance imaging (MRI) and magnetic resonance (MR) T2 relaxation time assessments to track the movement of oil in rock core plugs during waterflooding and polymer flooding processes, aimed at enhanced oil recovery (EOR). Polymer flooding, known for improving macro sweep efficiency, faces debates regarding its pore-level displacement efficiency. The research utilized MRI to monitor in-situ oil saturation during waterflooding and polymer flooding, employing MR T2 relaxation time measurements to understand pore-level changes in oil behavior and displacement mechanisms. Wettability, influenced by different oils, significantly impacted fluid flow behavior and polymer flooding effectiveness. The study employed water-wet Buff Berea and oil-wet synthetic core plugs, using Alcoflood 935 polymer for experiments. MRI revealed rapid oil saturation decrease during waterflooding, with polymer flooding

creating a "snowball" effect, more pronounced in crude oil. Oil-wet synthetic cores showed decreased oil saturation, unlike water-wet Buff Berea cores forming an oil bank. The study considered capillary end effects, correlating oil recovery rates with saturation profiles and using T2 log mean ratio for normalization. Overall, the research provides insights into polymer flooding's impact on oil recovery and pore-level fluid dynamics in different rock cores.

Juarez-Morejon et al., (2018) explored the impact of initial core wettability and the timing of polymer flooding on oil recovery, using homogeneous Bentheimer sandstones and partially hydrolyzed polyacrylamide (HPAM). Key findings include a substantial effect of polymer injection timing on final oil recovery, with early injection (secondary polymer flooding) exhibiting the best sweep efficiency. HPAM's viscosity variation and rheological behavior, influenced by factors like molecular weight and hydrolysis degree, are discussed. Polymer flooding aims to reduce water mobility and enhance macroscopic oil sweep efficiency. Different oil recovery behaviors are observed based on core wettability, emphasizing improved sweep efficiency with early polymer injection. The study concludes that early polymer injection enhances pore-scale sweep efficiency, achieving higher oil recovery, while the recovery rate decreases with increasing waterflooding maturity. Dispersion tests highlight polymer flooding's effectiveness at lower water saturations. Overall, the research underscores the significance of timing and wettability in polymer flooding for enhanced oil recovery, shedding light on factors influencing oil displacement and recovery efficiency.

Azad et al., (2018) investigated the impact of viscoelastic polymers, specifically hydrolyzed polyacrylamide (HPAM) and associative polymer, in enhanced oil recovery for heavy oil

reservoirs. It highlights the importance of viscoelasticity in influencing oil recovery in such reservoirs and the need for an analytical tool to characterize the extensional properties of polymers for better selection in EOR applications. The research, targeting heavy oil with viscosity exceeding 500 cP reservoirs employing polymer flooding, explores the shear-thinning regime of the polymers in porous media, transitioning to dilatant behavior at higher rates due to viscoelasticity. Core flooding experiments compare HPAM and associative polymer performance, revealing the latter's significantly higher pressure drop attributed to differences in extensional viscosity and polymer retention. Extensional rheology measurements using the Capillary Breakup Extensional Rheometer (CaBER) system confirm these differences. Despite a slightly higher oil recovery with the associative polymer (52.63% vs. 49.07%) during flooding, the study highlights the profound role of extensional viscosity on pressure drop rather than on oil recovery in homogeneous water-wet sand pack flooding.

Lee et al., (2019) investigated the effectiveness and the potential determining ions of low-salinity polymer (LSP) in improved oil recovery in carbonate oil reservoirs under different pH conditions. This approach combines polymer injection with low-salinity water injection to maximize EOR efficiency. Key findings include the application of polymers to improve water mobility in EOR, enhancing oil recovery by decreasing the mobility ratio. The study conducted experiments using Desert Pink rock carbonate cores, Middle East crude oil, and 800 ppm of a commonly used HPAM polymer. The LSPF experiments, designed to minimize capillary end effects, involved initial low-salinity water flooding followed by LSPF. The analysis considered polymer retention, permeability reduction, wettability alteration, and changes in residual oil saturation. The study concludes that LSPF,

particularly with a high concentration of SO_4^{2-} ions in neutral polymer solutions, significantly enhances EOR efficiency in carbonate oil reservoirs (12.3% IOR). It is noteworthy that this study differs from this research in the selection of polymer type, application of low unfavorable viscosity ratio condition, and the polymer's elasticity was not emphasized. The reported oil recovery is primarily attributed to enhanced polymer adsorption, that improved wettability.

Barri et al., (2023) investigated the impact of low molecular weight (MW) hydrolyzed polyacrylamide (HPAM) polymers on residual oil saturation (Sor) in low-permeability rocks (35 mD). Key findings include the examination of how the viscoelasticity of polymer solutions, particularly 6000 ppm of HPAM 3130 and 4500 ppm of HPAM 3230, influences Sor reduction. Core flooding experiments on a water-wet Berea sandstone core revealed that injecting a more elastic HPAM 3230 solution resulted in 2.9% more incremental oil recovery compared to a less elastic HPAM 3130 solution, highlighting the role of elasticity in mobilizing residual oil. The study emphasizes the significance of polymer viscoelasticity in enhancing oil recovery, suggesting that even polymers with lower elasticity contribute to additional recovery in low-permeability formations at Darcy velocity of 0.2 ft/day.

Seright et al., (2023) explored hydrolyzed polyacrylamide's (HPAM) rheological behavior in oil recovery, emphasizing its dynamics with residual oil and varying salinity/temperature. Using Berea sandstone cores, its studies shear-thickening velocities in polymer floods, their impact on HPAM injectivity, fracture initiation, and viscoelasticity in oil recovery. Addressing HPAM rheology differences in oil-free and oil-saturated media, it reveals that residual oil alters HPAM rheology, challenging certain shift factors' applicability. The study also scrutinizes salinity/temperature's influence on HPAM shear

thickening. Berea sandstone cores undergo diverse experiments, showcasing HPAM's rheological behavior under varying conditions. In oil-free settings, the study establishes a baseline for HPAM rheology, observing Newtonian behavior at lower rates, shear thinning as rates increase, and shear thickening at higher rates. Experiments with different oil saturations show that residual oil moderates shear thickening magnitude, challenging previous studies. The paper provides crucial insights into HPAM rheology in porous media, especially under residual oil, salinity, and temperature, with implications for polymer flooding in enhanced oil recovery.

2.6.1 Knowledges gap

Researches on viscoelastic polymers has been conducted using sandstone or artificially water/intermediate-wet cores. There have been only a few studies that have looked at viscoelastic polymer flooding in carbonate oil-wet rocks. The first study of this kind was conducted by Schneider & Owens, (1982), whose objective was to evaluate the relative permeability of oil and polymer. Lee et al., (2019) conducted a series of core flooding experiments using low-salinity polymer to determine the key ions affecting polymer displacement efficiency. They linked the additional recoveries achieved by the polymer to changes in wettability and the concentration of SO_4^{2-} ions. However, the role of polymer elasticity was not emphasized in this study. A gap in research can be found in the literature on the use of viscoelastic polymers in oil-wet heterogeneous carbonate rocks under high temperature (**Table 2.2**).

Table 2-2 Flooding parameters of key studies on viscoelastic polymer

Author	Type	K (md)	Flux rate (ft/day)	Mw/ conc.	Salinity	Temp.	IOR
<i>Lee et al (2019)</i>	Carbonate Oil-wet	50	1-2	8 MDa 800 PPM	6000	25	12.3%
<i>Han et al 1995</i>	Sandstone Water-Wet	500-760	1.6- 20	9 MDa	1000 PPM	30	20%
<i>Wang et al 2000</i>	micro-models Water-Wet	638	3.28	13 MDa 1000 PPM	800	N/A	14%
<i>Vermolen et al 2014</i>	Sandstone Water-wet	860	1-3	16 MDa 4230 PPM	6230	30	>15%
<i>Koh 2015</i>	Sandstone Water-wet	6000	1	20 MDa 3500 PPM	2000	40	>14%
<i>Clarke et al 2016</i>	Sandstone Water-wet	450	1	30MDa 640 PPM	4800	30	11%
<i>Qi et al 2017</i>	Sandstone Water- wet	2200	0.96	20MDa 2100 PPM	11000	30	10%
<i>Azad et al 2018</i>	Sand-pack Water-wet	1550	4.6	20 MDa 2000 PPM	0	30	39%
<i>Schneider & Owens, (1982)</i>	Sandstone Oil-wet	62	N/A	6 MDa 500 PPM	Low salinity	30	Final Sor: 14%

CHAPTER 3

Experimental Approach

Two Identical core flooding experiments were performed to evaluate the potential of viscoelastic advanced sulfonated polymer over biopolymer in reducing residual oil saturation. The experiment design focused on achieving similar in-situ apparent viscosity and using comparable porous media in all experiments. The specifics include the procedures for fluid preparation and measurement techniques, a description of the experimental apparatus utilized, and the methodologies applied for characterization.

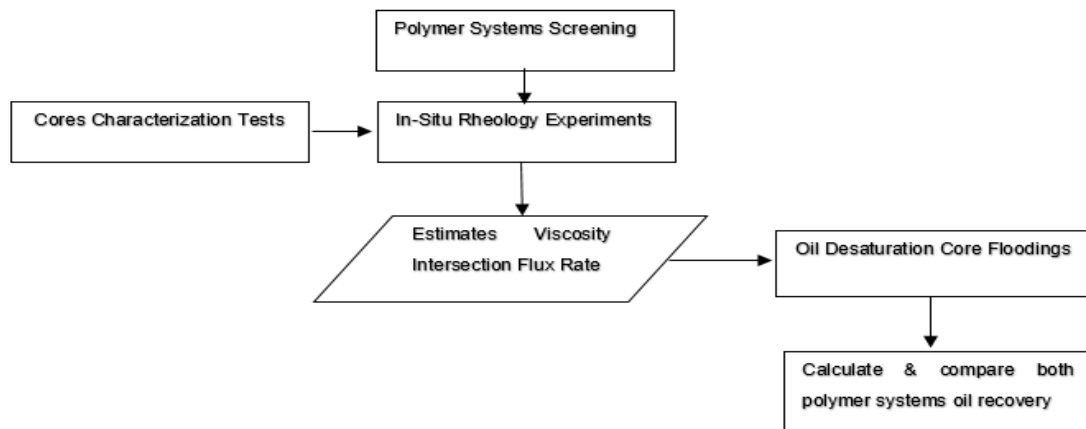


Figure 3-1 Study workflow

3.1 Fluids

This study incorporates various fluids to fulfill its research objectives, including brine, biopolymer, sulfonated polymer and light crude oil. The subsequent section outlines the preparation procedures for these fluids and provides an overview of their respective properties.

3.1.1 Brine

Brine solutions are made using an aqueous mixture containing the salts delineated in **Table 3.1**. These constituents were subjected to continuous stirring until the solutions achieved visual clarity. The low salinity brine is characterized by an estimated density of 1.127 g/cc and a viscosity of 0.97 cp at a standard room temperature of 25 °C. We primarily employed the low salinity brine for the synthesis of polymer samples, while high salinity brine was chosen for core saturation before oil saturation and flooding, mirroring the practical conditions prevalent in Gulf area reservoirs.

Table 3-1 brine solutions constituents

Ions	Field connate water, ppm	Low salinity brine, ppm
Sodium Na ⁺¹	59,491	1,830
Calcium Ca ⁺²	19,040	65
Magnesium Mg ⁺²	2,439	211
Sulfate SO ⁻²	350	429
Chloride Cl ⁻¹	132,060	3,220
Bicarbonate HCO ⁻¹	354	12
Total dissolved solids:	213,734	5,767

3.1.2 Polymers

Sulfonated polymer

The subject of investigation in this research pertains to advanced polymer materials specifically engineered to withstand rigorous carbonate-rich environments (high temperature & salinity) by adding a sulfonate group to the polymer chain. Sulfonated polymer AN-125 is utilized in this study. Various sulfonated polymer powder samples with

molecular weight variants were obtained from **SNF Floerger** company. The molecular weight spanning from low to exceedingly high molecular as shown in **Table 3.2**. The structural characteristics of these polymer varieties are shown in **Figure 3.2**.

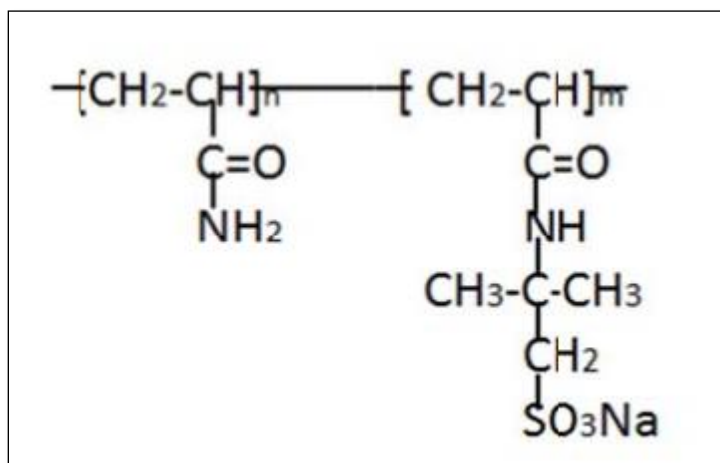


Figure 3-2 Chemical structure of sulfonated polymers AN-125

Table 3-2 Molecular weight ranges for available sulfonated polymers

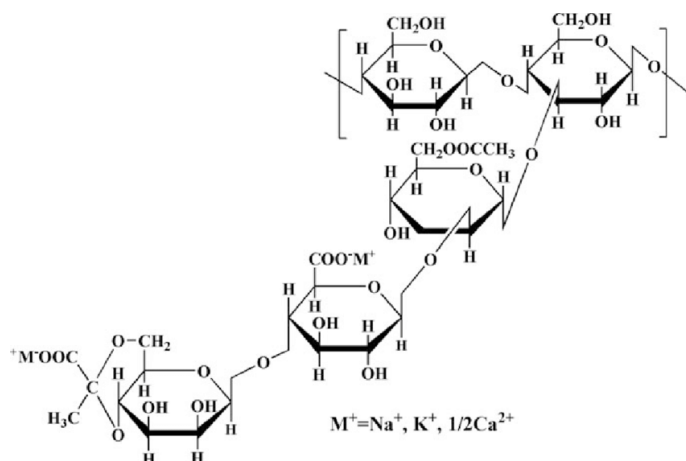
Molecular Weight Range	Polymer Name
Very high molecular weight >30 MDa	VHM
High molecular weight	SH
Medium to broad molecular weight	MPM
Standard molecular weight~8-12 MDa	STD
Very low molecular weight > 5MDa	VLM

For preparing different molecular weights and concentrations, polymer powder was carefully poured into the vortex wall of pre-prepared low-salinity brine solution, employing a high stirring rate of 600 rpm. After a period of 10 minutes at that rate, the stirring speed

was deliberately reduced to a lower rate of 250 rpm and kept for 24 hours covered with nylon to prevent oxidation. Every sample produced was subjected to rheological analysis using a rheometer to generate a steady shear rheology profile. Furthermore, small amplitude oscillatory shear tests, comprising dynamic strain sweep and dynamic frequency sweep assessments, were conducted.

Xanthan polymer

The xanthan polymer, categorized as a biopolymer, demonstrates a notable characteristic of viscosity reduction, manifesting as a thinning behavior in both porous media and bulk environments, the chemical structure of these particular polymers is visually depicted in **Figure 3.3**. The incorporation of this polymer was essential in order to establish a reference point for comparative analysis and to evident a scenario in which similar apparent viscosity as produced from the sulfonated polymer is maintained without any nonlinear viscoelastic effects. The selection of the concentration is carefully determined to achieve higher apparent viscosity in comparison to that of the sulfonated polymer within porous media under Newtonian flow conditions. Consequently, a particular concentration of 2000 ppm was chosen, where the two apparent viscosities are expected to intersect at high shear rates. The preparation protocols employed for these xanthan-based polymers are consistent with those used for the sulfonated polymer.



3.1.3 Crude Oil

Table 3-3 Oil characteristic analysis through SARA.

3.2 Displacing Fluid Screening and Rheology

The selection of polymer concentration and molecular weight for the viscoelastic polymer is determined through a systematic approach involving a series of bulk rheological assessments conducted across a spectrum of concentration and molecular weight variants. These rheological tests are executed with the utilization of Anton Paar rheometers, specifically the MCR-702 model, incorporating concentric cone and cylinder configuration, which accommodates a sample volume of 20 milliliters. The schematic representation below illustrates the rheometer geometry that is consistently employed in all the rheological characterizations (**Figure 3.4**).

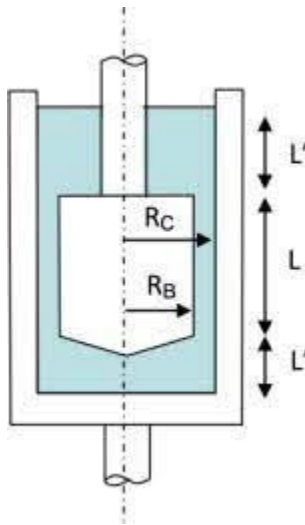


Figure 3-4 Schematic of rheometer cone & cylinder geometry

3.2.1 Steady Shear Rheology

Non-Newtonian fluids are characterized by their varying viscosity in response to changes in shear rates. Consequently, it is imperative to conduct steady shear rheology tests in order to elucidate the rheological profiles of each polymer sample. These tests serve two primary objectives within the scope of this study. The first practical aim is to identify the polymer concentration that yields a Newtonian viscosity exceeding that of the oil viscosity, thus

maintaining a favorable viscosity ratio during polymer flooding. The second objective involves characterizing the sulfonated polymer and drawing a comparative analysis between the relaxation time determined through steady shear testing and the characterization data obtained from oscillatory shear rheology. **Figure 3.5** shows the rheometer settings used in all steady shear rheology experiments, except for characterizing shear thickening onset for varying molecular weight, a linear ramp of shear rates, steady-shear rheological experiments are performed using denser sampling i.e., from shear rate of 300 to 600 s^{-1} , data points are collected for every 8 s^{-1} shear rates. A typical shear rheology profile is depicted in **Figure 3.6** for AN-125 SH 4000 ppm at 75 °C and low salinity brine.

The screenshot shows the rheometer settings interface. On the left, under 'Data points', the 'Number' is set to 30, 'Duration' is 'Constant', 'Point' is 1 min, and 'Interval' is 30 min. On the right, under 'Set value', the 'Variable' is $\dot{\gamma}$ Shear Rate, the 'Profile' is 'Ramp logarithmic', the 'Initial' value is 0.01 1/s, and the 'Final' value is 1000 1/s.

Data points		Set value	
Number:	30	Variable:	$\dot{\gamma}$ Shear Rate
Duration:	Constant	Profile:	Ramp logarithmic
Point:	1 min	Initial:	0.01 1/s
Interval:	30 min	Final:	1000 1/s

Figure 3-5 Snapshot of rheometer settings for steady shear rheology characterization.

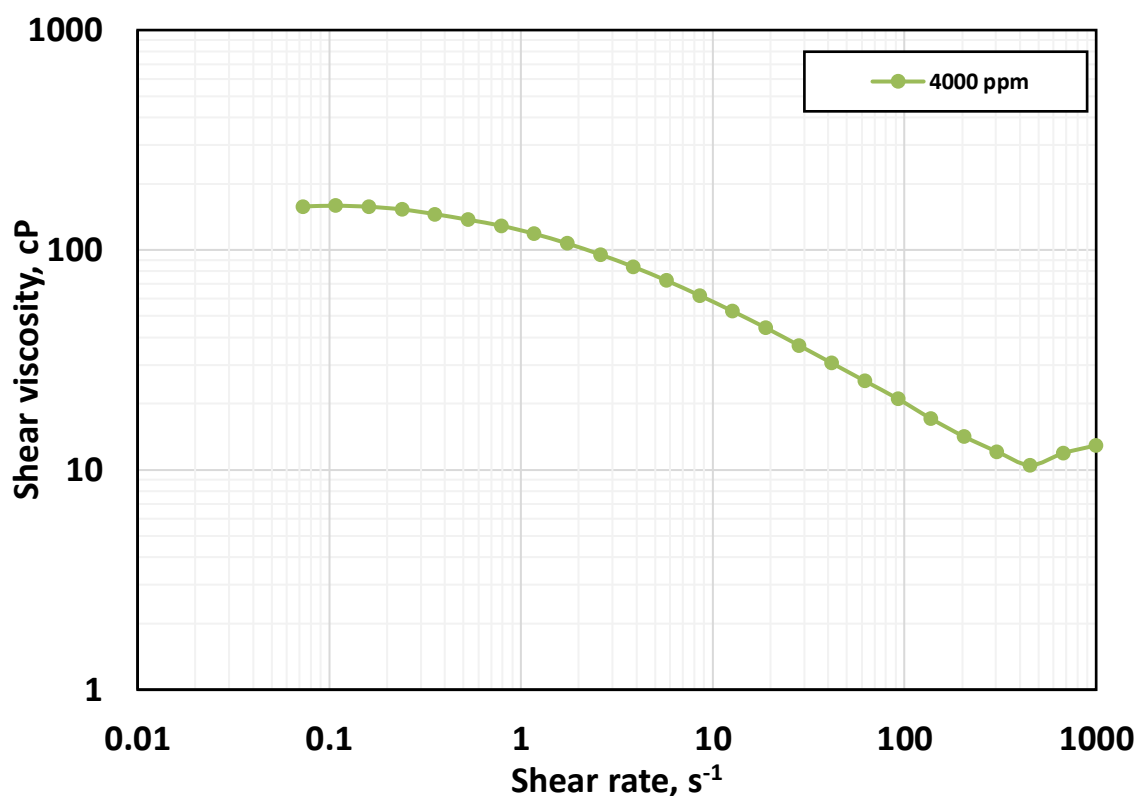


Figure 3-6 Steady shear rheology results for AN-125-SH 4000 ppm in LSW at 75 °C

3.2.2 Small Amplitude Oscillatory Shear Rheology (SAOS)

Small amplitude oscillatory shear rheology tests are experimental procedures executed at low magnitudes of shear rates, ensuring the preservation of the sample's integrity during the assessment. These tests are widely employed for characterizing complex fluids. The assessment comprises two sequential tests, each serving distinct purposes. The initial run, the dynamic strain sweep run, designed to identify the strain range that linearly correlates with the elastic modulus, is the initial phase. Following this, the second test, known as the dynamic frequency sweep test, employs the ascertained linear strain rate magnitude to evaluate the elastic and viscous moduli of the material across different frequencies. This thorough methodology plays a crucial role in uncovering the viscoelastic characteristics of the substance being studied.

The dynamic strain sweep run is conducted with the objective of determining the range of strains at which the polymer exhibits viscoelastic behavior under constant conditions of temperature ($^{\circ}\text{C}$) and frequency (rad/s). and Within this test, a strain situating within the linear viscoelastic regime is subsequently employed in performing dynamic frequency sweep tests.

The dynamic strain sweep test is carried out to identify the strain levels at which the polymer demonstrates viscoelastic behavior, keeping frequency (in radians per second) and temperature (in degrees Celsius) constant. In this test, a strain from within the linear viscoelastic range is selected for use in subsequent dynamic frequency sweep tests. For instance, **Figure 3.7** in the study illustrates the settings of the rheometer for the dynamic strain sweep tests conducted. Additionally, **Figure 3.8** presents a typical result from such a test, specifically for the AN-125 SH polymer at a concentration of 4000 ppm in low salinity brine at 75 degrees Celsius.

Data points		☒ Amplitude and frequency	
Number:	16	Variable:	γ Shear Strain (oscillating)
Duration:	None (set by devi...)	Variable:	ω Angular Frequency
		Profile:	Ramp logarithmic
		Profile:	Constant
		Initial:	0.1 %
		Value:	10 rad/s
		Final:	100 %

Figure 3-7 Snapshot of rheometer settings for dynamic strain rate sweep test.

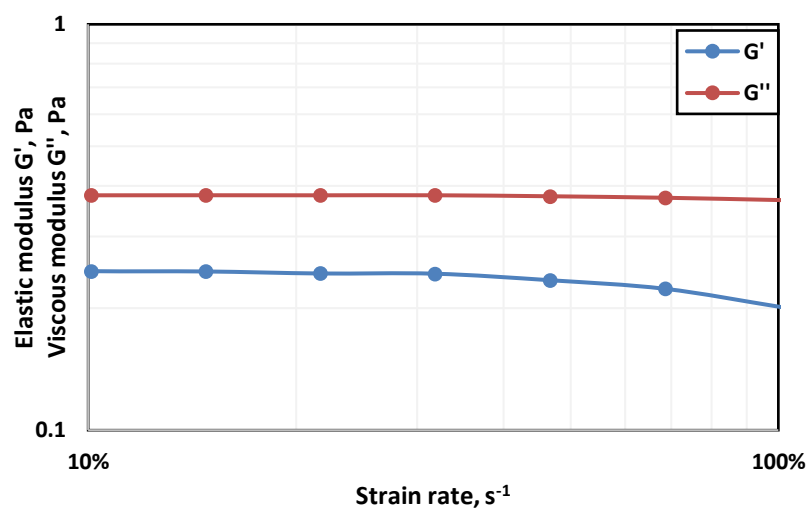


Figure 3-8 Amplitude sweep results for AN-125-SH 4000 ppm in LSW at 75 °C, the linear viscoelastic regime is between 10% -30%.

The dynamic frequency sweep run aims to measure the storage modulus (G') and the loss modulus (G'') across different oscillatory frequencies that are predetermined, while keeping the strain constant as established by the dynamic strain sweep test. The data obtained for G' and G'' at lower frequencies provide valuable insights into the behavior of the polymer under conditions of relatively low stress.

The point at which the G' and G'' curves intersect in the frequency domain is used in this study to calculate the polymer's relaxation time. The relaxation time corresponds to the reciprocal of this intersection frequency, the setting we adopt throughout all dynamic frequency sweeps is snapped in **Figure 3.9**.

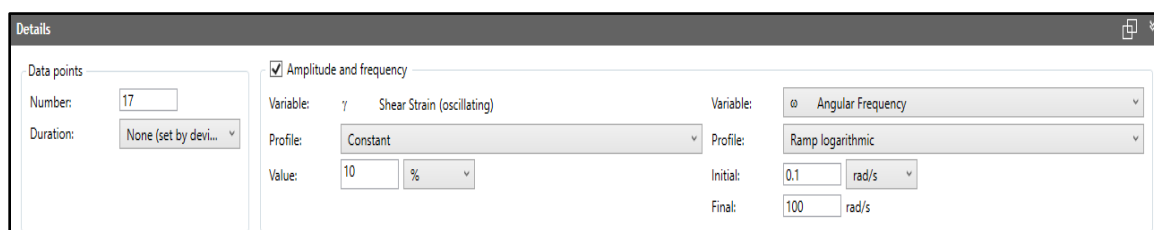


Figure 3-9 Snapshot of rheometer settings for dynamic frequency sweep run

When the loss modulus exceeds the elastic modulus ($G' < G''$), the solution displays liquid-like behavior. Conversely, when the elastic modulus is greater than the viscous modulus ($G'' < G'$), the solution exhibits characteristics more akin to a solid. Through most of the experiments carried out in this work we observed that fluid behaves solid-like at the beginning of the test and liquid-like when the relaxation time is exceeded a typical dynamic sweep profile is shown in **Figure 3.10** with the oscillatory profile of AN-125 SH 4000 ppm in low salinity brine at 75 °C, this phenomenon is noticeable in the presented result because of the high-temperature nature of our experiments. The choice of test temperature and constant strain rate dictate which behavior dominates, for instance, at high temperature or shear rates, the solid-like characteristic dominates before the intersection point.

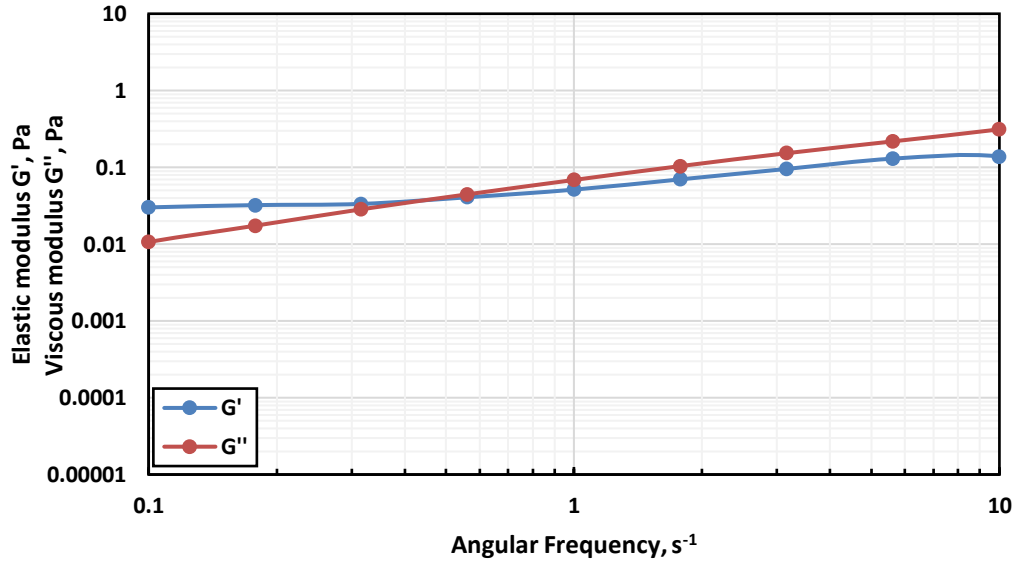


Figure 3-10 Frequency sweep results for AN-125-SH 4000 ppm in low salinity brine at 75 °C, relaxation time is the reciprocal of cross over point at $0.45 s^{-1}$

3.3 Porous Media Selection

The properties of porous media play a pivotal role in the investigation of polymer flow within such media. Core sample permeability, in particular, imposes constraints on the choice of polymer molecular weight that can be effectively injected into porous media.

As a general principle, lower permeability values correspond to a reduced maximum allowable molecular weight of the polymer for injection, as higher molecular weights can potentially lead to issues such as plugging or significant injection pressure. It is noteworthy that lower molecular weight polymers typically exhibit lower viscoelasticity. Therefore, it is essential to utilize core samples possessing sufficient permeability for these research purposes.

To fulfill this requirement, bulk samples were extracted from the Al-Lidam area located in the eastern region of Saudi Arabia, the location where the outcrop rock samples have been collected pinned in the map shown in **Figure 3.12 (a)**. The Lidam area rocks are stratigraphically equivalent to the Miocene Dam Formation and serve as hydrocarbon reservoir intervals within the Arabian Plate, specifically in Iraq and Iran, its mineral composition obtained from an X-ray diffraction test showing dominance of dolomite and some calcites as illustrated in **Figure 3.11** Subsequently, a series of 3x1.5-inch cores were made from these outcrop samples as shown in **Figure 3.13**, each possessing high permeability values spanning from 200 to 2 Darcy. Specific details regarding the cores employed at various stages of flooding are comprehensively provided in **Table 3.4**.

