QATAR UNIVERSITY

COLLEGE OF ENGINEERING

DEVELOPMENT OF POLYMERIC CROSSLINKABLE FORMULATIONS FOR CONFORMANCE CONTROL IN OIL AND GAS RESERVOIRS

BY

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ABSTRACT

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Title: Development of Polymeric Crosslinkable Formulations for Conformance Control In Oil and Gas Reservoirs

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Excessive water production from oil reservoirs is a main challenge facing the oil and gas industry nowadays. Polymers and crosslinkers are mixed to form gelants that are widely applied to seal water production zones leading to a more environment-friendly and economically-feasible production. While crosslinkers alternatives are limited and monopolized in the market, this thesis herein intends to explore other alternatives with improved performance for low and high temperature reservoirs. This thesis is divided into three main parts. The first part (chapter 4.a) intends to reinforce the conventional Polyacrylamide (PAM) /Polyethyleneimine (PEI) gelant using nanosilica as mechanical degradation is reported as shortcoming for this gel at high-temperature reservoirs. Differently sized nanosilica particles were investigated where the optimum reinforcement effect resulted from the 50 nm silica. The second part (chapter 4.b and 4.c) screens different functionalized silica based on the ability on crosslinking PAM. Gelation kinetics and rheological behavior of the newly developed systems were investigated nominating triamine-functionalized silica as an excellent replacement for Polyethyleneimine at high temperatures (>100 ^{o}C). The gel produced from PAM / triamine-functionalized silica was superior to all conventional gels with a gel strength of more than 5 times higher than the conventional PAM/PEI. The last part (chapter 4.d) screens different aluminum-based crosslinkers to replace the toxic chromium acetate, which is currently use. Aluminum Acetate (AlAc) was found to be the best among the screened inorganic crosslinkers in terms of gelation controllability, low settling rate, and viscoelastic behavior and temperature application window. Furthermore, PAM/AlAc gel was proven to be thermally stable in the range from 25 to 100 ^{o}C. Overall, the developed organic and inorganic crosslinkers have proven to work in the whole temperature range that is of interest to the oil and gas industry (25o-130oC) and have shown either equivalent or superior performance over the conventional crosslinkers. The application of the developed formulations is intended for water control as well as fracture sealing. The MS Thesis outcomes include: One filed US Patent, three published journal articles, and two submitted manuscripts.

***Key Words*:** Conformance Control, Water Shut-off, Gelation, Polyacrylamide, Polyethyleneimine, Nanosilica, Aluminum crosslinkers.

DEDICATION

I dedicate this work to my parents, my brother, and my sister for their endless support, and to my academic mentors, Prof. Ibnelwaleed Hussein and Dr. Mustafa Nasser for having their faith in my potentials

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

Chapter 1: Introduction

1.1. Research Overview

Natural gas and oil are expected to remain as the main contributors to the power generation industry for at least the next two decades, which creates a snowballing demand [1]. For decades, technologies and application techniques in the drilling and production of oilfields have developed to ensure a smooth, cost-effective, and optimized production. The field has widely broadened as polymers have been introduced serving many purposes and achieving many successes in the oil and gas industry [2]. The application of polymers extends to almost all stages in the lifetime of a reservoir. During the drilling stage, polymers are used as a main component in the drilling fluid serving as thickener besides other functionalities [3]. Moreover, polymers have been recently used as loss circulation materials (LCMs) and wellbore strengthening agents providing a smooth drilling operation [4]. Moving to the primary and secondary production stages, polymers are used in water-shutoff, aiming to decrease the percentage of water produced from oil reservoirs [5]. In tertiary recovery, most of the chemical treatments in enhanced oil recovery nowadays are polymer-based targeting reducing the affinity of oil-rock interaction [6]. Finally, polymers are also used in hydraulic fracturing for depleted reservoirs [7].

Excessive water production from oil and gas wells is considered as one of the main challenges that influences the feasibility of production. It is estimated that the daily global production of water from oil reservoirs is around 220 million barrels; confining to a global average of 3:1 water to oil ratio [8]. Processing this unwanted water, from separation to de-oiling and pumping, can be a lengthy and costly process that will increase the worldwide annual water handling cost to more than 40 billion dollars [9]. Beside the economic factor, the presence of water in the pipes and mid-stream facilities induces other problems including but not limited to, scale formation, corrosion, and microbial growth [10,11]. Reducing the quantity of produced water not only impacts the cost of operation, but it also enhances the lifetime of the well and increases the recovery factor [12]. Therefore, given the prevailing high water production and its associated problems as well as the strict environmental constrains of disposing it; there has been growing appeals for reducing the produced quantities to maintain an environment-friendly and a profitable operation [13].

Conformance control is generally defined as the measures taken to deal with excessive water production or poor sweep efficiency aiming to improve the productivity and stability of reservoirs [14]. Hamza et al. [15] have recently reported the main root causes for conformance control such as natural fractures, reservoir heterogeneity and behind pipe flow. Figure 1.1 shows the general classification of conformance problems. Determination of the type of conformance problem is the key to select the suitable polymer to be applied. A common strategy used to deal with such problems is the placement of crosslinkable polymeric systems.

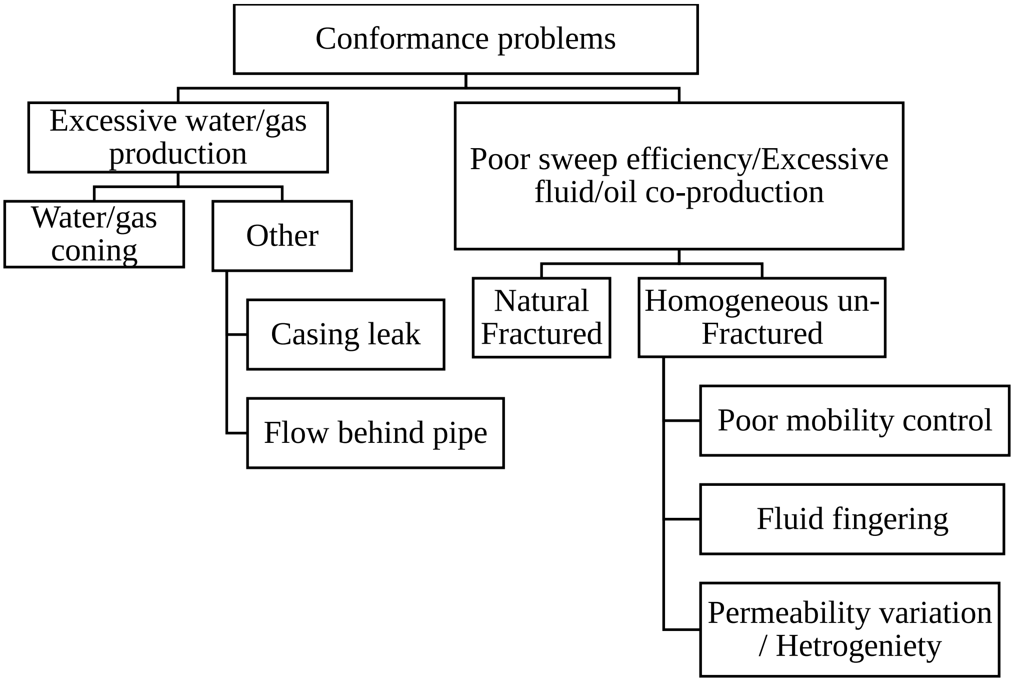


Figure 1.1 Classification of conformance problem

It’s crucial in the homogeneous formations to distinguish between high permeability regions and fractures. Furthermore, the formation anisotropic nature should also be considered in dealing with vertical and horizontal conformance problems properly. Generally, depending on the stress distribution at deep reservoirs the fractures tend to be vertically oriented, however, at shallow depths they are horizontal. Based on the geological conditions such as tectonic stress, the high permeability variations in the pay zone can include complex features such as channels, faults, vugular porosity, fracture networks which complicates the treatment process and requires an appropriate placement technique [16].

A whole range of different approaches to the problem are proposed and applied in oil reservoirs. Several industries have proposed the use of mechanical treatments such as the use of packers and inflow control devices, which selectively passes the oil over other fluids [17,18]. Nevertheless, Chemical treatments have been shown to cope with the problem more efficiently [15]. In-situ crosslinkable polymers have been widely used for water shut-off where the formulation is designed to be injected as a liquid and the gelation is to be complete in the designated area leading to plugging the water-producing zone [5]. Recently, in-situ gelants have also been proposed to be used for other applications in oilfields such as wellbore strengthening and as loss circulation materials giving it the advantage of broad applicability [19,20].

Polyacrylamide (PAM) is the most abundantly used base polymer for water control purposes due to the low cost it has as well as the commercial availability [14]. Over the last three decades, researchers have successfully investigated many crosslinkers, which can be classified generally into organic and inorganic crosslinkers. Organic crosslinkers, such as Polyethyleneimine (PEI), hydroquinone (HQ), and hexamethylenetetramine (HMTA), have achieved many successes in conformance control applications [21,22]. Nonetheless, organic crosslinkers are unfavored in reservoirs characterized with moderate to low temperatures ($<80^{o}$C) due to the long gelation time it has at these conditions [15]. On the other hand, inorganic crosslinker are best suited for such reservoirs where the temperature allows for a controllable gelation time [13]. Inorganic crosslinkers form a colloidal dispersion in the polymeric solution; they are described by having a multivalent metallic base (M^{n+}) associated to ligand where the crosslinking is achieved by the initiation of coordination bonds between the metal and the functional groups on the base-polymer [23].

Upon a complete crosslinking process, petroleum engineer has a coding system for the gels based on the physical appearance the was first established by Sydansk [24]. The assessment is done through a bottle test where the test tube is flipped and the gel code is assigned based on the gel behavior as in Table 1.1.

Table 1.1 Gel coding system

Gel code	Gel description
A	No detectable gel formed
B	Highly flowing gel
C	Flowing gel
D	Moderately flowing gel
E	Barely flowing gel
F	Highly deformable nonflowing gel
G	Moderately deformable nonflowing gel
H	Slightly deformable nonflowing gel
I	Rigid gel

1.2. Tangible Objectives

The overall goal of this to provide practical solutions for the shortcomings of the currently existing crosslinkers, which are mainly the shear-degradation of Polyethyleneimine (PEI) in high-temperature reservoirs and toxicity of chromium acetate used in moderate to low temperature reservoirs. Therefore, the three sub-objectives for this thesis are:

1. To provide a physical reinforcement for the conventional PAM/PEI to enhance the final gel strength and shear resistivity. This is achieved by introducing nanosilica of different sizes to the gelling system. The mature gel is assessed based on the viscoelastic behavior and the stability of nanoparticles in aqueous solutions are evaluated using zeta potential.
2. To screen different functionalized silica with different functional groups, namely Tri-amine, Guanidine, and TAAcONa) based on their crosslink-ability with PAM. The gelation kinetics is to be studied using Differential Scanning Calorimeter (DSC) and compared with PEI. The rheological behavior of the crosslinkable systems are investigated and benchmarked with PAM/PEI system.
3. To investigate the ability of aluminum-based crosslinkers on providing a rate-controllable gelation and high gel strength. Aluminum associated with Acetate, Amino-Acetate, Nitrate, and Lactate are screened with polyacrylamide. The gelling systems are to be evaluated based on the physical stability of the colloidal gelants, the gelation rate, operating pH and temperature conditions, and the final gel strength.

1.3. Research Contributions

Current practice in gel treatments suffers from the limited available options for crosslinkers. For moderate to low temperature reservoirs (< 90^{o}C), chromium acetate is mostly used. The higher oxidation state of chromium is highly toxic and the tendency of Cr(III) to oxidize to Cr(IV) limits its applicability. Moreover, Cr(III) itself can be destructive to aqua life, and therefore using it in offshore operations can jeopardize the environment and ecosystem. Aluminum on the other side is a more environment friendly material that can be used to replace chromium acetate. Aluminum acetate is introduced in this thesis as crosslinker to polyacrylamide with a wide temperature-window of applicability between 25-100 ^{o}C. For the high-temperature reservoirs, Polyethyleneimine is the most abundantly used crosslinker. Field trials showed that PAM/PEI system is only effective for a limited period of time in the very high temperature reservoirs (>130^{o}C) since the gel degrades within months due the continuous mechanical and thermal stresses. Nanosilica has been studied in gelling systems showing the good reinforcement effect it has. Nevertheless, the effect of nanosilica size was not addresses before. This study provide a thorough investigation on the rheological behavior of nanosilica reinforced PAM/PEI gel. Morever, PEI market is monopolized and the available alternatives for high-temperature applications are limited. Therefore, a new functionalized-silica based crosslinker is crosslinker is introduced where it can compete and replace PEI for reservoirs characterized with temperatures higher than 100 ^{o}C.

1.4. Research Outcomes

Patents

1. A. Hamza, I.A. Hussein, **M. Shamlooh**, M.S. Nasser, M. Magzoub, S. Salehi, Polymeric Gels for Oil and Gas Conformance Control Applications and Methods of Making Same, USPTO 62/880,845, 2019. Provisional Application.

Journal Papers

2. **Shamlooh, M.,** Hamza, A., Hussein, I.A., Nasser, M.S., Magzoub, M., Salehi, S., 2019. Investigation of the Rheological Properties of Nanosilica-Reinforced PAM /PEI Gels for Wellbore Strengthening at High Reservoir Temperatures. Energy & Fuels. https://doi.org/10.1021/acs.energyfuels.9b00974
3. Hamza, A., **Shamlooh, M.,** Hussein, I.A., Nasser, M., Salehi, S., 2019. Polymeric formulations used for loss circulation materials and wellbore strengthening applications in oil and gas wells: A review. Journal of Petroleum. Sci. & Eng. https://doi.org/10.1016/j.petrol.2019.05.022
4. Hamza, A., **Shamlooh, M.**, Hussein, I.A., Nasser, M., Salehi, S., 2019. Rheology of Triamine Functionalized Silica Reinforced Polymeric Gels developed for Conformance Control Applications. Energy and Fuel. https://doi.org/10.1021/acs.energyfuels.9b03625
5. **Shamlooh, M.**, Hamza, A., Hussein, I.A., Nasser, M.S., Salehi, S., 2020. Gelation Kinetics of Functionalized Silica Crosslinked Polymeric Gels used in Conformance Control Applications. Journal of Thermal Analysis and Calorimeter. Under Review.

6. **Shamlooh, M.,** Hussein, I.A., Nasser, M.S., Magzoub, M., Salehi, S., 2020, Development of pH-Controlled Aluminum-Based Polymeric Gel for Conformance Control in Sour Gas Reservoirs. Journal of Natural Gas Science and Engineering. Under Review.

Conference Papers

7. **Shamlooh, M.**, Hamza, A., Hussein, I.A., Nasser, M.S., Salehi, S., 2019. Overview of Polymers for Improved Oil Recovery Treatments, in: Third EAGE WIPIC Workshop: Reservoir Management in Carbonates, Volume 2019, p.1-4. https://doi.org/10.3997/2214-4609.201903133
8. **Shamlooh, M.**, Hamza, A., Hussein, I.A., Nasser, M.S., Salehi, S., 2020. Reinforcement of Polyacrylamide-co-tert-butyl Acrylate Base Gel Using Nanosilica for Conformance Control at Low and High Reservoir Temperatures, in: SPE International Conference and Exhibition on Formation Damage Control. https://doi.org/10.2118/199324-MS.

Chapter 2: Literature Review

2.1. Introduction to crosslinkable gelants used for conformance control

Polymers are used in many applications in the oil and gas industry because of their relatively low cost compared to other chemicals. Moreover, their physical and chemical properties make them suitable for an operational purpose specifically their pump-ability. Polymers have reasonable viscosity, which provides them with the ability to penetrate deep in the formation without losing their properties. In general, polymers can have a high molecular weight which might reach millions of Daltons and some of them can be dispersed in liquids which cause the solution viscosity to increase [25].

There are many classifications of polymers because of their variety. For instance, polymers can be classified based on their origin, structure, molecular forces, mode of polymerization, diversity of monomers structure. Both bio-polymers such as xanthan gum (XG) and synthetic polymers such as acrylamide-based polymers are used for conformance control enhancement.

Polyacrylamide (PAM) is a simple chemical structure of acrylamide polymers. PAM cost is relatively low and has stable chemical properties at high temperature, saline conditions and under high shear rates. It is considered as cationic in low and medium pH value. When the percent of carboxylate groups to the acrylamide groups is 1:1000, PAM is known as ultra-low hydrolysis polyacrylamide. If the carboxylate ratio in PAM overcomes 2 %, it can be denoted as partially hydrolyzed PAM (HPAM). Figure 2.1 illustrates the chemical formula of PAM and HPAM.

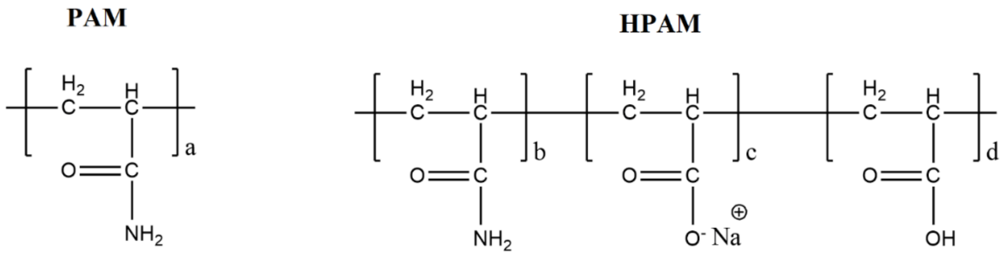


Figure 2.1 Chemical structure of PAM and HPAM polymers

2.1.1. Polymeric gel systems and base-polymers

Polymeric gel systems consist of a base polymer and crosslinker combined. They usually consist of crosslinked monomers and other reagents. Generally, polymer gel systems are classified based on the crosslinking process into in-situ crosslinked polymer gels (immature gels), pre-formed gels (mature gels) and foamed gels [12]. Each polymer has unique chemical properties. For instance, PAM has difficulty in crosslinking because of its neutral amide. On the other hand, the percentage of carboxylate groups in HPAM (up to 60 %) determines the suitable crosslinker to be used.

Polymer gel treatments have been implemented widely in the petroleum industry such as in water shut-off, sand control, cementing and well stimulation treatments over a wide range of temperature from 21°C (70°F) to 177°C (350°F). The temperature as well as pH and crosslinker concentration have great influence on the crosslinking and gelation process. At high temperatures (> 80^{o}C (176^{o}F)), some polymers such as xanthan and PAM degrade or form precipitations.

The type of crosslinker affects the gel physical and thermal stability. For example, at temperatures in the range of 60 - 80°C (140 - 176^{o}F), in-organically crosslinked polymer gels have considerably short gelation time which causes pumping difficulties. In contrast, organically crosslinked polymer gels are more stable at reservoir temperature (above 80°C (176^{o}F)) compared with the inorganically crosslinked ones.

Many researchers in the past decade focused on polymeric formulations for water-shut-off applications. El-karsani et al., (2014) gave a comprehensive review on recent water shut-off publications and classified them into two general systems, polymeric gels for near-wellbore crosslinked organically or inorganically, and gels for deep reservoir penetration (micro gels) [5].

One of the polymers used for gelation purposes in water control applications is the copolymer, which consists of acrylamide and t-butyl acrylate (PAtBA) (Figure 2.2). Experimental investigation of this system proved a wide range of temperature applicability (30-177^{o}C (86-338^{o}F)) [26]. However, low temperatures compromise the strength of the produced gels. Then it has been applied in many fields over the past decade [14,27].

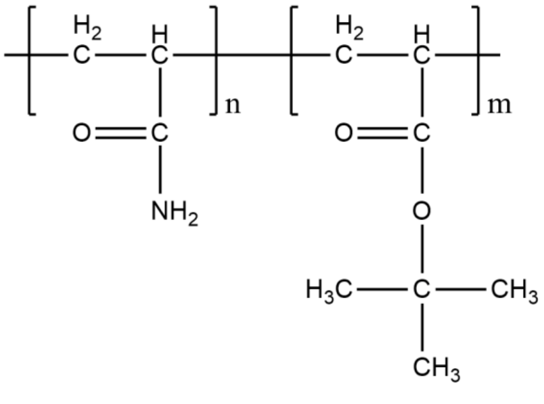


Figure 2.2 Chemical structure of PAtBA

Focus has shifted to the homopolymer, which is the PAM due to the significant difference in the price although PAtBA is a better crosslinkable polymer [5].

All of the polymers described above are synthetic polymers that are mostly designed to be used in the industry. Nevertheless, natural polymers have a potential to be adapted for wellbore strengthening application due to their availability and low cost. Many studies have investigated the crosslinkability of natural polymers including, but not limited to, polysaccharides such as starch, sucrose and guar. Polysaccharides are natural polymers that have a cyclic hexagonal carbon structure as a backbone (Figure 2.3) where one polysaccharide differs from another by the difference in the functional groups “R” as well as in the branching.

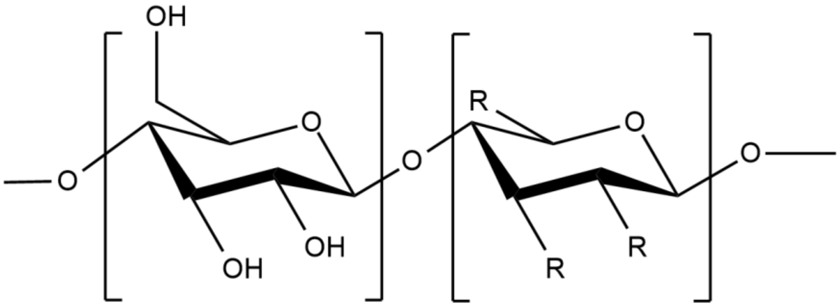


Figure 2.3 Polysaccharide structure

Azeredo and Waldron (2016) in their review have presented many crosslinkers used in the food industry to crosslink polysaccharides to enhance some properties such as water sensitivity [28]. Aldehydes (such as glutaraldehyde and montmorillonite) were found to be very effective in crosslinking polysaccharide with many suggested reaction mechanisms depending on the functional group present in the polymer. However, aldehyde use is limited in the food industry due to the fact that it might be toxic as well as the fact that harsh conditions of low pH and high temperature is needed for the crosslinking reaction to take place. Zhao et al., (2012) reported the crosslinking of alginate, which is a polysaccharide with a hydroxyl group via condensation reaction with cystamine producing a hydrogel with an ultimate stress of around 6 kPa [29].

Additionally, some researchers investigated physical crosslinkers. Yu et al., (2015) used tea catechins as a crosslinker to methylcellulose where crosslinking takes place by hydrophobic interaction between the two compounds forming a hydrogen bond, which was described by physical crosslinking [30]. Likewise, Zhang et al., (2013) reported physical crosslinking of polysaccharides under cryogenic conditions at temperatures reaching as low as - 20^{o}C (- 4^{o}F) forming what was described as cryogels. Many polysaccharides (e.g. XG, carboxymethylated cellulose, locust bean gum) were reported and some have been proved to form a strong cryogel reaching a storage modulus (G´) of up to 1500 Pa [31].

2.1.2. Inorganic Crosslinkers

The use of inorganic crosslinkers has been investigated broadly nominating chromium acetate to be the best in terms of controllability [23,32]. The presence of acetate provides a better gelation control since it has a similar structure to the carboxylate groups on PAM making the crosslinking reaction slow [13]. One of the main drawbacks of using chromium as a crosslinkers is that the higher oxidation state (Cr^{6+}) is very toxic. Although the used Cr^{3+} has an acceptable toxicity limit, it have a tendency under some conditions to oxidize as well as the fact that Cr^{3+} itself poses a destructive risk on the marine life when disposed even at low concentrations [15]. Therefore, Aluminum, the third most abundant element in earth's crust [33], can be of less environmental impacts, which motivated some researchers for proposing it as an alternative to chromium [34].

Sun et al., (2016) analyzed the HPAM/chromium acetate system and studied the effect of polymer hydrolysis degree on the gelation time [35]. In this experimental study, bottle test was used, this is a common visual technique used to assess the status of the formed gel following a coding system that was first developed by [24]. Sydansk assigned a letter to the gel varying between "A" (no detectable gel formed) and "I" (Rigid gel). It was concluded that the gelation time of this system can be monitored between 8 to 30 days reaching up to letter "F" (highly deformable non flowing gel) in the bottle test and was found to have a better functionality at low reservoir temperature (65^{o}C (149^{o}F)).

Pu et al., (2019) also examined the preparation of micro gels from PAM and chromium acetate and verified that this system is independent of salinity [36]. Micro gels in this system showed unique swelling properties that match the need for water control applications. However, this study lacks the investigation of rheological properties of the system. Other chromium crosslinkers were also investigated such as chromium malonate, chromium chloride and aluminum chloride with a gelation time that can be controlled between 1 hour and 6 days. Nevertheless, these systems are only proven to have a good thermal stability at low temperature [12].

2.1.3. Organic Crosslinkers

Organic crosslinkers in some cases are preferred as they have higher temperature applicability range. PEI (Figure 2.4) was under the scope recently as it is more environmentally friendly than other organic crosslinkers as well as it produces a gel that is thermally stable in the long term under high temperature (130°C (266°F)) [12,26].

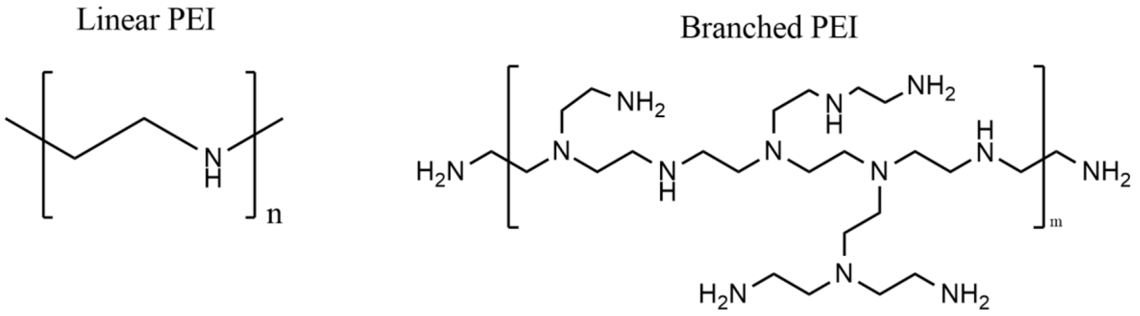


Figure 2.4 PEI chemical structure

ElKarsani et al., (2015) found that the best formulation for the application of PAM/PEI system in water-shut-off is 9 wt. % PAM with 1 wt. % PEI in seawater as it gave a solid ringing gel that is thermally stable under 150°C (302°F) [37]. The effect of different salts was evaluated and found to have a retarding effect by delaying the gelation time; ammonium chloride was the most effective for the retarding purposes. El-Karsani et al., (2014) introduced a new method for evaluating the properties of gels using thermal analysis and proved its effectiveness [38].

Reaction mechanism between amide and amine groups is believed to be dependent on "transamination mechanism" by which the amine group on PAM is replaced by nucleophilic amine nitrogen from PEI [23,39]. The chemistry of PAM-PEI crosslinking is shown in Figure 2.5 below. Organic crosslinkers such as PEI are triggered by high temperatures of above 80 ^{o}C, where the reaction rate becomes significant, and the cross-linking process is accomplished by covalent bonding [40].

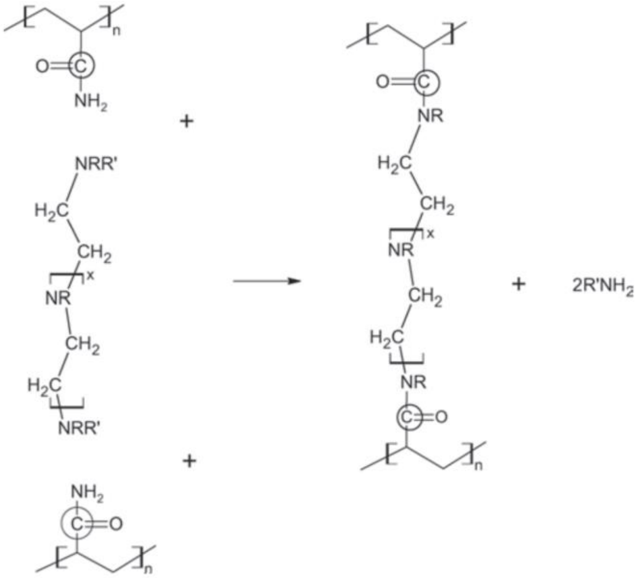


Figure 2.5 PAM/PEI crosslinking mechanism [39]

2.1.4. Thermal stability of polymeric solutions

Heat is released because of the crosslinking process during the gelation. El-Karsani et al. [38] investigated the gelation kinetics of PAM/PEI using Differential Scanning Calorimeter (DSC) technique where it proved its reliability. Both endothermic and exothermic peaks were observed as a consequence of hydrolysis and crosslinking, respectively [41]. DSC was also proved to be able to detect multi-crosslinking developed during the use of polymer mixed with multiple cross-linkers such as PEI and Cr^{3+} [40,42].

Thermal analysis using (DSC) can simulate reservoir conditions by using a defined incremental temperature increase. DSC has verified the good thermal stability of the PAM/PEI system and the good retarding effect of ammonium chloride. Mohamed et al., (2015) used the same technique to test the performance of emulsified gel, which has a smart selectivity by blocking water and allowing hydrocarbons to flow in low permeable zones [42]. Gelation time in the presence of the surfactant in a 9:1 PAM:PEI ratio was found to be 2 to 4 hours compared to 1.5 hours in the absence of the surfactant [24]. Jia et al., (2016) studied the same PAM/PEI system at low temperature (40°C (104°F)), results revealed that code "I" (Rigid gel) can be reached for this system if a high molecular weight polymer is used (8 million Da) [43]. However, it takes around 20 to 30 days to reach this strength, as the crosslinking rate is very low at this low temperature.

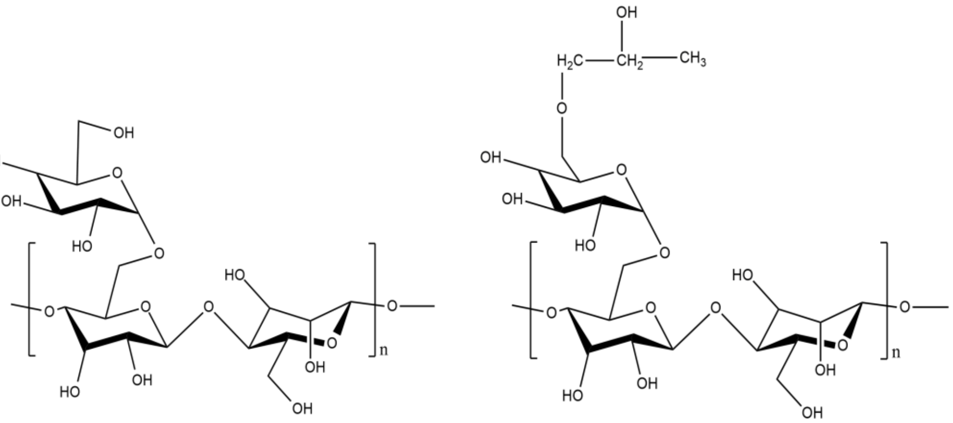
2.1.5. Gel physical stability

The most common issue faced in the in-situ gels are the gelation time as the gelant usually is highly sensitive to the reservoirs conditions such as the temperature, pH, salinity and the type of materials that exist in the reservoir, which may affect the stability of the gel [5]. A proposed solution is to inject mature micro-gels that penetrates through the formation and then plugs the fracture by swelling water and expanding. Methylene bisacrylamide is the most commonly used crosslinker for such systems [44,45]. The most important parameters in developing a performed or a mature gel are the swelling capacity and the strength of the swelled gel [45]. Bai et al., (2007) performed a test on the transport mechanisms of mature microgels and proved through core flooding experiments that the mature gel can penetrate through pores with diameters smaller than the microgels due to the elastic properties, which makes it applicable in a wide range of wells with different permeability values [46]. Consequently, mature gels have been applied in many fields and proved its reliability [44,45].

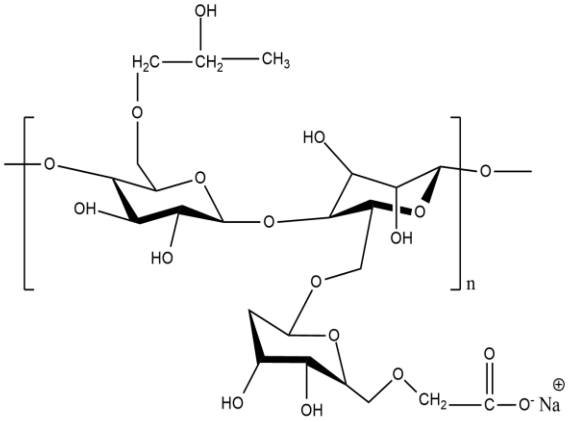
The next stage after developing a system that can be gelled is to enhance its properties such as the gelation time, mechanical strength, sensitivity, gelant stability, and long-term thermal stability; this could be achieved through additives. Retarders are most commonly added in water shut-off applications to delay gelation time for fast crosslinking gelants, ammonium chloride was found to have a good retarding effect in comparison with other salts as well its compatibility in the PAM/PEI system [47]. Other effective retarders such as polyamines and sodium carbonate were also reported [48,49]. Another type of additives are the chelating agents, which have the main function of providing a system with a better thermal stability on the long run by hindering the syneresis. many substances were tested such as ethylenediaminetetraacetic (EDTA), salicylate, and oxalate proved to have a remarkable effect by delaying the syneresis from 4 days to more than one year in one of the cases [50].

2.1.6. Emerging Green Formulations

Biopolymers are gaining more attention because they are environmentally friendly. Polysaccharides such as starch, latex and guar gum and its derivatives such as hydroxyalkyl guar and carboxyalkylhydroxyalkyl guar have been explored as crosslinkable polymers [51–53]. Figure 2.6 shows the structure of guar and some guar derivatives. They are also mixed with nanoparticles (NPs) to improve their properties [54]. Anhydrous sodium tetraborate such as colemanite ($Ca_2B_6O.5H_2O$) and ulexite ($NaCaB_5O.8H_2O$) as retarders with guar and guar derivatives [55]. Alsabagh et al., (2014) investigated the use of natural polymers such as cellulosic polymers (CMC, guar gum and potato starch) to mitigate loss circulation [56]. Rheological enhancement was achieved by using 0.1 % CMC, which showed the best results compared to 0.3 % guar gum and 0.6 % potato starch. Guar was mixed with different crosslinkers such as borax, sodium alginate, ammonium alginate and calcium citrate and all the obtained gels were firm. 0.285 to 0.57 wt. % of guar was mixed with 0.0285 – 0.057 wt. % borax. It was observed that the gels formed rapidly [57]. Moreover, chitosan has been proposed recently to replace PEI as a crosslinkers since PEI is planned to be phased out from some Scandinavian countries due to toxicity issues in offshore reservoirs [5].



Guar **HydroxyPropyl Guar Gum (HPG)**



CarboxyMethyl HydroxyPropyl Guar (CMHPG)

CarboxyMethyl Cellulose (CMC) **CarboxyMethyl HydroxyPropyl Cellulose (CMHEC)**

Figure 2.6 Guar and Guar derivatives chemical structures

2.1.7. Pilot and Field applications

Although developing the polymeric formulation is an essential step in the process of chemical reservoir treatment, its success in the bench-scale does not guarantee success in the field trials. Therefore, the next step in the process is the pilot-scale where the actual field conditions of the mimicked to address all the possible challenges for scaling the application up. Finally, when the technology is well characterized and understood, it is then tested in field applications. Nevertheless, the application of new technologies in actual fields is usually risky due to the possibility of causing unrecoverable formation damage, which makes the pilot-scale characterization essential to address all the different aspects of the application.

The main challenge in field applications is controlling the gelation time. Fast gelation may cause plugging the injection pipes and the failure of the whole operation, while very slow gelation, on the other hand, may cause a further delay in the operation leading to an increase in the non-productive time [58]. Another major problem is the degradation of polymers with time, while the continuous shearing leads to the decomposition gels leading to an increase in the water-cut again [5]. Additionally, a major challenge in the chemical treatments is the long-term stability in high-temperature reservoirs. Al-Muntasheri et al.[21] reported that although successful treatment was achieved upon placing the gelant by reducing the water cut by more than 40%, the gel has broken several months later due to the high temperature there (150 ^{o}C). This was attributed to the syneresis of gel caused by exposure to the continuous thermal stresses at such harsh conditions.

Table 2.1 Summarizes 11 case studies of pilot and field-testing for some crosslinkable polymeric systems.