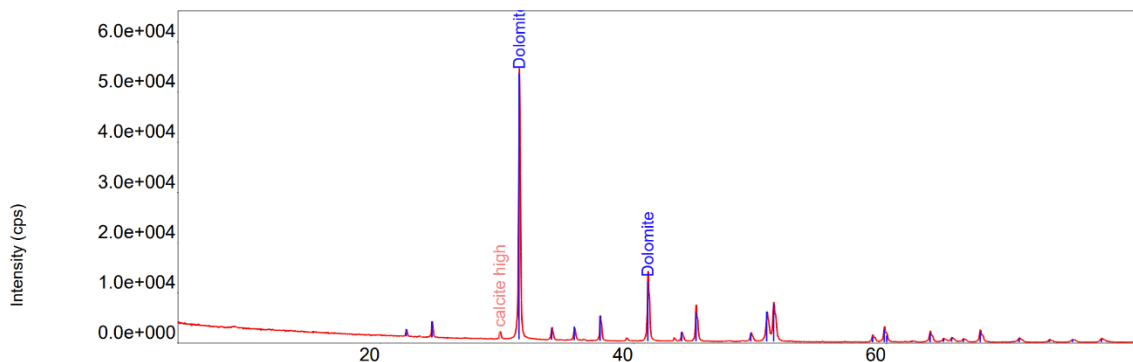


Figure 3-11 XRD analysis of rock sample from Lidam area showing dominance of dolomite.

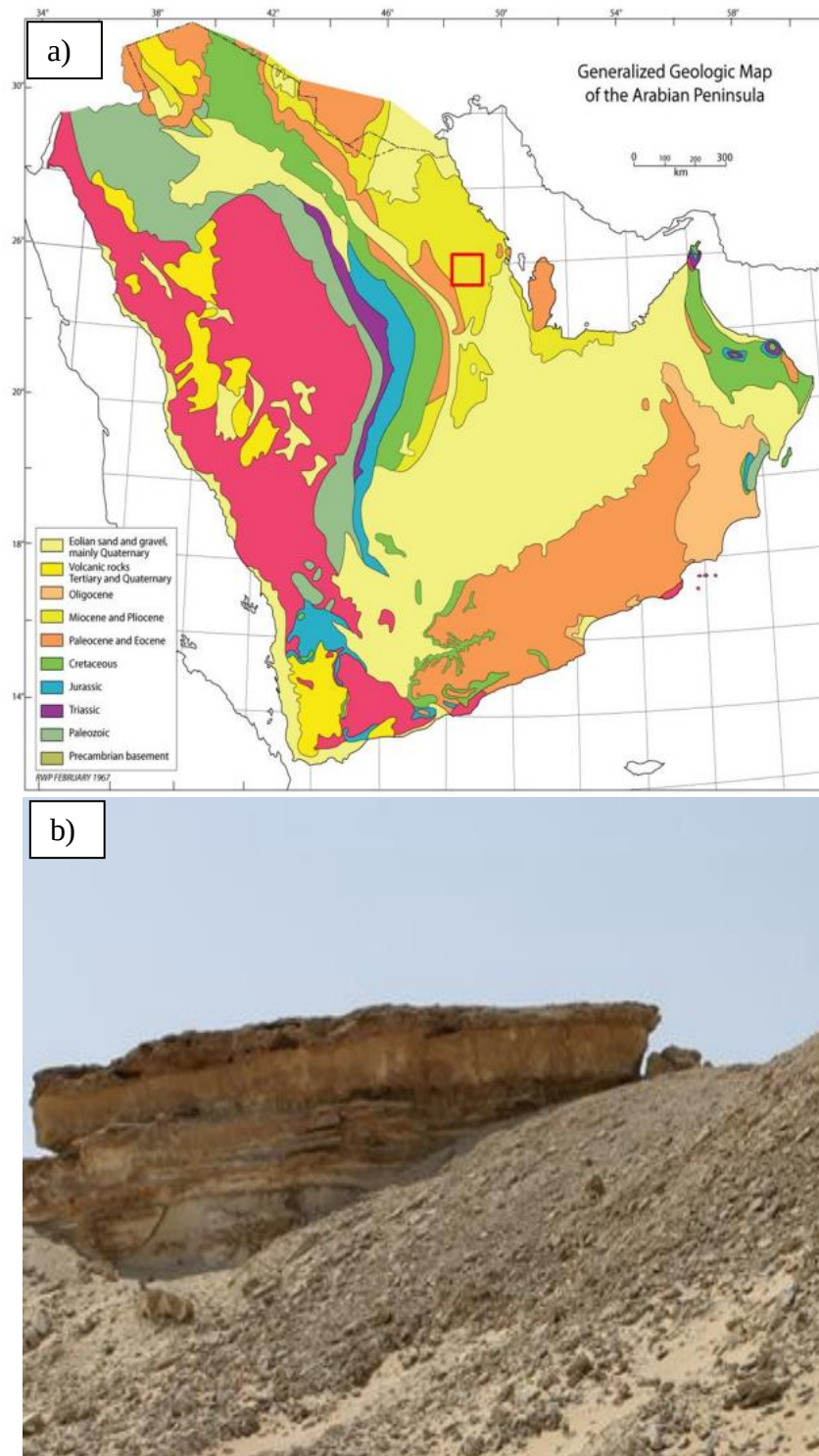


Figure 3-12 a) Map view showing the location of Lidam area b) Picture showing the Lidam carbonate outcrop in eastern Saudi Arabia.



Figure 3-13 Cores extraction from outcrop rock sample after slabbing.

Table 3-4 Core sample characteristics

No.	Core Name	Length, (inch)	Diameter, inch	porosity	Liquid Permeability, mD	Pore Volume, ml
1	F2 ^(S)	3	1.5	42.21%	1375	36.31
2	F3	3	1.5	43.36%	1077	38.75
3	F6	3	1.5	42.52%	1616	34.76
4	F21 ^(S)	3	1.5	33.44%	1362	28.4
5	F20	3	1.5	32.89%	1296	28.58
6	F1	3	1.5	37.43%	2308	31.23
7	F1+F20 ^(F)	6	1.5	39.82%	1434	67.54
8	F3+F6 ^(F)	6	1.5	42.94%	1278	73.51

F = cores for two-phase flooding
S = cores selected for single-phase flooding

3.4 Single/Two-Phase Flooding Setup

A schematic representation of the core-flood setup is visually presented in **Figure 3.14**. This configuration comprises several critical elements, including an accumulator for fluids, syringe pump, a holder for the core, devices to measure pressure differences (pressure transducers), connecting tubes, and devices for collecting fractions of the fluid. During the operation, the syringe pump administers either brine or a polymer-based solution from the fluid reservoir into the core placed within its holder. The pressure transducers are utilized to gauge the variations in pressure throughout various parts of the core. Additionally, the device designed to collect fractions systematically gathers effluent samples. This collection process enables the subsequent assessment of the samples' viscosity, which is then compared against the characteristics of the fluid initially introduced into the system.

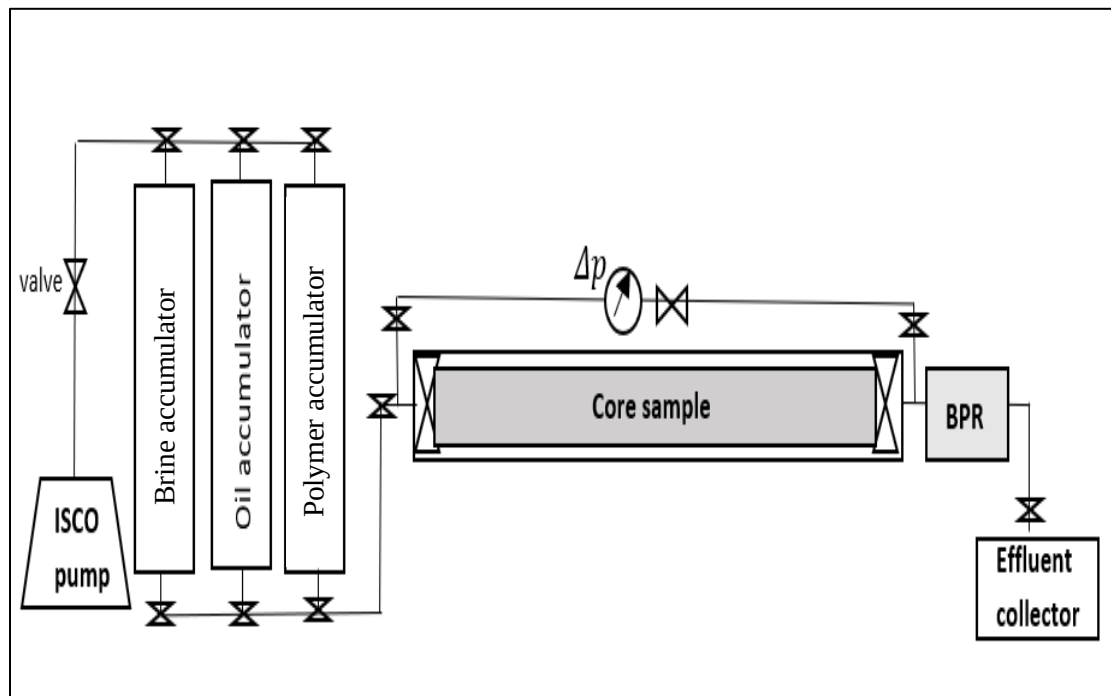


Figure 3-14: core flooding setup.

3.4.1 Core Flooding Phases

In-Situ Rheology

Understanding the rheological behavior of the sulfonated polymer within porous media with permeability comparable to that utilized in the oil recovery experiments has significant importance. This helps in identifying the thickening regime flow rates for conducting the oil recovery experiments. In this specific study, a concentration of 2500 ppm of AN-125 SH polymer was chosen as the displacing polymer, as detailed in Chapter 4. This polymer was employed in a flooding experiment conducted on core sample F21, as described in **Table 3.4**. Importantly, core sample F21 shares comparable permeability characteristics with the cores used in the oil recovery experiments involving the same polymer (F1-F20). Comparable permeability allows for ensuring that the polymer will exhibit shear thickening behavior due to its viscoelasticity when flooding a core at the same flux rate.

The polymer is injected into core sample F21 at various interstitial flux rates, commencing from a high Darcy flux rate of 100 ft/day and gradually decreasing to 1 ft/day. During this process, the stable pressure values are consistently monitored and recorded via pressure transducers. The pressure differentials observed at each flux rate are then converted into apparent viscosity, by Darcy law, attributing all pressure drops to the viscosity of the polymer.

The identical procedures are applied to the biopolymer, xanthan Gum, where a solution of 2000 ppm xanthan (as detailed in Chapter 4) is injected into core sample F2, which shares comparable permeability characteristics with cores

F3-F6, used in the oil recovery experiments involving xanthan Gum (**Table 3.4**). The flux rates are gradually reduced, following the same pattern as in the AN-125 SH case, ranging from 100 ft/day to 1 ft/day, to closely monitor the fluid behavior within the porous media and pinpoint the flux rates at which this shear-thinning effect occurs. Simultaneously, to identify the point where this shear-thinning behavior intersects with the thickening behavior exhibited by AN-125 SH.

Oil Flooding

The cores designated for two-phase core flooding experiments are completely saturated with high salinity brine, commonly referred to as "field connate water" in **Table 3.1** to simulate practical reservoir conditions. Following this saturation process, the cores are subsequently loaded into the core flooding system (**Figure 3.14**).

The cores are subjected to flooding with a light crude oil that contains hydrocarbon components, as outlined in **Table 3.3**. The oil injection is commenced at a low rate of 0.5 cc/min until no further water production is observed, the oil injection is stopped after 2 PV of the last water volume observed. when the initial oil saturation is achieved, the cores are then transferred into an aging cell, where they are maintained at a constant temperature of 75°C for a period of one calendar month. Another cycle of oil injection is done before core flooding for one hour at 0.5 cc/min.

Water Flooding

After the aging with oil, the cores in the two recovery experiments undergo a low salinity brine flooding at an elevated temperature of 75 °C. This brine solution

is composed of salts as specified in **Table 3.1**. The water flooding is extended with the objective of attaining residual oil saturation within the oil-wet cores. The water flooding is executed at a velocity of 2, 4 and 8 ft/day (Darcy velocity) to minimize capillary end effect. The flooding continues for 2 PV after the recovery of oil ceases.

AN-125 SH Flooding

Following water flooding injection in the viscoelastic polymer core flooding experiment, 2500 ppm of AN-125 SH (screening is detailed in Chapter 4), was chosen for the purpose of residual oil recovery. The polymer flooding was carried out at a Darcy flux rate where shear thickening behavior was anticipated in the porous media based on the in-situ rheology core flooding experiment (chapter 5). Three different Darcy velocity were applied during this phase of flooding, first flooding rate was approximately 4 ft/day followed by 20 ft/day were a clear viscosity advantage is being given to biopolymer to recover oil, the last rate applied was the flux rate where intersection occur at 32.5 ft/day. All applied flux rates were maintained at a high temperature of 75 °C and continued until no further oil production was observed for 2 PV.

Xanthan Gum Flooding

In the second core flooding experiment, a biopolymer, xanthan Gum, was selected for flooding. Notably, xanthan Gum does not exhibit elastic behavior at relatively high shear rates. Following the water flooding phase, the biopolymer solution was introduced to recover residual oil, with the flooding conducted at a high temperature of 75°C. The polymer flooding in this scenario was executed at

the same different three constant Darcy velocities of 4, 20, 32.5 ft/day, mirroring the conditions used for the viscoelastic polymer AN-125 SH. This approach was chosen to ensure that the apparent viscosity of both polymers in the porous media remains comparable as shown in in-situ rheology experiments for both solutions, despite the different underlying phenomena driving viscosity changes. In the first experiment, viscoelasticity is at play, whereas in the second experiment, shear thinning behavior is the key factor. The polymer flooding continued until 2 pore volumes (2 PV) after no further oil production was observed.

3.4.2 Core Flooding Calculation

The calculations for the core flood experiments involve various parameters, including pore volume, porosity, liquid permeability, and oil saturation and recovery. The specific calculations and parameters are described and detailed below.

Bulk & Pore Volume

The bulk volume of rock encompasses both the volume of the grains and the voids in between, whereas the pore volume specifically refers to the volume of the pores within the core sample. Pore volume is calculated by saturating the cores with known-density brine and measuring the weight difference in dry and wetting cases, those measurements are confirmed through helium porosimeter. The bulk volume is measured through core dimensions.

$$V_p = \frac{M_{sat} - M_{dry}}{\rho_w} \quad (3.1)$$

Where

V_p = pore volume, ml

M_{sat} = saturated core weight, g

M_{dry} = Dry core weight, g

$$V_b = \pi r^2 L \quad (3.2)$$

Where

V_b = Bulk volume, cm^3

r = Core radius, cm

L = Core length, cm

Porosity & Liquid Permeability

The permeabilities of cores to brine solution were measured using a permeameter in which a brine is injected at different flow rates and the pressure drop is measured at each flow rate, the permeability is calculated through the slope of plotting q vs ΔP . The porosity is calculated through equation (3.3) and confirmed through helium porosity.

$$\Phi = \frac{V_p}{V_b} \quad (3.3)$$

Where

Φ = Porosity, %

V_p = pore volume, ml

V_b = bulk volume, ml

$$q = \frac{kA\Delta p}{\mu L} \quad (3.4)$$

Where

k = brine permeability, D

A = Core cross sectional area, cm^2

q = Flow rate, cm^3/min

L = Core length, cm

μ = brine viscosity, cP

ΔP = pressure drop across core length, psi

Apparent Viscosity

Non-Newtonian fluid's viscosity changes with injection rates and porous media characteristics, when a polymer is flown in a core sample its viscosity changes and is reflected through pressure drop. To calculate this apparent viscosity Darcy equation was used as shown below.

$$\mu_{app} = \frac{kA\Delta p}{qL} \quad (3.5)$$

Where

μ_{app} = apparent viscosity, cp

Porous Media Shear Rate

The Cannella model (Cannella, 1988) is employed to convert the flow rate of the polymer into shear rate (measured in s^{-1}), enabling a comparison between bulk and in-situ rheology.

$$\gamma = c \left(\frac{3n+1}{4n} \right)^{\frac{n}{n-1}} \frac{u}{\sqrt{k\Phi}} \quad (3.6)$$

Where

γ = porous media shear rate, s^{-1}

c = shear correction factor, commonly = 6.

n = shear thinning index.

u = flux rate, ft/day

Carreau Model

In the Cannella model, the shear thinning index (n) is ascertained by aligning bulk rheological experimental data with the Carreau model, which is utilized for forecasting the shear viscosity of non-Newtonian fluids.

$$\mu = \mu_{\infty} + (\mu_0 - \mu_{\infty})(1 + (\gamma\lambda)^2)^{\frac{n-1}{2}} \quad (3.7)$$

Where

μ = Shear Viscosity, cP

μ_0 = Zero Shear Viscosity, cP

μ_{∞} = Infinite Shear Viscosity, cP

λ = characteristic time, s

Oil Saturation and Recovery

Oil saturation at any time during water and polymer flooding was calculated using the following equation, at the initial setting the produced oil V_o was zero and the resultant saturation is the initial oil saturation.

$$S_o(t) = \frac{OIC(t) - V_o}{V_p} \quad (3.8)$$

Where

OIC = Oil volume residing in core, ml

S_o = Oil saturation at any given time.

V_o = volume of produced oil, ml

The oil recovery factor at the end of the water and polymer flooding phase was calculated using equation (3.9). The following formula determines each flood's incremental oil recovery over its preceding flood.

$$RF = \frac{V_o}{OOIC} \quad (3.9)$$

$$IOR = V_o(t) - ORIC \quad (3.10)$$

Where

$OOIC$ = Oil volume initially residing in core, ml

IOR = Incremental oil recovery, %

$ORIC$ = Oil remaining in the core after the last flooding.

RF = Oil recovery, %

CHAPTER 4

POLYMER SYSTEMS CHARACTERIZATION

In this section, we conduct steady shear rheological characterization of the AN-series polymers and a xanthan gum, each characterized by distinct viscoelastic properties. Our objective is to analyze if the rheological outcomes align with the theory, wherein higher molecular weights correspond to increase non-linear viscoelastic effects. Following this, our practical objective is to select a specific polymer's molecular weight and conduct extensive concentration screening to determine the optimal polymer concentration for achieving a favorable polymer-oil ratio in subsequent two-phase single-rate core flood experiments. Throughout the extensive concentration screening, we gathered linear and non-linear viscoelastic property data. Subsequently, we perform linear-oscillatory rheological experiments on the low-salinity polymer systems, comparing the shear linear relaxation time with the oscillatory linear relaxation time. Additionally, we compare the shear linear and non-linear relaxation times to gain further insights into the rheological behavior of the polymer systems. **Table 4.1** summarizes the polymer systems that have been tested in this study.

Table 4-1 Polymer systems rheological characterization matrix in low salinity brine and 75°C (SRT indicates steady shear rheology test, DFST indicates dynamic frequency sweep test and DSST indicates dynamic strain sweep test).

Polymer system	SRT	DSST	DFST
AN-125 VHM 3000 ppm	Y	Y	Y
AN-125 SH 3000 ppm	Y	Y	Y
AN-125 STD 3000 ppm	Y	Y	Y
AN-125 MPM 3000 ppm	Y	Y	Y
AN-125 VLM 3000 ppm	Y	Y	Y
AN-125 SH 10,000 ppm	Y	Y	Y
AN-125 SH 5000 ppm	Y	Y	Y
AN-125 SH 4000 ppm	Y	Y	Y
AN-125 SH 3500 ppm	Y	Y	Y
AN-125 SH 3000 ppm	Y	Y	Y
AN-125 SH 2500 ppm	Y	Y	Y
AN-125 SH 2000 ppm	Y	Y	Y
AN-125 SH 1000 ppm	Y	Y	Y
AN-125 SH 500 ppm	Y	Y	Y
AN-125 SH 100 ppm	Y	Y	Y
AN-125 SH 60 ppm	Y	Y	Y
AN-125 SH 25 ppm	Y	Y	Y
Xanthan gum 2500 ppm	Y	X	X
Xanthan gum 2000 ppm	Y	X	X
Xanthan gum 1650 ppm	Y	X	X

4.1 Viscoelastic Polymer System Screening

The rheological characterization of Enhanced Oil Recovery (EOR) polymers is crucial for understanding the resistance factor they are expected to offer in porous media (Azad and Trivedi, 2019a). Steady-shear rheogram provides insights into the polymer's Newtonian viscosity and shear-thinning behavior (Delshad et al., 2008; Seright et al., 2011). In recent studies, steady shear rheograms have also been utilized to assess the non-linear viscoelastic properties of EOR polymer systems (Azad, 2023; Barri et al., 2023).

4.1.1 Effect of Sulfonated Polymer's MW on Steady Shear Rheology

Figure 4.1 illustrates the impact of polymer molecular weight (Mw) on steady shear rheology, utilizing logarithmic sampling points. The associated parameters, including Newtonian viscosity, shear characteristic time, and non-linear relaxation time, all are compiled in **Table 4.2**. While the exact Mw values of those polymers are unknown, the trend indicates that higher Mw values correspond to elevated Newtonian viscosity and increased linear relaxation time, as depicted in **Figures 4.1 -4.2**.

Interestingly, the pattern differs for the viscoelastic onset rate, as shown in **Figure 4.3**. Despite increasing Mw, the viscoelastic onset rate remains relatively consistent in steady shear rheology when sampling points are logarithmically ramped, leading to comparable non-linear relaxation times across different molecular weights.

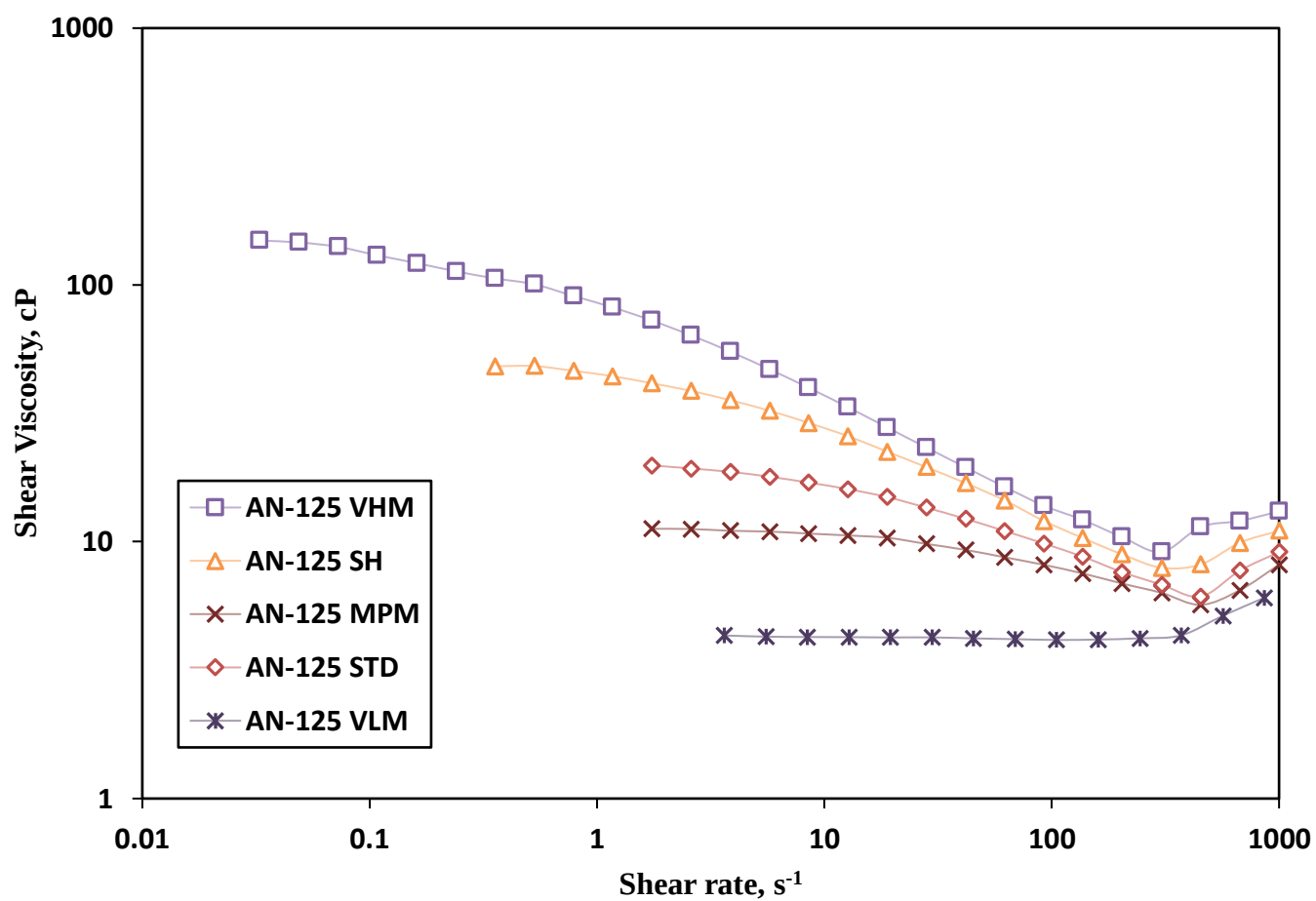


Figure 4-1 Effect of Molecular weight on steady-shear rheology of AN-125 polymers prepared with 5767 ppm brine at 75°C.

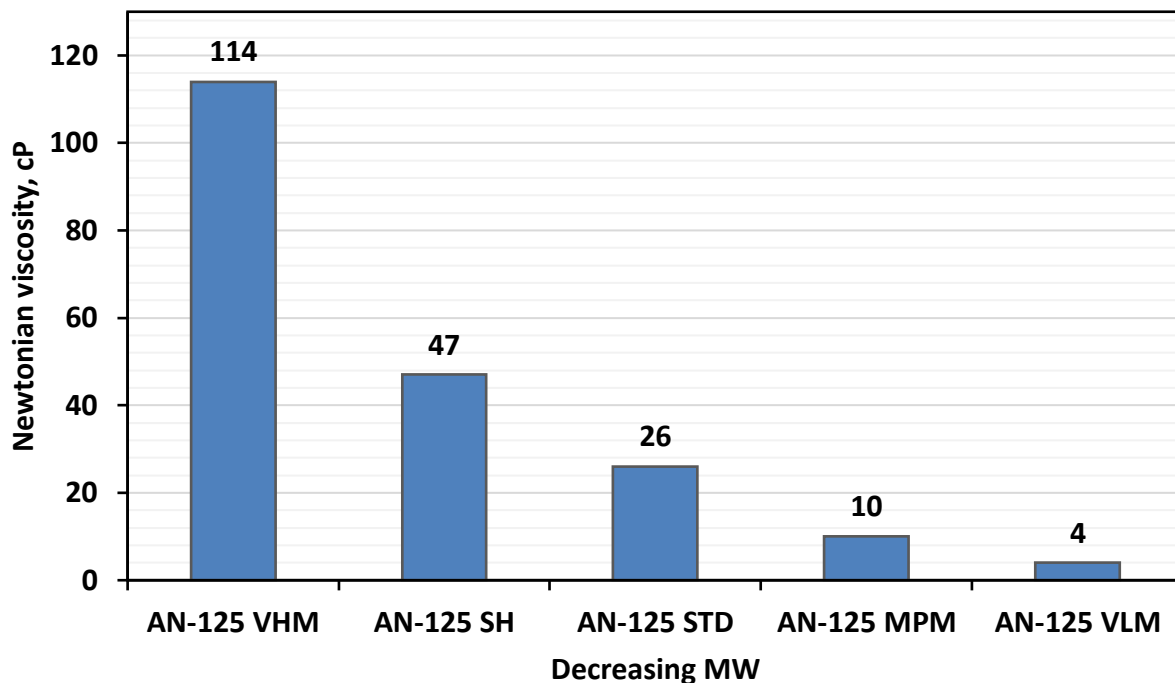


Figure 4-2 Effect of Molecular weight on the Newtonian viscosity of AN-125 polymers prepared with low salinity brine of 5767 ppm brine.