Table 2.1 Summary of pilot and field trials used for water shutoff

Formulation (Base polymer/ Crosslinker)	Test type/ Application	Conditions	Observations	Ref
PAM/organic crosslinker	Field (30 wells - US) / water shut-off	Average temperature of 60 ^oC	• Successful treatment in carbonate and sandstone formations • Poor characterization of some wells led to formation damage in some pay-zones	[59]
PAM/ Chromium acetate	Field (7 wells- US) / water shut-off	Temperature of 43 ^oC with the presence of H_2S	• The gel produced can handle the harsh reservoir conditions (high salinity, pH, and presence of H_2S)	[60]
PAtBA/PEI	Field (Norway) / water shut-off	The formation is characterized by high porosity	• Stability of the gel depends on the acidity (stable at pH>7) • Successful chemical treatment by reducing the water cut to 0%	[61]
PAtBA/PEI	Field (Saudi) / water shut-off	Horizontal natural gas well with a maximum temperature of 150 ^oC	• Water cut was decreased from 100% to less than 60% within 3 days of treatment • Incompatibility of polymeric formulation with sodium carbonate	[21]
PAtBA/PEI	Field (Mexico) / water shut-off	Oil wells with the highest reported temperature of 177 ^oC	• The organically crosslinked system should good stability at high temperatures • The water-cut was decreased to <1% over	[58]

Table 2.1 Summary of pilot and field trials used for water shutoff

Formulation (Base polymer/ Crosslinker)	Test type/ Application	Conditions	Observations	Ref
			a period exceeding 3 years	
PAtBA/PEI	Field (37 wells - Mexico)/ water shut-off	Depleted highly fractured wells with a maximum temperature of 120 ^{o}C	• Effectiveness of treatment for fractured carbonate reservoir as well as high permeable sandstone formations • Water-cut reduced by more than 80% in some of the wells. • The gel showed high stability in most of the wells after one year of treatment	[62]
PAM/PEI	Pilot/water shut-off	High temperature & high salinity conditions	• Thermal stability for more than 600 hours at a temperature of 85 ^{o}C • Addition of silica nanoparticles supported the gel structure and gave it more endurance	[63]
PAM/HMTA	Pilot/In-depth fluid diversion	Neutral pH (6-8) with a temperature of 95 ^{o}C	• Gelation time of around 3-4 days to reach maximum maturing • The final gel showed good durability	[64]

Table 2.1 Summary of pilot and field trials used for water shutoff

Formulation (Base polymer/ Crosslinker)	Test type/ Application	Conditions	Observations	Ref
FLOPERM (commercial polymer)/ formaldehyde	Field (Venezuela) / conformance control	Limestone formation with a temperature of 140 ^{o}C	• Additional oil production of 36,000 barrels annually with 15% reduction in water-cut	[13]
Fibrous gelling system (undeclared)	Field (Middle East) / Lost circulation	-	• Successful treatment in two wells • Loss rates were decreased from 200 bbl/hr to zero. • The gel was designed to degrade after several months which was achieved since the production rate was as predicted with no remedial actions	[65]
Crosslinked polymer (ASDOBC2C)	Field (Italy) / Lost circulation	Vuggy limestone formation	• Achieved full sealing in the fracture • Polymer degradation was achieved during the production stage leaving the formation undamaged	[66]

2.2. Introduction to the factors that influence polymer system in oilfield chemical treatments

Various factors should be considered when selecting a polymer for successful polymeric treatment at high-pressure high temperature reservoirs. These parameters can be categorized into fluid stability and fluid-rock interactions. Many factors have an influence on the performance of the gelled polymer such as type and concentration of the crosslinker and the polymer, degree of hydrolysis, additives, pH, temperature and salinity [67].

The ideal polymeric formulation should be efficient in sealing unconsolidated sandstone as well as vugs and natural fractures in carbonate formations under low and high differential pressure conditions. Moreover, the strength of the formulated gel should support the overburden pressure; however, the formed filter cake should be easily removed by chemical or mechanical means. In addition, polymer systems should satisfy rheological features of the effective sealant solution to plug fractures with different width sizes. The polymeric solution should have low density, high viscosity, be crosslinkable at low shear rates and show shear thinning behaviors at high shear rates. The lubricity of the polymer should be high enough to avoid drill string sticking [68].

Many experimental studies were curried out to demonstrate the effect of different variables on the gelation kinetics of polymer solutions. Al-Muntasheri et al., (2008) studied the gelation kinetics of PAM/PEI mixture for HPHT applications at 15.2 s^{-1} [39]. The results showed that PEI can crosslink PAM at 130°C (266°F) and 435 psi with thermal stability up to 8 weeks. The system was able to totally plugging Berea sandstone core sample at 90°C (194°F) and 1000 psi pressure drop with thermal stability up to 21 days. For low temperatures, raising the polymer wt. % increases the gelation time, whereas for high formation temperatures the gelation time can be extended by decreasing the polymer ratio. However, the gel strength will be questionable. At 130°C (266°F), no syneresis was observed for 7 - 9 wt. % PAM / 0.2 - 3 wt. % PEI and Sydansk [24] code "I" (rigid gel) was observed. The time required for the gelation process can be customized by varying the concentration of the cross linker. For 5 – 7 wt. % PAM the degradation was observed when the PEI concentration reached 4 wt. % at 130°C (266°F). Moreover, adding NaCl to the solution retarded the gelation time from 0.67 hour for 7 wt. % PAM/0.3 wt. % PEI without any salt to 4.4 hrs and 6.8 hrs after adding 30,000 and 50,000 ppm of NaCl at 120°C (248°F), respectively.

Furthermore, Gelation parameters in inorganically crosslinked systems, namely gel strength and gelation time, are highly affected by the surrounding conditions. Although some researchers reported the ability of PAM / Cr (III) system to produce a gel at high pH values of up to 12.5 [24], Other researchers noted that the stability of chromium colloids decreases in aqueous solutions when the pH exceeds 5.5 compromising the feasibility of the operation [69]. Additionally, Nijenhuis et al. (2003) reported that the PAM / Cr(III) system can only crosslink at pH conditions between 5 to 9 [70] while Karimi et al. Suggested that the pH range between 5.5-7.5 produces the most stable gel [71]. Hence, the behavior of inorganic complexes in aqueous solutions is not yet well understood. Apart from the stability of particles, crosslinking of the inorganic crosslinkers was found to be pH triggered having the gelation time decreased as the pH increases [72]. The effect of pH is believed to result from the hydrolysis of PAM that is increased at high pH leading to the conversion of more amide groups to carboxylate groups resulting in more crosslinkable sites [35,73]. Moreover, the crosslinking reaction follows Arrhenius's equation where the increase in the temperature increases the crosslinking rate [74,75]. While pH and temperature have the most significant effect on gelation time, other factors influence the equilibrium gel strength such as salt type and content, and polymer to crosslinker ratio [71,74,76].

The high salinity formation water delays the gelation time at high temperatures because of the hydrolysis of PAM, which produces HPAM and NH_3 in high pH conditions. The negative charge in the produced carboxylate group increases the polymer hydrodynamic volume while the positively charged sodium ions reduce the HPAM size and hence provides extended gelation time. Consequently, increasing the degree of hydrolysis decreases the gelation time. It was reported that the minimum hydrolysis rate of PAM is at initial pH of 7 due to that the gelation time of 7 wt. % PAM / 0.3 wt. % PEI was the longest compared with initial high and low pH. However, the effect of salts on the gelation time varies with different types of polymer systems [43]. Table 2.2 illustrates the effect of some salts on the gelation time of polymer solutions. El Karsani et al., (2014) reported that of NH_4Cl increased the hydrolysis, gel strength and gelling time of 20 wt. % PAM more than NaCl at 120^oC (248^oF) [47]. Na_2CO_3 was not compatible with the PAM/PEI gel.

Table 2.2 Effect of salts on the gelation time of polymer solutions

Polymer / Crosslinker	Temp. (°C)	Salt	Gelation Time	Comments	Ref
HPAM/Cr^{3+}	25	Synthetic brine	Decrease	-	[43]
HPAM/Cr^{3+}-methanol	32	NaCl	Decrease then increase	Different NaCl concentration ranges have different effects on gelation rates because the effect of promoting ionization and electrostatic shielding effect.	[77]
HPAM/ $ZrOCl_2$	28	NaCl $CaCl_2$, $MgCl_2$	Decrease	Added ions in this system decrease the repulsive forces between ions which makes the crosslinking reaction faster	[78]
HPAM/PEI	40 – 65	NaCl	Increase	-	[43]
PAtBA/PEI	120 – 150	NaCl KCl $CaCl_2$	Increase	Retardation was found to increase with the charge density (charge/ ion size)	[79]

Table 2.2 Effect of salts on the gelation time of polymer solutions

Polymer / Crosslinker	Temp. (^oC)	Salt	Gelation Time	Comments	Ref
HPAM/ Rescorinoll/ Phenol-formaldehyde	65	NaCl	Decrease	Polymer chains at high total dissolved solids rolls due to the decrease in the repulsive forces which increase the chances of collisions between polymer and crosslinker	[80]
HPAM/ Rescorinoll/ Formaldehyde / NH_4Cl	30	NaCl KCl	Increase	In the presence of both NH_4Cl and NaCl, Increasing NaCl will increase the total dissolved solids and accordingly the gelation time, compared to when NH_4Cl is used alone. Na^+ has better retardation effect than K^+ because of the higher charge density	[43]

Table 2.2 Effect of salts on the gelation time of polymer solutions

Polymer / Crosslinker	Temp. (^oC)	Salt	Gelation Time	Comments	Ref
HPAM/PEI	130	NH_4Cl	Increase	NH_4Cl accelerates hydrolysis reaction however it has a good retardation effect (better than NaCl).	[47]
PAtBA/PEI	176	Carbonate salt	Increase	Successfully applied in a Mexican field.	[81]

Polymer to crosslinker percentage is essential for polymer gel stability. Very low concentrations cause weak gel that might need a long duration for the gelation process. In contrast, very high polymer concentration might end with gel shrinkage and syneresis [82]. Vasquez et al., (2003) extended the gelation time of an acrylamide and t-butylacrylate (410 gal/Mgal) crosslinked by PEI which was applied in the field at 135^{o}C (275^{o}F) to 20 hours after mixing it with acrylamide acrylamide-2- methylpropane sulfonic acid (AMPS) [67]. The results proved the thermal stability of the base and developed solution up to 176.7^{o}C (350^{o}F). However, increasing the crosslinker concentration and temperature would reduce the gelation time significantly to about 2.5 hours at 176.7^{o}C (350^{o}F) by using 10-20 gal/Mgal of PEI. Moreover, decreasing the concentration of the polymer base to 150 gal/Mgal and the concentration of the crosslinker to 10 gal/Mgal increased gelation time to more than 9 hours.

As a rule of thumb in the field practice, the size of sealing materials in fractured should be selected to be either equal to or greater than third of the pore throat size or fracture width [83]. Sanders et al., (2003) stated that fibrous/polymer based crosslinked solutions should be engineered based on the fracture size and rate of losses for the flowing wells [84]. High molecular weight crosslinking polymers were recommended for vugular or natural fractured zones and low molecular weight types for induced and micro-fractures. The final objective is to set a soft-medium gel strength for naturally fractured zones while developing higher strength is desired for micro-fractures. However, the great challenge is in shale formation where limited leak off is available for the trapped fluid within the fractures [85]. Low molecular weight PAM crosslinked with chromium acetate provides stronger gels than high molecular weight PAM [74].

Metal cations have measurable effect on the properties of the polymers. Omer and Sultan (2013) examined the effect of metal cations such as manganese, calcium, and magnesium on the rheological and thermal stability of PAM [86]. It was noticed that that adding 0.05 wt. % of Ca^{2+}, $Mg^{2+,}$ and Mn^{2+} separately to 0.95 wt. % of PAM decreased viscosity by about 42 %, 31 %, and 10.9 % respectively. Adding 0.25 wt. % of the counter-ions reduced the viscosity by almost 100 % compared with 1 wt. % pure PAM solution. Moreover, increasing the wt. % of these cations reduced the thermal stability of the formed solution compared with the pure polymer case. For example, the thermal stability for 1 wt. % PAM dropped from 70^{o}C (158^{o}F) to 66^{o}C (150.8^{o}F) for 0.85 wt. % PAM/0.15 wt. % Ca^{2+}, 50^{o}C for 0.75 wt. % PAM/0.25 wt. % Mg^{2+} and the lowest value was recorded for 0.75:0.25 wt. % of PAM: Mn^{2+} which was about 39^{o}C (102.2^{o}F). These results will help in understanding the effect of the formation water and chemical additives on the rheology and thermal stability of polymer systems.

2.3. Polymers used in loss circulation and fracturing

Polymeric materials has been used in hydraulic fracturing to transport proppant inside the fractures. Moreover, crosslinkable systems has also been used as loss circulation material (LCM) to seal the thief zones during the drilling operation. Polymers used for these operations have the potential to be implemented for water shutoff through deep investigation of their properties.

2.3.1. Polymers in Hydraulic Fracturing

In hydraulic fracturing, the fluid is designed mainly to carry the proppant inside the fracture and then it will be broken to allow proppant settling. Moreover, most of the fracturing treatment is carried out in deep formations where the temperature is high. For water shutoff, the interest is to maintain the rheological and thermal stability of the formed gel. Therefore, polymeric solutions can be adjusted to be used for conformance control and seal the water production-zones properly.

Al-Muntasheri (2014) reviewed polymer based hydraulic fracturing fluids that can be used for very low permeability zones such as guar, hydroxypropyl guar (HPG) and carboxy methyl HPG (CMHPG) [7]. Table 2.3 comprises a list of the polymeric formulations reviewed by Al-Muntasheri et al. (2014) [7]. PAM based polymers are preferred for high reservoir temperatures because they the formed gel can withstand up to 232.2^{o}C (450^{o}F).

Table 2.3 Polymeric systems used in hydraulic fracturing

Polymer	Crosslinker	Polymer, (wt. %)	Crosslinker, (wt. %)	Temp. (^oC)	Ref.
PAM-based	Zr	1	0.04	132 – 232	[79]
PAM-based	Zr and Activator	1.04	0.041 – 0.044	38 – 132	
Linear bio-polymer	-	0.479 – 0.839	-	< 93	
CMHPG	Zr	0.359	0.04	< 149	
Low molecular weight HPG	Borate	-	-	90 – 135	
AMPS-vinyl phosphonate	Zr	0.479	-	218	
Linear guar	-	0.395	0	< 79	
Guar	Boronic acid functionalized NPs	0.359	0.0002	37	
HPG	Borax	0.5	0.1	30-100	[87]
HPG	Zr	0.5	0.4	140	[88]

Table 2.3 Polymeric systems used in hydraulic fracturing

Polymer	Crosslinker	Polymer, (wt. %)	Crosslinker, (wt. %)	Temp. (^{o}C)	Ref.
HPG	Ti Ti-acetyl acetonate	0.48	0.2		[89]
Guar gum HPG	KH_2PO_4	0.4	0.025 0.031	25 - 121	[90]
HPG	Borate/ functionalized nano-silica	0.3	0.02	25 - 80	[91]
HPAM, XG, Guar Gum, TVP and AMPS	GLDA, EDTA and DTPA	0.43	20	148.9	[92]

2.3.2. Polymers in lost circulation

Loss circulation is one of the most common problems faced during the drilling of oil and gas wells. It occurs when the mud escapes what is known as “thief zones” instead of returning to the surface. LCMs are injected as a remedial action upon noticing a partial or full loss of drilling fluid during the operation. The severity of loss circulation depends highly on the geographic nature of the drilled reservoir. For example, carbonate reservoirs have a high possibility to encounter the issue of losing the drilling fluid since they are characterized by the presence of vugs and natural fractures [93]. Besides, lost circulation can also be attributed to other thief zones such as cavernous formations, induced fractures, and high permeable formations. Lost circulation can is usually detected by monitoring the pressure inside the well and the flow rate of the returning mud. One of the main functions of the drilling fluid is to keep the pressure in a window above the pore pressure and below the fracturing pressures, thus, escaping into the formation may cause a drop in the static pressure which jeopardizes the stability of the well. Therefore, LCMs are introduced with a main function of sealing the thief zones and strengthen the wellbore which widens the mud weight window.

Boukadi et al. [94] presented many materials used as LCM. Conventionally, solid wastes such as sawdust, rubber and packing pellets were injected during the downtime of operation to seal the fractures. However, they are generally described as poor performance LCMs due to the lack of ability to seal micro-fractures as well as the fact that they do not provide the required strength to ensure smooth operation. Additionally, cementing is one of the most commonly known cures to treat loss circulation problems. However, cementing has the potential of damaging production zones, which will worsen the matter. Recently, the focus has shifted to the polymeric system due to its ability to function in a very wide range of applications. The targeted systems for such applications are gelants that are crosslinkable polymers that can be injected as a liquid and then forms a gel when it reaches the designated zone at those conditions. Many polymeric systems have been suggested to be used as LCM such as a copolymer of sodium acrylate and potassium acrylate [56], hydrocarbon-based polymeric gelant [95] and styrene-butadiene copolymer [96]. Polymeric systems are advantageous over the conventionally used materials due to the high success rate it obtains. Table 2.4 summarizes some of the polymeric systems used as LCMs.

Table 2.4 Summary of polymeric solutions used as LCMs

Polymer(s) / Crosslinker(s)	Temp. (^oC)	Gel strength / Gelation time	Ref.
3 wt. % HPAM / 1.2 wt. % PEI.	120	9.8 times the base solution / 200 minutes.	[82]
2 wt. % HPAM-derivative / 1.2 wt. % PEI	100	3 times the base solution / 204 minutes.	
0.5 wt. % PAM / (0.4 gm) phenol and (0.37 gm) formaldehyde.	Room temperature.	Code C / -	[97]
Multifunctional gel solution.	up to 100	-	[98]
HPAM / chromic III carboxylate. Synthetic water hydrated polymer.	-	400 times the original size.	[99]
CACP mixed with retarder, fibrous cellulose polymer and polymer with calcium carbonate.	90	3 to 7.5 MPa.	[100]
Modified polymer.	-	-	[68]
Urethane 902, Butyl Sealant, polysulfide polymer and Hotpour 164.		Gelation time about 5 to 30 minutes.	[94]

Table 2.4 Summary of polymeric solutions used as LCMs

Polymer(s) / Crosslinker(s)	Temp. (^oC)	Gel strength / Gelation time	Ref.
7 wt. % copolymer of acrylamide and PAtBA, 2 wt. % KCl and 8 wt. % carbonate retarder.	Up to 176.7	40 minutes without retarder and 600 minutes with 8 wt. % carbonate retarder at 176.7^{o}C.	[81]
Smart anionic shape memory polymer activated by heat.	70	34.5 MPa.	[83]
The oil-absorbent polymer formed by 6 gm of MMA, 18 gm of HMA and 16 gm of BA and 5 gm of EAC.	300	Increased from 3 to 9 Pa after using 3 wt. /vol. % of the oil absorbent polymer.	[101]
0.7 wt. % lignosulfonate/acrylamide graft copolymers	30 and 55	-	[102]
5.72 kg/m^3 (HPS) (not recommended for drilling), 2.85 kg/m^3 CMC and XG.			[103]
acrylamide-based solution mixed with hydroxyl and carboxyl based ingredients (commercially named as XNGJ-3).	Became a gel at 80.	bear up to 21 MPa	[104]

2.4. Introduction to Functionalized or Unfunctionalized Nanomaterials

Nanoparticles have physical and chemical properties such as high surface area and very tiny size, which make them very efficient in pore throat plugging. Nanoparticles can be combined with polymer systems in different concentrations to improve their rheological properties and reduce the friction losses [105].

Silica NPs have been investigated widely due to their relatively low cost. Liu et al., (2017) studied the effect of silica on the PAM/HMTA-HQ in-situ (immature) system for water control purposes and found an amount of 0.3% silica is the optimum for that system enhancing several properties [106]. The produced gel was highly affected by the presence of silica as the storage modulus increased from around 10 Pa to more than 30 Pa. In addition, silica has improved the thermal stability allowing the system to tolerate a temperature of 155^oC (311^oF) compared to 138^oC (280.4^oF) without silica. Moreover, investigating different amounts of added silica led to a conclusion that the more silica added the less the gelation time which opposes the retarders effect. Dai et al., (2016) experimented the effect of silica on PAM/phenol system and concluded that 0.2 wt. % silica (15 nm) is the optimum amount for that system [107]. Core flooding experiments showed that silica has facilitated the injectivity in the PAM/phenol system which can withstand a temperature up to 110^oC (230^oF) and a total salinity of more than 200,000 mg/L.

Silica NPs in mature gels were also evaluated, Adibnia and Hill (2017) tested nano-silica (≅100 nm) in PAM/bisacrylamide and deducted that silica alone in the absence of a crosslinker (bisacrylamide) is unable to crosslink PAM [108]. However, it enhances gel strength, as less amount of the crosslinker is needed in the presence of silica NPs. Testing rheological behavior of the gel showed that silica increases both the loss and storage modulus, which makes it effective for strengthening purposes in mature gels. Tang et al., (2018) verified the same result in a system of acrylamide monomer, ammonium persulphate initiator, bisacrylamide crosslinker and hydroxyl –functionalized silica NPs (30 nm) [109]. The test revealed that silica increases the crosslinking density, which facilitates the gelation and strengthens the formed gel. NPs functions did not stop in enhancing the mechanical and thermal properties, it was also reported that clay NPs are used to crosslink polymers [110]. Thoniyot et al., (2015) explained this phenomenon by the existence of free radicals on the clay that initiate the polymerization in the presence of monomers and then crosslinking takes place [111].

Ma et al., (2017) presented a nano-conformance control system consisted of 1 wt. % HPAM / 0.2 wt. % PEI combined with colloidal silica (9-12 nm) for high-temperature high salinity formation [112]. Increasing the concentration of the nano-silica prolonged the gelation time significantly, 0.63 wt. % of nano-silica was reported as the optimum concentration and the gelation time of the polymeric nano-solution at this concentration was 132 hours.

Lecolier et al., (2005) used environmentally friendly nano organic/non-organic gel crosslinked by chromium acetate that has colloidal and swellable particles [113]. PAM based solutions mixed with crosslinked polymer grains (100 microns) showed increasing pressure drop resistance to 10 MPa/m for fracture width of 1 millimeter. Furthermore, increasing the concentration of the crosslinker improved the gel strength almost by the same percent. In contrast to the crosslinked polymer, salinity did not influence the gelation kinetics of the nano-based pills. However, a decrease in the viscosity by 20 % of one of the solutions was observed before gelation. Aging of the nano-compositions for 16 hours at 120^{o}C (248^{o}F) illustrated the stability of the solutions at high temperatures because the gel strength was only dropped by 20 %. Silva et al., (2013) utilized oxidized nano carbon black, with a concentration in the range 0.05 to 0.50 wt. %, as an additive for saline muds having 1 wt. % Poly(acrylamide-co-acrylic acid) [114]. The laboratory tests showed that the black carbon NPs raised the viscosity by 25 % and maintained the stability of the prepared fluids for about 5 months.

Table 2.5 summarizes the polymeric solutions and nano-material used with nanoparticle size. Although the NPs are very small in size, they can withstand the closure stress applied to them inside the fracture. Despite the fact that NPs improved the thermal and rheological properties of the drilling fluids, there are many technical challenges that can be encountered such as nanoparticle dispersion hence the stability of the nanofluids. Moreover, identification of the optimum concentration of the NPs is difficult because relatively low percentages are used. In addition to that, the relatively high cost of nano-fluids limited their implementation commercially at the field scale. Preparation and measurements of such fluids do not have standard procedures, which make the process of performance evaluation very complex.

Table 2.5 Summary of polymer systems combined with NPs and its size

Polymer System	Nano-material	Size	Notes	Ref.
1 wt. % HPAM / 0.2 wt. % PEI	0.63 wt. % colloidal silica	9 - 12 nm	The gelation time 132 hours. Increasing the concentration of the nano-silica prolonged the gelation time significantly.	[112]
PAM base mixed with nanoparticle and chromium acetate	PAM grains	∽ 100 micron	Increase of pressure drop resistance to 10 MPa/m. Not affected by salinity. Gel strength was only dropped by 20 % after aging for 16 hours at 120^{o}C (248^{o}F).	[113]
PAM/phenol	0.2 wt. % silica	15 nm	system which can withstand a temperature up to 110^{o}C (230^{o}F) and a total salinity of more than 200,000 mg/L.	[107]
PAM/bisacrylamide	Silica	About 100 nm	Enhances the gelation. silica increases both the loss and storage modulus	[108]

Table 2.5 Summary of polymer systems combined with NPs and its size

Polymer System	Nano-material	Size	Notes	Ref.
acrylamide monomer, ammonium persulphate initiator, bisacrylamide crosslinker	Silica	30 nm	silica increases the crosslinking density, which facilitates the gelation and strengthens the formed gel.	[109]

2.5. Health and environmental risks

Evaluating the rheological and thermal characteristics of polymeric formulations is common among researchers; however, toxicity of the systems is usually ignored. Nevertheless, regional and international regulations are getting strict which limits the freedom in using some chemicals [5]. **Table 2.6** compares the different types of crosslinkers discussed before based on the lethal dose (LD_{50}). LD_{50} represents the amount of chemical in mg per kg of body (rats in this case) needed to kill 50% of the population. Thus, the less the value of LD_{50}, the more hazardous the material is.

Chromium in its high oxidation state (6+) is the most toxic among the compared chemicals. Although chromium 3+ is the one used for crosslinking where its toxicity lies within the same range of other crosslinkers. However, chromium has a tendency to oxidize to the higher oxidation state when it leaches to water having an oxidizing environment giving

Cr^{6+}, which has fatal consequences. Moreover, the lethal concentration (LC_{50}) of some marine creatures such as algae can reach as low as 0.032 ppm, which creates a problem disposing such water [115]. On the other hand, organic crosslinkers are relatively safer option giving that PEI has the lowest toxicity among the conventionally used crosslinkers. However, some governments such as Norway are applying some stricter laws on the usage of PEI [5]. Therefore, chitosan, which is highly safe, is considered as a promising alternative to replace PEI.

Table 2.6 Toxicity comparison between different types of crosslinkers used for gelation

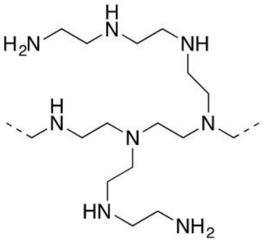
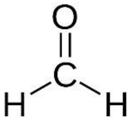
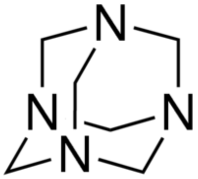
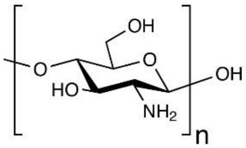
	Crosslinker	Chemical formula	LD_{50} (mg/kg body)	Ref.
Inorganic	Chromium	Cr^{3+}	185-615	[116]
		Cr^{6+}	20-250	
	Aluminum	Al^{3+}	200-1000	
	Zirconium	Zr^{4+}	> 1000	[117]
Organic	PEI		2200	[5]

Table 2.6 Toxicity comparison between different types of crosslinkers used for gelation

Crosslinker	Chemical formula	LD_{50} (mg/kg body)	Ref.
Formaldehyde		300-1300	[118]
Hydroquinone (HQ)		300-1300	[119]
Hexamethylenetetramine (HMTA)		200-450	[120]
Chitosan		16000	[5]

Chapter 3: Materials and Methods

3.1. Materials

PAM with high Mw (>1,500,000 Da) and degree of activity of 12 - 15 wt. % and low Mw (700,000 Da) with a concentration of 20 wt. % was obtained from SNF Floerger, France. PAtBA with a molecular weight of around 100,000 Da and activity content of 20 wt.% was also obtained from the same company. The viscosity of the low and high Mw PAM at 170.3 s^{-1} and 24^oC is 72 and 195 cP, respectively. PEI of Mw of 750,000 Da is used as a cross-linker with a concentration of 33.3 wt. % is from Polyscience Company, Canada. Non-functionalized nano-silica in liquid form with different sizes of 8, 20, 50 and 85 nm were used to reinforce the cross-linked polymer obtained from NYACOL Nano Technologies, Inc, Canada. Table 3.1 summarizes the properties of the different types of functionalized silica screened in chapter 4.b. Also, The aluminum complexed used in chapter 4.d are summarized in Table 3.2 below.

Table 3.1. Summary of all types of silicon used in the investigation

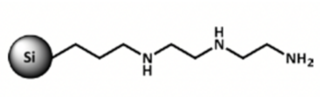
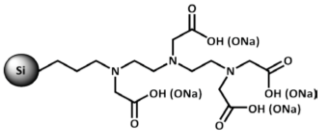
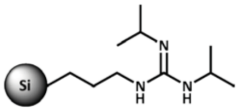
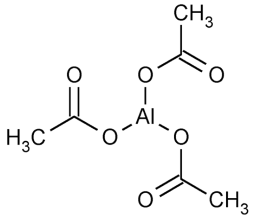
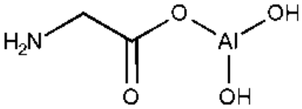
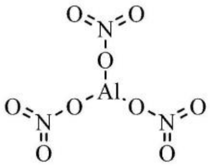
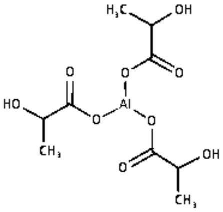
Functional group	Size (μm)	Molecular loading (mmol/g)	Pore size (Å)	Density (g/mL)	Structure
Triamine (TRI)	40-63	1.11	60	0.736	
TAAcONa (TAC)	40-63	0.41	60	0.712	
Guanidine (GUA)	40-63	0.80	60	0.732	

Table 3.2 Aluminum based crosslinkers used in the study

Scientific Name	Supplier	Purity	Appearance	Structure
Aluminum Acetate [*AlAc*]	Glentham, England	99%	White Powder	
Aluminum tris(2-AminoAcetate) [*Al-AmAc*]	iChemical, China	97%	White to yellowish powder	
Aluminum Nitrate Nonahydrate [*AlNt*]	iChemical, China	100%	White Crystals	
Aluminum Lactate [*AlLc*]	iChemical, China	>90%	White Powder	

All the materials were used as received. The solutions were prepared using deionized water, unless mentioned otherwise.

3.2.Methods and Experimental procedures

3.2.1. Gelants preparation procedures

Predetermined amounts of each samples constituents was added in the following order: base polymer, water, nanosilica, crosslinker, and then the other additives. A stirring time of 10 minutes was allowed after the addition of each component. Moreover, the sample is sonicated for 10 minutes after the addition of nanosilica and the colloidal crosslinkers to enhance their stability in the aqueous solutions. Seawater used is synthetic based on the composition showed in Table 3.3.

Table 3.3. Composition of synthetic seawater [121]

Salt	Concentration, g/L
$NaHCO_3$	0.2382
Na_2SO_4	6.5754
$CaCl_2.H_2O$	2.3945
$MgCl_2.6H_2O$	18.0539
NaCl	40.2738
TDS	67.2976

For pH adjustments, Highly concentrated solutions of HCl (39 M) and KOH (20 wt%) were used to adjust the pH when needed. Pre-calibrated Hach 2100 pH-meter was used for measurements.

3.2.2. Mature gel preparation

Test tubes, which can withstand up to 180oC, were filled by the polymeric solution before immersing into an oil bath. The temperature was gradually increased, over a period of 20 minutes, to 130oC to avoid thermal shock and glass breaking. This temperature was selected to represent high temperature oil and gas reservoirs. Silicon caps that can withstand high pressures are used, as due to the high water content in the used polymeric formulation, pressure tends to increase inside the tubes which inhibits polymeric hydrolysis at this high temperature. 24 hours was set as curing time, unless mentioned other wise, to ensure a complete gelation process. After that, the gel strength of mature gels was measured using a Rheometer.

3.2.3. Viscoelastic Behavior of Mature Gels

Anton Paar MCR 302 rheometer was used to conduct all the rheological experiments. Frequency sweep tests were conducted at 25^{o}C and atmospheric pressure using the parallel plate geometry with a 25 mm diameter and 2 mm gap. The motor adjustment was done first before installing the parallel plate geometry. Zero gap and reset force was performed before each set of runs. Samples were loaded and trimmed carefully to fill the area of the parallel plate. All tests were implemented on mature gels where the strain was fixed at 10 %, which is within the linear region and the frequency was varied in the range between 0.25 to 100 Hz. Storage modulus at a frequency of 10 Hz was used to compare the gel strength of the different formulations. Storage modulus represents the elastic behavior of the produced gel as well as the amount of stored energy in the system. In engineering terms, the more the storage modulus is, the higher stresses the gel can withstand. Thus, it will result in higher well stability.

3.2.4. Stability of colloidal crosslinkers in gelling samples

Some separation was observed is some samples leaving a part of the sample to be poorly crosslinked, therefore, the percentage of the separated phase is reported to reflect the stability of the system after being aged for 24 hours (Figure 3.1).

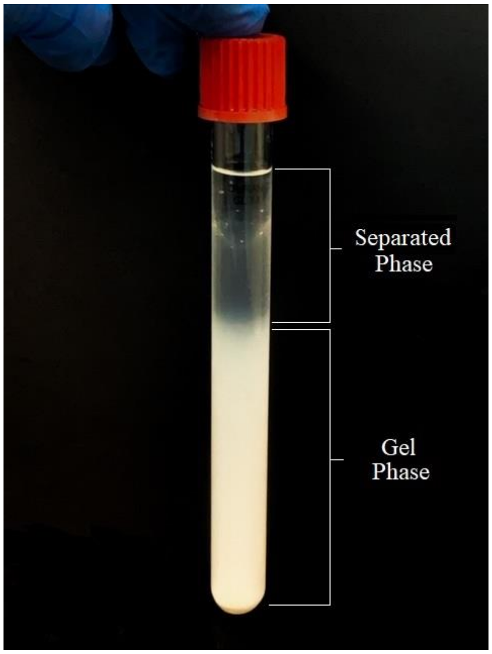


Figure 3.1 Separation in the gel sample due to the settling of colloids

3.2.5. Differential Scanning Calorimeter (DSC) experiments

DSC experiments were done on TA micro DSC (MCDSC) using a high-pressure ampule at a constant pressure of 500 psi applied using nitrogen. It is used to examine the gelation kinetics of the newly developed crosslinkers. For all experiments, the MDSC was first equilibrated for 10 minutes at room temperature followed by ramping the temperature to the target temperature at a rate of 2^{o}C/min. When the final temperature is reached, the mode is switched to isothermal where the temperature is kept constant for a period until the baseline is reached again which indicates no further thermal interactions.

3.2.6. Zeta Potential measurements

Zeta potential reflects the electric double layer surrounding the particles in the suspended system where the higher the magnitude is, the more stable the colloidal system is. To assess the stability of the colloidal crosslinkers in the aqueous solutions, the zeta potential of the inorganic particles was tested. Zeta potential tests were performed in Malvern nanosizer at room temperature. For nanosilica, the stock solutions was diluted 10 times and then tested. For the aluminum-based colloidal crosslinkers, a solution of 3 mg/L particles in water was prepared, and then the pH of the system was adjusted from low to high pH values where each where tested to create a pH response of the colloidal crosslinkers. Zeta potential experiments were conducted at ambient conditions.

3.2.7. Thermogravimetric Analysis (TGA)

The thermal stability of crosslinkers is measured through TGA technique using Perkin Elmer Pyris 1 TGA equipment. Nitrogen gas was used as purging gas at a rate of 35 ml/min .The samples were heated from 25 ^{o}C to the predetermined final temperature at a rate of 10 ^{o}C/min. For aluminum based crosslinkers, the samples where kept at an isothermal mode at a temperature of 105 ^{o}C, after the heat scanning, for one more hour to ensure the evaporation of all volatile compounds.

3.2.8. Scanning Electron Microscope (SEM)

SEM has been proved to be an effective imaging technique used to examine the micro structure of hydrogels. As the conventional SEM doesn’t accept humid sample, the tested hydrogel was dried in the following procedure: 1) The sample was dried in a regular freezer at a temperature of -20 ^{o}C for 48 hours 2) The sample was then freeze at -40 ^{o}C under vacuum conditions using VirTis Freeze Drying Equipment. The SEM tests were then conducted using Nova Nano SEM 450, FEI.

Chapter 4: Results and Discussion

4.1. Part A: Reinforcement of PAM/PEI system using nanosilica for high-temperature reservoirs

4.1.1. Introduction

As nanomaterials have been proved to be a good physical enforcer in conformance control [122], many researchers have studied the effect of introducing nanosilica to gelling systems. Various mechanisms have been proposed to explain the effect of silica in a polymeric system. Conradi suggested that physical enforcement happens in the presence of a polar group in the polymer which creates an electrostatic bond between silica and the polymer matrix which makes it more compacted and stronger [123]. Chen et al. explained the reaction between PAM/PEI and silica in a way that the multiple silanol groups on silicon create a hydrogen bond with the amide group [124]. Furthermore, they claimed that silica contributes to what is explained as "cross-linking reaction" where the presence of silicon in the backbone of the polymer gives the gel additional strength. Wei et al. have further studied this mechanism computationally, where the binding energy on the atomic level was calculated for sizes between 20.06 – 36.75 Å (2.006 – 3.675 nm) [125]. The results indicated the presence of physical bonds in the form of van der walls interactions between the hydroxyl groups on silica and the functional groups on PAM. The peak appeared at a bond length of 1.8 – 3.1 Å, which was designated as hydrogen bonding.

The main limitation faced in a polymeric system with nanosilica is the agglomeration and the difficulty in the dispersion. Tadano et al. investigated the behavior of 15 nm silica in a polymeric system and found the percentage of agglomeration to be a function of the concentration of the polymer and Mw as the more entangled the polymer chains are the more suspended silica is found [126].