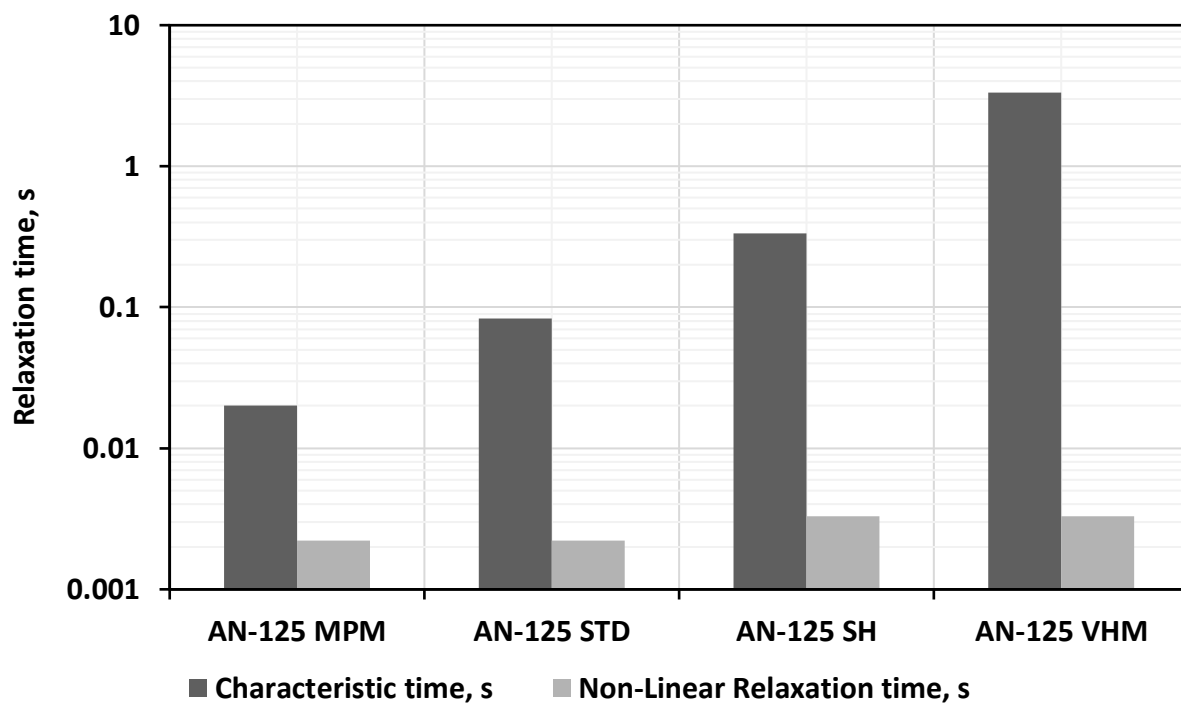


Figure 4-3 Effect of Molecular weight on linear characteristic time and non-linear relaxation time of AN-series of polymers at low salinity of 5767 ppm brine

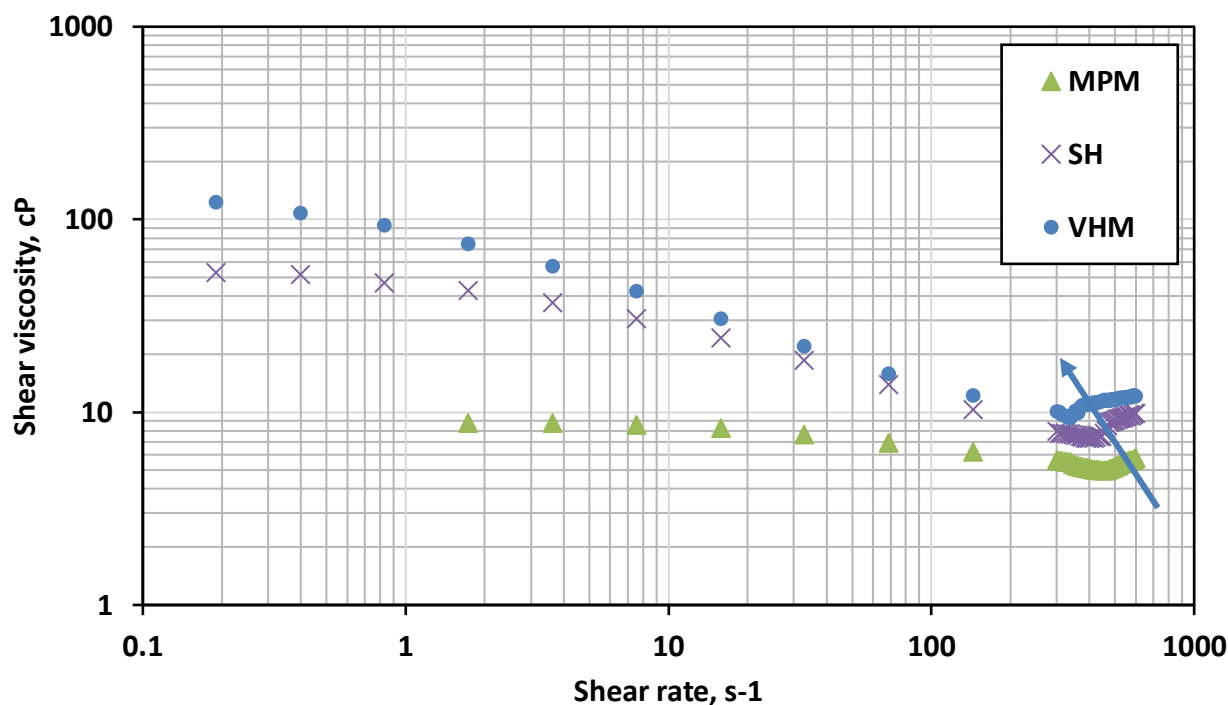


Figure 4-4 Effect of Molecular weight on steady-shear rheology of AN-125 polymers prepared with 5767 ppm brine using linear sampling at high shear rate.

Upon closer examination of **Figure 4.3**, it becomes evident that the non-linear relaxation time remains consistent for AN-125 MPM and AN-125 STD. Conversely, for AN-125 SH and AN-125 VHM, the non-linear relaxation times are higher but similar. This observation deviates from the theoretical expectation, which suggests that higher molecular weight (M_w) should lead to increased non-linear relaxation time (Howe et al., 2015).

To gain deeper insights, steady-shear rheological experiments are conducted with denser linear sampling. Data points are collected in a narrower range, specifically from a shear rate of 300 to 600 s^{-1} , with data points collected for every 8 s^{-1} shear rate (**Figure 4.4**). This refined analysis aims to explore whether the onset rate falls within a narrow range of adjacent shear rates, potentially contributing to the observed behavior.

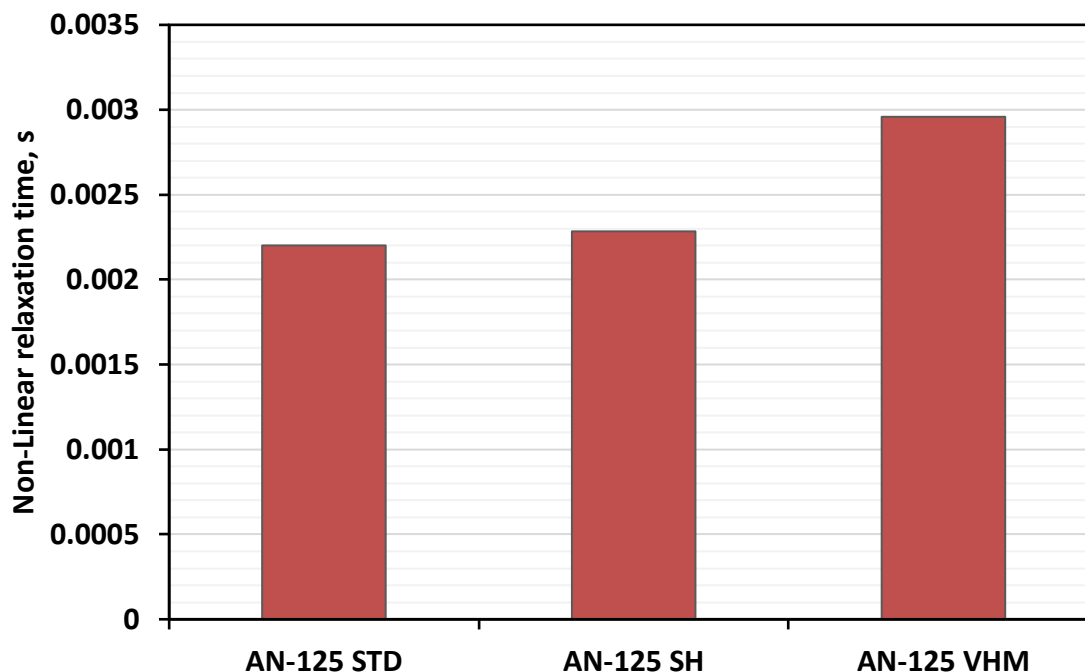


Figure 4-5 Effect of Molecular weight on non-linear relaxation time of AN-125 polymers prepared with 5767 ppm brine using denser sampling

As anticipated, a denser sampling reveals varying onset rates for the AN-series polymers. Specifically, the onset rates for VHM, SH, and MPM AN-series polymers are 333, 434, and 454 s^{-1} , respectively. The inverse of the onset rate increases with higher molecular weight (Mw), as illustrated in **Figure 4.5**. All experiments are conducted with a gap distance of 0 mm. In this study, we explore different gap distances between the cylinder and geometry, specifically 0 mm, 10 mm, and 20 mm, during the steady-shear rheological characterization of AN-125 SH polymer, as depicted in **Figure 4.6**.

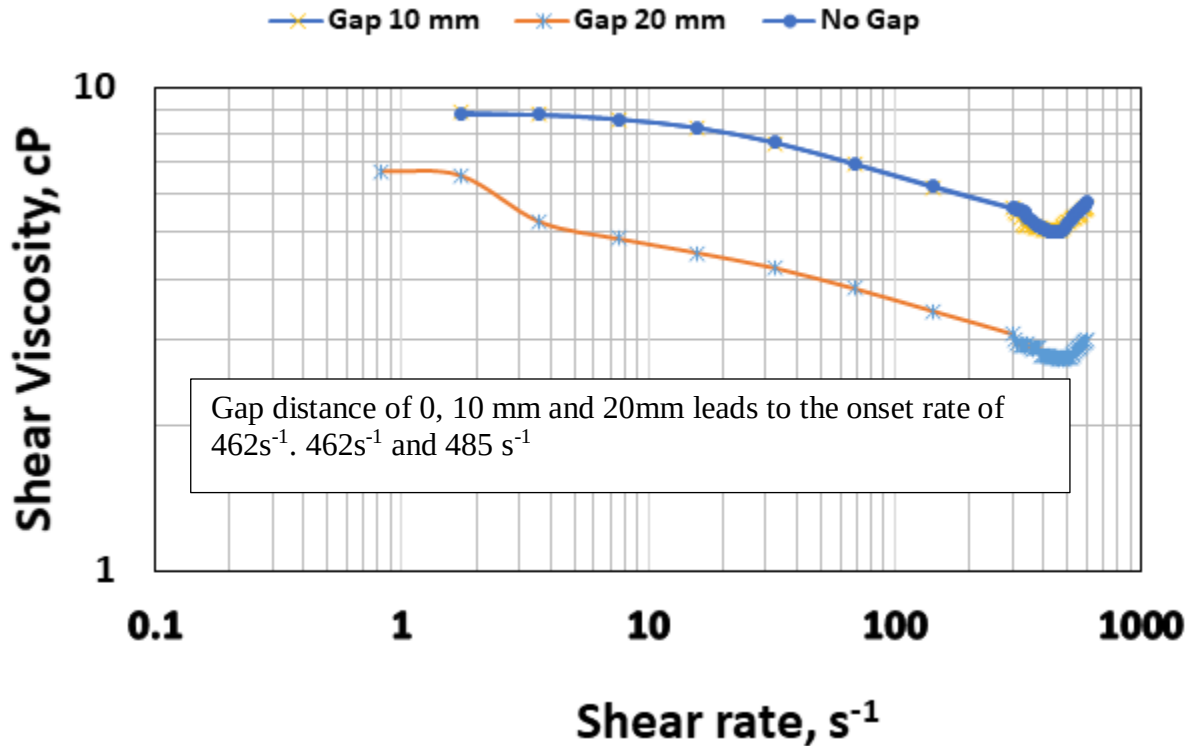


Figure 4-6 Effect of gap distance on shear thickening onset rate for AN-125 SH polymer prepared in 5767 ppm brine at 75°C

The onset rate of 462 s^{-1} is observed with the imposed gap distance of 0 and 10 mm. However, with 20 mm gap distance, a delayed onset was observed. It is important to note that a gap distance of 20 mm means the cylinder needs to be lifted. However, with the gap distance of 10 mm, the cylinder is well-with in the geometry. Since we didn't observe the differences in the onset rate between the imposed gap distance of 10 mm and zero gaps, we went with zero gap in all the subsequent experiments.

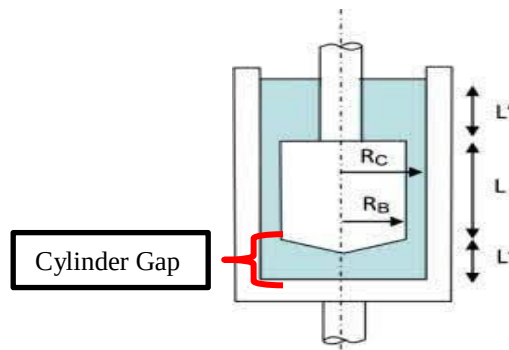


Figure 4-7 Varying gap distance of concentric cylinder and cone rheometer geometry.

4.1.2 Effect of sulfonated polymer's MW on Oscillatory Shear Rheology

Oscillatory shear rheology has long been a fundamental method for characterizing the linear viscoelastic relaxation time (Garrouch and Gharbi, 2006; Magbagbeola, 2008; Delshad et al., 2008; Qi et al., 2017; Erincik et al., 2018). Two rheometric techniques are applied to determine the linear relaxation time. Initially, the linear viscoelastic regime (LVE) is identified through an amplitude sweep, measuring storage (elastic) and loss (viscous) modulus as functions of strain. The LVE regime encompasses regions where both moduli remain constant. Once the strain corresponding to LVE is determined, a frequency sweep is conducted at that constant strain percentage. This sweep plots elastic and loss moduli against frequency to find the intersection point, and the inverse of this intersection frequency yields the linear relaxation time. For AN 125-SH, AN 125-VHM, and AN 125-STD, elastic and loss moduli are plotted against frequency at a specific strain of 10 per second (**Figures 4.8 to 4.10**). As anticipated, the linear relaxation time of the polymer increases with higher molecular weight.

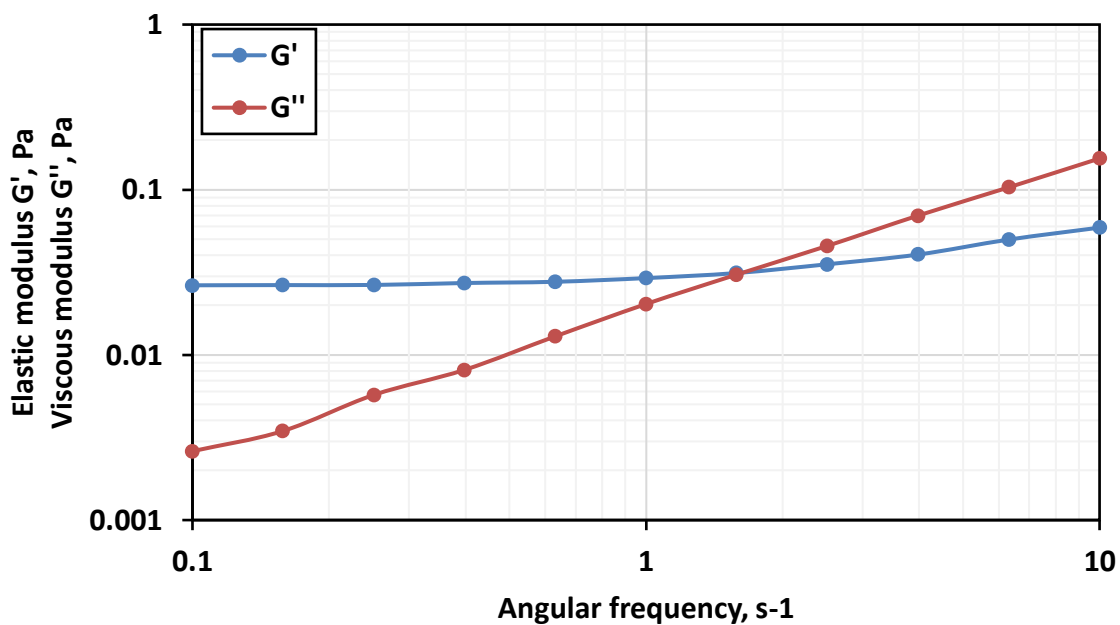


Figure 4-8 Storage Modulus and loss modulus as a function of Angular Frequency for 3000 ppm AN-125 STD Polymer in 5767 ppm brine at 75°C

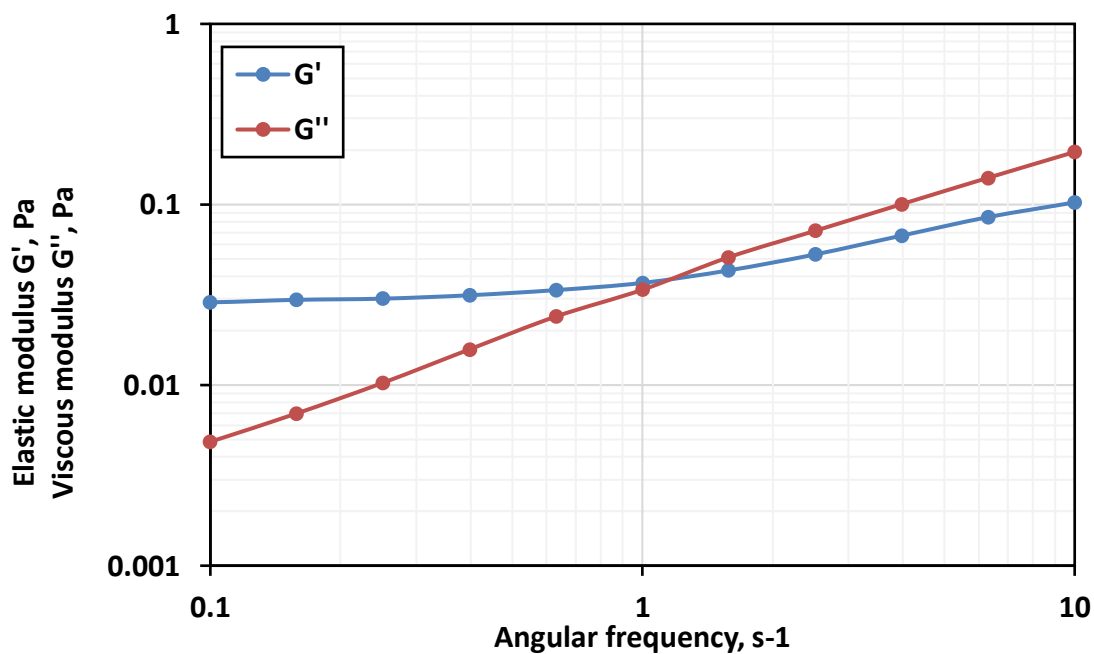


Figure 4-9 Storage Modulus and loss modulus as a function of Angular Frequency for 3000 ppm AN-125 SH Polymer in 5767 ppm brine at 75°C

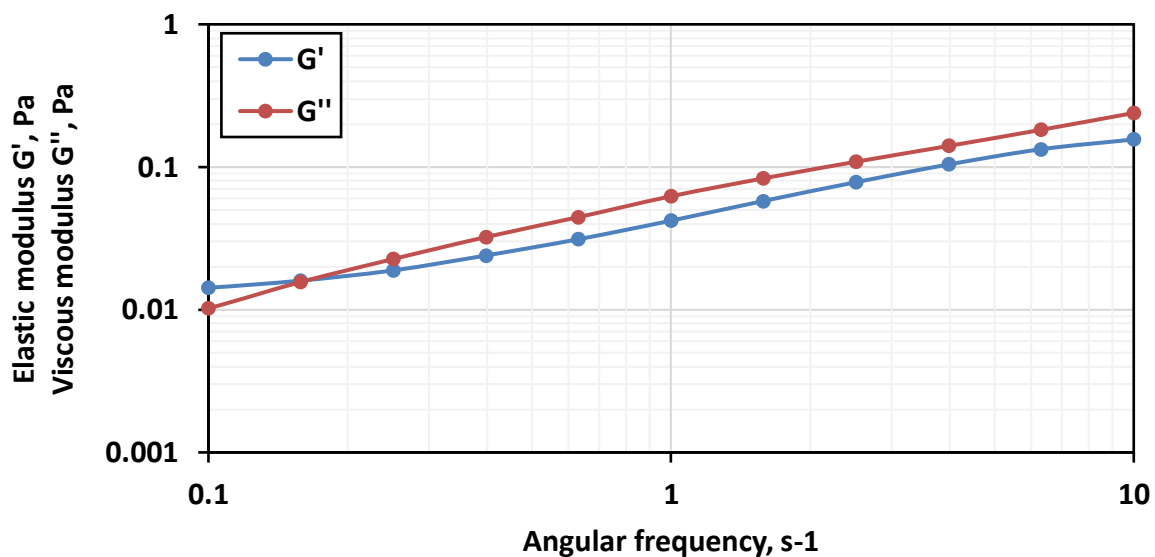


Figure 4-10 Storage Modulus and loss modulus as a function of angular frequency for 3000 ppm AN-125 VHM Polymer in 5767 ppm brine at 75°C

4.1.3 Relaxation Times Comparison

The impact of molecular weight on various relaxation times is depicted in (Figure 4.3). As observed, an elevation in Mw leads to an increase in linear relaxation time. Notably, the non-linear relaxation time exhibits a magnitude significantly smaller than that of linear relaxation times. A careful comparison of linear relaxation times obtained from oscillatory and steady-shear methods reveals that oscillatory relaxation time demonstrates a higher magnitude, as illustrated in Figure 4.11.

Table 4-2 Rheological properties of AN polymers of varying Mw at 5767 ppm salinity at 75°C

Polymers	Zero shear viscosity, cP	Linear characteristic time, s	Amplitude, %	Linear oscillatory relaxation time, s	Shear thickening onset-rate, s ⁻¹	Non-linear relaxation time, s	Non-linear relaxation time, s
AN-125 VHM	114	3.33	10	6.33	333.33	0.0033	0.003
AN-125 SH	47	0.33	10	0.833	434.8	0.0033	0.0023
AN-125 STD	26	0.083	10	0.633	454.5	0.0022	0.0022
AN-125 MPM	10	0.02	10	NA	NA	0.0022	NA

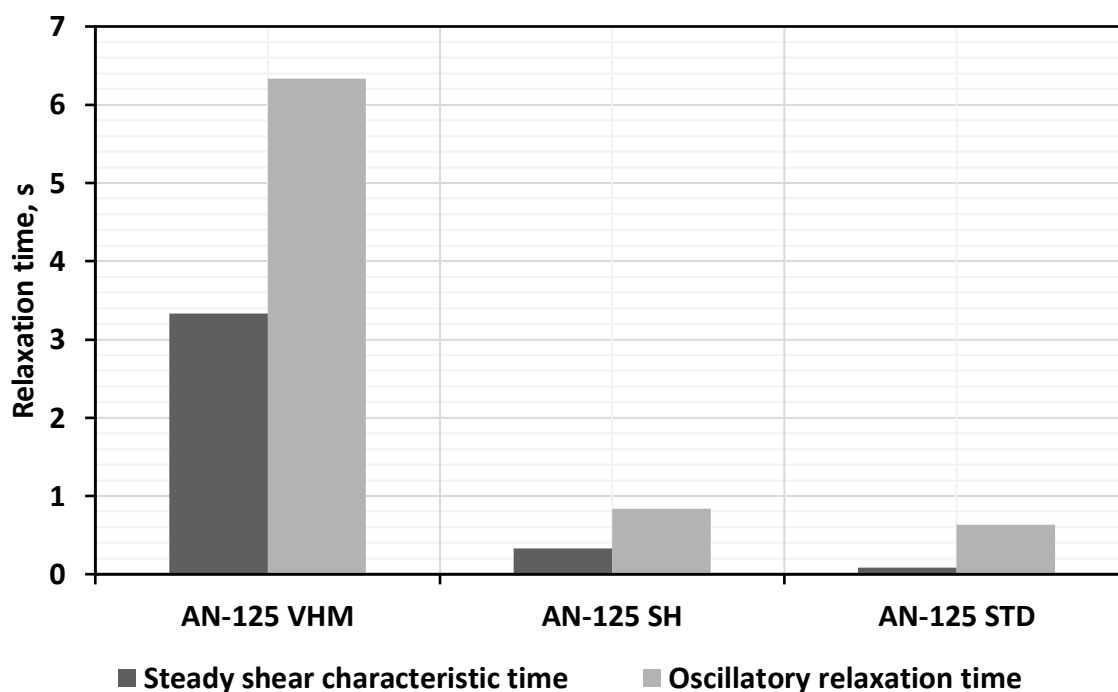


Figure 4-11 Linear relaxation time obtained using steady-shear and oscillatory rheometry for AN-125 polymers system prepared in 5767 ppm brine at 75°C

Although AN-125 VHM polymer provided higher viscosity and linear and non-linear viscoelasticity because of its highest Mw, AN-125 SH polymer was considered for consideration for further screening and subsequent core flooding. This is to make sure the injected polymer propagates freely without plugging in the rocks with a permeability greater than 100-200 mD (Figure 15 on clarke et al. 2015).

4.1.4 Effect of Sulfonated Polymer's Concentration on Steady Shear

Rheology

The effect of concentration on the shear rheograms for AN-125 SH is shown (Figure 4.12). The concentration ranges between 25 ppm to 10,000 ppm. An increase in concentration leads to an increase in Newtonian viscosity (Figure 4.13), and increased linear characteristic time (Figure 4.14) but not the non-linear relaxation time. The trend of

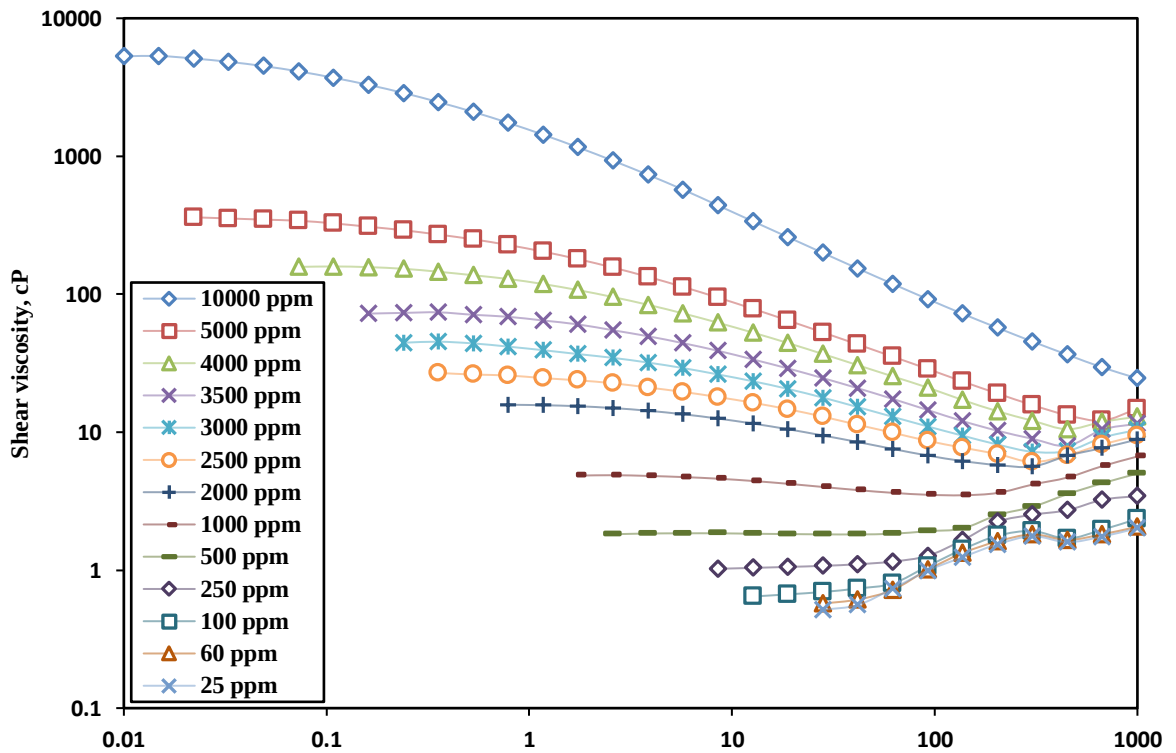


Figure 4-12 Effect of Concentration on the steady-shear rheological behavior of AN-125 SH polymer at 5767 ppm brine at 75°C

concentration on Newtonian viscosity, linear characteristic time, and core relaxation time can be found in Howe et al. (2015). The reason behind the decrease in non-linear relaxation time with respect to the increase in concentration could be attributed to the decreased stretching offered by the polymer solutions.