Previous studies have addressed the effect of adding nanosilica to reinforce polymeric solutions using a fixed particle size. In this study, the effect of particle size on the rheology and cross-linking of PAM/PEI system is investigated using different sizes of nanosilica. Moreover, the combined effect of polymer size and silica size is studied by examining nanosilica in low and high Mw PAM. Therefore, the detailed objectives of this work are to: (i) Study the effect of particle size of various nanosilica particles on the viscoelastic behavior of PAM /PEI at high temperature. (ii) Examine the efficiency of nanosilica in reinforcing polymeric gels with different nanosilica loading. (iii) Investigate the influence of nanosilica on strengthening low and high Mw PAM. (iv) Explore the impact of nanosilica size on the crosslinking of PAM/PEI and identify the controlling mechanisms.

4.1.2. Sydansk codes for nanosilica reinforced gels

In Table 4.1, the gel codes are shown for the different systems after an aging time of 24 hours in an oil bath at a temperature of 130^{o}C. Compared to the baseline, which is a PAM/PEI system with a 9/1 concentration; all reinforced systems exhibited a noticeable increase in the gel strength upon addition of nanosilica. However, among the experimented systems, the maximum strength was achieved using nanosilica of sizes 20 and 50 nm. The increase of silica concentration to levels of up to 2 wt. % has enhanced the gel strength of the base polymer solution from Sydansk code “F” to a rigid gel of code “I”.

Table 4.1 Sydansk codes for the produced gels

	Nano-Silica concentration, wt. %				
Size, nm	0.1	0.25	0.5	1	2
8	G	G	G	G	G
20	H	H	H	I	I
50	H	H	H	I	I
85	G	G	G	G	H

4.1.3. Storage Modulus

Rheological tests for the produced gel were in agreement with the above Sydansk test results as the middle-sized silica achieved the best results (Figure 4.1). The dashed line in Figure 4.1 indicates the base line followed which is a system of 9% of PAM with 1% of the cross-linker (PEI) in which a gel with a storage modulus of 1644 Pa was produced. The highest gel strength was achieved for the system with 50 nm silica at a concentration of 2 wt. % reaching a storage modulus value of 5481 Pa which is more than 300 % higher than PAM/PEI base solution. Figure 4.2 shows the frequency sweep tests performed to evaluate the strength of the mature gel. There was no significant change of storage modulus noticed upon changing the frequency. Hence, the gel produced is stable in the tested range.

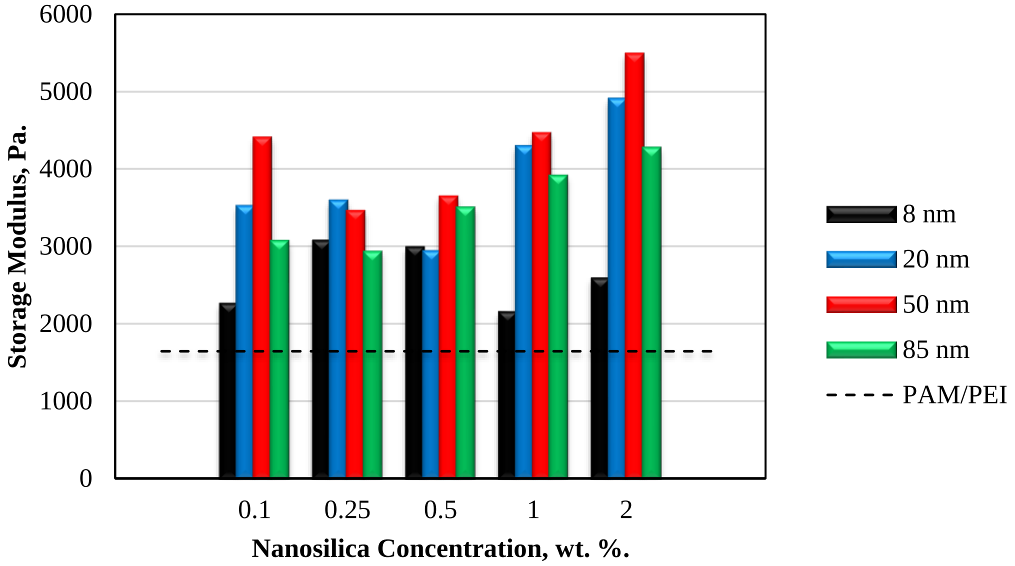


Figure 4.1 Effect of silica size and concentration on storage modulus

The impact of silica addition on gel strength could be divided into three regimes as shown in Figure 4.3. First, a slight increase in the gel strength is observed followed by a small drop and then a constant increase in the gel strength of the gel with the addition of more silica. Figure 4.3 illustrates this behavior where the effect has been clearer for the 8 nm silica. It is believed that in the first period, silica enhances the cross-linking reaction, which is initiated by the PEI, and creates hydrogen bonds between silanol groups and the polymers. This interaction gives extra strength to the polymer.

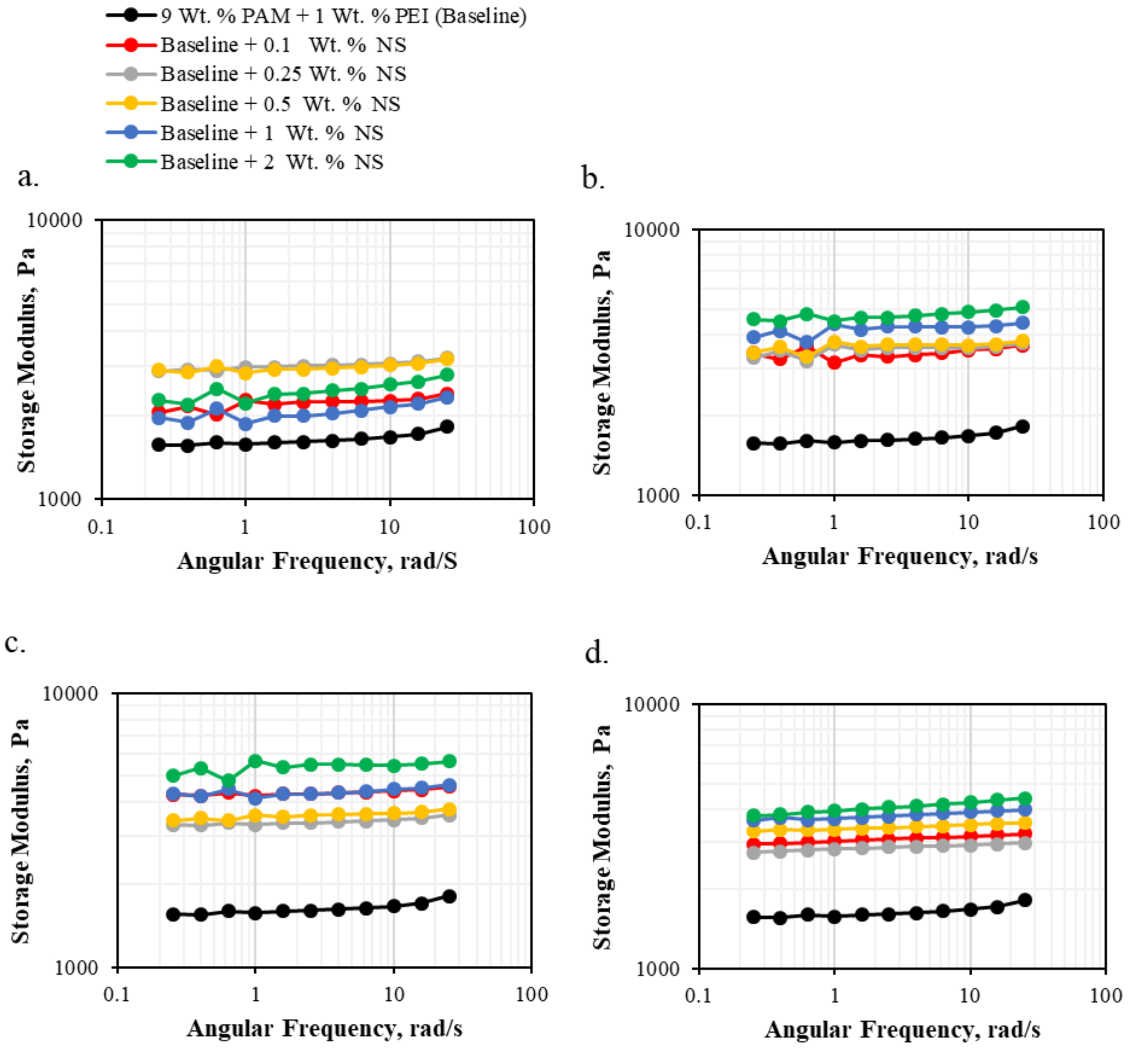


Figure 4.2 Frequency sweep test of 9:1 wt. % PAM/PEI combined with nanosilica (NS) at a range of concentration from 0.1 to 2 wt. % and different sizes a) 8 nm. b) 20 nm. c) 50 nm. d) 85 nm.

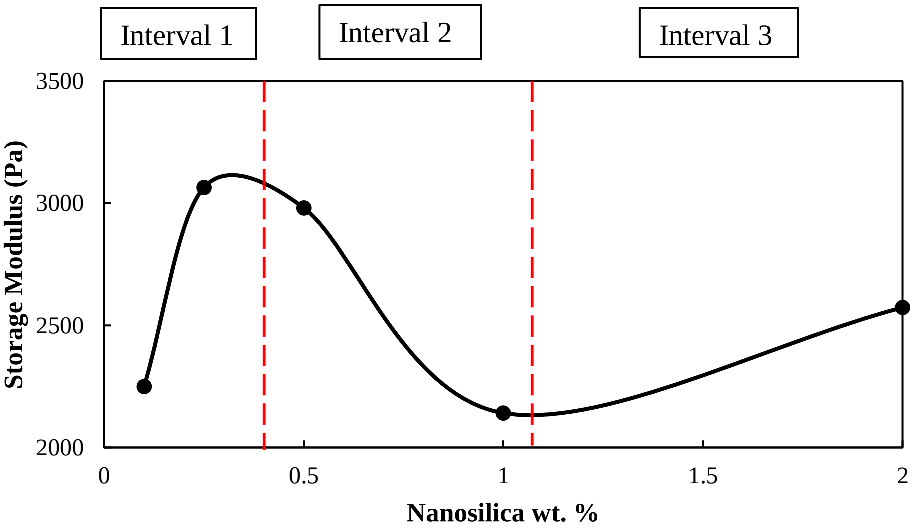


Figure 4.3 Rheological behavior of gel with the variation in concentration of 8 nm silica

A similar observation was noticed by Adibana and Hill where they claimed that silica in the presence of a small amount of cross-linker is able to chemically cross-link the polyacrylamide [108]. In the second interval, Increasing the amount of nanosilica in the system further decreases the possibility of interaction between the polymer and the cross-linker, which results in the observed drop in elasticity. Further increase in silica will no longer affect the crosslink-ability, and additional silica in the third interval leads to an increase in the strength. This is mainly due to the increase in the total solid contents in the system as well as the creation of hydrogen bonding between silica and the cross-linked polymer. This observation was also reported by Chen et al. where it was suggested that the controlling mechanisms of adsorption of PAM on the surface of nanosilica are [124]:

a. Binding through hydrogen bond between nanosilica and PAM

b. Hydrophobic interaction

c. Based on the charge on the polymer chains, electrostatic binding.

However, these forces are competing with each other because even with anionic polyacrylamides such as HPAM interacted with nano-silica with a negative charge on its surface. From the electrostatic point of view, this interaction is not desired; however, it has no effect on the adsorption of anionic polymers on silica. The adsorption mechanism for anionic polymers is accomplished through hydrogen bonding between the carbonyl on PAM chains with the silica which is stronger than the electrostatic repulsion23.

Weakening of the electrostatic repulsion is favorable because many attachment points are easy to form via hydrogen bonding between PAM and nano-silica, which is preferred for better gel reinforcement. Increasing the size and concentration of silica will increase the surface area and consequently the total charge. Therefore, the optimum concentration significantly depends on the size and concentration of the silica because they control the adsorption of PAM on silica surface and directly affect the controlling mechanisms, which in turn influence the gel strength.

The concentration ranges of these three intervals were observed to shift to lower values as the size of nanosilica is increased (Figure 4.4). The trend of the 20 nm reinforced gel (Figure 4.4.a) shows a shrinkage in the first interval as it ended at a concentration below 0.25 wt%, followed by the second and the third intervals. While in the 50 and 85 nm (Figure 4.4.b and Figure 4.4.c), the first interval has disappeared which indicates its existence at lower concentrations than the studied range. Finally, the second interval has further contracted to a smaller range for the 85 nm silica (Figure 4.4.c). This behavior could be directly linked to the surface area per unit mass where it is higher for smaller particles. The higher the surface area, the higher the cross-linking inhibition in the second interval, which shifts the whole range to higher concentrations. For the same reason, inhibition of cross-linking takes place at a lower concentration for the larger particles (50 and 85 nm).

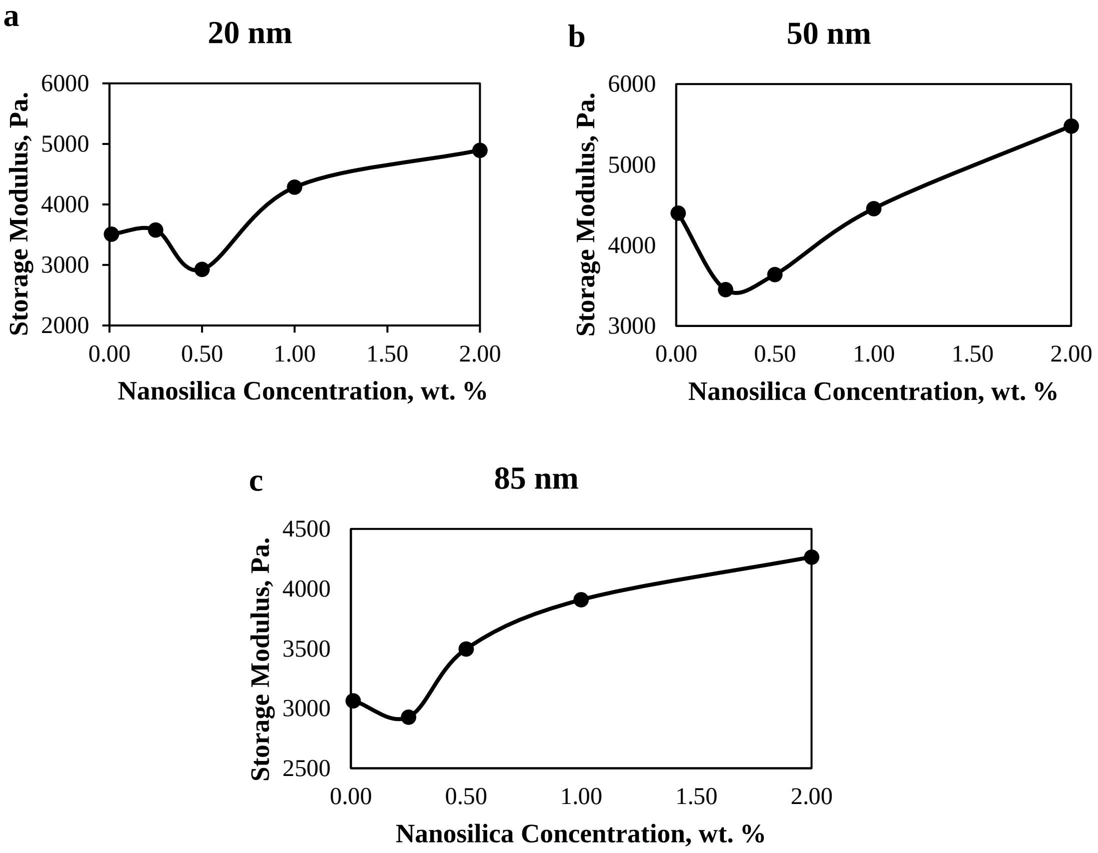


Figure 4.4 Rheological behavior of gel with the variation in concentration of a) 20 nm b) 50 nm c) 85 nm silica

Coil contraction phenomena were reported after intramolecular hydrophobic interactions. However, it was confirmed that there is a "critical association concentration", above which a stable network structure will be formed resulting in substantial viscosity enhancement and hence polymer solution reinforcement [63,127]. Moreover, nanosilica also has a critical concentration above which the nanoparticles will adsorb PAM chains because of the hydrogen bonding between the silanol group and carbonyl groups [128].

Similar strengthening effect was noticed upon adding fly ash, which consists mainly of silica and alumina, to the PAM/PEI crosslinked system. Adewunmi et al. have verified through XRD test that ash particles disperse in the polymeric network which indicates the existence of physical or chemical bonds. Moreover, polymeric systems tend to shift to more crystalline rather than amorphous upon the addition of fly ash [129]. These observations verifies the polymer-silanol interaction mechanisms discussed above.

4.1.4. Stability of Nanosilica Solutions using Zeta Potential

For further understanding of the reinforced systems, zeta potential (ζ-potential) of the stock solutions of nanosilica in water was tested. Figure 4.5 revealed that the 50 nm size is the most stable size in water as it has shown the highest magnitude of ζ-potential of - 42.8 mV. These results were compatible with the rheological results as the 50 nm showed the highest gel strength. The 8 nm silica showed the least stable state between the tested nanoparticles which is again was reflected in rheology by producing the weakest gel. This is mainly interpreted by the fact that the more stable the system is, the easier is its dispersion through the viscous polymer solution resulting in improved bonding and higher strength. The high values of ζ-potential suggest that the effect of the hydrophobic interaction of all systems is negligible which means that no phase separation will occur. Accordingly, silica settling has not been observed for all samples even at high silica concentrations of the largest studied size, which was 85 nm.

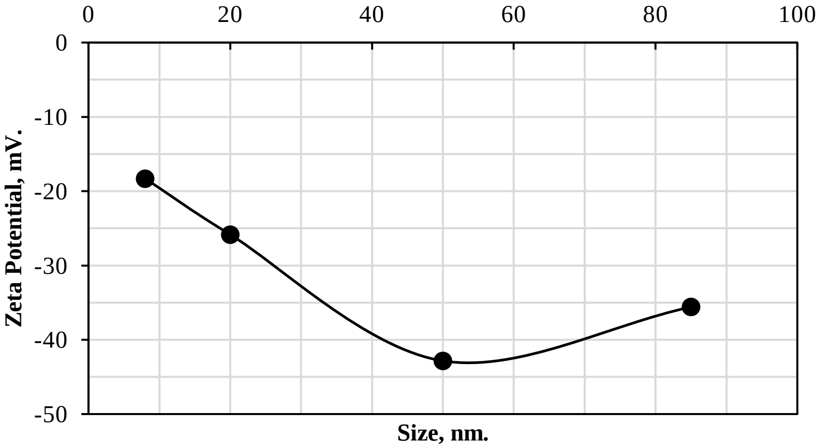


Figure 4.5 Zeta potential of nanosilica in water

4.1.5. Loss factor

Loss factor, or mathematically tan (δ), is a good representation of the degree of viscoelasticity as described in **Eq. 4.1**.

$$\tan(\delta) = \frac{G''}{G'} \tag{4.1}$$

Figure 4.6 shows that all the tested samples had a tan (δ) of less than 1 which indicates the solid-like behavior of the gels which is expected as the tests were performed on a mature gel.

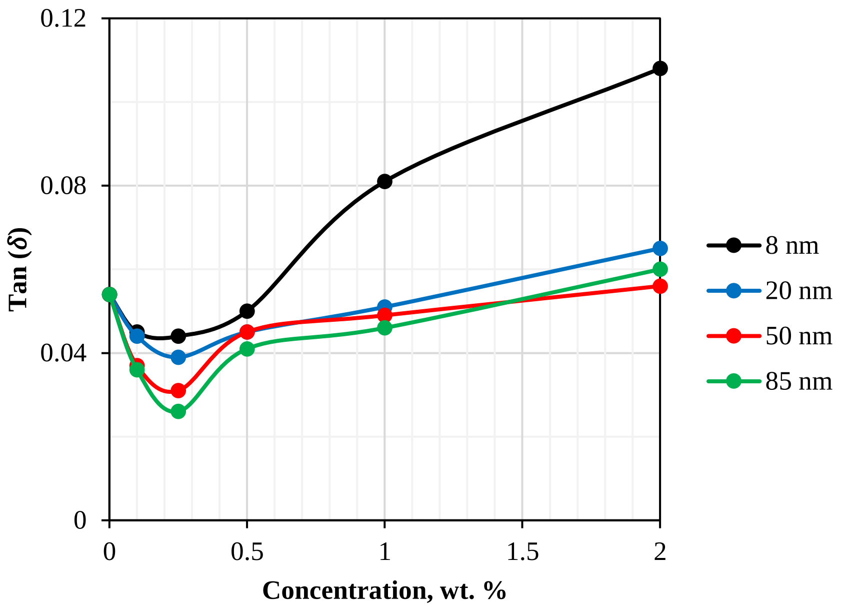


Figure 4.6 Loss factor as a function of nanosilica concertation

Figure 4.7 shows that there is a clear trend followed by the magnitude of the loss factor as it decreases with the increase of nanoparticle size for a fixed amount of added silica. These results reflect that the produced gel shows a more solid-like behavior when larger particles of nanosilica are added. From another perspective, varying the concentration for a fixed nanosilica size showed a polynomial-like trend where there is a minimum value mirroring an optimum concentration that shows the most solid-like behavior. This optimum concentration was found to be between 0.25 and 0.5 wt. % for all sizes. The addition of more silica showed a higher strength in the rheological tests due to the increase of van der Waal forces between the silica and the polymeric matrix. However, the presence of silica hinders the cross-linking reaction, which is reflected in the shift of elasticity towards the viscous side.

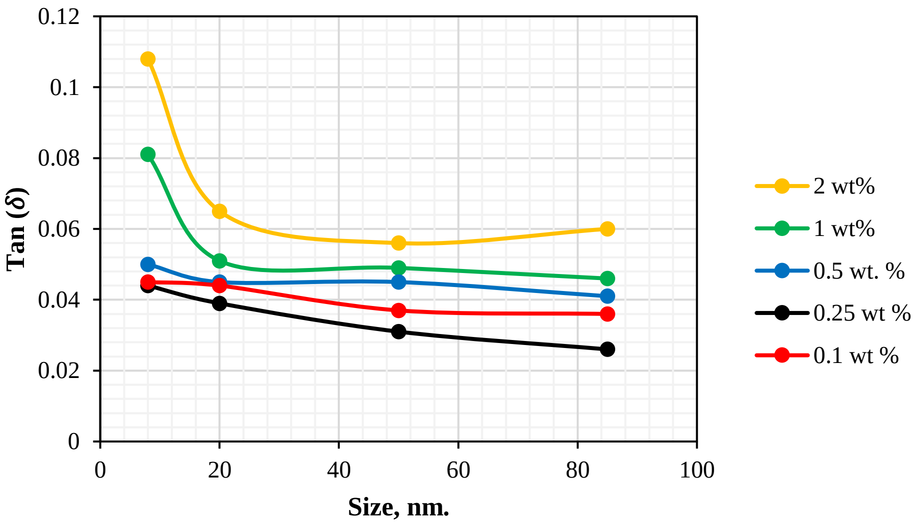


Figure 4.7. Loss modulus as a function of nanosilica size

4.1.6. Effect of PAM molecular weight

On one hand, high Mw PAM cross-linked with PEI without the addition of any silica showed a significant increase in the strength of the final gel (Figure 4.8). The same ratio of PAM/PEI was used and the Mw of PAM was the only variable. Thus, the final polymeric matrix produced by the high Mw PAM was stronger with the gel strength of the high Mw PAM being more than 200 % higher than the gel with low Mw PAM. On the other hand, upon the addition of silica to PAM, the high Mw PAM showed different behavior than the low Mw system. Previous research suggested that the addition of silica to polymers leads to increase in the hydrodynamic radius of the polymer due to the bridging connection between nanosilica and PAM which increases the length of the molecular chain as well as the hydrophilic interaction of nanosilica and PAM [124].

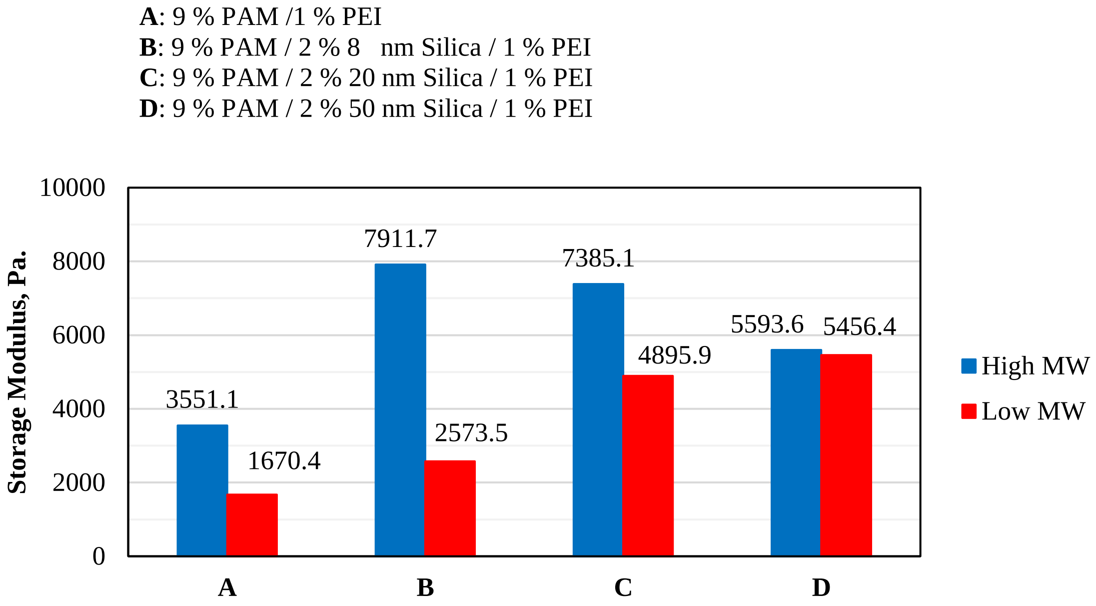


Figure 4.8. Effect of Mw on storage modulus.

Based on zeta potential results, the bridging connection is proposed to be the dominant mechanism because of the negligible effect of the hydrophilicity as suggested by Chen et al. [124]. At high Mw, the coil contraction of PAM intermolecular chains would greatly influence the network structure because the chains would be extended. High strength was achieved using the high Mw PAM; however, using this system might result in problems with injectivity due to the high viscosity despite its favorable high strength.

For the high Mw PAM, Figure 4.8 shows a decrease in gel strength with the increase in particle size while the reverse is observed for the low Mw PAM. In the case of high Mw polymer, increasing the size of silica provides fewer cross-linkable sites since it hinders the accessability of PEI to PAM chains and hence the coil contraction will be significant. On the other hand, using the 8 nm size silica provides more PEI accessability for chemical cross-linking with PAM and higher surface area/mass for the physical carbonyl-silanol hydrogen bonding. Thus, the ease of penetration, which is reflected in the size of silica, is the dominant factor in the high Mw system.

In contrast, for low Mw PAM, chain are shorter and the number of PAM chains is high so even large particles will have enough space to penetrate through the polymeric matrix. Therefore, the degree of suspension and stability of silica will be the determining step for the low Mw polymeric matrix.

Figure 4.9 shows a schematic description of the effect of the small and large size of nanosilica on the adsorption of PAM and network structure of reinforced composite. Similar mechanism was reported by Chen et al. using 28.6 nm silica, and the same previous approach has been extended in this study to explore the effect of size [124].

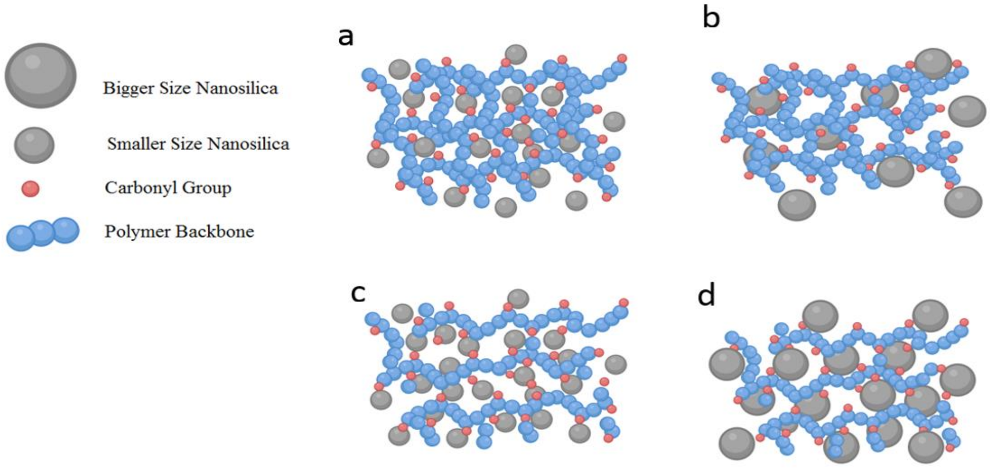


Figure 4.9. Schematic representation of the dispersion of a) small size nanosilica in high Mw polymer b) large size nanosilica in high Mw polymer c) small size nanosilica in low Mw polymer d) large size nanosilica in low Mw polymer.

4.1.7. Effect of Aging Time on the Gel Strength

Th**e** thermal stability of PAM/PEI system has been studied by exposing the gelled systems to high temperature for different aging times. Figure 4.10 shows that nanosilica has enhanced the thermal stability of the 9 wt. PAM / 1 wt. PEI at different aging times. The base solution PAM/PEI showed slight decrease in the storage modulus after a day of aging at 130^{o}C and the same trend can be clearly observed after the addition of 8 nm compared with the gel strength after 12 hours. Similar behavior was reported by El-Karsani et al. for the base solution at different aging times at 150^{o}C [37]. The ratio of gel strength reduction was 35.54 % for the base fluids, however, adding 2 wt. % of the smallest size nanosilica showed about 19.9 % drop which indicates the effect of silica in enhancing the thermal stability. For the bigger sizes (20, 50 and 50 nm) the gel strength increased linearly with time for the whole studied range. This behavior indicates that the presence of silica has delayed the thermal decomposition of the gel to more than 24 hours. Additionally, the trend of gel strength for different aging times (Figure 4.10) was the same having the 50 nm silica as the optimum size which revealed significant gel strength increase by 67.75 % after raising the aging time from 1 hour to 24 hours. Moreover, the produced gel with 50 nm silica after 1 hour was stronger by 81.62 % compared to the mature gel obtained from 9 wt. % PAM / 1 wt. % PEI. Therefore, such gels can be used for treatment of lost circulation since they produce stronger gel in a short time; hence reduce the drilling downtime.

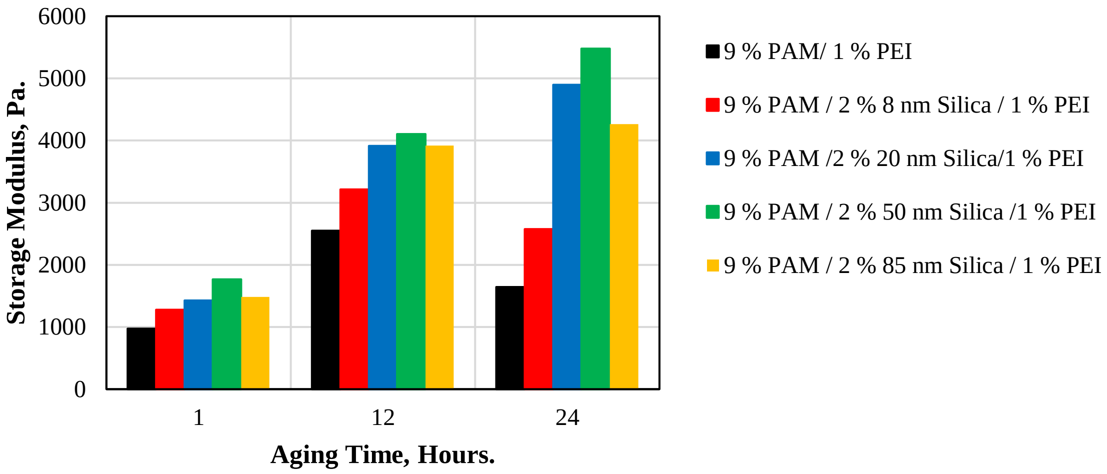


Figure 4.10 Effect of aging time on the gel strength of 9 wt. % PAM / 1 wt. % PEI with 2 wt. % nanosilica with different sizes at 130°C.

Gelation time of the studied system can be fast for deep reservoir applications where the system will form gel before reaching the designated area. Nevertheless, gelation time can be controlled through addition of retarders. Many retarders has been proposed in the literature such as ammonium chloride and sodium carbonate [15].

4.1.8. Conclusions

In this work, nanosilica with sizes in the range 8-85 nm were used to reinforce a polymer solution consisting of 9 wt. % PAM and 1 wt. % PEI. The polymer and the cross-linker are examined for potential wellbore strengthening applications at elevated temperature (130°C). Such conditions are representative of deep reservoir conditions. Different concentrations between 0.1 and 2 wt. % of various sizes were investigated. Although different metrics were used to evaluate the studied systems such as zeta potential, loss factor and storage modulus, the last had always gave the conclusive decision, as gel strength is the targeted property in this study. Based on the findings of this study, it could be concluded that:

1. Nanosilica with the studied nano sizes range is an efficient reinforcing agent for 9:1 wt. % PAM/PEI solution for high temperature wellbore strengthening applications and could be used to seal the fractures inside the reservoir because of the observed high gel strength. Sydansk code “G” to “I” were observed for all mature gels after adding nanosilica compared to code “F” for the base polymeric formulation.
2. Addition of 2 wt. % of 50 nm silica to the base polymer/cross-linker solution has improved the storage modulus by more than 3 folds. Whereas, the minimum gel strength enhancement was recorded after adding 1 wt. % of 8 nm silica to the PAM/PEI solution which was stronger by 1.3 times compared to the polymeric solution at the same conditions. Thus, the optimum nanosilica size is 50 nm for the high Mw PAM/PEI system.
3. Increasing the size of nanosilica in the polymeric system tend to increase the elasticity. Adding 2 wt. % of small size nanosilica to high Mw PAM increased the gel strength. However, for the high Mw PAM the increase in the size of nanosilica leads to initial increase in gel strength followed by a drop for the large size silica with an optimum size of 8 nm. On the other hand, the optimum for the low Mw PAM was observed at 50 nm in agreement with zeta potential results. These observations are correlated to PAM chain size and ease of mobility of silica particles within the shorter chain of the low Mw PAM.
4. Hydrogen bonding between silanol group and a carbonyl group on PAM was suggested to be the dominant mechanism that forms a stable network structure in which nanosilica

physically reinforces the new formulated systems with different nano sizes. Therefore, the gel strength developed due to the chemical cross-linking of PAM/PEI has further been enhanced by the addition of silica.

5. The effect of silica was not limited to the physical enhancement, as it has also extended to enhancing the thermal stability of the gel. The storage modulus of the gel in the absence of silica was noticed to start decreasing after 24 hours of aging under 130 ^{o}C. Yet, adding silica to the same system has extended this degrading effect to longer periods beyond the studied range (24 hours) as the storage modulus was found to be proportional to the aging time within the first 24 hours. The results suggest that the optimum size of nanosilica that leads to the highest gel strength depends on PAM Mw.

4.2. Part B: Screening of organic functionalized silica crosslinkers and study of gelation kinetics

4.2.1. Introduction

Traditionally, models have been developed to study the crystallization which has been widely applied and proved its reliability [130–132]. Nevertheless, El-Karsani et al. [38] have adapted this technique to study gelation kinetics then followed by few studies applying the same approach [40,42]. The physics of polymer crystallization involves the formation of solids from a polymer melt due to cooling, in a process that is initialized by nuclei formation. Similarly, gelation involves the formation of solid-like structure from a liquid due to heating. The similarity of the physics of gelation and crystallization attracted our group to use the same models, developed earlier for describing polymer crystallization kinetics, in describing gelation kinetics [38,42].