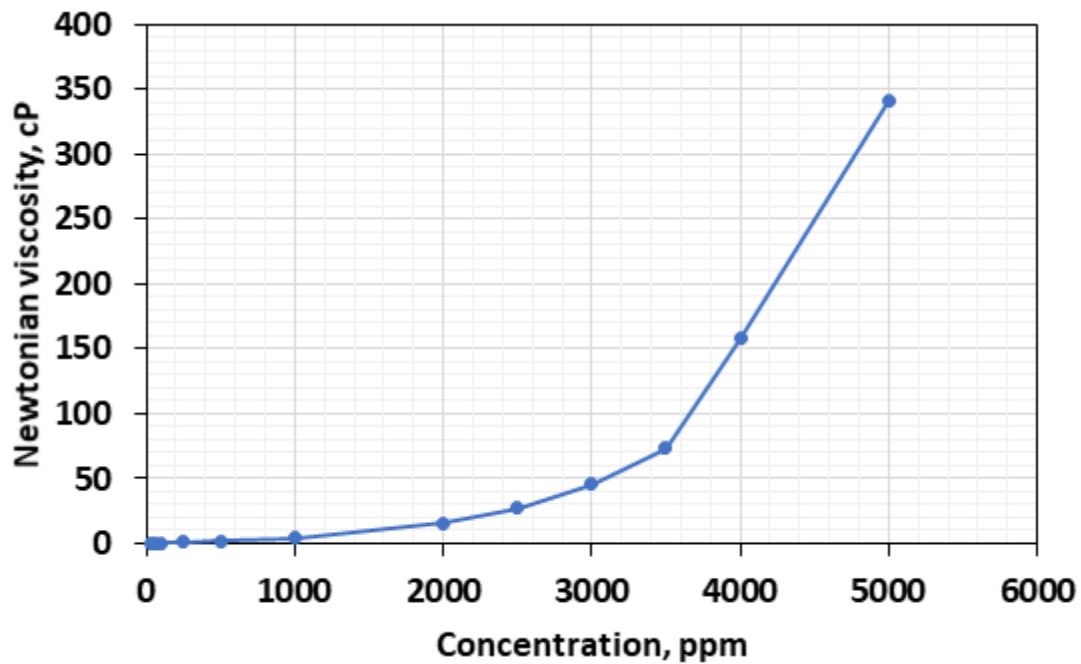


Figure 4-14 Effect of Concentration on the Newtonian viscosity of AN-125 SH polymer at 5767 ppm brine at 75°C

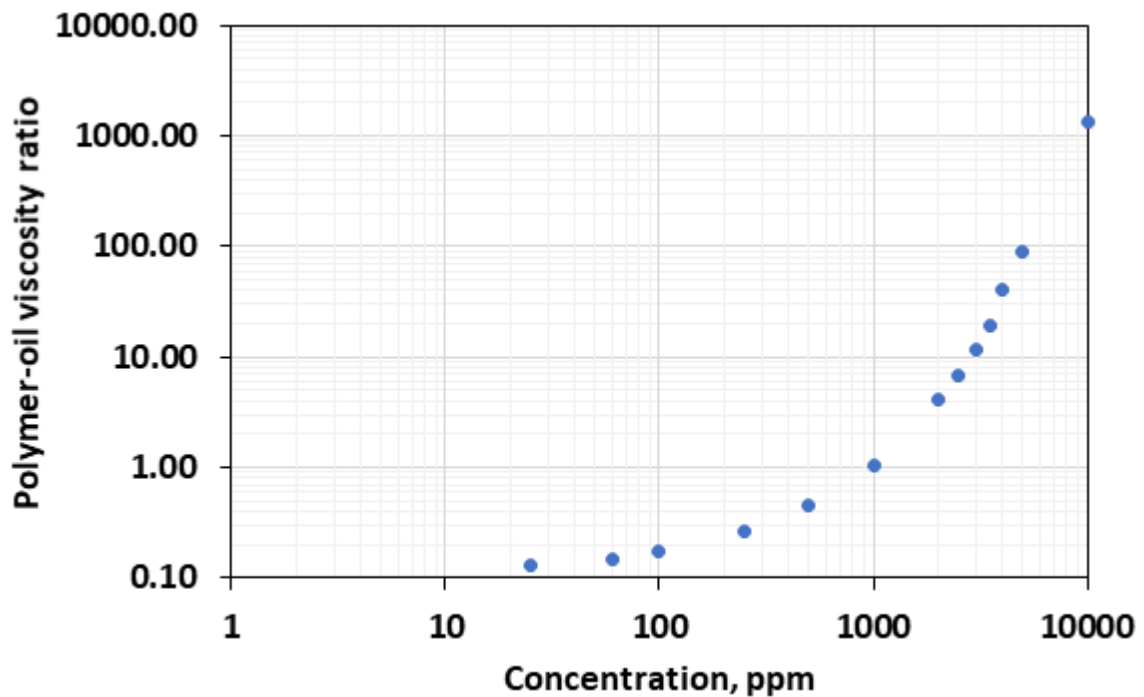


Figure 4-13 Effect of Concentration on the Polymer-oil viscosity ratio using 4 cP oil at 75°C

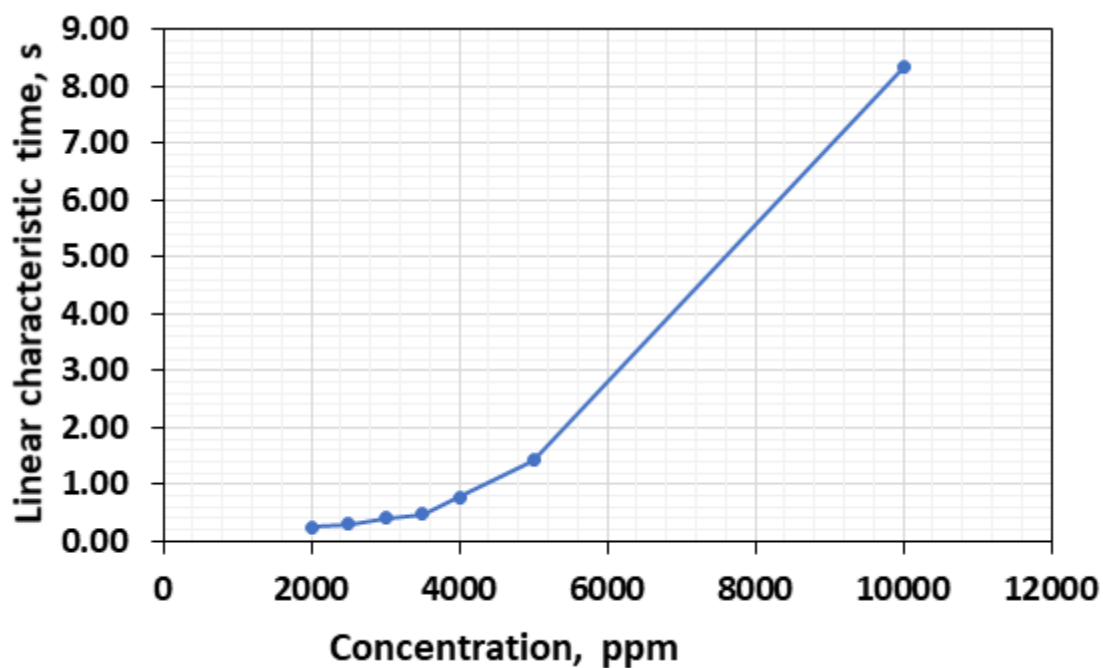


Figure 4-15 Effect of Concentration on the linear characteristic time of AN-125 SH polymer at 5767 ppm brine at 75°C

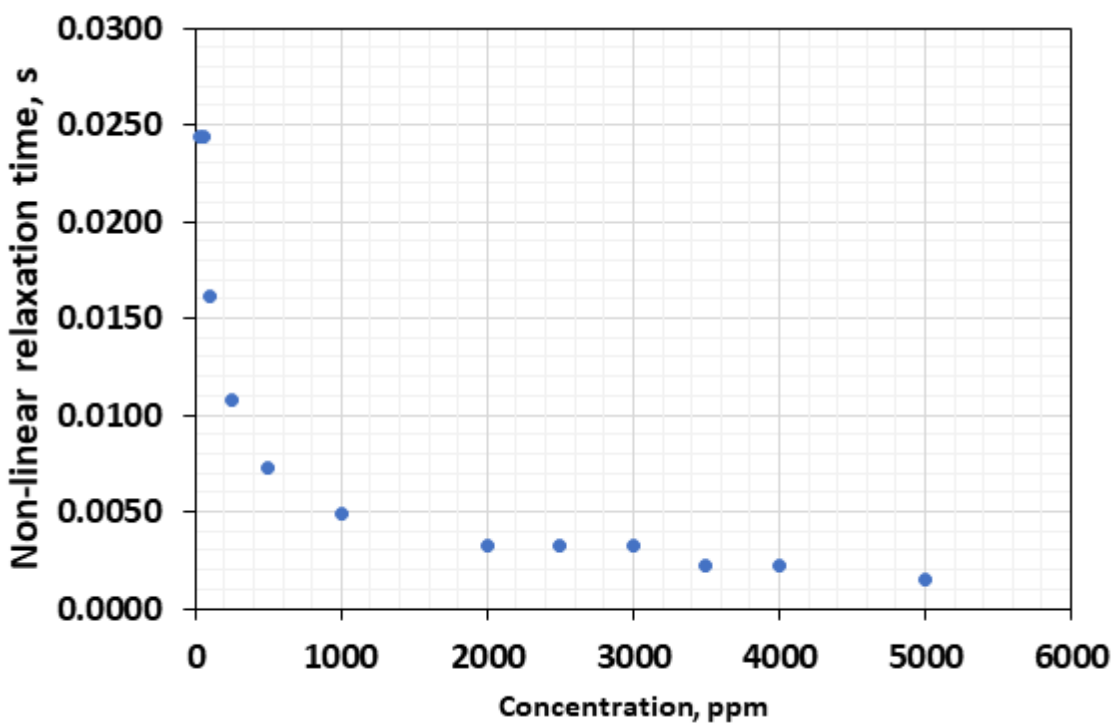


Figure 4-16 Effect of Concentration on the non-linear relaxation time of AN-125 SH polymer at 5767 ppm brine at 75°C

4.1.5 Effect of Concentration on Oscillatory Shear Rheology

The effect of AN-125 SH polymer's concentration on linear oscillatory rheology is studied by varying the concentration from 25 ppm to 10,000 ppm. As previously discussed, the determination of linear relaxation time involves conducting an amplitude test followed by a frequency sweep. The results of AN-125 SH different concentrations are documented in the **Appendix A**, an illustrative example of these tests is provided for 10,000 ppm of AN-125 SH polymer in **Figures 4.17 and 4.18**. The linear relaxation time, obtained when a small strain is imposed, is showcased as a function of polymer concentration in **Figure 4.19**. These values can be determined through both steady-shear rheology and oscillatory rheology.

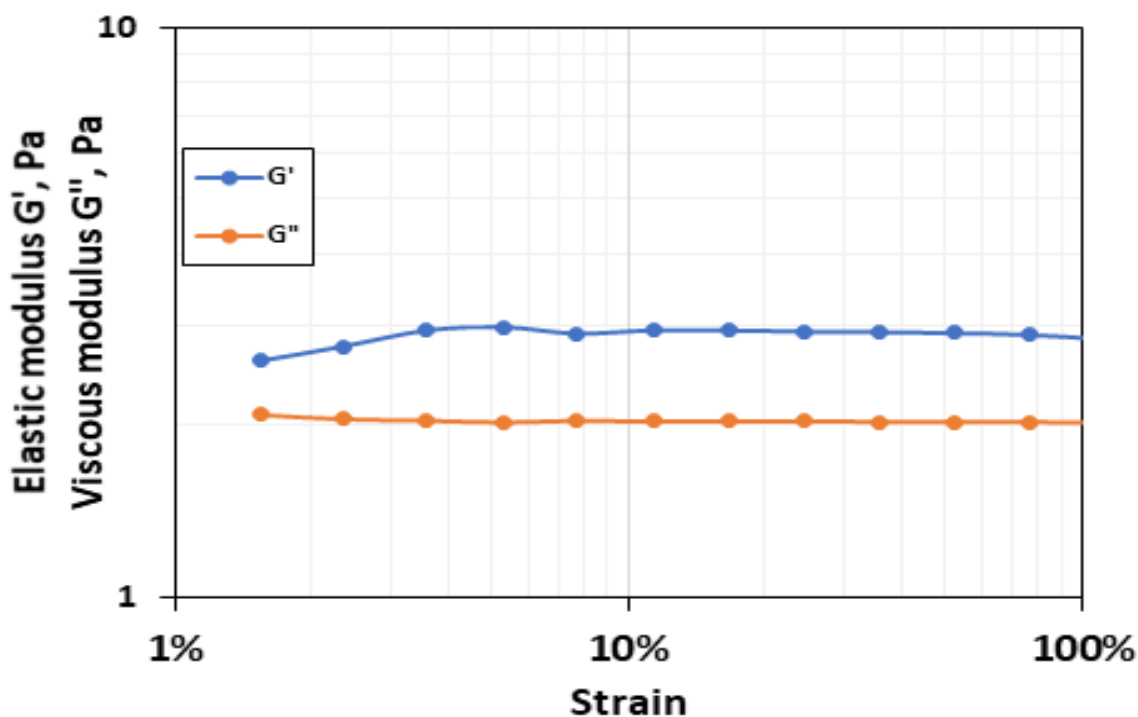


Figure 4-17 Amplitude test for 10,000 ppm AN-125 SH polymer at 5767 ppm brine at 75°C

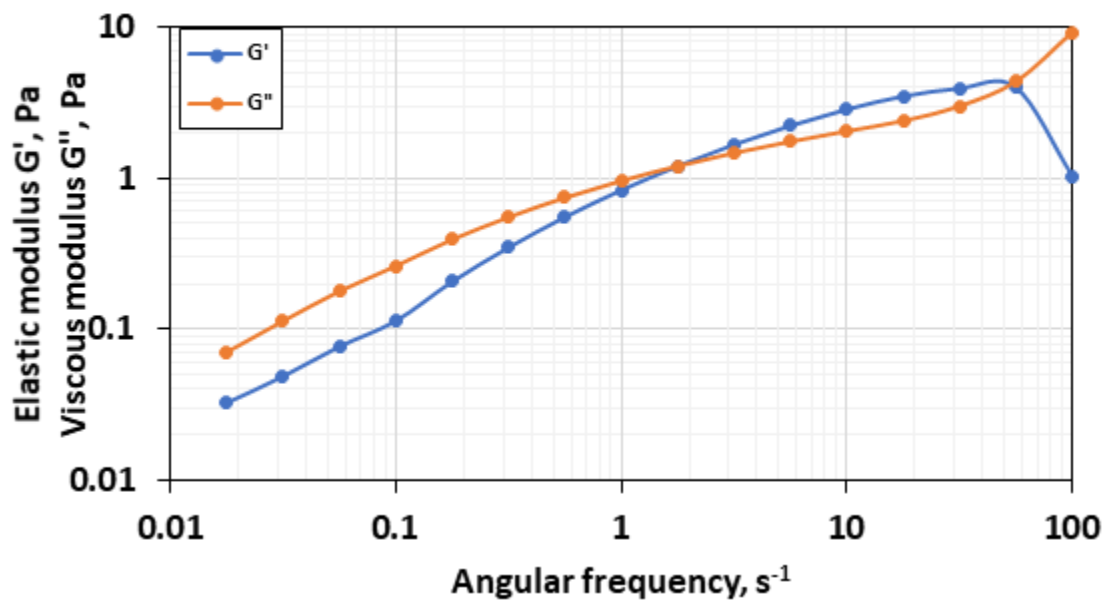


Figure 4-18 Frequency test for 10000 ppm AN-125 SH polymer at 5767 ppm brine at 75°C

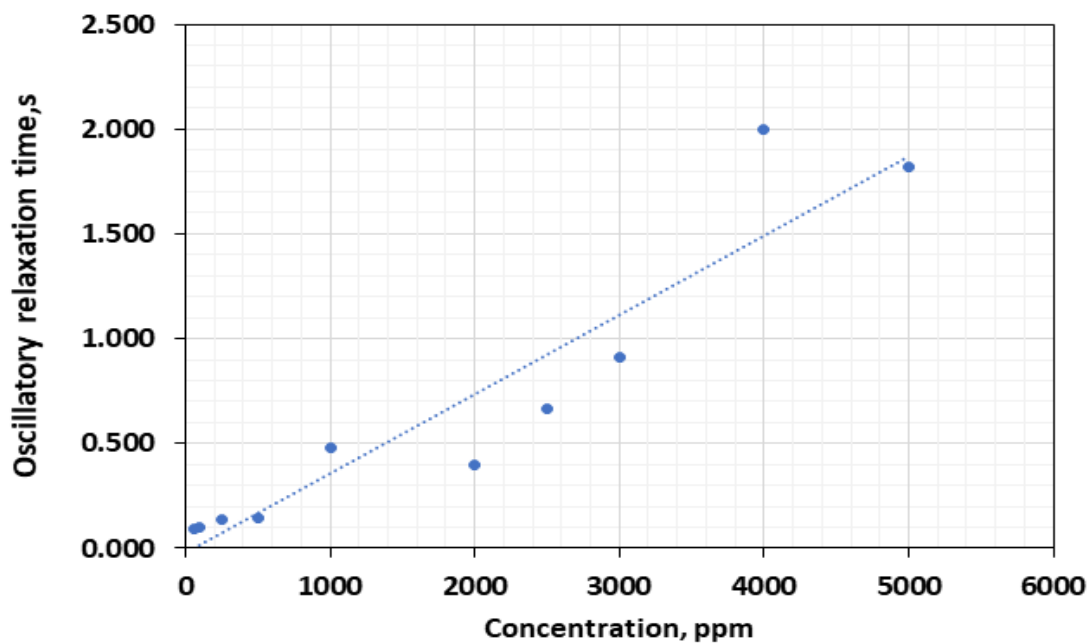


Figure 4-19 Linear oscillatory relaxation time as a function of concentration for AN-125 SH polymer-5767 ppm brine at 75°C

4.1.6 Relaxation times comparison

Figure 4.20 and **Table 4.3** present the comparison of linear relaxation time obtained as a function of concentration using oscillatory shear rheometry and steady-shear rheometry. Interestingly, oscillatory relaxation times are typically higher. A detailed listing of Newtonian viscosity, linear-steady shear relaxation time, oscillatory relaxation time, and non-linear relaxation time is given in **Table 4.3**. One interesting finding is that as concentration increases, non-linear relaxation time either stays constant or gets smaller. AN-125 SH polymer at a concentration of 2500 ppm, exhibits a Newtonian viscosity of 26 cP. This establishes a favorable viscosity ratio of 7 in porous media (**Figure 4.13**), considering the oil viscosity to be 4 cP at 75 °C, this concentration is chosen for use as the viscoelastic polymer in the subsequent two-phase flooding.

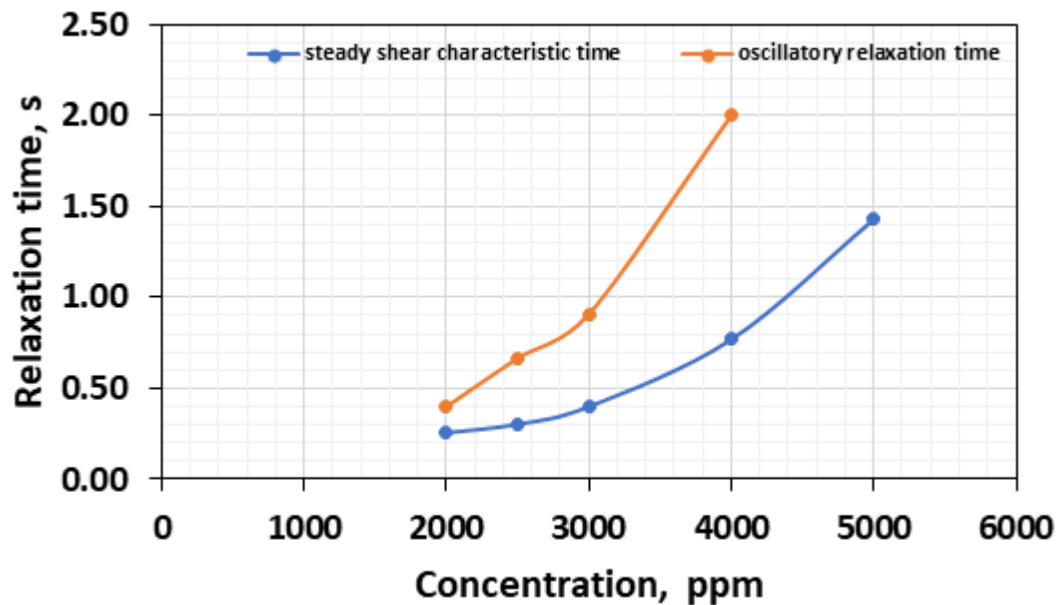


Figure 4-20 Linear oscillatory and linear steady-shear relaxation time as a function of concentration for AN-125 SH polymer-5767 ppm brine at 75°C

Table 4-3 Steady-shear and oscillatory rheological parameters for varying concentrations of AN-125 SH polymer systems at 75°C

Concentration ppm	Zero shear viscosity (cp)	visc. Ratio	Characteristic time, s	Amplitude, %	Cross over point	Linear Relaxation time, s	Thickening onset rate, 1/s	Non-linear relaxation time, s
10000	5298	1358	8.33	10	1.78	0.562	N/A	N/A
5000	340.9	87	1.43	10	0.55	1.82	672	0.0015
4000	157.8	40	0.77	10	0.5	2	452	0.0022
3500	73.2	19	0.48	10	2.5	0.4	452	0.0022
3000	45.3	12	0.40	10	1.1	0.91	304	0.0033
2500	26.9	7	0.30	2.5	1.5	3.45	304	0.0033
2000	15.7	4	0.26	30	2.5	0.40	304	0.0033
1000	4	1	N/A	30	2.1	0.48	204	0.0049
500	1.8	0	N/A	10	7	0.14	137	0.0073
250	1.02	0	N/A	30	7.3	0.14	92.4	0.0108
100	0.67	0	N/A	30	10.2	0.1	62	0.0161
60	0.57	0	N/A	30	10.7	0.09	41	0.0244
25	0.51	0	N/A	50	9.5	0.10	41	0.0244

For AN-125 SH concentrations lower than 2000 ppm, achieving a linear viscoelastic regime within low strain rates proved challenging. Consequently, a higher strain rate was employed, despite the data's unreliability at this elevated rate, as indicated by the rheometer. It is noteworthy that both steady shear and oscillatory linear time exhibit a consistent rise with concentration, particularly evident in the steady shear tests. However, in the oscillatory tests, a clear trend was not uniformly established across all concentrations, as depicted in Figure 4.19. With increasing concentration, the gap between elastic and viscous moduli diminishes. This is notably pronounced in the highest molecular weight

polymer, where the difference in values becomes exceedingly small compared to polymers of moderate or light molecular weight as observed in the case of AN 125-VHM, SH and STD (**Figures 8-10**).

4.2 Biopolymer System Screening

To explore the potential of viscoelastic polymers in reducing residual oil saturation, a comparable flooding experiment using a polymer with the same apparent viscosity in porous media but without non-linear viscoelasticity is required. xanthan gum is suitable for this purpose, and the chosen xanthan concentration ensures that the bulk viscosity of this polymer is higher than the viscoelastic bulk rheogram, allowing for viscosity intersection in the viscous-elastic regime of each polymer. **Figure 4.21** illustrates different concentrations of xanthan gum overlaid with AN-125 SH. It is evident that a xanthan concentration of 2000 ppm exhibits a higher rheogram profile that will inevitably intersect with 2500 ppm of AN-125-SH at high shear rates, resulting in similar apparent viscosity despite the two polymers exhibiting contradicting phenomena (shear thinning and thickening).

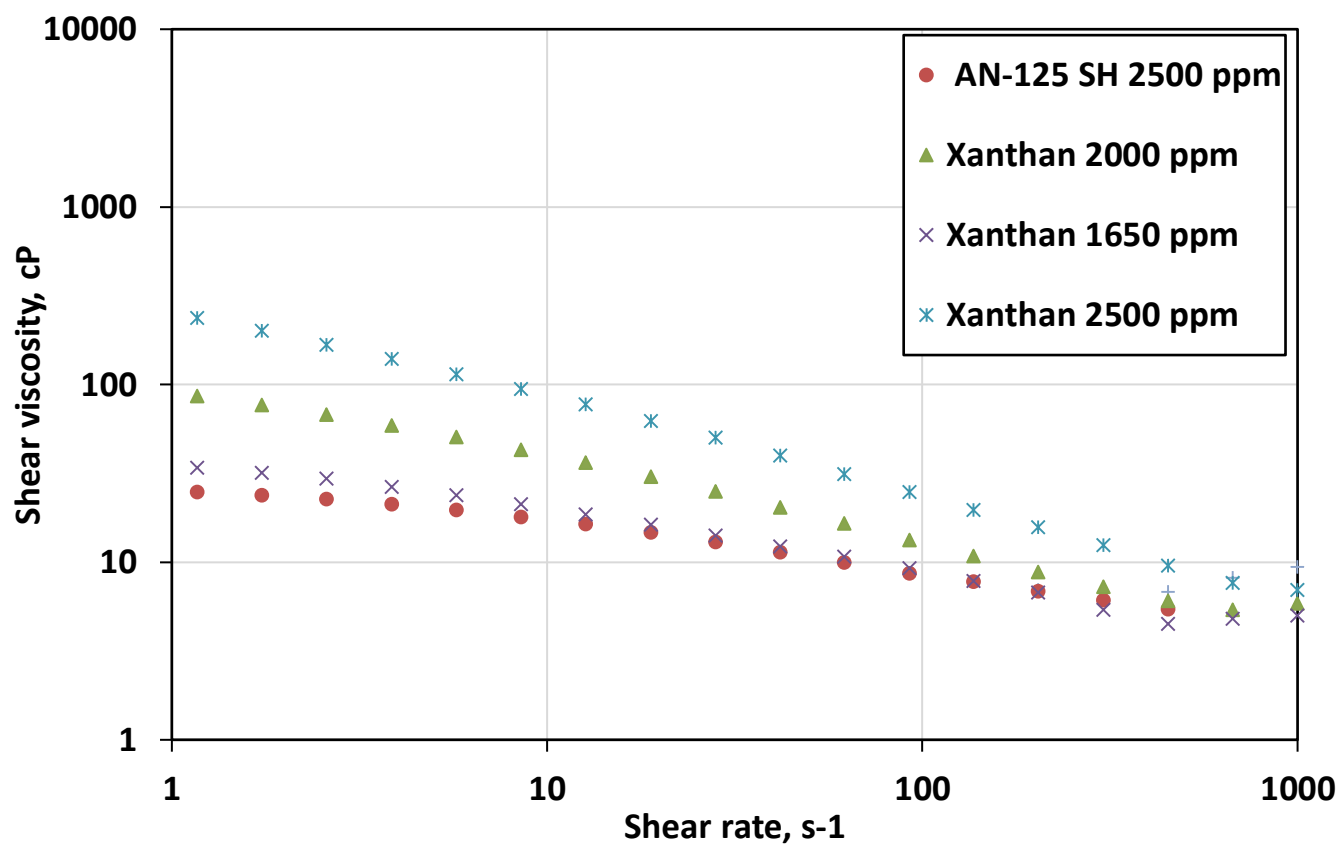


Figure 4-21 Set of xanthan gum rheology profiles for different concentration in comparison with 2500 ppm of AN-125 SH polymer at 5767 ppm brine and 75°C

CHAPTER 5

In-Situ Rheology and Oil Recovery of EOR Polymers

This chapter outlines the results from single-phase core flooding experiments conducted to examine the in-situ behavior of two distinct types of polymers. Additionally, it includes findings from oil recovery experiments that were designed based on how each polymer performed during the in-situ tests in similar porous media. This approach provides an indication of the potential of viscoelastic polymers in reducing difficult residual oil in an oil-wet setting. Building on the insights from the previous chapter, we have identified the concentrations of both polymer systems. These parameters were chosen for their ability to demonstrate two distinct phenomena while yielding similar apparent shear viscosities within core samples.

5.1 In-Situ Rheology

Synthetic polymers composed of acrylamide monomers with a portion hydrolyzed, exhibits complex rheological properties as in long-chain polymers. Under extremely low shear rates, it demonstrates a Newtonian behavior, typically indicated by a plateau. In low shear rates, from over 100 per second, it shows pseudoplastic or shear-thinning characteristics. When subjected to higher shear rates, dilatant or shear-thickening behavior becomes apparent and appears clearly in core flooding experiments, when the elastic limit of the polymer chain reached it enters mechanical degradation regime. These various behaviors are illustrated in the provided stylized plot (**Figure 5.1**) from (2022). In the other

hand, biopolymers are rigged chains that's only show shear thinning when subjected to monotonic elevated shear rate.

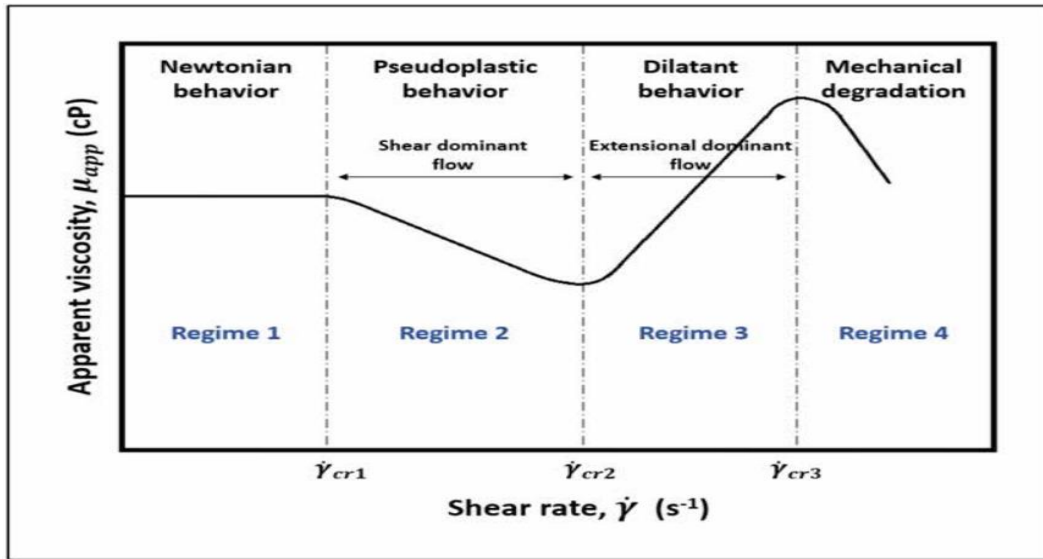


Figure 5-1 Typical behavior of synthetic polymers when flowing in porous media from Sheng, (2011)

Biopolymers and synthetic polymers serve as common Enhanced Oil Recovery (EOR) fluids. To assess the potential viscoelasticity of synthetic polymers over biopolymers in recovering residual oil within oil-wet reservoirs, it is crucial that both polymers exhibit similar apparent viscosity in comparable porous media. For this purpose, a series of cores were extracted from an outcrop and employed in this study, possessing high permeability within the range of 1-1.3 Darcy. Six cores with comparable properties were selected to conduct single and two-phase flooding experiments. Cores F21 and F2 were specifically utilized to generate the in-situ rheology profile of AN-125 SH and xanthan gum, with their respective properties detailed in **Table 5.1**.

Table 5-1 Properties of core samples used for single-phase flooding

Core #	Polymer type	K, mD	ϕ	PV	L, in	Dia, in
F21	AN-125-SH	1296	33%	28	3	1.5
F2	Xanthan	1375	42%	36	3	1.5

5.1.1 Biopolymer-Xanthan gum 2000 ppm

In order to characterize the rheological behavior of xanthan polymer within porous media, a fully saturated core with formation water was loaded into the core flooding setup. Subsequently, the core was subjected to high salinity water flooding, utilizing salts specified in **Table 3.1**. Subsequent to water flooding at elevated temperature of 75 °C, 2000 ppm of xanthan polymer was introduced to the core at progressively decreasing flux rates, ranging from 34 ft/day to 0.8 ft/day Darcy velocity. The observed pressure drop after stabilization was then reverse-calculated to determine viscosity, considering the known liquid permeability. As anticipated for biopolymers, the apparent viscosity exhibited shear thinning behavior with increasing shear rates. The observed behavior within the tested flux rates is illustrated in **Figure 5.2**.

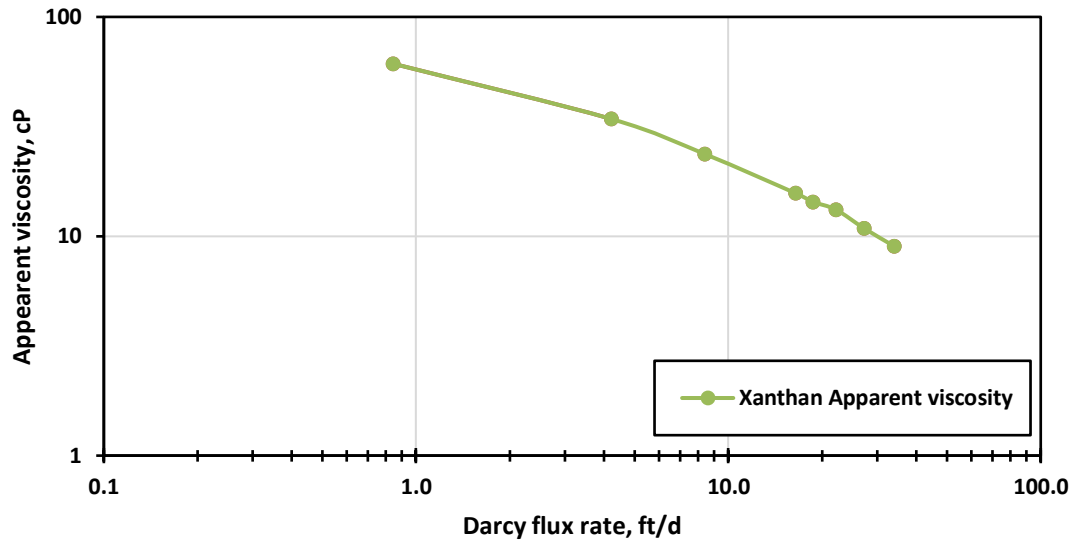


Figure 5-2 Polymer apparent viscosity at 75 °C for 2000 ppm of xanthan gum in low salinity brine (TDS=5957) flowing in ~1.3 D permeability sample.