Avrami Model

Avrami model [133] is described by **Eq. 4.2**.

$$1 - \mathrm{x_T} = \exp(-\mathrm{k_T} \cdot \mathrm{t^n}) \tag{4.2}$$

Where $\mathrm{k_T}$ the rate constant, n is the gelation exponent and t is the time of gelation. Equation 1 could also be used for non-isothermal gelation by switching from time scale to temperature scale using the scanning rate R ($^{\mathrm{o}}$C/min). $\mathrm{x_t}$ in equation 1 describes the fractional gelation which is the percentage of the heat released or absorbed at time t to the total heat released when the gelation is complete. **Eq. 4.3** explains the mathematical expression of the fractional gelation at time t.

$$x_t = \frac{\int_{t_0}^{t}\left(\frac{dH}{dt}\right)dt}{\int_{t_0}^{t\infty}\left(\frac{dH}{dt}\right)dt} \tag{4.3}$$

Eq. 4.2 could be linearized by applying double logarithmic which is described in **Eq. 4.**

$$\ln(-\ln(1 - x_t)) = \ln(k_t) + n\ln(t) \tag{4.4}$$

Vyazovikin and Sbirrazzuoli Model

Vyazovikin and Sbirrazzuoli [134] developed a model to describe the secondary crystallization. Unlike Avrami model which describes the whole crystallization process to be linear, this model assumes the crystallization process to be more restricted as the fractional crystallinity increases. This phenomenon was interpreted physically due to the increase in the difficulty of molecular diffusion as the crystal grows. The mathematical model is described in **Eq. 5**, which relates the activation energy to the systems temperature.

$$\Delta E_x = U^* \frac{T^2}{(T-T_\infty)^2} + K_g R \frac{T_m^2 - T^2 - T_m T}{(T_m - T)^2 T}$$

(4.5)

Whilst activation energy can be computed as a function of fractional crystallization using **Eq. 4.6.**

$$-\frac{E}{R} = \frac{d\ln(\frac{dX}{dt})}{dT^{-1}}$$

(4.6)

While T_m represents the melting point of the polymer, U^* is the partial activation energy describing the limitation in diffusion, K_g is nucleation parameter, E is the activation energy, R is the universal gas constant and T_∞ is commonly described to be (T_g – 30 K) where T_g is the glass-transition temperature [132].

This model has been widely applied in literature to describe the crystallization kinetics [131,132,135]. However, in this study, it will be adapted to describe gelation kinetics of PAM crosslinked with PEI as well as with functionalized silica. Melting point in the model was replaced by the final gelation temperature while T_g was replaced by the initial gelation point to simulate the crystallization process.

4.2.2. Heat flow of PAM in water

The heat released or absorbed of a single system containing 9 wt. % PAM diluted in water during both the non-isothermal and isothermal intervals is shown in Figure 4.11. The first interval is the heating from 25^{o}C to 130^{o}C at a constant heating rate of 2^{o}C and the second interval is isothermal at 130^{o}C. The first interval resembles the injection of the gelant in oil and gas wells where the temperature increases till it reaches the reservoir temperature. The second interval simulates the gelling solution when it reaches the target zone and the temperature remains constant for a fixed period of time before the formation of the 3D gel structure. The heat released by pure PAM is used as a baseline for the analysis of gelling systems to identify the heat related to the heat capacity and PAM hydrolysis. A clear endothermic peak appeared signifying the hydrolysis of PAM which is in agreement with previous literature reports of El-Karsani et al [15] where hydrolysis of PAM was described to be an endothermic reaction. Heat absorbed by the system during the course of hydrolysis was found to be 357.8 J/g. These results are comparable to another study in which the hydrolysis of 20 wt. % PAM in water was 375 J/g [35]. The small variation in the results is attributed to the difference in the molecular weight of PAM used, scanning rate and the active content in the studied systems.

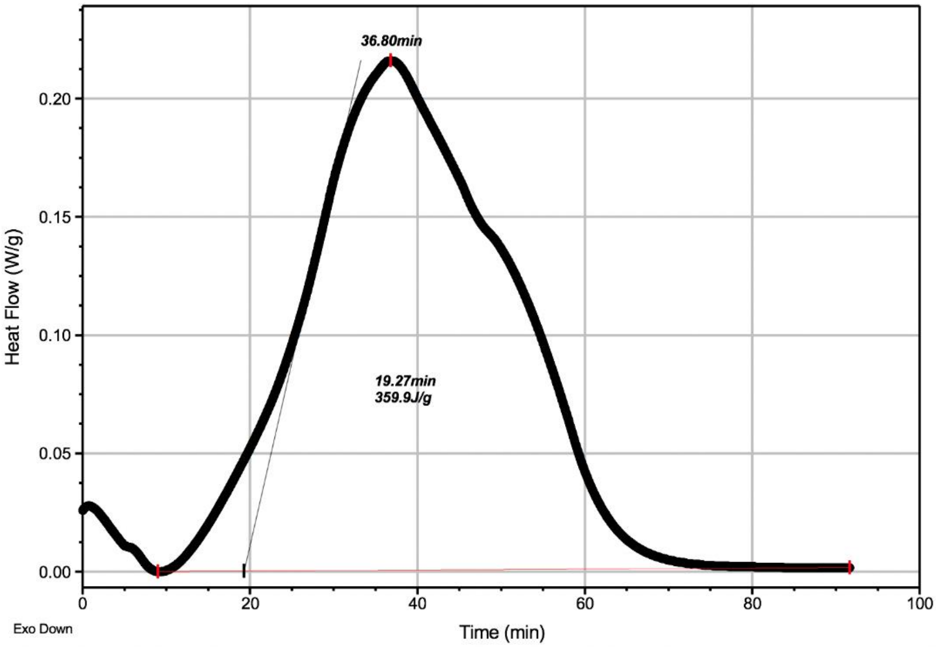


Figure 4.11 Heat flow of 9% PAM in water

4.2.3. PAM/PEI-gelant heat flow analysis

Figure 4.12.a represents the gelation of 9:1 wt % PAM:PEI and the results have followed with the same trends of El-Karsani et al. [38]. However, a new approach of analysis is followed here by using PAM hydrolysis data (Figure 4.11) as a baseline that results in Figure 4.12.b. Analysis has been done based on the heat flow with temperature (Figure 4.12.b) to determine the temperature at which the heat released as a result of the crosslinking reaction is detectable. Figure 4.12.b shows the onset of the crosslinking of PAM/PEI system as 84.2^{o}C which is in alignment with field applications where this system is only suitable for high reservoir temperatures [12]. Besides, an extra endothermic peak has been attained upon introducing PEI to the system, this is due to the increase in the total alkalinity of the system. Similar behavior was reported in the literature [136]

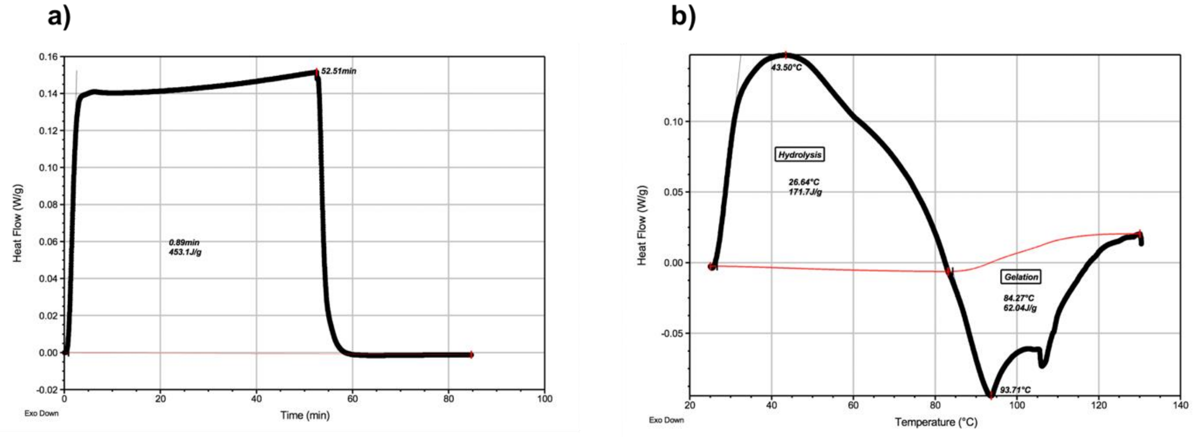


Figure 4.12. Heat flow of PAM:PEI system at a ratio of 9:1 a) Unsubtracted data b) subtracted data from the baseline

4.2.4. Heat flow of PAM/functionalized-silica systems

Among the three types of functionalized silica investigated in this study, TRI was the only material to crosslink producing a stable gel at 130^{o}C (Figure 4.13). Table 4.2 describes the physical states of gels produced using Sydansk system of coding [24]. PAM/TRI system was able to produce a gel with code E which is comparable to the benchmark system, PAM/PEI, that produces a gel of code F. Due to the instability of triamine-functionalized silica in water, some particles have precipitated. However, due to the presence of viscous PAM as well as the initial sonication, some particles remained dispersed in the solution, which was enough to produce a gel. This precipitation of TRI leads surly to a decrease in the number of crosslinkable site, thus, a stronger and more stable gel can be attained by stabilizing the silica in the solution.

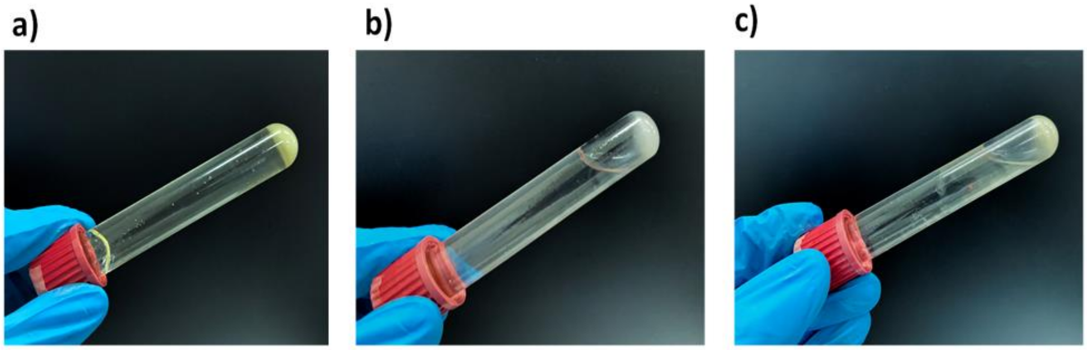


Figure 4.13. Systems of PAM and silica functionalized with a) TRI b) TAC c) GUA, after aging for 24 hours at 130°C

Table 4.2 Sydansk codes for screened systems

System	Sydansk code	Physical Interpretation
9% PAM 1% PEI	F	Highly deformable non-flowing gel
9% PAM 2% TRI	E	Barely flowing gel
9% PAM 2% TAC	A	No detectable gel formed
9% PAM 2% TAC	A	No detectable gel formed

Figure 4.14 shows the course of interaction between PAM and the different types of the functionalized silica. As the chemistry of triamine is close to that of PEI, it is proposed that the mechanism of the crosslinking is the same, which is suggested to be through transamination [137]. This observation could be deduced from the heat flow of both

systems (TRI in Figure 4.14.a and PEI in Figure 4.12.b) since the relatively follow the same trend. In addition, the onset of the exothermic peak, that indicates the crosslinking reaction, was 80.1°C, which is close to that of PAM/PEI (84.27°C). Although PEI has the advantage of having long chains which creates more possibilities for crosslinking sites but most likely less chain mobility due to the high viscosity of PAM/PEI in comparison with PAM/TRI. TRI, on the other side, has the advantage of the presence of silica that can have a reinforcement effect as well as enhancing the thermal stability of the system. Although both TAC and GUA failed to produce gelling systems, exothermic peaks were detected in both systems (Figure 4.14.b - Figure 4.14.c) which can be attributed to the early decomposition of functional groups.

4.2.5. Thermal stability of functionalized silica

The high stability of silica is clearly shown in Figure 4.15 where the functionalized silica is heated up to a temperature of 900°C. Two regions of significant weight loss have been observed for all types of silica as indicated in Figure 4.15.b. The first region is at a temperatures of ~ 100°C, which is associated to evaporation of water. The second region occurs at high temperatures of more than 200°C, which is a reflection to the detachment, and decomposition of the organic functional groups. TRI functional group was the most stable among the three where the decomposition was detected at a temperature of 425 °C, while TAC and GUA decomposed at temperatures of 350°C and 220°C, respectively. Silica particles have, however, remained intact up to a temperature of 900°C as all systems kept more than 75% of its original weight up to the final temperature. Most importantly, triamine functional group is stable at the region of interest, which is up to a temperature of 150°C representing high reservoir temperatures.

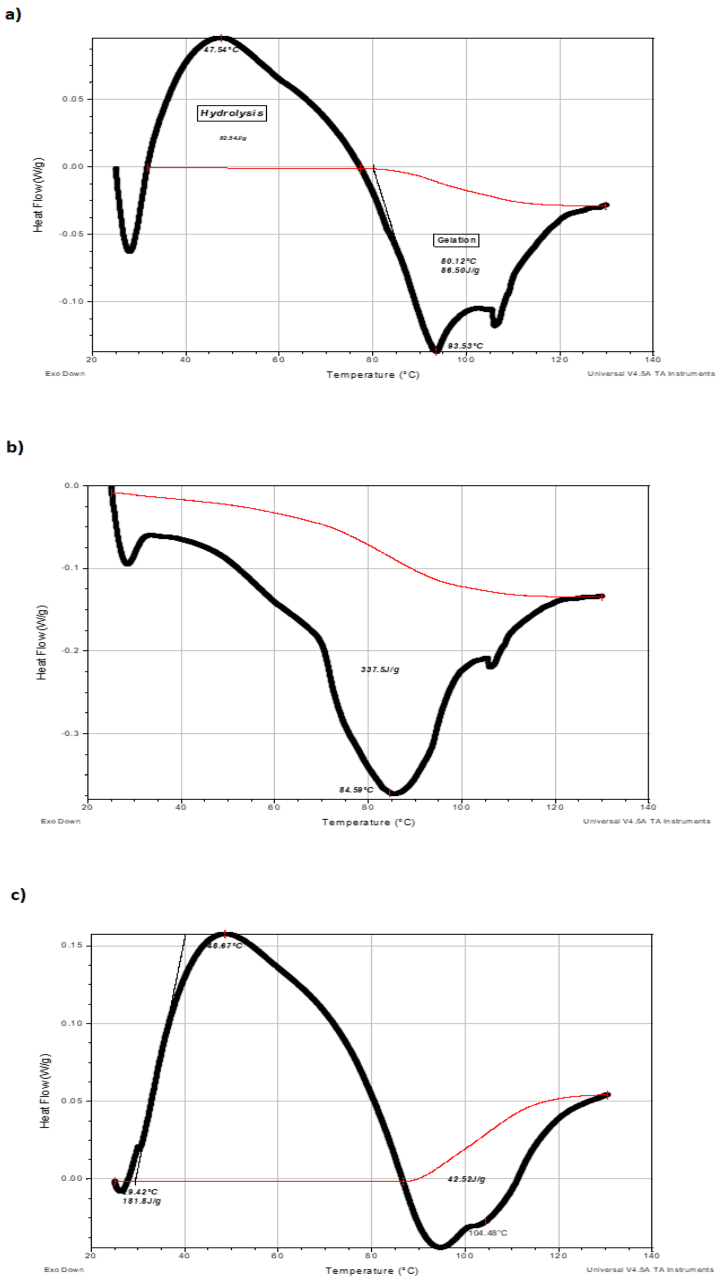


Figure 4.14. Heat flow of PAM 9% with 2% silica functionalized with a) Triamine b) TAAcONa c) Guanidine

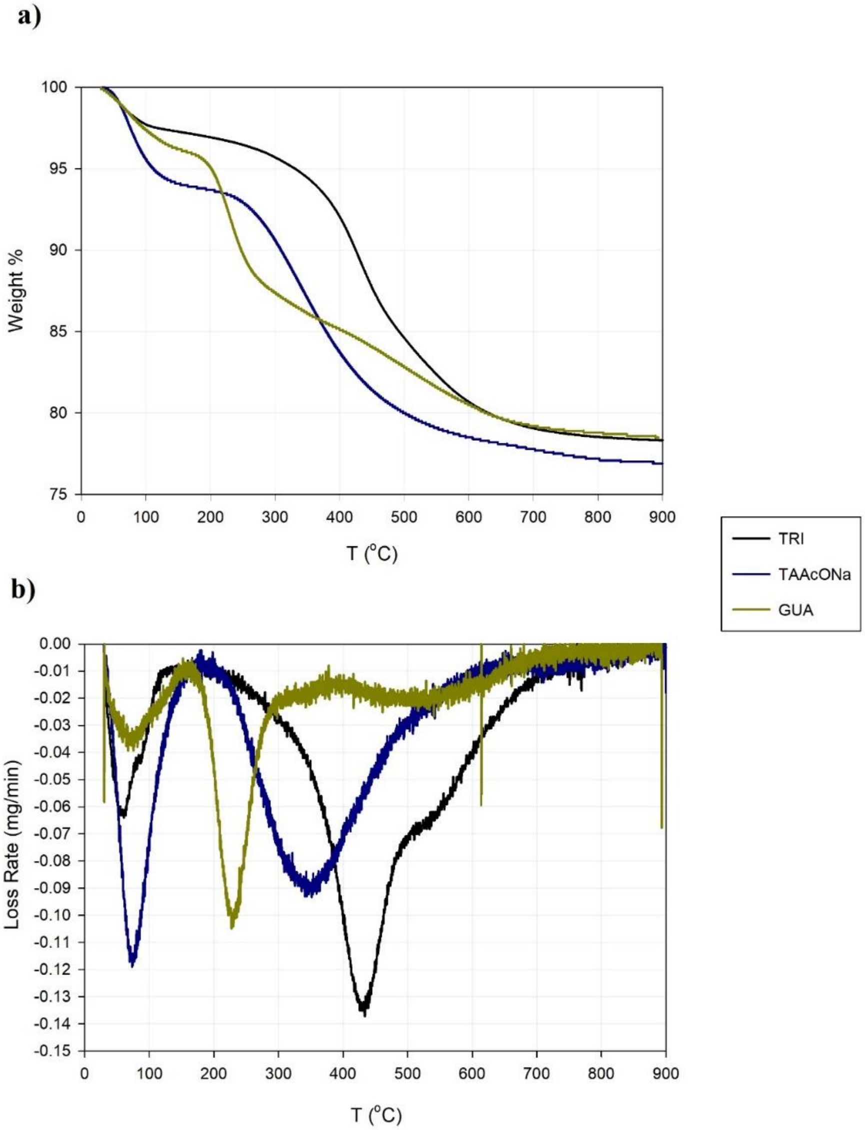


Figure 4.15. Thermogravimetric analysis for functionalized silica a) Weight Percent b) Loss Rate.

4.2.6. Kinetic models

The gelation for PAM crosslinked by PEI and TRI systems is given in Figure 4.16. The gelation time for PAM/TRI is around 60 minutes while it is 70 minutes for PAM/PEI system. A sudden jump in the PAM/PEI system was observed after reaching a plateau at around 60% fractional gelation, which can be explained by the thermal triggering resulting from reaching the temperature 130 °C. Fast gelation at constant temperature could be responsible for the sharp increase in gel strength. Avrami, and Vyazovikin and Sbirrazzuoli kinetic models are applied as an attempt to better understand the course of gelation in both systems.