5.1.2 Synthetic Polymer-AN-125 SH

To investigate the in-situ rheological properties of a synthetic polymer within porous media, an initial step involved saturating a core with formation water within the core flooding setup. Using a flood of highly salinized water using the salts specified as connate field brine in **Table 3.1**. After the water flooding, conducted at a raised temperature of 75 °C, the core was injected with 2500 ppm of AN-125 SH polymer. This injection was carried out at gradually decreasing flow rates, varying from 34 ft/day to 0.8 ft/day in Darcy velocity. The viscosity was then determined using the resulting stable pressure drop across the core, taking into account the established liquid permeability. In line with typical behavior of synthetic polymers, the apparent viscosity of the polymer exhibited shear-thinning at lower shear rates, transitioning to shear-thickening as the shear rate increased

beyond the critical shear rate of 18.7 ft/day. This specific rheological behavior across the tested range of flow rates is illustrated in **Figure 5.3**.

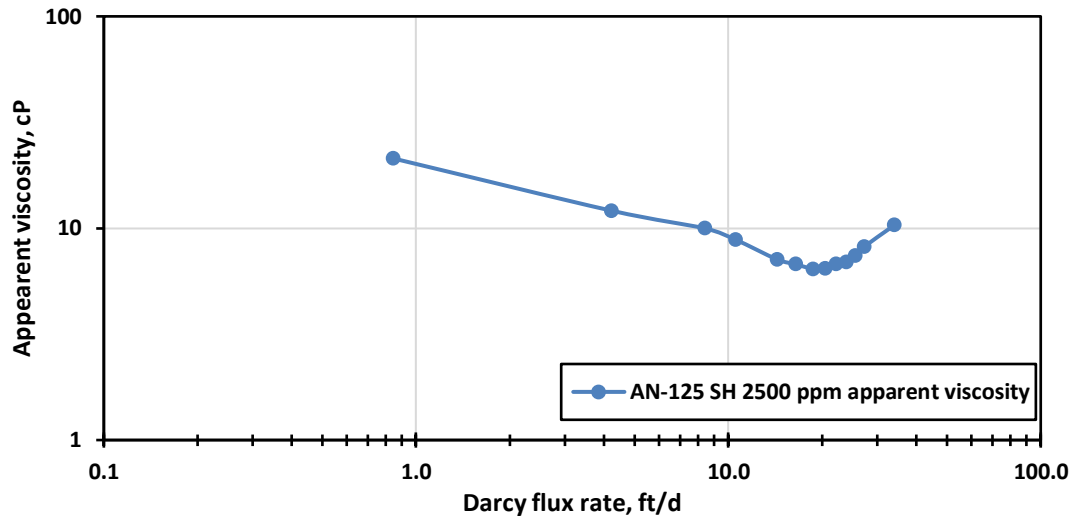


Figure 5-3 Polymer apparent viscosity at 75 °C for 2500 ppm of AN-125 SH in low salinity brine (TDS=5957) flowing in ~1.6 D permeability sample.

5.1.3 Comparison of in-situ rheology

The purpose of conducting identical single-phase flooding experiments in analogous media is to identify the flux rate at which the two polymers intersect. The apparent viscosity of each polymer is influenced by distinct phenomena; xanthan gum experiences reduced viscosity under elevated shear due to its chain nature, whereas AN-125 SH, under high shear, gains viscosity and resistance to flow owing to the elasticity of its chains. As shown in **Figure 5.4**, the apparent viscosity profiles of the selected concentrations intersect at 31.5 ft/day, equivalent to an injection rate of 7.78 cc/min, aligning with the anticipated behavior. A shear rate correction factor of 6 was determined to be optimal for aligning the bulk shear rheology with the in-situ rheology. The calculation of the porous media shear rate was performed using the Cannella conversion model. **Figure 5.5** displays the overlaid graph of the bulk shear and apparent viscosity of the two polymers utilized in the study. It is

noteworthy that the bulk rheology of the biopolymer closely resembles the in-situ profile. A comparable observation aligns with findings from prior studies by Cannella et al. (1986), Azad & Trivedi (2019), and Clarke et al. (2016). Each of these studies utilized high permeability rocks during in-situ flooding, reporting permeability values of 300, 465, and 552 Darcy, respectively. The high permeability of the porous media used is 1.3 Darcy, this hinders polymer deformation within the rock sample, as indicated by NMR tests (**Figure 5.7**) revealing a dual porosity system with medium and macro porosity. The highest peak corresponds to high T_2 relaxation time, indicative of high pore size or fractures, suggesting an easier path for fluid flow (Elsayed et al., 2022). This reduces polymer deformation in porous media, aligning its rheological behavior with that tested through the bulk rheometer. For AN-125 SH, despite the high permeability, an early onset is observed in porous media compared to bulk rheology. This implies that in such rock samples, activating polymer elasticity requires a higher shear compared to lower permeability rocks, where tight pores aid in stretching and launching elasticity at relatively lower rates.

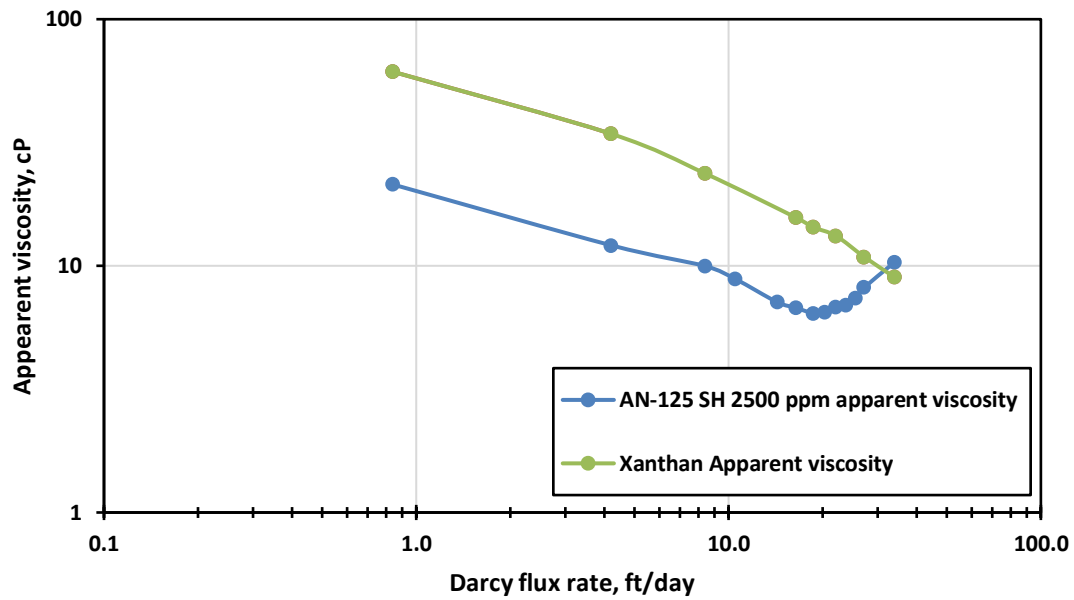


Figure 5-4 Comparison of polymer apparent viscosity at 75 °C between 2000 ppm of xanthan gum and 2500 ppm of AN-125 SH in low salinity brine (TDS=5957) flowing in comparable samples in term of permeability showing intersect at high flux rates at 31.5 ft/day.

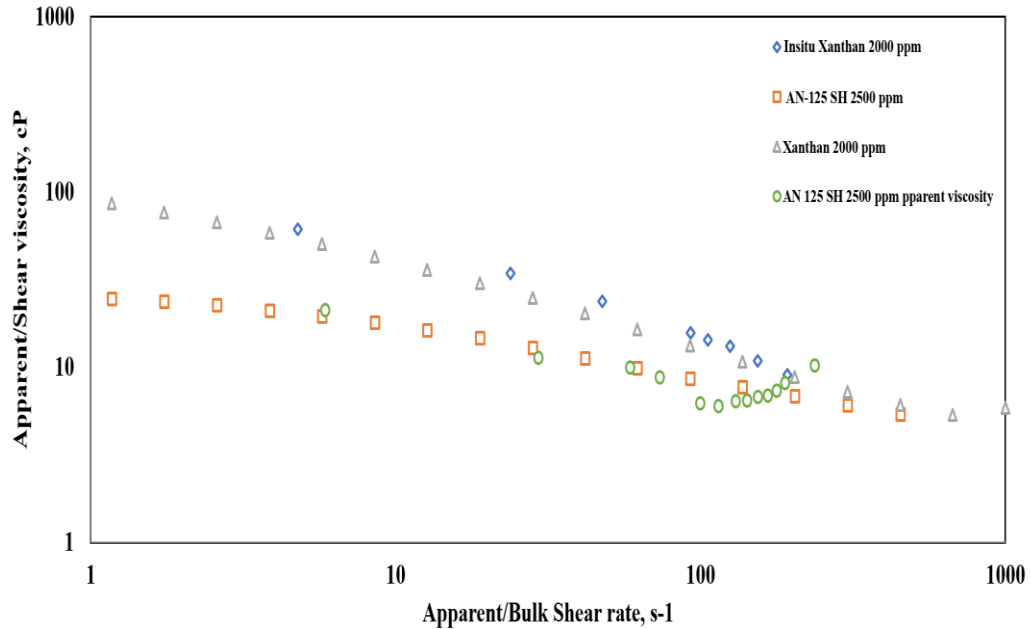


Figure 5-5 Shear and apparent viscosity of core flooding polymers; xanthan 2000 ppm and AN-125-SH 2500 ppm at 75 °C

5.2 Oil Recovery Flooding Experiments

This section presents and interprets the outcomes derived from a series of oil recovery core flooding experiments. Two identical core flooding trials were executed to evaluate the efficacy of viscoelastic polymers in diminishing residual oil presence within oil-wet environments. This evaluation was compared against the performance of a non-elastic biopolymer. These experimental investigations were conducted under elevated temperature conditions of 75 °C, incorporating three distinct flux rates that correspond to specific regimes within the polymer's in-situ profile, as elucidated in the preceding section. The parameters of the polymer system, as identified in the previous chapter, were strategically chosen to ensure favorable viscosity ratio between the injected polymer and the residing oil under the specified flooding conditions. Throughout each experimental iteration, both the overburden and back pressures were maintained at constant levels (Overburden pressure: 1500 psi, Back pressure: 950 psi). The injection protocol replicated the sequence established in the initial experiment: initiating with water flooding at flux rates of 2, 4, and 8 ft/day, subsequently followed by polymer flooding at increased rates of 4, 20, and 32.5 ft/day. This systematic approach facilitated a comprehensive assessment of the polymers' performance in enhancing oil recovery.

The porous media used in these experiments were obtained from an outcrop, as detailed in the methodology chapter. A set of core samples with similar permeability was selected for generating the polymer in-situ profile and conducting the oil recovery experiments. The characteristics of the core samples are presented in **Table 5.2** below. The flooding process was conducted using a composite sample comprised of two 3-inch plugs, facilitating an in-depth characterization of the rock's properties. This was achieved through Nuclear

Magnetic Resonance (NMR) scanning, a technique employed to evaluate the pore size distribution within these core samples. The T_2 relaxation time results showcased in **Figure 5.6**, indicate the presence of a dual porosity system characterized by dual peaks. Such a feature suggests the potential existence of fractures or vugs within the rock structure having a relaxation time near 1000 ms (Elsayed et al., 2022), providing valuable insights into its porous nature.

Table 5-2 The properties of outcrop core samples used in core flooding

Property	Core #1 (F1+F20)	Core #2 (F3+F6)
Core 1 PV	31	30
Core 2 PV	28	34
Total PV	59	64
L, in	6	6
Diameter, in	1.5	1.5
Composite k, D	1.2	1.4
Avg Porosity	35%	42%
S_{wi}	0.492	0.6094
S_{oi}	0.508	0.3906

In this study, selected core samples were initially flooded with formation brine to simulate the saline connate water conditions typical in carbonate reservoirs. Subsequently, these cores were flooded with crude oil possessing a viscosity of 26 cP at ambient conditions and 4 cP at 75 °C. During the initial permeability assessments, several cores experienced fracturing or damage due to the application of high confining pressures. This led to the observation that such cores are fragile and particularly sensitive to stress. Consequently,

incidents of core damage necessitated a more cautious approach in handling and preparing the cores for subsequent flooding experiments. This included the application of lower confining and back pressures during the oil injection phase prior to aging, aimed at minimizing core damage. However, the reduced back pressure during the oil flooding phase adversely impacted the oil's ability to effectively displace the pre-existing water within the cores, resulting in suboptimal initial oil saturation levels. For the aging process, the cores were placed in a transfer cell and subjected to a temperature of 75 °C for a duration of one month, facilitating the conversion of the core's wettability into oil-wet conditions. As per the review by Alameer et al. (2023), an aging period exceeding 20 days at temperatures above 60 °C is generally considered adequate for achieving the desired oil-wet alteration in such scenarios. **Table 5.3** details the properties of fluids involved during core flooding experiments.

Table 5-3 General information of fluids injected during core flooding experiments

Fluid	Information
AN-125 SH	Newtonian viscosity is 26 cP at 75°C / 2500 ppm
Xanthan	Newtonian viscosity is 85 cP at 75°C /2000 ppm
Low salinity brine	Viscosity at 75°C is 0.57 cP / TDS is 5767 ppm
Oil	Crude oil that has an ambient viscosity of 26 cP and 4 cP at 75°C

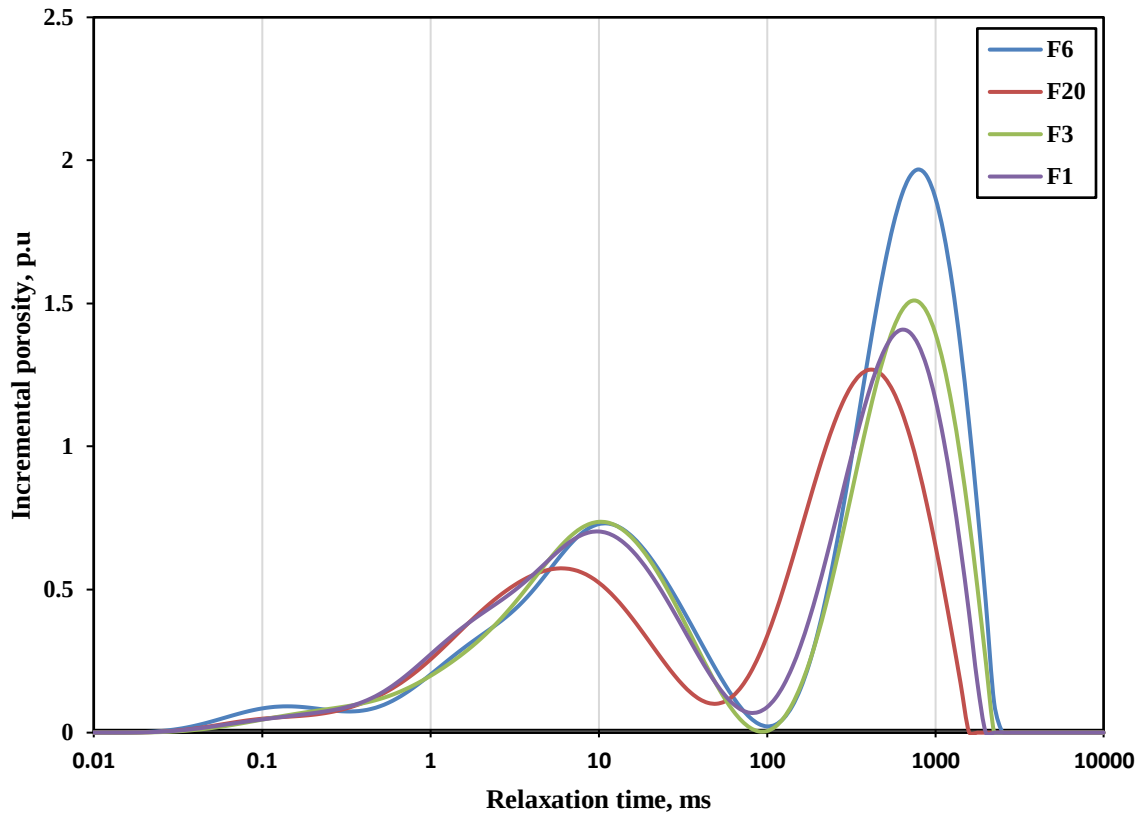


Figure 5-6 NMR scan results using T_2 relaxation time on dolomite cores obtained from an outcrop, indicating dual porosity system and large pore size distribution that dominates 97% of the core samples.

5.2.1 Biopolymer-Xanthan gum

In this study, xanthan gum at a concentration of 2000 ppm was selected as the representative viscous polymer, based on the screening process detailed in the preceding chapter. The experimental protocol commenced with the injection of oil at various rates for a duration of one hour. Subsequently, low salinity brine was injected at three distinct flow rates, with each rate maintained for about 4 pore volumes (PV) in order to ascertain the residual oil saturation and optimize the extraction of movable oil. The transition to polymer injection occurred after approximately 2 PV of oil cut was observed in the effluent collector at each water flooding rate, signifying the end of oil production. The initial injection rate of polymer was fixed at 4 feet per day,

corresponding to an early point within the shear thinning regime as identified in the in-situ rheological profile. At this stage, the polymer exhibited a viscosity of approximately 34-cP, in contrast to the 4-cP viscosity of the oil at the experimental temperature. Subsequent polymer injection rates were increased to 20 and 32.5 ft/day, each continued for around 2 PV past the point where oil production ceased. The highest rate corresponds to a lower viscosity regime (approximately 9-cP) for the polymer, as this type of polymer demonstrates significant shear thinning only under conditions of elevated shear.

Figures 5.7 to 5.9 provide a comprehensive visual representation of the oil recovery factors, oil saturation profiles, and the overall pressure drop observed throughout the various phases of injection during the experiment. Initially, the water flooding at a rate of 2 ft/day Darcy velocity resulted in a reduction of oil saturation from approximately 40% to 35%. This equates to an 11% recovery of the initial oil in the core, a consequence largely attributed to the core sample's high heterogeneity, the initially low oil saturation, and its oil-wet characteristics. Despite no additional oil being produced at the second rate, increasing the velocity to 8 ft/day led to an enhanced oil recovery of 16.1%, marking a 5% incremental oil recovery attributed to the higher flux rate. The oil remaining in the core at this point is challenging to categorize as residual oil saturation, primarily due to the core's pronounced heterogeneity, which rendered it resistant to mobilization by water at varying rates.

Subsequently, after 13 pore volumes of injection, 2000 ppm of xanthan gum was introduced at a 4 ft/day flux rate. As a consequence, the oil recovery increased significantly to 24.6% of the initial oil in the core at a pressure gradient of about 0.85

psi/ft. This marked improvement can be explained by the high viscosity of xanthan at this particular shear rate coupled with the low injection rate, both of which contributed to enhanced sweep efficiency in the heterogeneous porous media. The second injection rate of xanthan polymer produced only a marginal increase in oil volume, bringing the total recovery to 25.1% at pressure gradient of 2 psi/ft, oil recovery remained unchanged even after the third and higher injection rate (32.5 ft/day) of xanthan at higher pressure gradient of 2.6 psi/ft.

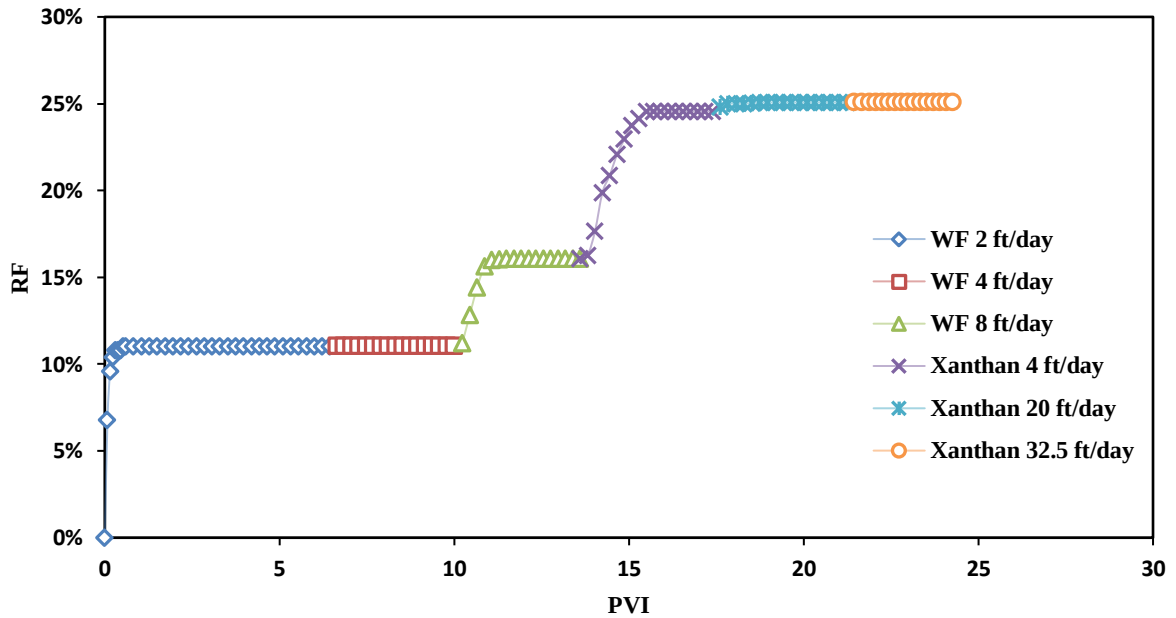


Figure 5-7 Oil recovery factor of Low Salinity Water and 2000 ppm xanthan Gum Flooding at 75 °C in Composite Core Samples (F3-F6).

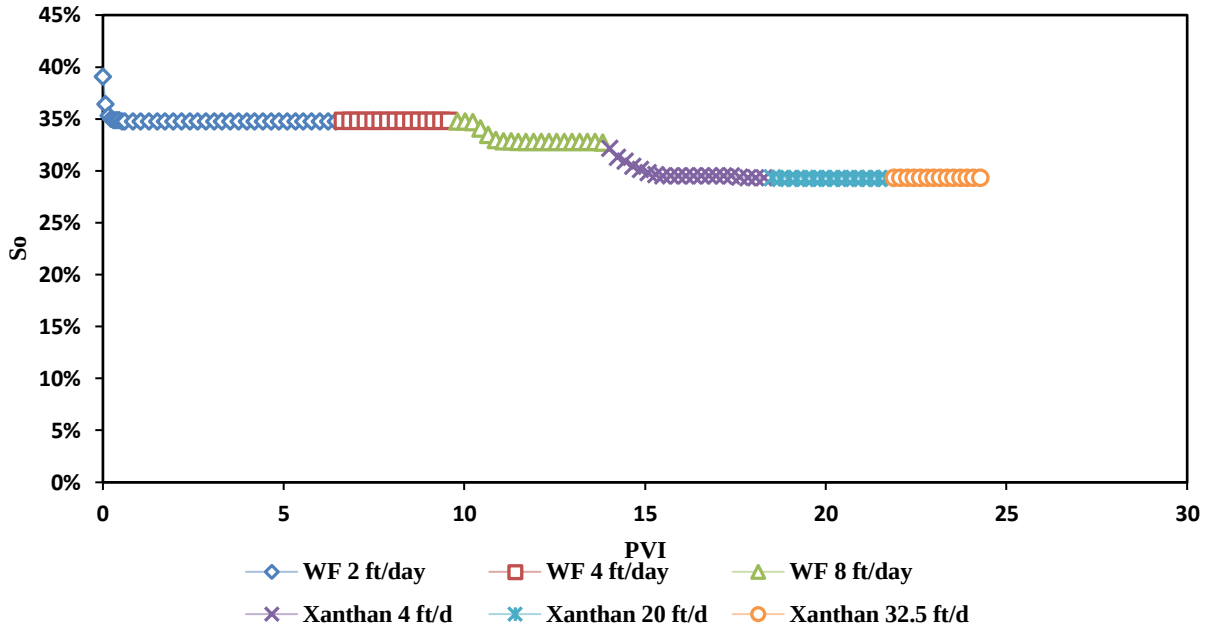


Figure 5-8 Oil saturation profile of low salinity water and 2000 ppm xanthan gum flooding at 75 °C in composite core samples (F3-F6).

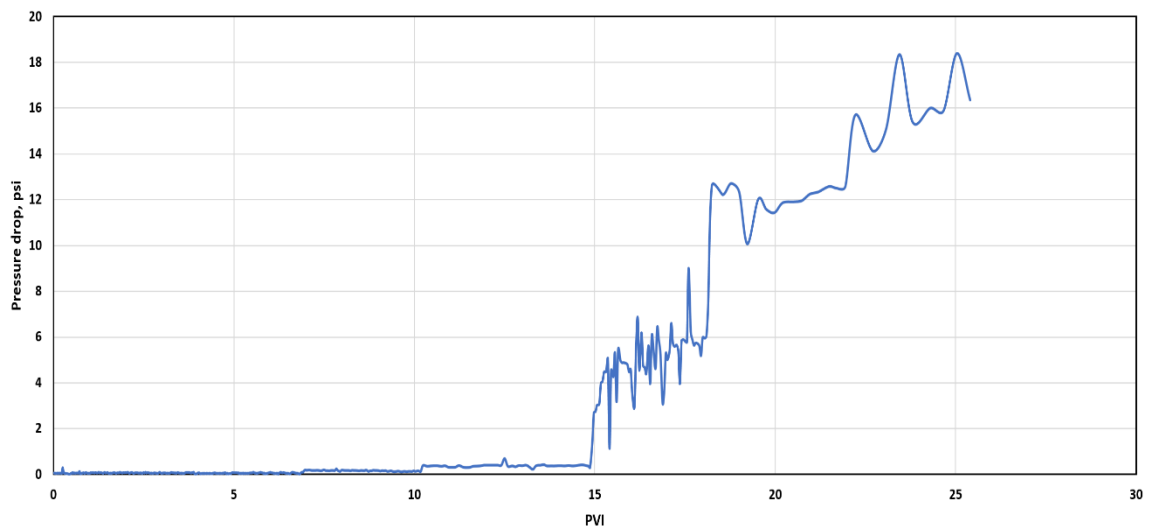


Figure 5-9 Pressure drop profile of low salinity water and 2000 ppm xanthan gum flooding at 75 °C in composite core samples (F3-F6).

5.2.2 Synthetic Polymer-AN-125 SH

Conversely, the main focus of this study with the sulfonated polymer AN-125 SH, chosen for its viscoelastic properties at a concentration of 2500 ppm, as determined from the screening process outlined in the previous chapter. The experimental approach adopted for AN-125 SH mirrored that of the xanthan gum injections, commencing with oil injection at varying rates for an hour. This phase was followed by injecting low salinity brine at three separate flux rates for ~ 4 pore volumes (PV) each, aiming to establish residual oil saturation and maximize the recovery of mobile oil. The shift to polymer flooding was initiated once a 2 PV past the last oil drop in the effluent collector was noted for each rate of water flooding.

The initial rate of polymer injection was established at 4 ft/day, aligning with an initial phase in the shear thinning regime, as indicated by the in-situ rheological profile (**Figure 5.4**). At this shear rate, the polymer's viscosity was approximately 12-cP, contrasting with the oil's 4-cP viscosity at the test temperature. The polymer injection rates were subsequently escalated to 20 and 32.5 ft/day corresponding to apparent viscosity of 6.5 and 9.8 cP respectively, each maintained for about 2 PV after the cessation of oil flow. The maximum rate was associated with the highest-pressure gradient (around 30 psi/ft) owing to polymer elasticity, which exhibits notable shear thickening behavior particularly under high shear conditions.

Figures 5.10 - 5.12 provide graphical depiction of the oil recovery factors, profiles of oil saturation, and the pressure drop monitored across the different injection stages in the experiment. The initial phase of water flooding, conducted at a Darcy velocity of 2 ft/day, led to a decrease in oil saturation from roughly 50.8% to 44%. This corresponds to

an oil recovery of 13% from the original oil in the core, a result predominantly ascribed to the core's significant heterogeneity, the initial low oil saturation, and its intrinsic oil-wet nature. Despite the absence of further oil extraction at the second rate, an escalation in the rate to 8 ft/day settled in a boosted oil recovery of 17%, accounting for a 4% incremental recovery owing to the elevated flux rate.

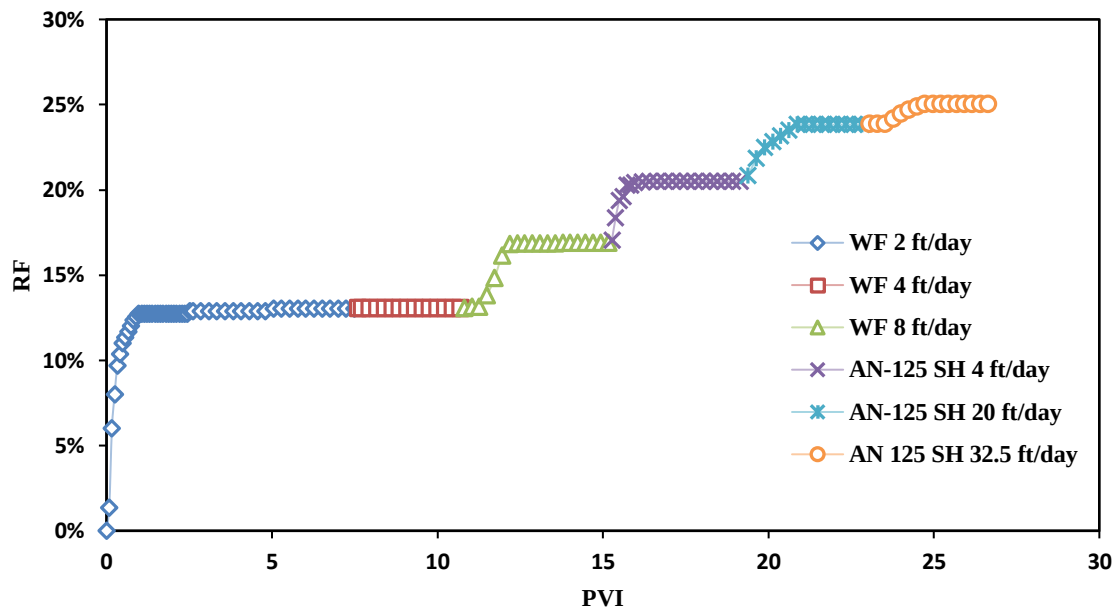


Figure 5-10 The profile of oil recovery factor of low salinity water and 2500 ppm AN-125 SH polymer flooding at 75 °C in composite core samples (F1-F20).

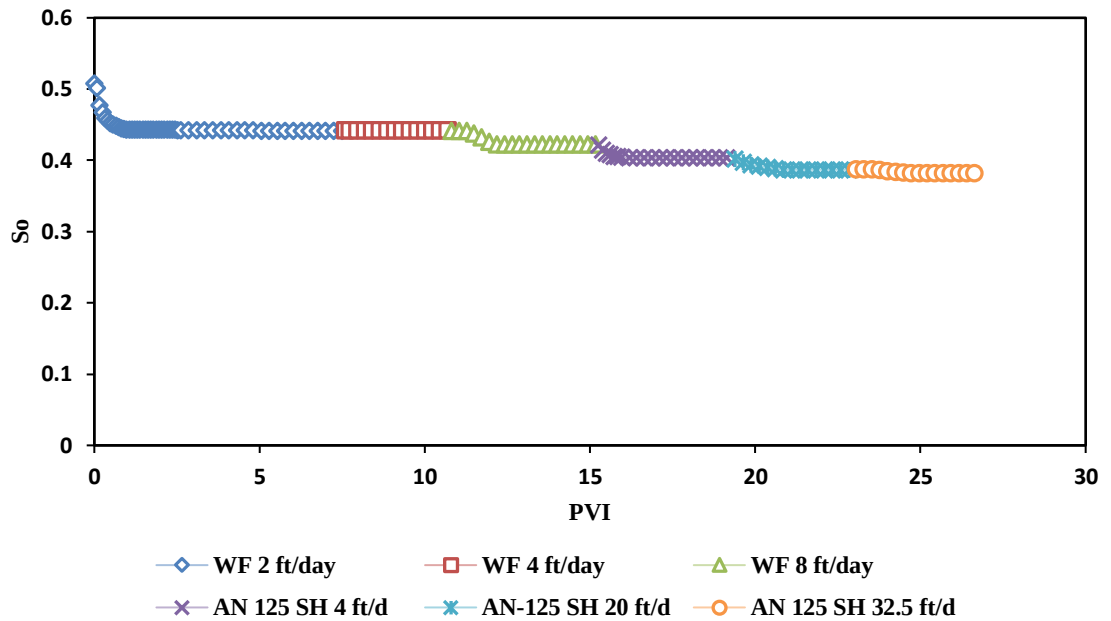


Figure 5-11 Oil saturation profile of low salinity water and 2500 ppm AN-125 SH polymer flooding at 75 °C in composite core samples (F1-F20).

The introduction of 2500 ppm of AN-125 SH into the system, at a flux rate of 4 ft/day, resulted in an enhanced oil recovery while maintaining a pressure gradient of approximately 0.67 psi/ft. This injection achieved a recovery factor of 20.5% of the core's initial oil content. The observed increase in recovery is largely due to the mobilization of oil, facilitated by the low rate of injection within the heterogeneous media. An increase in the injection rate of the sulfonated polymer further improved oil recovery, raising the total to 23.8% at a pressure gradient of 3.3 psi/ft. This recovery pertains to the residual oil that was not extracted by the previous rate, with a consistent plateau in oil recovery observed for about 2 pore volumes (PV). Remarkably, the oil recovery underwent a notable increase upon implementing the third and highest injection rate of 32.5 ft/day. This rate aligns with the regime where the elastic effects, as identified in the in-situ rheological profile, became prominent. The application of

this elevated injection rate propelled the oil recovery to 25%, accompanied by the highest-pressure gradient observed in the experiment, reaching 30 psi/ft. This phase of the experiment highlights the impact of polymer elasticity activated by high flux rates on enhancing the recovery of residual oil in complex reservoir conditions.

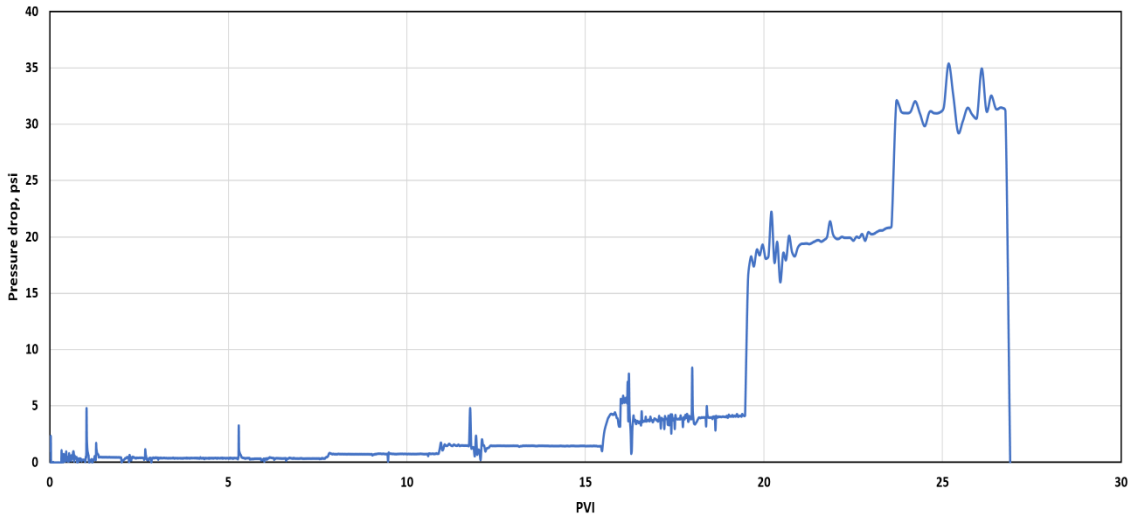


Figure 5-12 Pressure drop profile of low salinity water and 2500 ppm AN-125 SH polymer flooding at 75 °C in composite core samples (F1-F20).

5.2.3 Comparative discussion

In this section, a comparative analysis of oil recovery is made, with a particular focus on the incremental oil recovery facilitated by an elastic polymer and a biopolymer, linking these findings with analogous studies in existing literature. Despite the inherent oil-wet conditions and the prevalence of large pore sizes within the core samples, both experimental setups resulted in a total oil recovery plateauing at 25% of the initial oil content in the core, as illustrated in **Figure 5.13**. This figure elucidates the percentage increase in oil production attributable to polymer injection in both instances.

A notable difference however, is observed in the incremental oil recovery realized by the two polymers. Xanthan gum, on one hand, accomplished the majority of its total recovery

during the initial injection rate of 4 ft/day, which corresponds to the highest viscosity observed during the experiment's injections phases. This is consistent with the in-situ rheological profile depicted in **Figure 5.4**, where this rate is situated within the initial phase of the shear-thinning regime. Such behavior suggests that the gained oil recovery at this rate is a result of improved sweep efficiency due to the viscous nature of the flooding.

Conversely, subsequent xanthan flooding rates (20 and 32.5 ft/day) yielded minimal additional oil recovery, with no oil production detected at the highest injection rate. In contrast, the viscoelastic polymer AN-125 SH was subjected to flooding at three rates, with the elevated rates selected based on their alignment with the onset of the polymer's elastic effects as indicated in the in-situ rheological profile.

Figure 5.13 provides a comparative analysis of incremental oil recovery percentages post water flooding for two polymers, 2500 ppm AN-125 SH and 2000 ppm xanthan gum, under varying flux rates post-water flooding at 75 °C. Key observations include AN-125 SH were able to reduce oil saturation more effectively relative to xanthan gum, this increase in oil recovery can be attributed to polymer viscoelasticity since polymer shear thickening onset occurred at 18 ft/day **Figure 5.4**. While xanthan gum, especially at 4 ft/day, as shown in **Figure 5.14** achieve higher recovery percentage this is explained by the drastic viscosity ratio difference between AN-125 and xanthan. Increasing flux rate does not significantly impact xanthan incremental oil recovery **Figures 5.15-5.16**. the end point oil saturation and oil recovery of each particular flood is tabulated in details in **Table 5.4**.

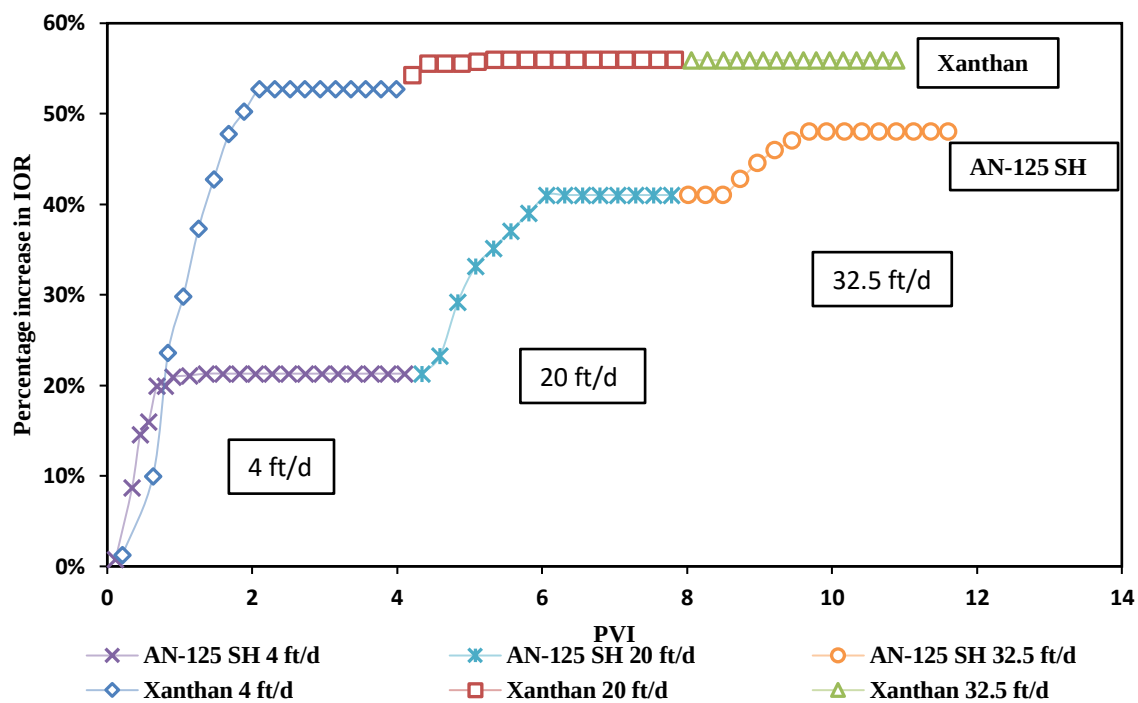


Figure 5-13 Comparative of incremental oil recovery percentage for 2500 ppm AN-125 SH and 2000 ppm xanthan gum solutions at flux rates of 4, 20, and 32.5, post-water flooding, at 75 °C

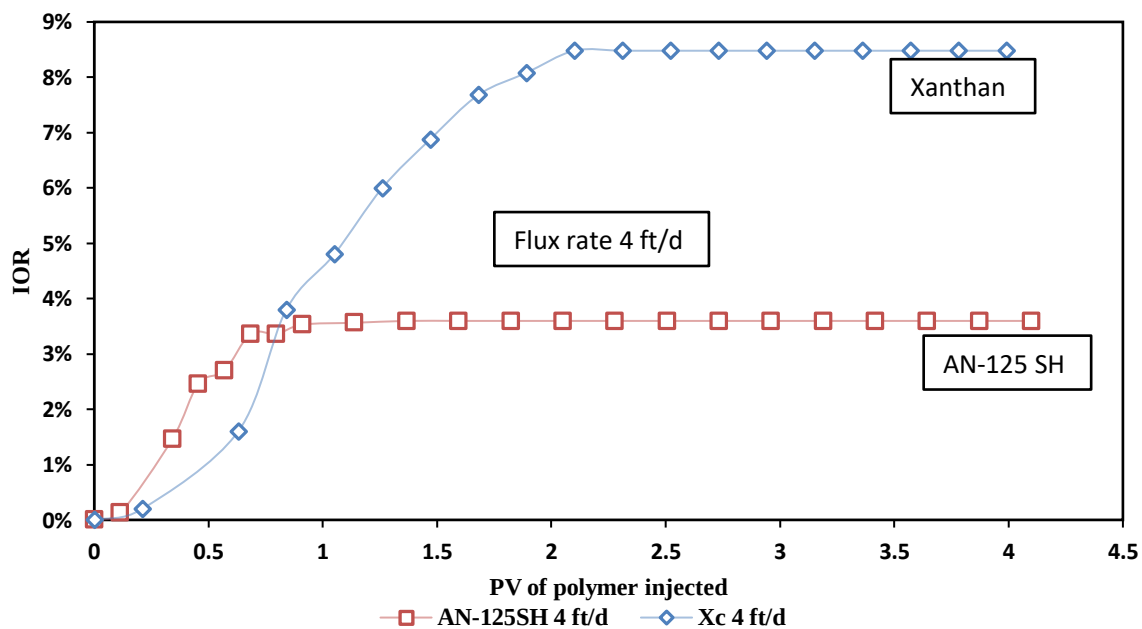


Figure 5-14 Comparison of incremental oil recovery for 2500 ppm AN-125 SH and 2000 ppm xanthan gum solutions at shear thinning regime (4 ft/day) at 75 °C

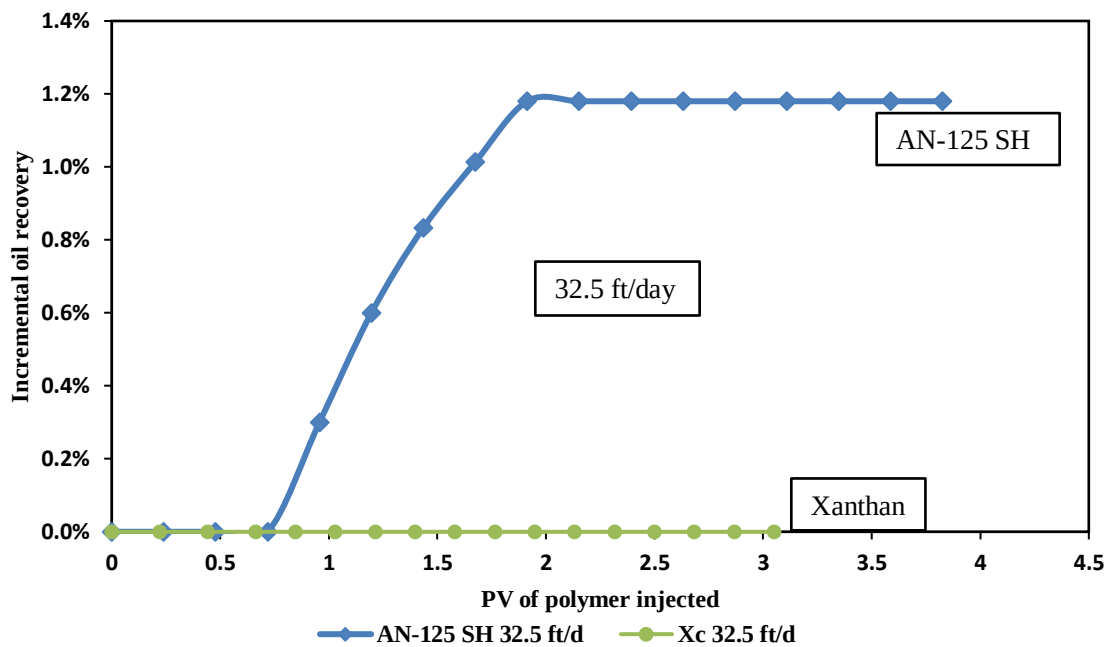


Figure 5-16 Comparison of incremental oil recovery for 2500 ppm AN-125 SH and 2000 ppm xanthan gum solutions at intersection flux rate of polymers apparent viscosities (32.5 ft/day) at 75 °C

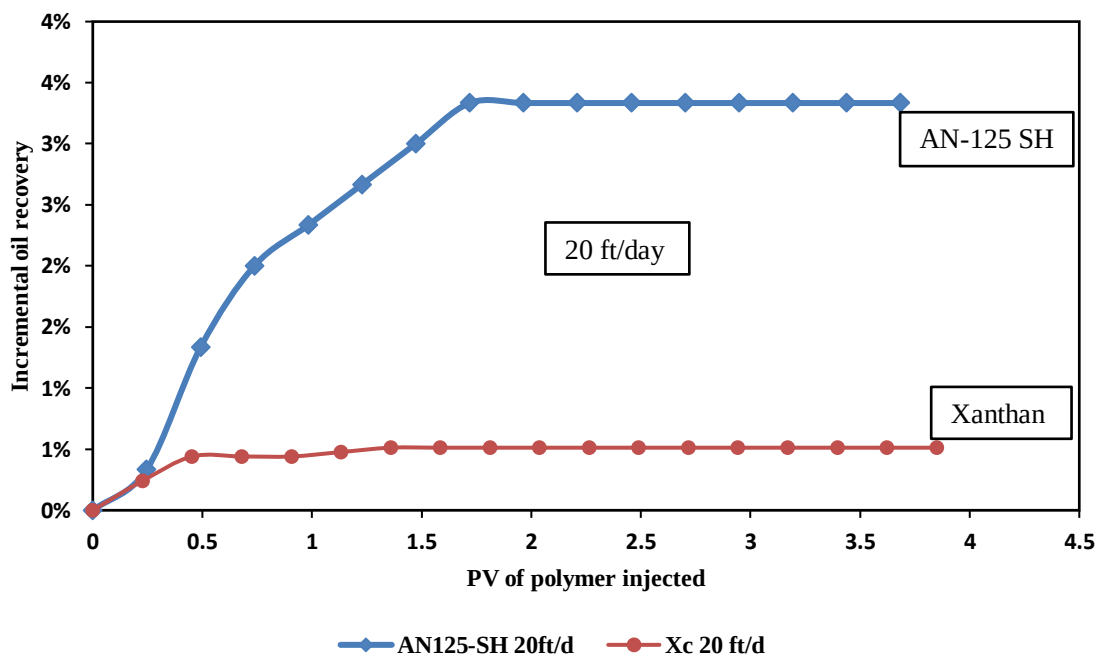


Figure 5-15 Comparison of incremental oil recovery for 2500 ppm AN-125 SH and 2000 ppm xanthan gum solutions at 20 ft/day at 75 °C

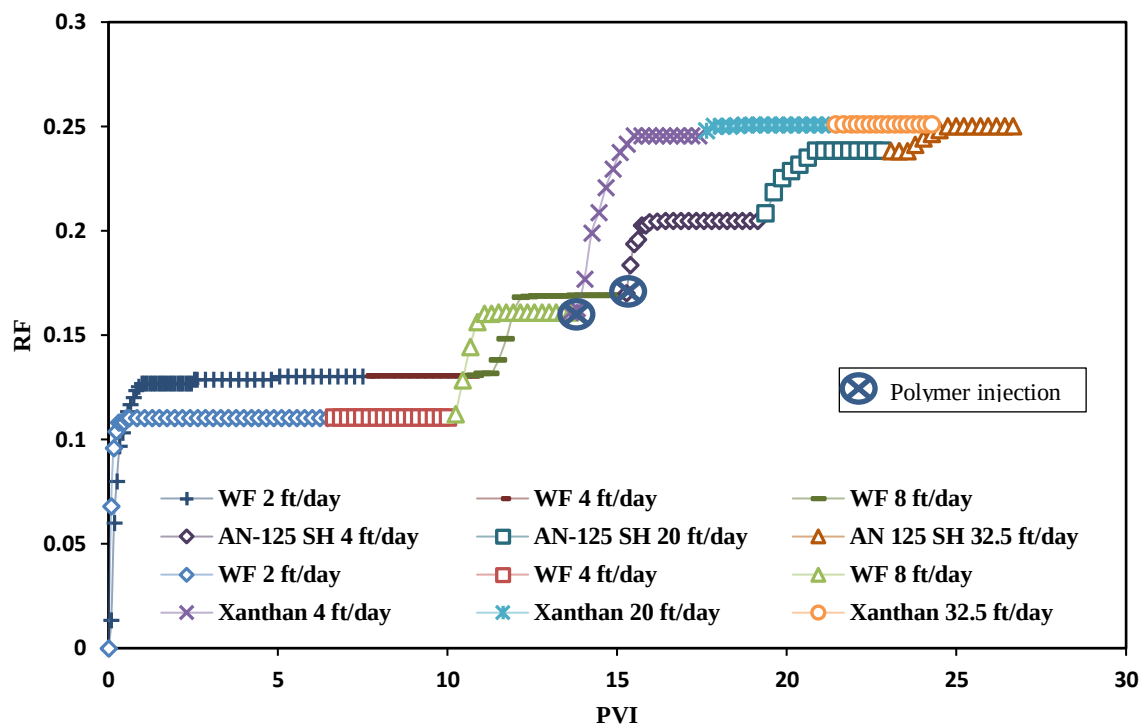


Figure 5-17 Comparison of oil recovery factor for 2500 ppm AN-125 SH and 2000 ppm xanthan gum solutions at different water and polymer flux rates at 75 °C

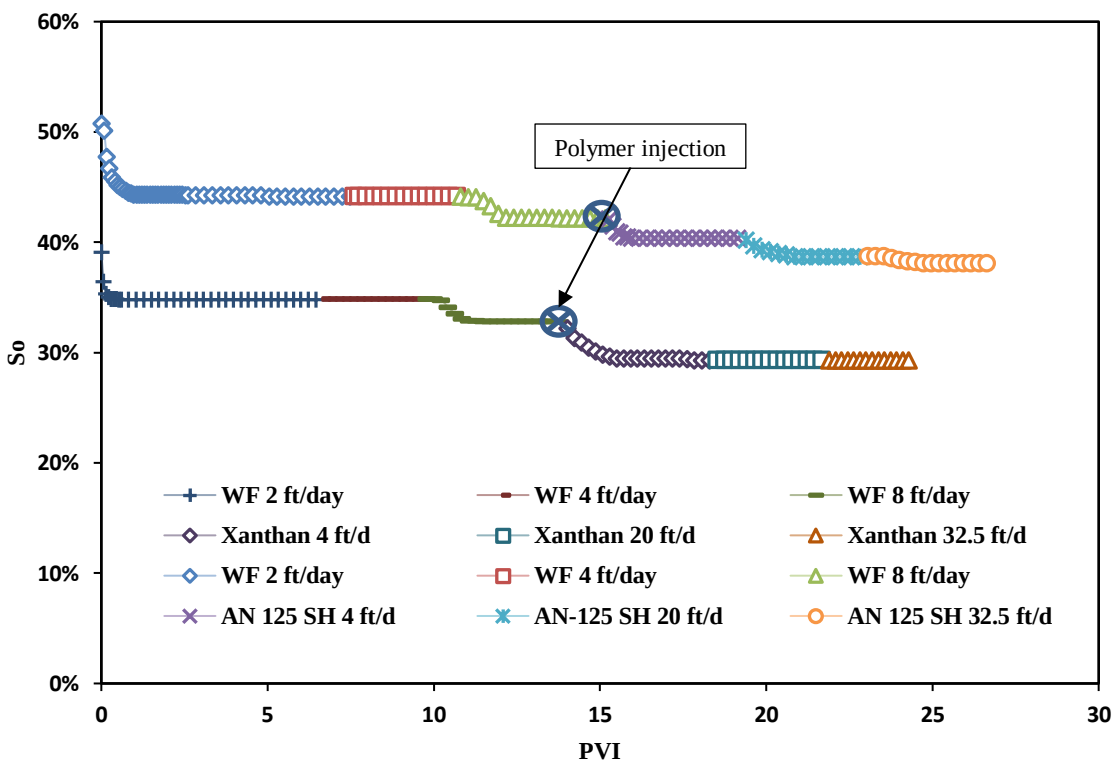


Figure 5-18 Comparison of oil saturation profile for 2500 ppm AN-125 SH and 2000 ppm xanthan gum solutions at varying flux rates at 75 °C

Table 5-4 Summary of core flooding experiments results

Exp #	Flood type	Viscosity, cP	Injection rate, ft/day	RF	End point S_o	IOR	Pressure gradient, psi/ft
Core #1 AN-125 SH 2500 ppm	WF1	0.57	2	13%	44%	N/A	0.14
	WF2	0.57	4	13%	44%	N/A	1.4
	WF3	0.57	8	17%	42%	4%	2.8
	P1	12	4	20.5%	40%	3.6%	8.1
	P2	6.5	20	23.8%	38.6%	3.3%	39.4
	P3	9.2	32.5	25%	37.9	1.2%	62
Core #2 Xanthan 2000 ppm	WF1	0.57	2	11%	35%	N/A	0.1
	WF2	0.57	4	11%	35%	N/A	0.4
	WF3	0.57	8	16.1%	33%	5%	0.8
	P1	34	4	24.6%	30%	8.5%	10.24
	P2	13.8	20	25.1%	29%	0.5%	24.6
	P3	9.8	32.5	25.1%	29%	0.0%	31.4

The results of this study contribute to the existing body of knowledge by demonstrating that viscoelastic polymers have the capacity to extract residual or challenging-to-recover oil in oil-wet settings. This is in comparison to biopolymers, even when both are subjected to identical injection conditions, within comparable porous media, and exhibit similar apparent viscosities within the core samples. Polymer flooding, a technique commonly employed within the petroleum industry, has traditionally been regarded as a method to enhance sweep efficiency, primarily targeting the recovery of mobile oil. Historically, it was not considered effective for recovering oil beyond what water flooding could achieve (Taber 1969; Lake 1989). However, several studies focusing on water-wet rocks has consolidated the understanding that viscoelastic polymers can indeed reduce residual oil saturation at higher fluxes due to their elastic properties at higher fluxes/ higher pressure gradients (Wang et al., 2000; Urbissionova et al., 2010; Clarke et al., 2016; Erincik et al., 2018; Qi et al., 2017; Koh et al., 2018; Barri et al., 2023).

Elastic effects in polymer flooding are typically induced by either high shear rates or by low-permeability conditions that cause polymers to stretch within constricted pore spaces, even at relatively low flux rates. In the study by Barri et al. (2023), the notable incremental oil recovery was achieved due to viscoelastic polymer injection at relatively low pressure gradient when compared to preceding viscous polymer injection. This could be due to the sample's low permeability (35 mD) where viscoelastic polymer can experience more stretchability. despite the application of relatively low Darcy flux rate of 0.2 ft/day. Further, the study by Clarke et al. (2016) conveyed that viscoelastic polymer can lead to relatively high residual oil recovery than a viscous polymer in 435-465 mD rock at the Darcy velocity of 0.23 ft/day. This despite the fact that the viscous polymer was exhibiting higher shear viscosity than the viscoelastic polymer around the flooding velocity. Although both sets of experiments were conducted using water-wet homogeneous sandstone cores, this present study shows positive impact of viscoelasticity on the mobilization of residual oil only in higher Darcy fluxes (20,32.5 ft/day) in non-water wet heterogeneous carbonate core samples.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

This research examines the role of viscoelastic polymers in mobilizing residual oil saturation within oil-wet carbonate rock samples and correlate the findings with those obtained using a biopolymer. The investigation was structured around two identical designed core flooding experiments. The polymer concentrations were carefully selected to ensure they yielded analogous apparent viscosities within the core samples, a fact substantiated by single-phase flooding experiments within comparable porous media. Additionally, this study delves into the influence of varied molecular weights and concentrations on the relaxation times of the sulfonated polymer AN-125, utilizing both steady shear and oscillatory rheological methods. The insights gained from this work are summarized below:

- 1- The non-linear relaxation time of AN-125 SH polymer, exhibits an increase with the polymer's molecular weight, a trend that becomes particularly evident when data is densely sampled during steady shear rheometry.
- 2- Variations in the gap of the concentric cone and cylinder geometry utilized in testing do not influence the non-linear relaxation time of AN-125 SH.
- 3- There is a direct correlation between the concentration of AN-125 SH polymer and its linear relaxation time, with this relationship being more pronounced and consistent when observed through steady shear rheometry rather than oscillatory shear.

- 4- At shear thinning flux (4 ft/day) xanthan gum led to higher recovery compared to viscoelastic sulfonated polymer.
- 5- When compared to xanthan gum, sulfonated viscoelastic polymer led to higher oil recovery factor of 1.2% and 3.3% respectively only at shear thickening fluxes (Darcy) of 20 and 32.5 ft/day, thereby conveying that viscoelastic effect gets dominated only at high fluxes in the candidate heterogeneous carbonate rock.
- 6- The heterogeneity and the high pore sizes of the core samples hinders oil saturation levels. The overall efficiency of the sweep during the flooding process were lower than what is usually reported with standard sandstone cores in the literature.

6.2 Proposed future works

As a complementary of this work, it is advisable to pursue additional exploration into the use of viscoelastic polymers for mobilization of residual oil in oil-wet carbonate formations, some additional aspects are required to better understand and verify the reported findings.

- Verify the oil wettability of the samples by assessing the Amott index using Amott-Harvey cell.
- Explore and compare the mobilization of residual oil using high salinity viscoelastic polymers at high shear rates, ensuring the viscosity ratio is similar to this work.
- Assess the oil recovery capabilities with viscoelastic polymers in homogeneous core samples, across both low and high salinity environment.
- Determine the effectiveness of oil mobilization with viscoelastic polymers at practical flooding rates.
- Investigate the combined use of conformance control fluids and oil mobilization fluids to enhance recovery in heterogeneous, fractured reservoirs.

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Appendix A

Amplitude & Frequency sweep tests for AN-125 SH 10,000 ppm

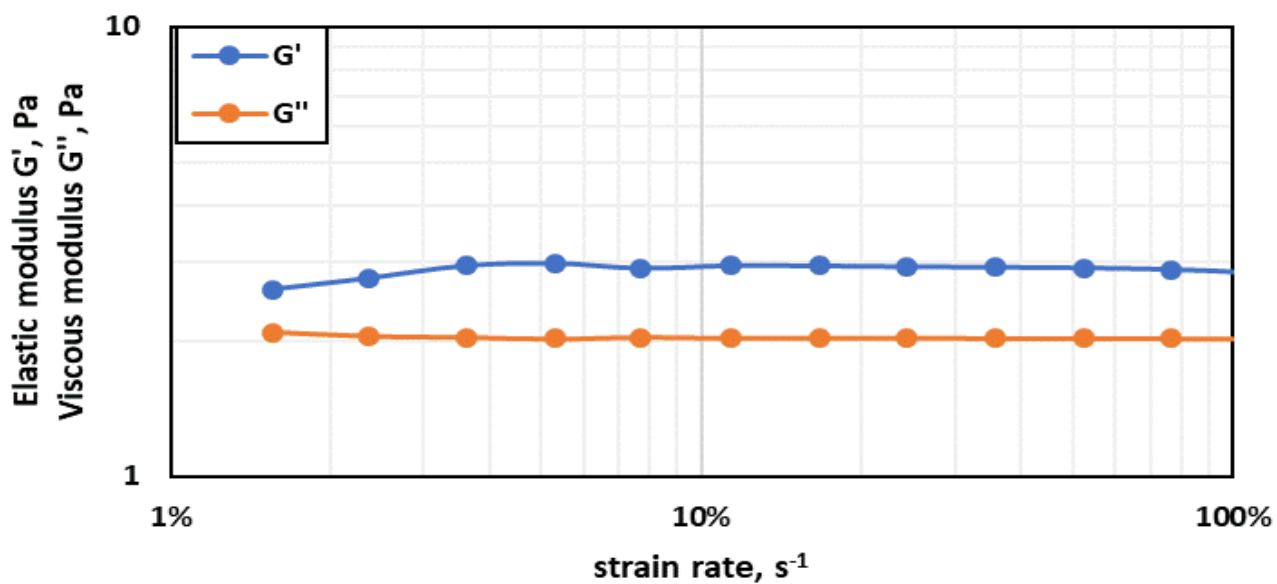


Figure 0-1 Amplitude sweep for 10,000 ppm AN-125 SH polymer at 5767 ppm brine at 75°C

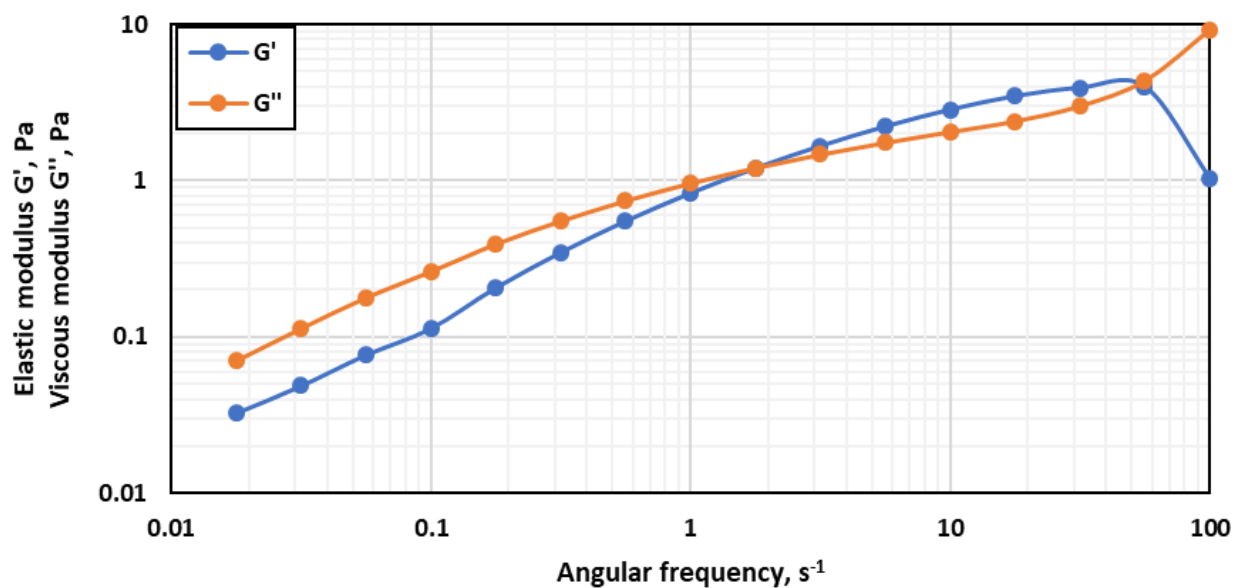


Figure 0-2 Frequency sweep for 10000 ppm AN-125 SH polymer at 5767 ppm brine at 75°C

Amplitude & Frequency sweep tests for AN-125 SH 5000 ppm

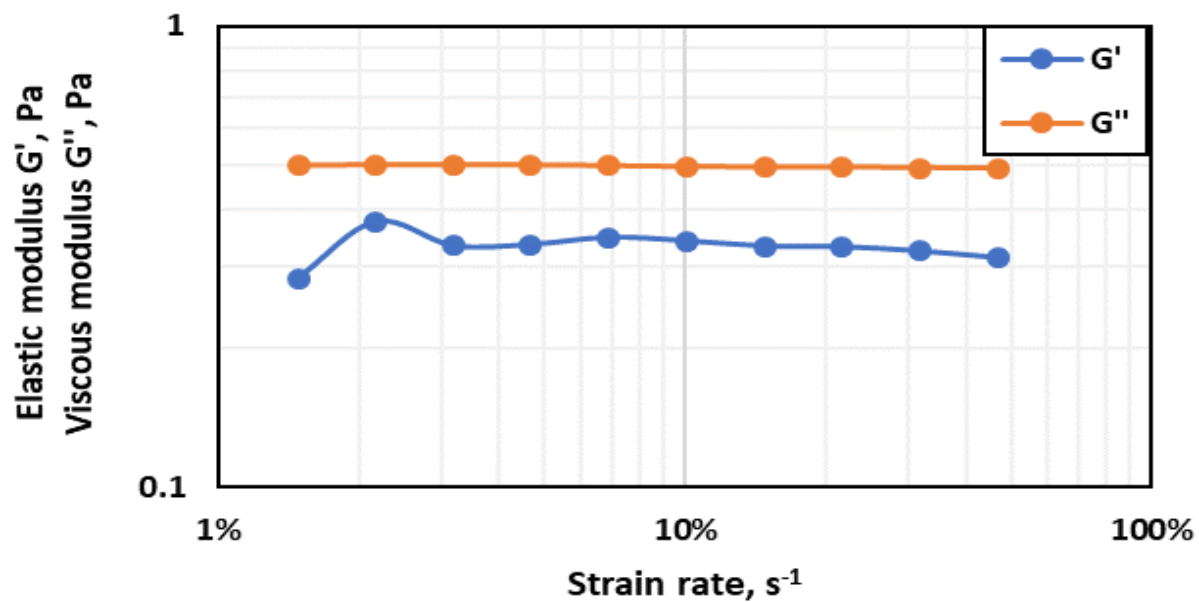


Figure A-3 Amplitude sweep for 5000 ppm AN-125 SH polymer at 5767 ppm brine at 75°C

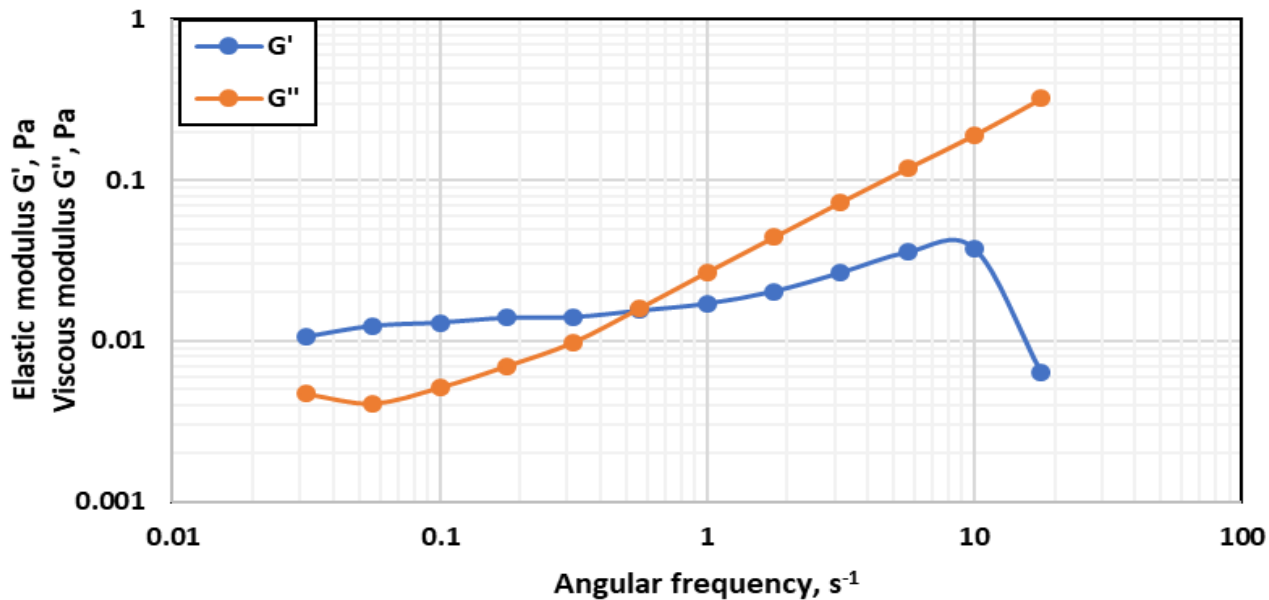


Figure 0-4 Frequency sweep for 5000 ppm AN-125 SH polymer at 5767 ppm brine at 75°C

Amplitude & Frequency sweep tests for AN-125 SH 4000 ppm

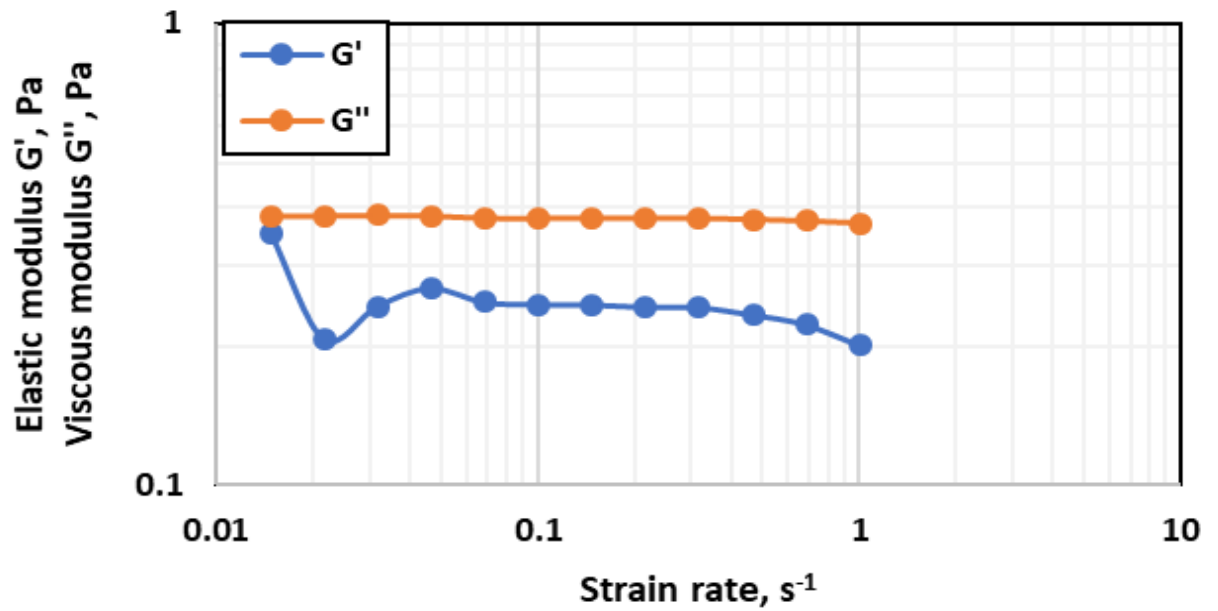


Figure 0-5 Amplitude sweep for 4000 ppm AN-125 SH polymer at 5767 ppm brine at 75°C

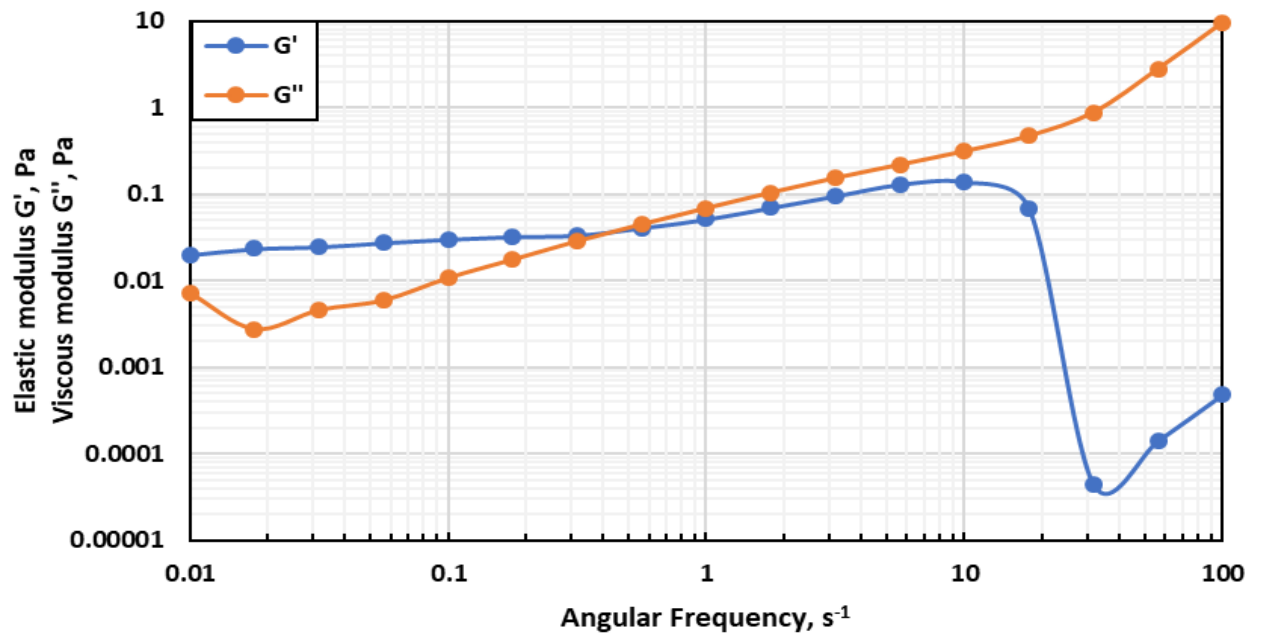


Figure 0-6 Frequency sweep for 4000 ppm AN-125 SH polymer at 5767 ppm brine at 75°C

Amplitude & Frequency sweep tests for AN-125 SH 3500 ppm

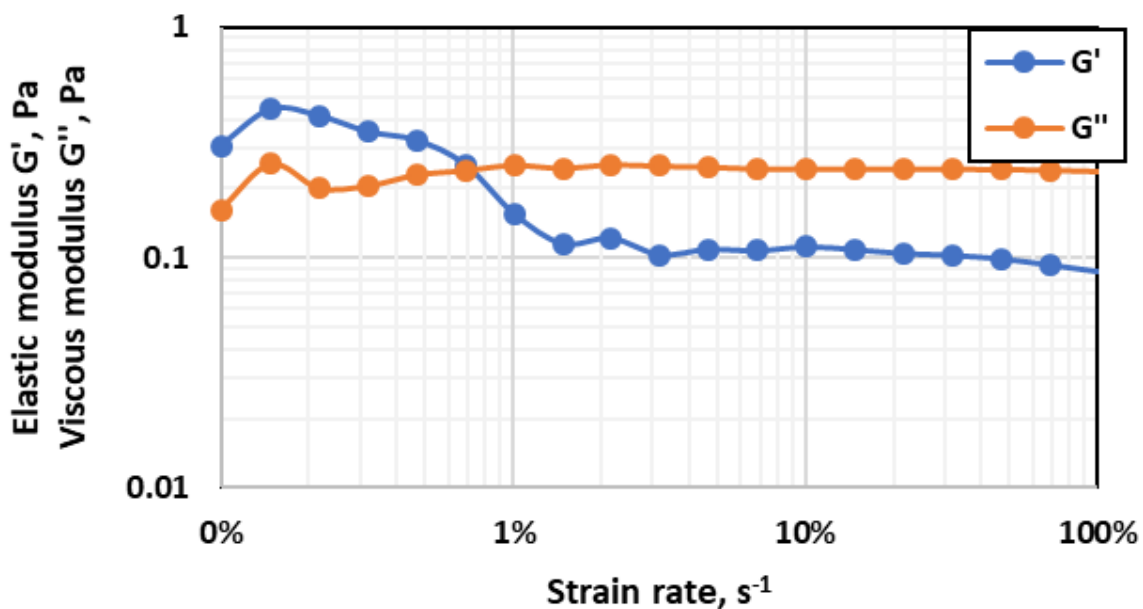


Figure 0-7 Amplitude sweep for 3500 ppm AN-125 SH polymer at 5767 ppm brine at 75°C

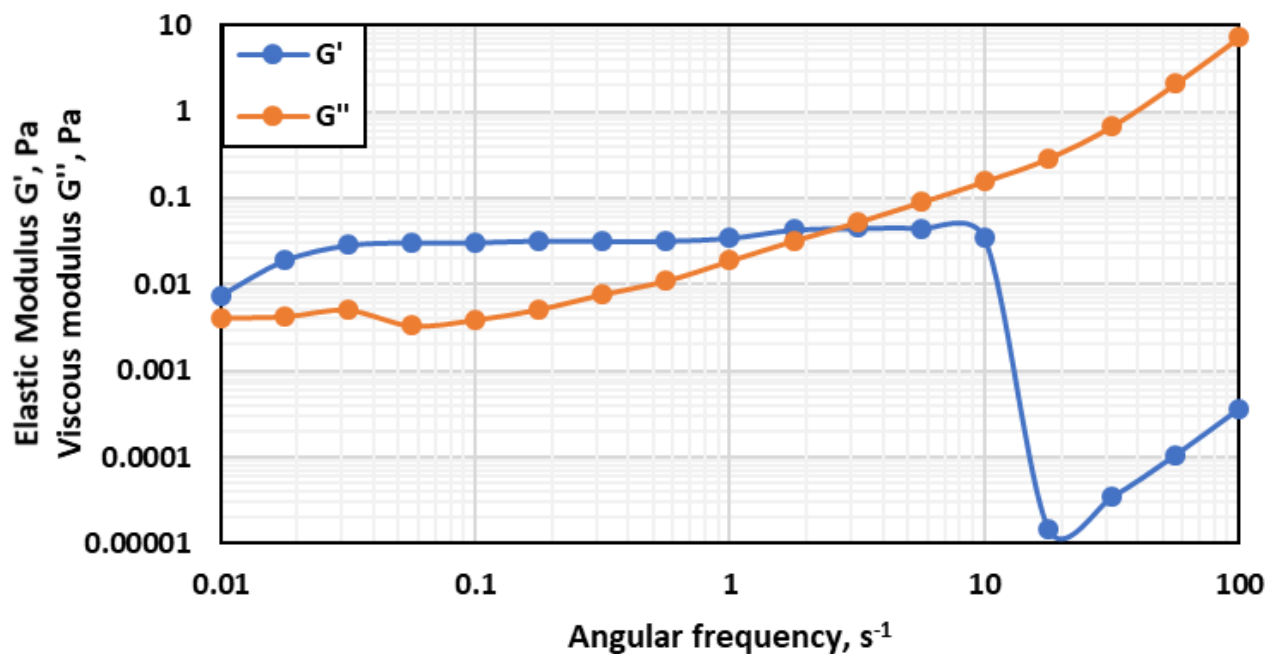


Figure 0-8 Frequency sweep for 3500 ppm AN-125 SH polymer at 5767 ppm brine at 75°C

Amplitude & Frequency sweep tests for AN-125 SH 3000 ppm

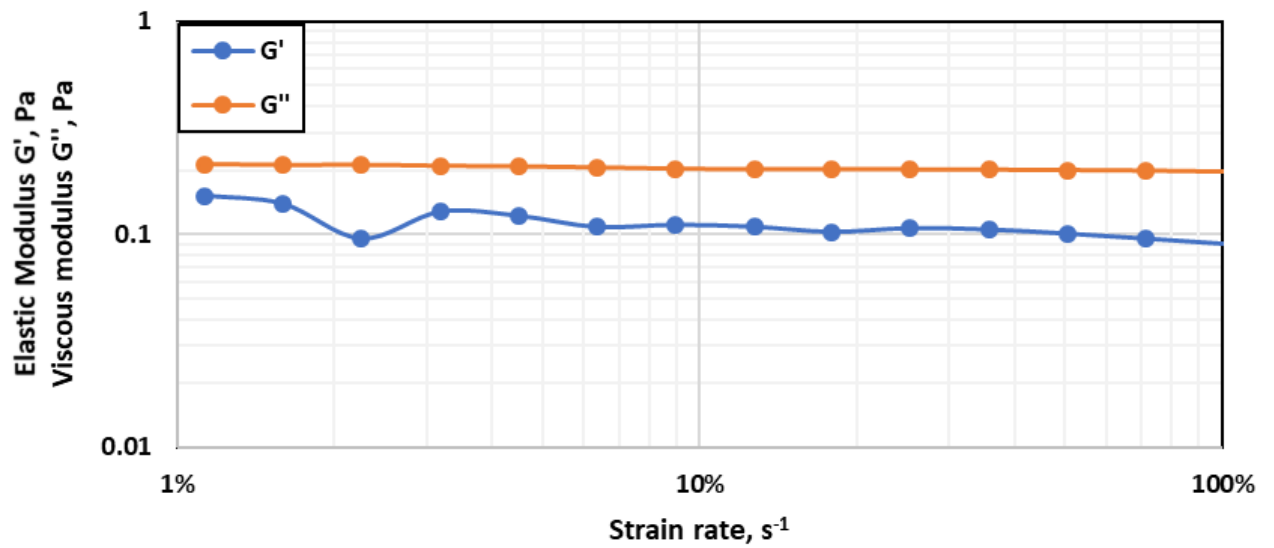


Figure 0-9 Frequency sweep for 3000 ppm AN-125 SH polymer at 5767 ppm brine at 75°C

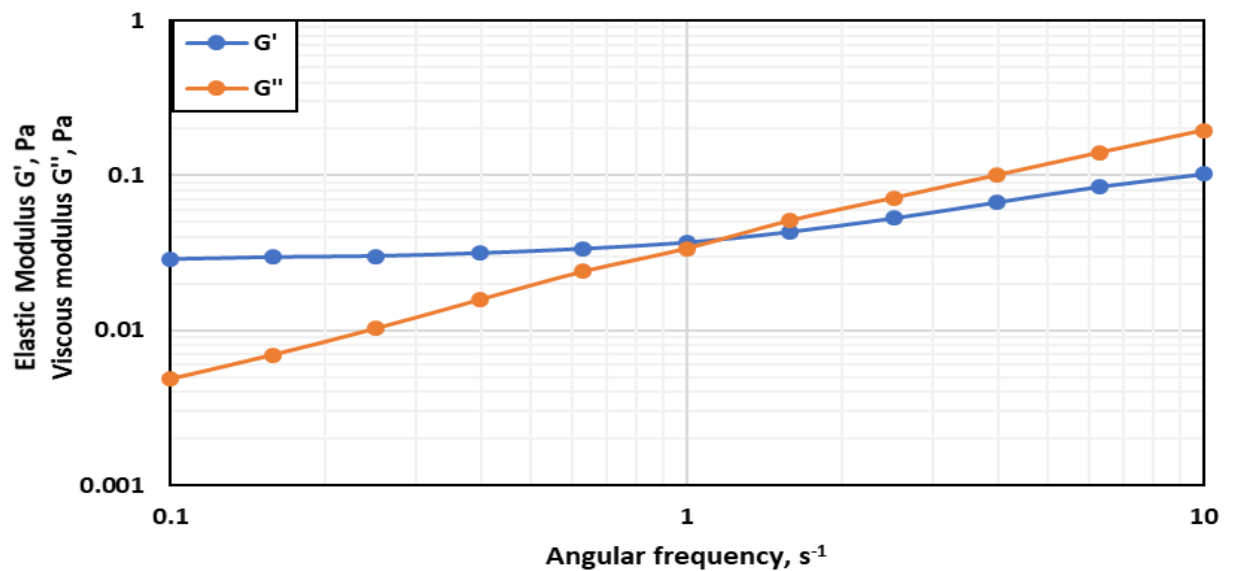


Figure 0-10 Frequency sweep for 3000 ppm AN-125 SH polymer at 5767 ppm brine at 75°C

Amplitude & Frequency sweep tests for AN-125 SH 2500 ppm

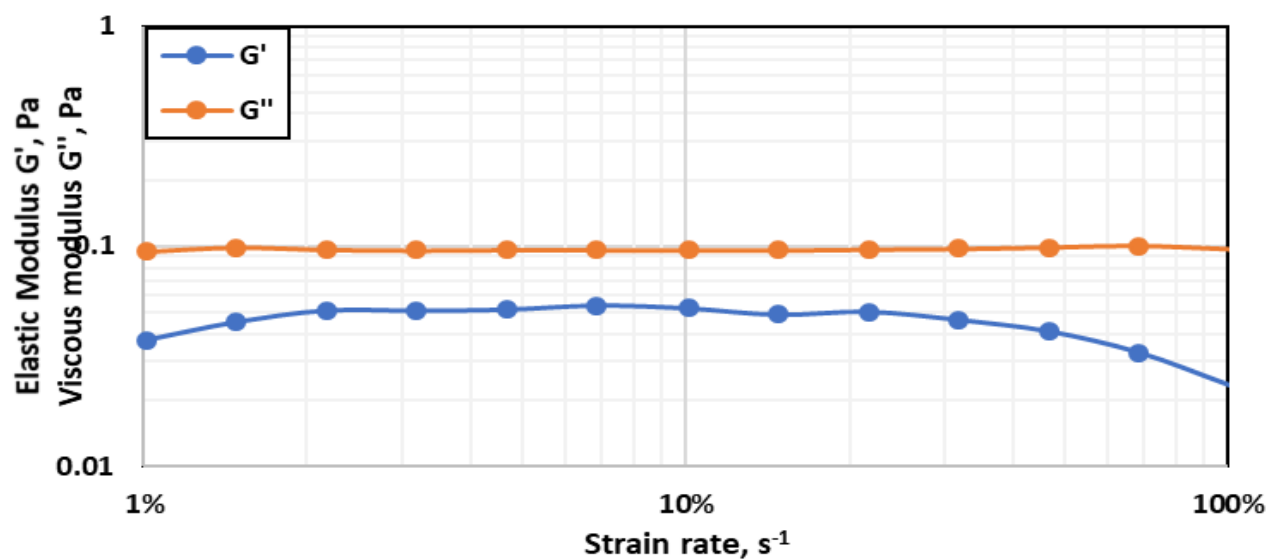


Figure 0-12 Amplitude sweep for 2500 ppm AN-125 SH polymer at 5767 ppm brine at 75°C

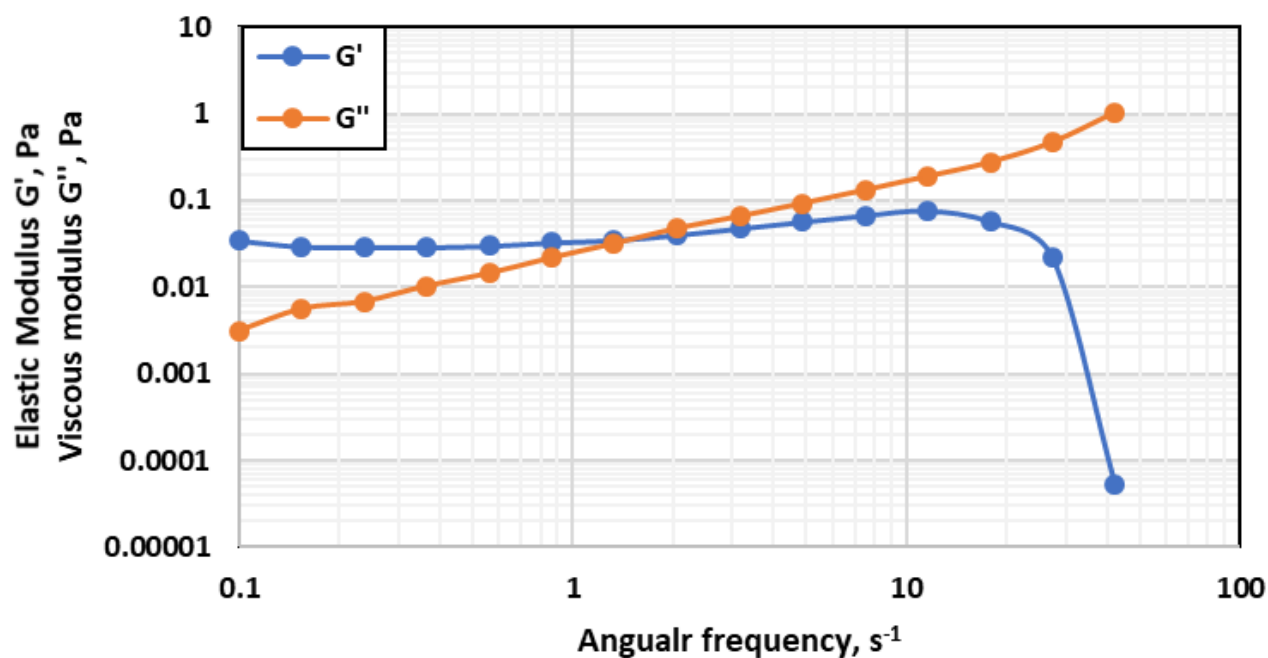


Figure 0-11 Frequency sweep for 2500 ppm AN-125 SH polymer at 5767 ppm brine at 75°C

Amplitude & Frequency sweep tests for AN-125 SH 2000 ppm

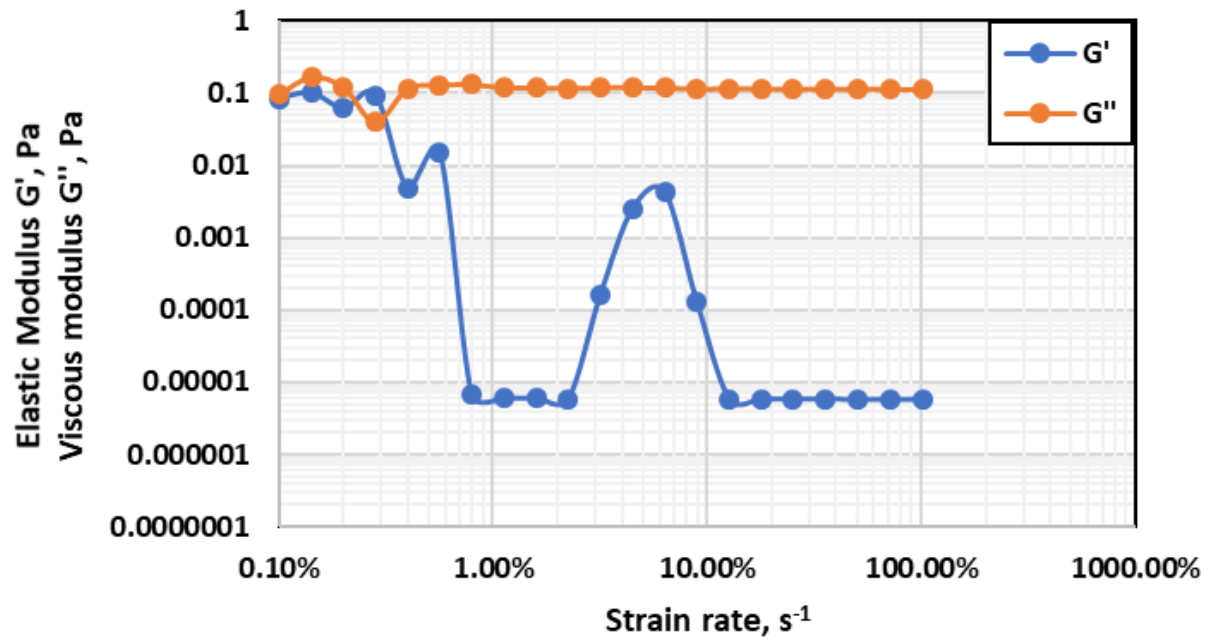


Figure 0-13 Amplitude sweep for 2000 ppm AN-125 SH polymer at 5767 ppm brine at 75°C

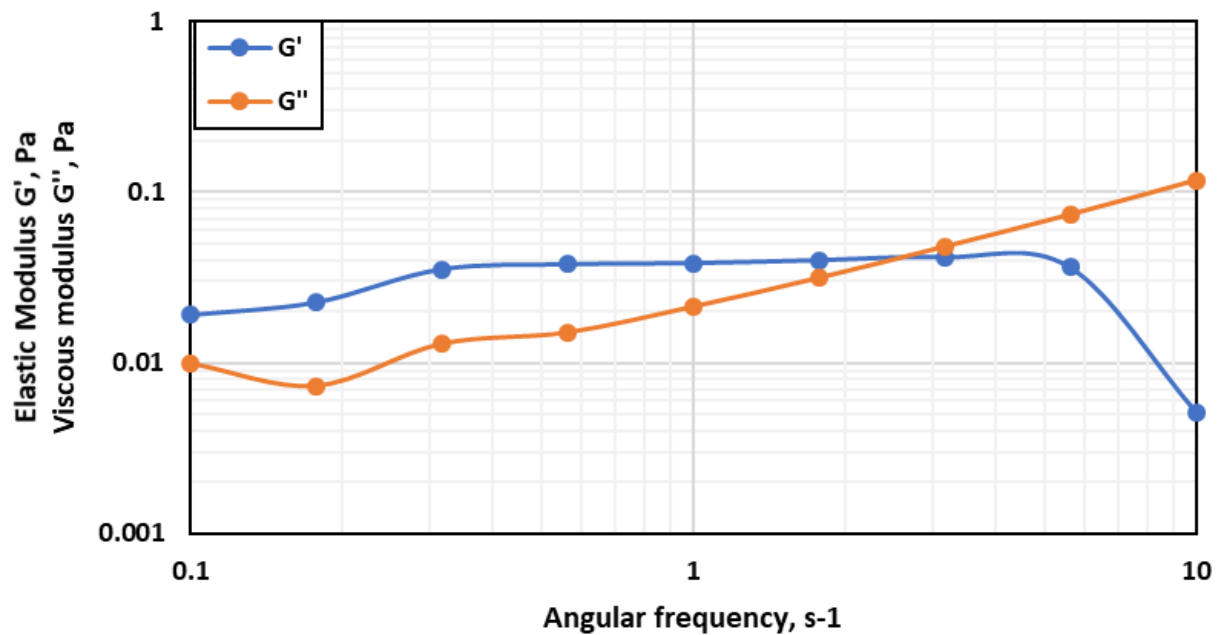


Figure A-14 Frequency sweep for 2000 ppm AN-125 SH polymer at 5767 ppm brine at 75°C

Amplitude & Frequency sweep tests for AN-125 SH 1000 ppm

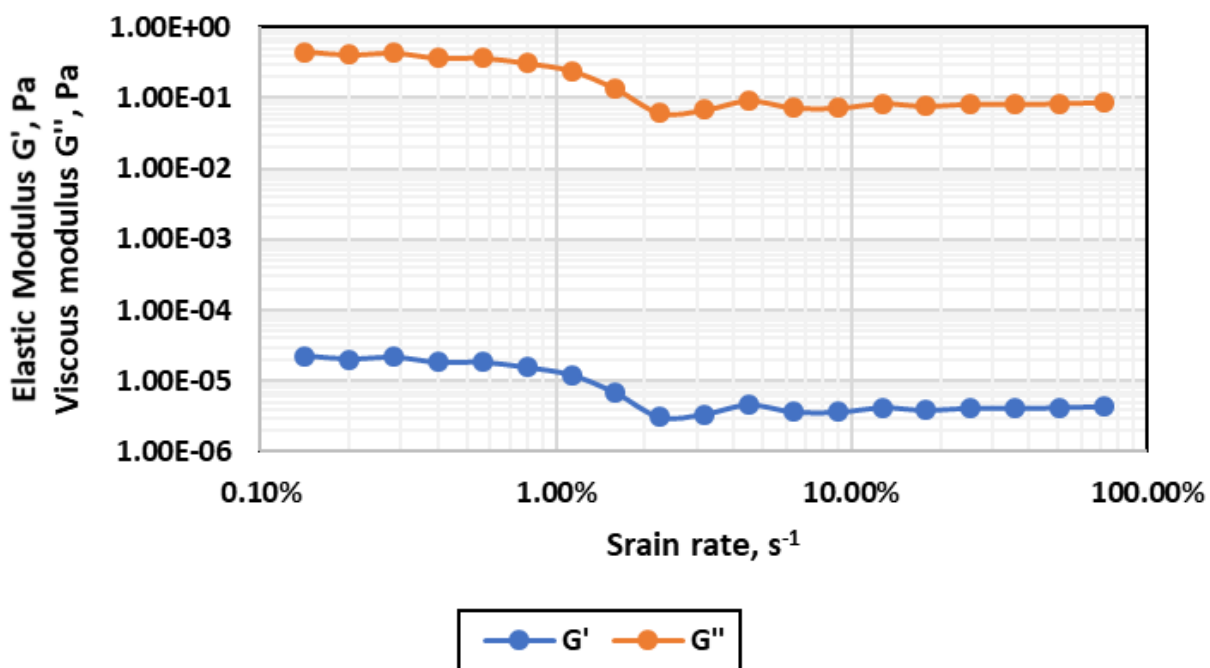


Figure 0-15 Amplitude sweep for 1000 ppm AN-125 SH polymer at 5767 ppm brine at 75°C

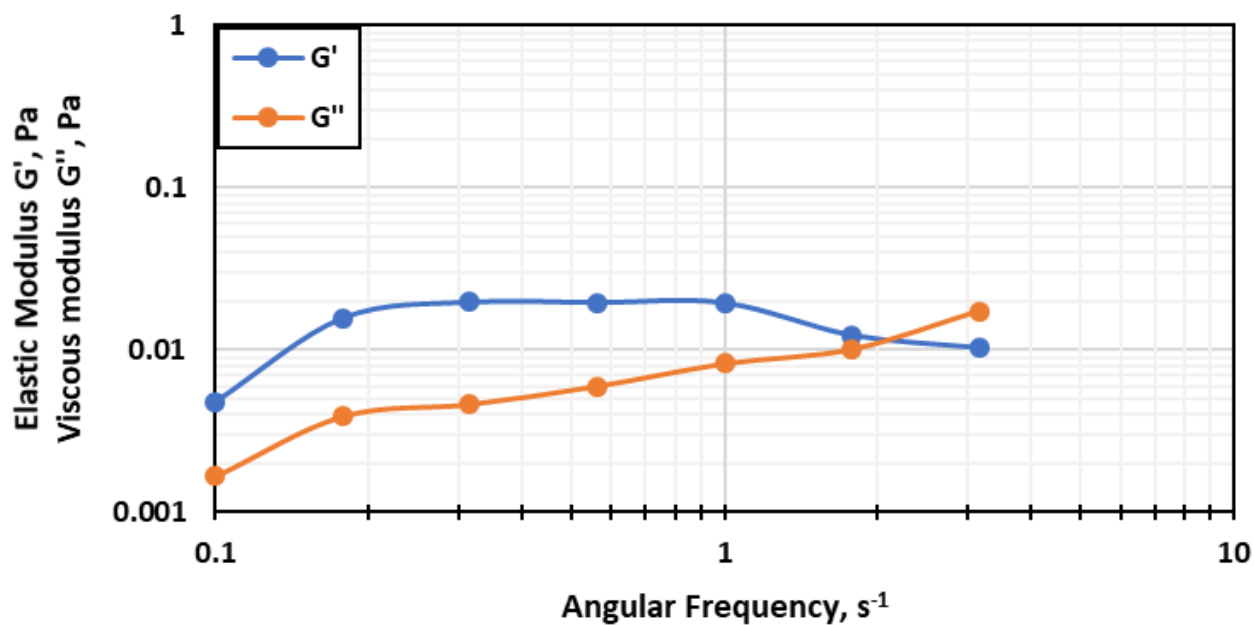


Figure 0-16 Frequency sweep for 1000 ppm AN-125 SH polymer at 5767 ppm brine at 75°C

Amplitude & Frequency sweep tests for AN-125 SH 500 ppm

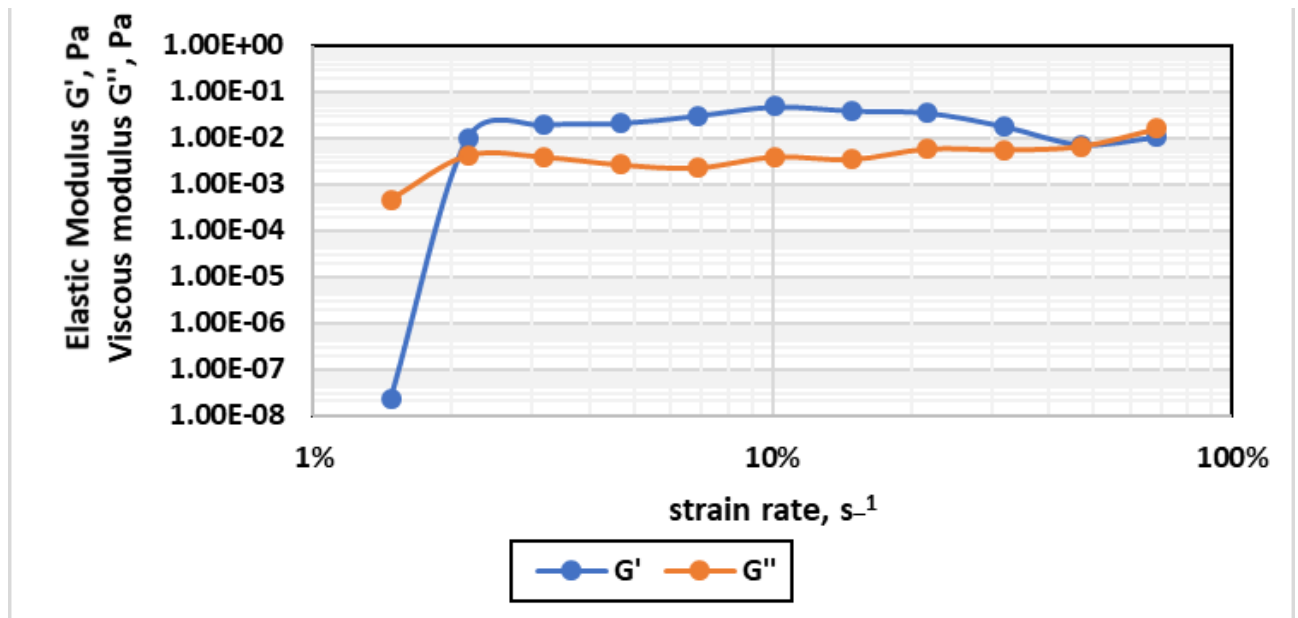


Figure 0-17 Amplitude sweep for 500 ppm AN-125 SH polymer at 5767 ppm brine at 75°C

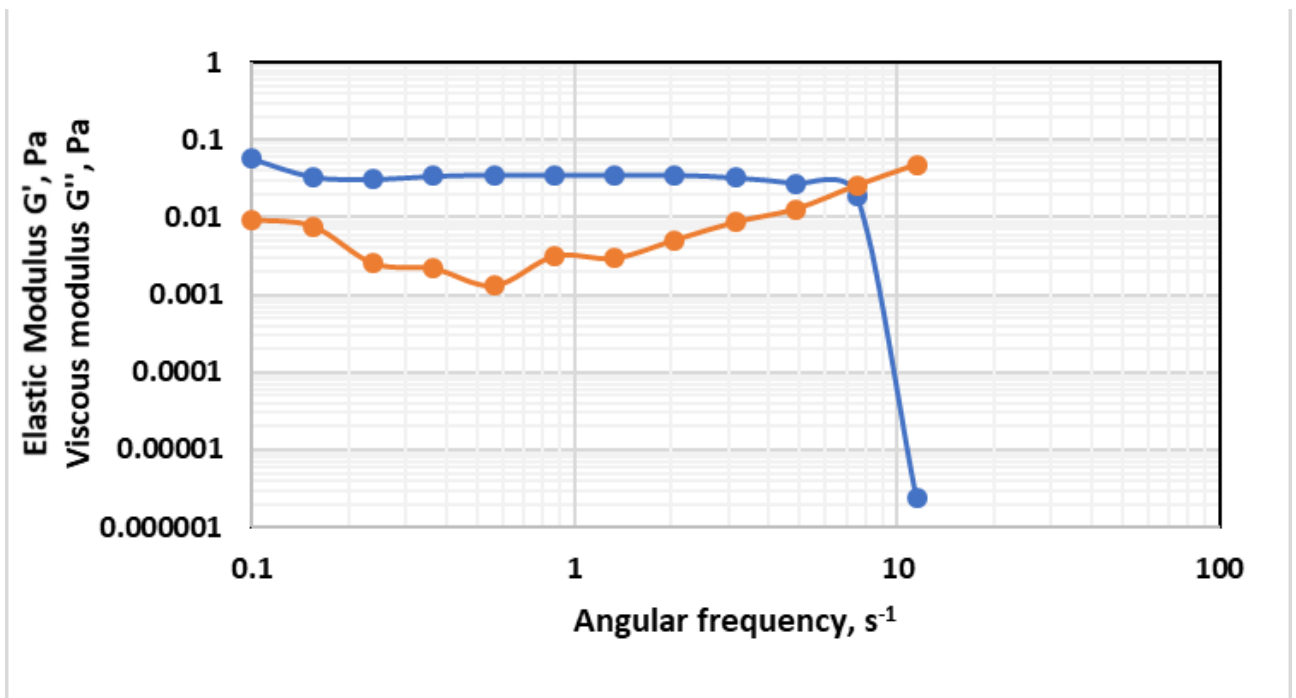


Figure 0-18 Frequency sweep for 500 ppm AN-125 SH polymer at 5767 ppm brine at 75°C

Amplitude & Frequency sweep tests for AN-125 SH 250 ppm

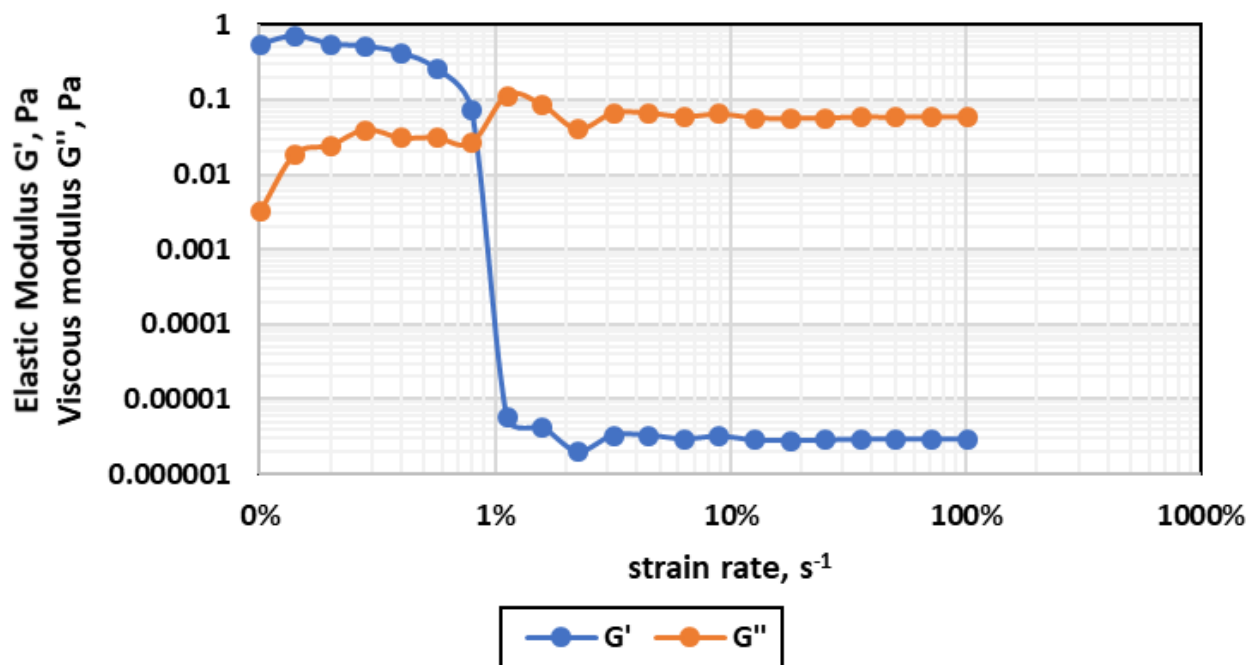


Figure 0-19 Amplitude sweep for 250 ppm AN-125 SH polymer at 5767 ppm brine at 75°C

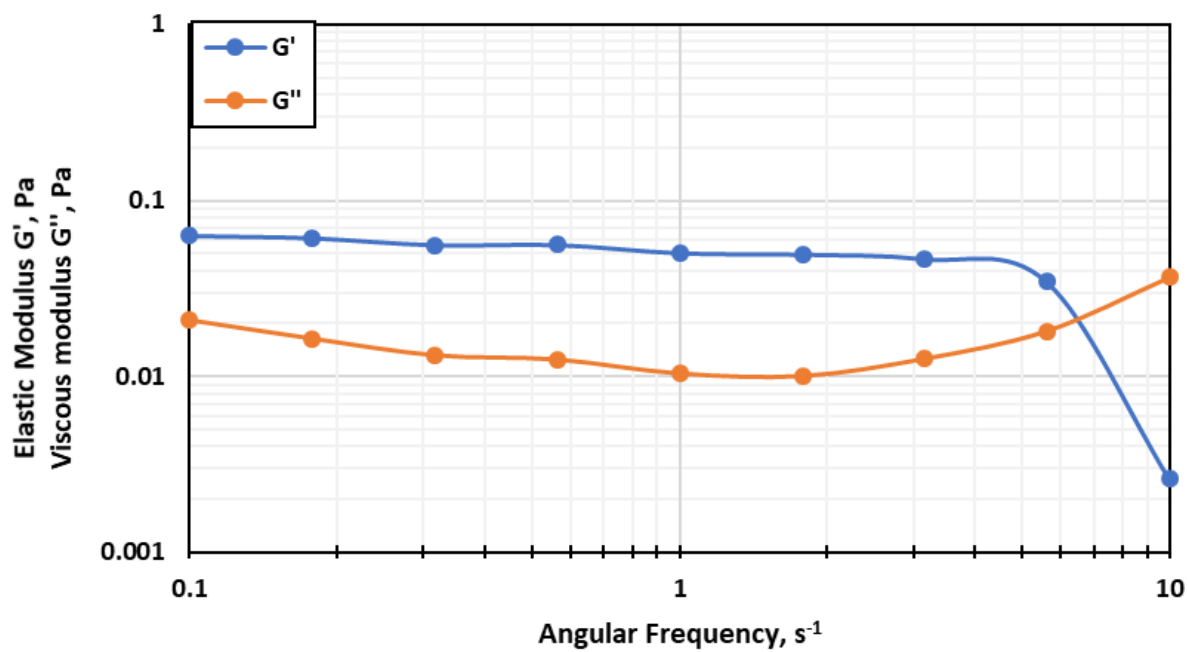


Figure 0-20 Frequency sweep for 250 ppm AN-125 SH polymer at 5767 ppm brine at 75°C

Amplitude & Frequency sweep tests for AN-125 SH 100 ppm

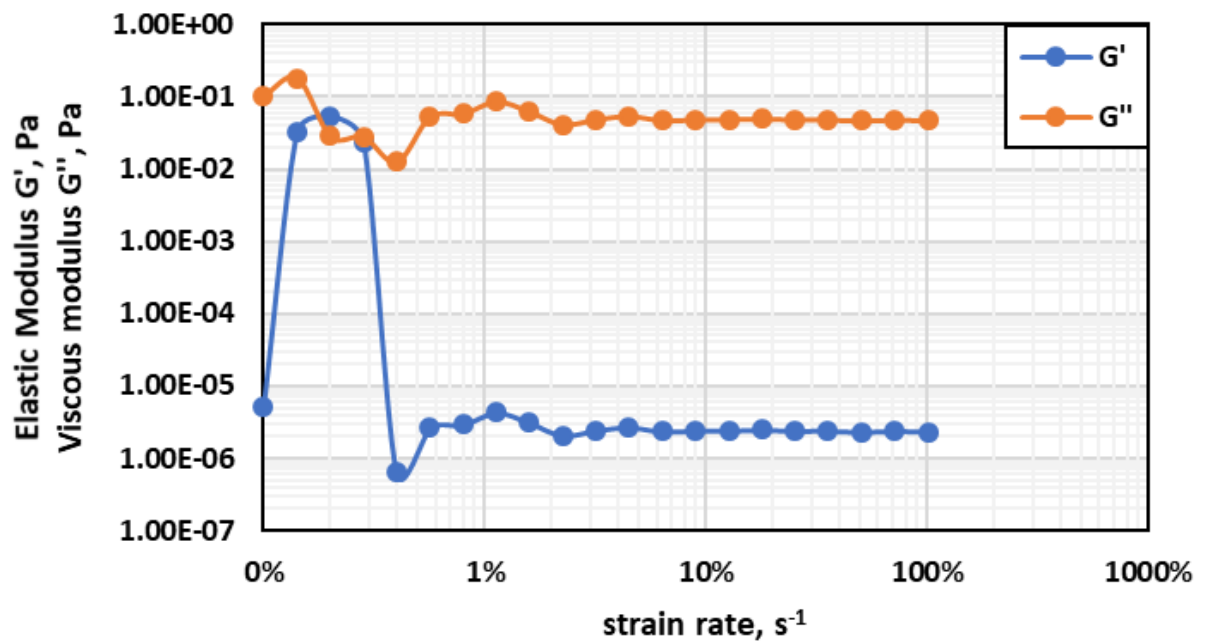


Figure 0-21 Amplitude sweep for 100 ppm AN-125 SH polymer at 5767 ppm brine at 75°C

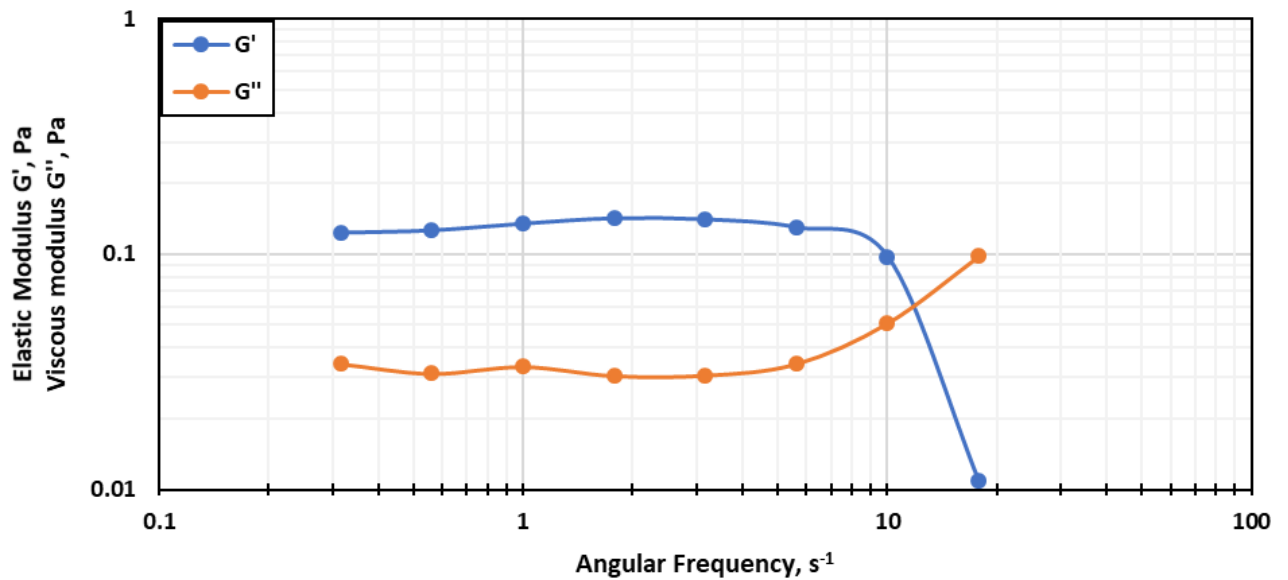


Figure 0-22 Frequency sweep for 100 ppm AN-125 SH polymer at 5767 ppm brine at 75°C

Amplitude & Frequency sweep tests for AN-125 SH 60 ppm

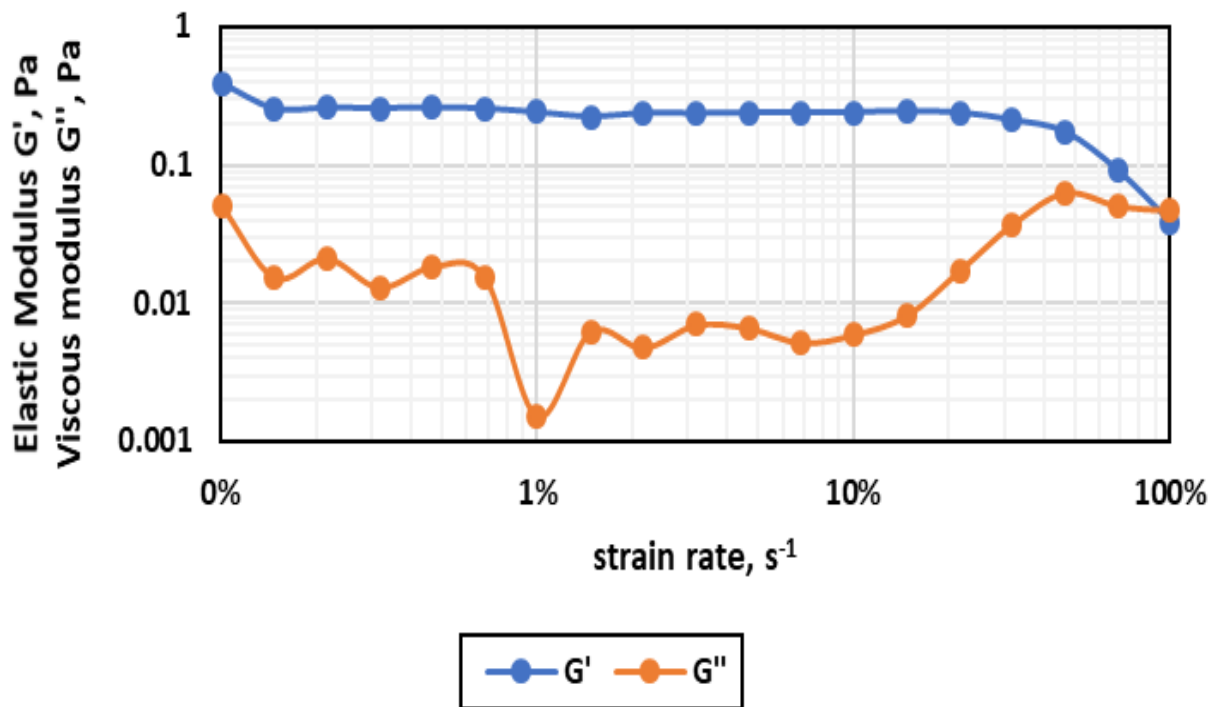


Figure 0-23 Amplitude sweep for 60 ppm AN-125 SH polymer at 5767 ppm brine at 75°C

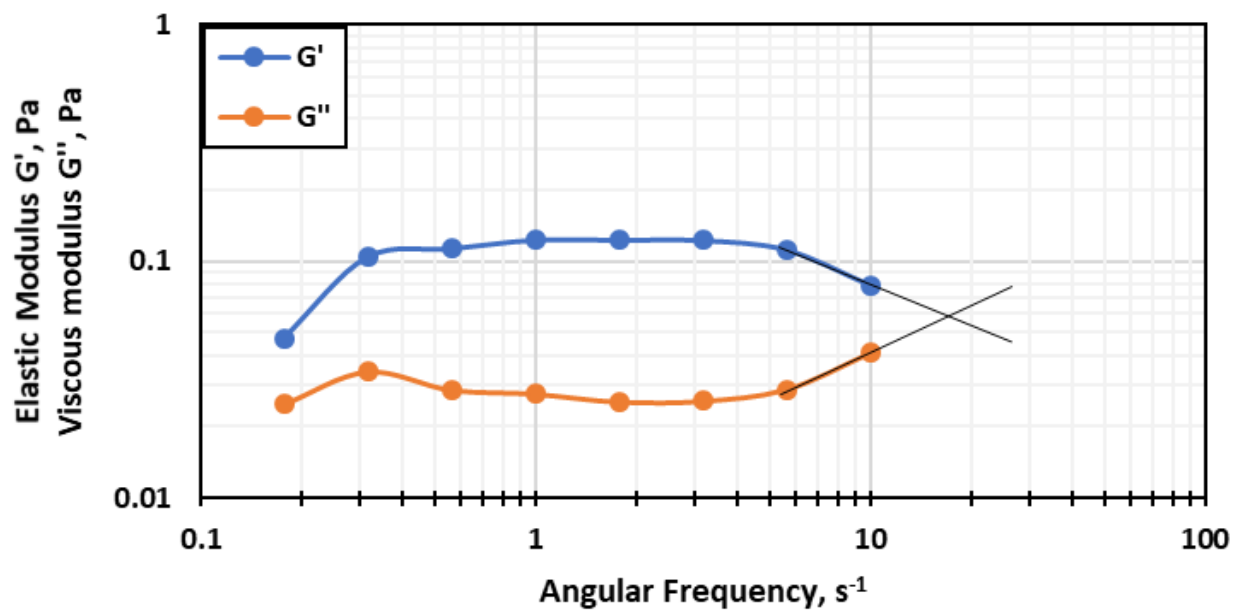


Figure 0-24 Frequency sweep for 60 ppm AN-125 SH polymer at 5767 ppm brine at 75°C

Vitae

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Publications

1. Alvayed D., Khalid M.S., **Dafaalla, M.**, Ali, A., Ibrahim, A., Weijermars, R. 2023, "Probabilistic estimation of hydraulic fracture half-lengths. Validating the Gaussian pressure transient method with the traditional RTA-method. (wolfcamp case study)" Journal of Petroleum Exploration and Production Technology _ **Published.**
2. **Moaz Dafaalla**, Madhar Sahib Azad, Syed Rizwan, Dhafer Al-Shehri, Subhash Ayirala, Mohammed Mahmoud, Ali Al-Yousef, "Does Core-Length Matter for Mobility Control Displacements in Core?" **Accepted-after revision** in Arabian Journal for Science and Engineering.
3. Oil recovery potential of viscoelastic sulfonated polymer in Heterogeneous carbonate reservoir (**in prep.**).
4. Examining the utility of oscillatory and steady-shear rheometry to measure linear viscoelastic properties for HPAM polymer (**in prep.**).