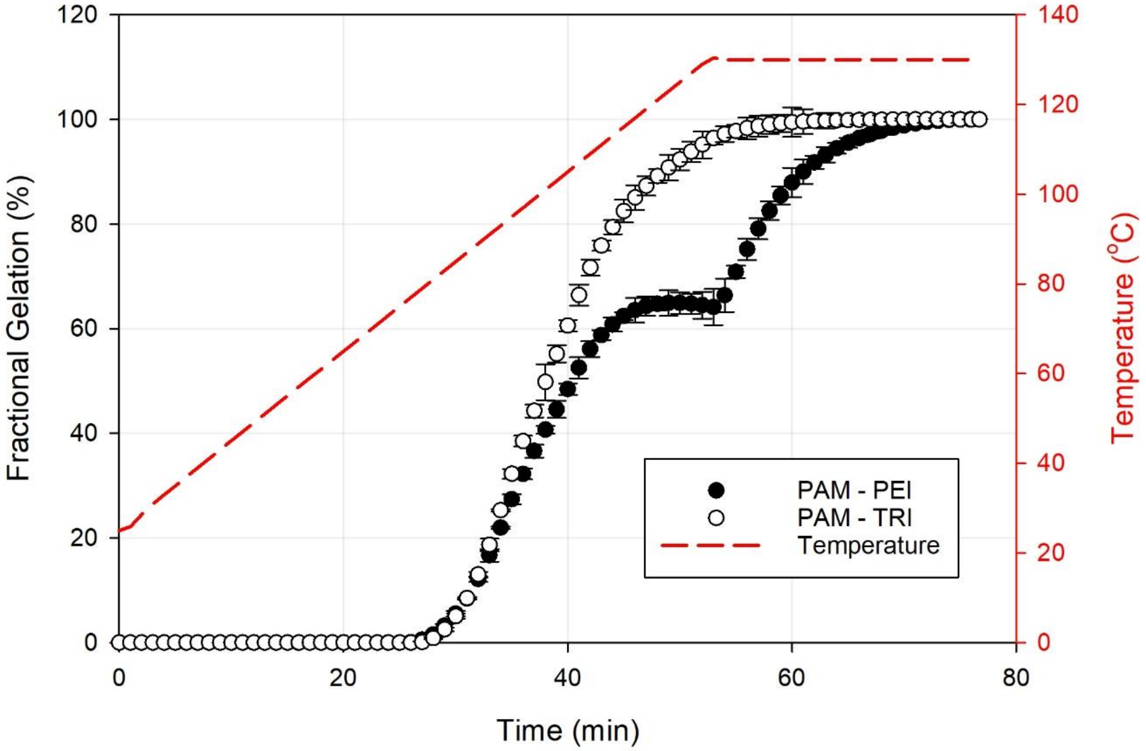


Figure 4.16. Fractional gelation as a function of time for PAM crosslinked with different crosslinkers

The application of Avrami’s model for both systems is shown in Figure 4.17 where the data points represent the experimental part while the lines represent the fitting. A comparison of the two systems shows high similarity, which can be interpreted as another indicator of the similarity of the reaction mechanisms. Avrami’s model suggest that the degree of gelation has slightly increased from ~3.7 in the PAM/PEI system to ~4.2 in the new system, which could be attributed to the presence of silica. A significant deviation in the gelation rate constant was noticed decreasing from $0.0064 \times 10^{-4}\ \mathrm{min}^{-1}$ for the PAM/PEI system to $0.0013 \times 10^{-4}\ \mathrm{min}^{-1}$ for the PAM/TRI system. These values were found comparable to similar systems studied in literature [38]. Overall, Avrami’s model failed to represent accurately PAM/PEI gelation kinetics, which can be a basis to point out that the gelation reaction is not of single step. Overall, Avrami’s model fits better in PAM/TRI system (R^2= 0.966) than it does in PAM/PEI system (R^2=0.826). This is likely due to the mass transfer limitations upon gelation, which are likely higher in PAM/PEI in comparison with PAM/TRI. This observation supports the previous finding that the onset temperature of PAM/TRI is lower than that of PAM/PEI, which is believed to be due to limitation of PEI chain mobility in the viscous PAM/PEI system.

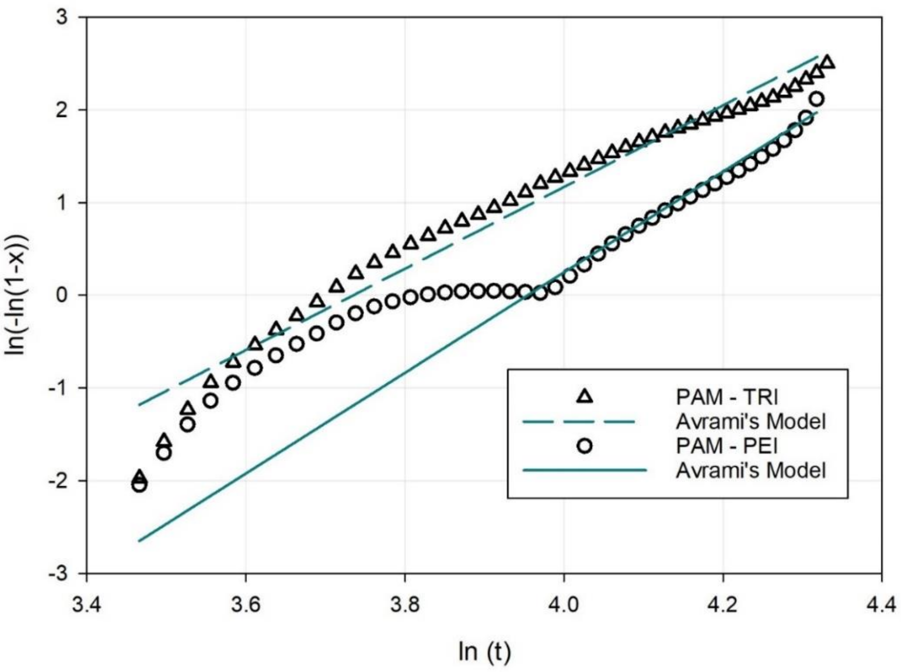


Figure 4.17. Application of Avrami’s model on the gelling systems

To further understand the gelation mechanism, Vyazovikin and Sbirrazzuoli model, which takes into consideration mass transfer limitations at high gel fractions, was applied in an attempt to generate more explanatory gelation mechanism [132]. Figure 4.18 represents the application of Vyazovikin and Sbirrazzuoli model on both PAM/PEI and PAM/TRI systems.

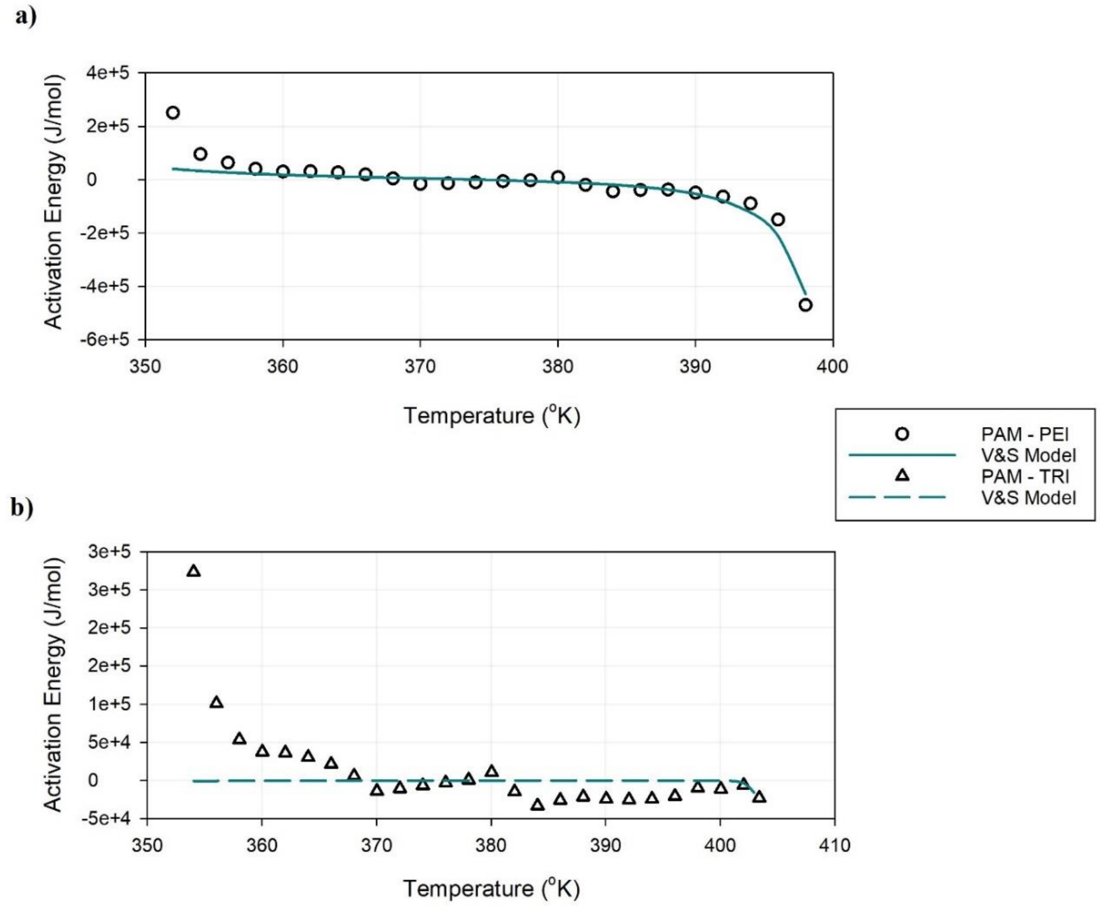


Figure 4.18. Application of Vyazovikin and Sbirrazzuoli model for gelling systems a)PAM-PEI b)PAM-TRI

While the Vyazovikin and Sbirrazzuoli model shows better fitting than Avrami's in PAM/PEI system (R^2=0.904), it failed to fit PAM/TRI system data (R^2=0.131). This observation can help in understanding both systems at the micro-level. A possible interpretation to these results is that in PAM/PEI system, where both polymers have long chains, the formation of gel forms a barrier, which inhibits the accessibility to the crosslinking sites. This behavior can explains the good fit (R^2 = 0.9) in the Vyazovikin & Sbirrazzuoli model where it accounts for the mass transfer limitation. Thus, crosslinking reaction of PAM/PEI is of two steps where it is diffusion-limited once the gel start forming. This behavior can also be observed in Figure 4.16 where the gelation is inhibited when it reaches a fractional gelation of around 60%. The presence of gel acts as a barrier limiting the interaction of crosslinkable functional groups. On the other side, silica in PAM/TRI system could be fully dispersed throughout the system before the onset of gelation. This results in less difficulties in diffusion at later stages of gelation. Since the mass transfer limitation is very low in this system, Vyazovikin and Sbirrazzuoli model failed to predict the gelation behavior and the elementary gelation mechanism suggested by Avrami model is better in predicting the behavior of such systems. Figure 4.19 show a schematic diagram representing the proposed crosslinking mechanism of PAM/TRI system.

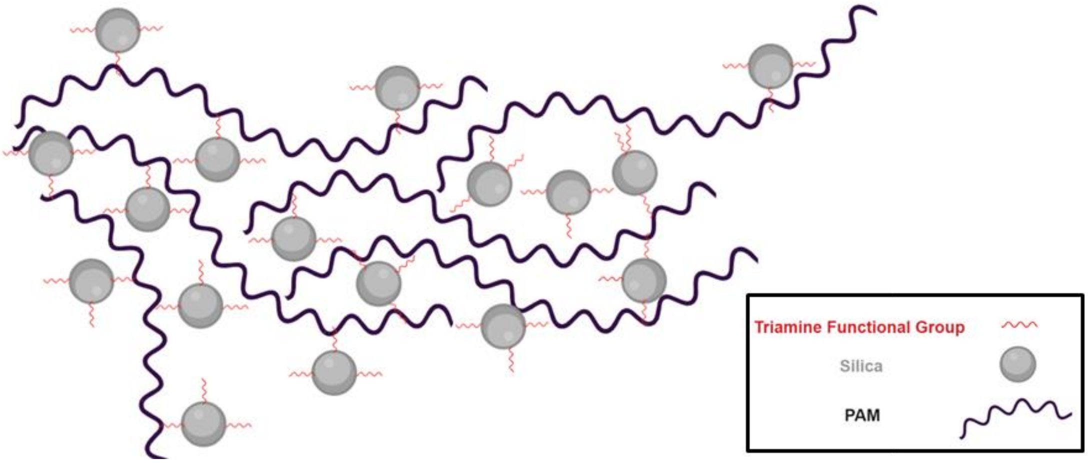


Figure 4.19. Schematic diagram of PAM/TRI crosslinked system

Therefore, observation of heat development through the gelation reaction on PAM/PEI (Figure 4.16) suggest the diffusion limitation as the gel develops. This observation has been supported by Vyazovikin and Sbirrazzuoli model (Figure 4.18.a). This behavior is believed to be a result of the entanglement of the long-chained PEI, where the difficulties in reaching the functional groups in PAM increases as the gel develops. Nevertheless, TRI has the advantage of the presence of short-chained functional groups where the initial dispersion of silica in the system ensures the accessibility of these groups to crosslink PAM with no diffusion limitation.

4.2.7. Conclusions

In this study, the ability of different functionalized silica as crosslinkers for PAM polymer has been investigated at a temperature of 130^{o}C for wellbore strengthening applications. Furthermore, the gelation kinetics of the gelling system is analyzed using DSC. It can be concluded that:

1. 2 wt. % of TRI, TAC and GUA with an average size of 40–63 μm were used to crosslink 9 wt. % PAM. TRI was the only functional group that was able to crosslink with PAM and produced a gel
2. The gel produced from PAM/TRI was evaluated to have Sydansk code of “E” and storage modulus about 677 Pa which is 41.18 % less than the strength of 9 wt. % PAM / 1 wt. PEI system at similar gelation time (70 minutes).
3. The endothermic peak due to the crosslinking reaction between TRI and PAM was detected at 80.1^{o}C by DSC, which is less by about 4^{o}C than that of PEI crosslinking temperature.

4. TGA analysis showed that all the functionalized silica types were thermally stable after heating to 200°C reaching a maximum weight loss of 6 wt.% due to the degradation of the functional groups at elevated temperatures of more than 200 °C.
5. According to Avrami model, the gelation rate of PAM/TRI has a gelation rate of $0.0013 \times 10^{-4}\ \mathrm{min}^{-1}$,however, it failed to accurately predict PAM/PEI system due to the diffusion limitation.
6. Based on Vyazovikin and Sbirrazzuoli model, diffusion is proposed to have the dominant effect in the crosslinking of PAM/PEI system as the fractional gelation increases. In contrast, PAM/TRI system was affected by the initial dispersion of silica in the system.

4.3.Part C: Rheology of Triamine Functionalized Silica Reinforced Polymeric Gels

4.3.1. Introduction

Functionalized silica with different functional groups has been recently introduced to the oil and gas industry. Hu et al. succeeded in the synthesis of a cyclodextrin functionalized nanocomposites targeting the enhanced oil recovery (EOR) application [138]. Cyclodextrin functionalization was reported to be able to increase the oil recovery by more than 6% compared to the reference system that uses unfunctionalized nanocomposites. Cao et al. have functionalized nanosilica with amino groups which was tested as an additive for acrylamide based fluid used in EOR [139]. The investigation revealed that functionalized nanosilica has significantly enhanced the thermal stability of the fluid as both the nanosilica and the amino group have contributed to this effect. The baseline acrylamide based fluid system was less resistive toward thermal degradation than the system with unfunctionalized silica, however, amino-functionalized silica showed the most degradation resistance.

In this study, a new crosslinker, which the gelation kinetics was studied in Part B, is introduced. The crosslinker combines the presence of the functional group (amine) responsible for crosslinking in PEI attached to silica particles that enhance reinforcement and thermal stability. Thus, triamine silica (TRI) is introduced to replace PEI for the purpose of enhancing both the strength as well as the thermal stability of the produced gel especially at high temperatures (>100^{o}C). The rheology and gelation of the developed system are investigated. Moreover, the effect of water salinity and possible ways of reducing formation damage are examined.

4.3.2. Crosslinkability of Different Polymers Using TAS Crosslinker

Polyacrylamide polymers crosslink with PEI via an amine group. The ability of triamine functionalized silica to crosslink with two polyacrylamide based polymers (PAM and PAtBA) was evaluated using 9 wt. % of the polymer and 2 wt. % TAS at 130^{o}C and compared with conventional PAM/PEI system. Figure 4.20 displays the gel samples produced using the new crosslinker. Although triamine functionalized silica has been able to crosslink both PAM and PAtBA. Yet, it is clear from the figure that settling of silica is an issue. The settling behavior can be attributed to the micro size of the functionalized silica (> 40 µm) and the high concentration. Even though, the amount of silica that remained suspended was enough to crosslink both polymers producing weak gels as shown in Figure 4.20.

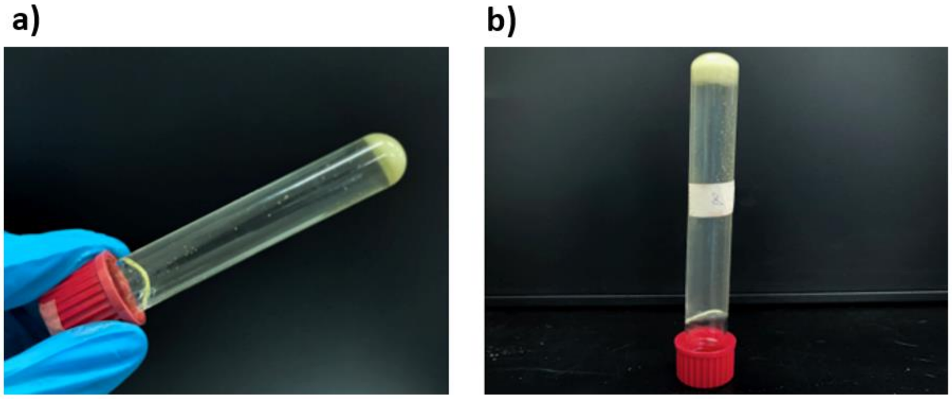


Figure 4.20. Gel produced using 2% Triamine silica (TAS) crosslinker with 9% of the polymer a) Polyacrylamide (PAM) and b) Polyacrylamide tert-butyl (PAtBA)

The rheological behavior of these gel samples was tested. Figure 4.21 clearly indicates that the gel produced from crosslinking PAM is more rigid than the second system with PAtBA. This behavior was mainly referred to as the settling of functionalized silica particles since precipitation was noticed to be more in PAtBA. The difference in molecular weight between the two systems played an important role as the higher molecular weight polymer (PAM), which has a higher viscosity, was able to suspend more silica particles resulting in more crosslinking. These interactions were reflected by the higher gel strength achieved in PAM (659 Pa) compared to PAtBA (136 Pa).

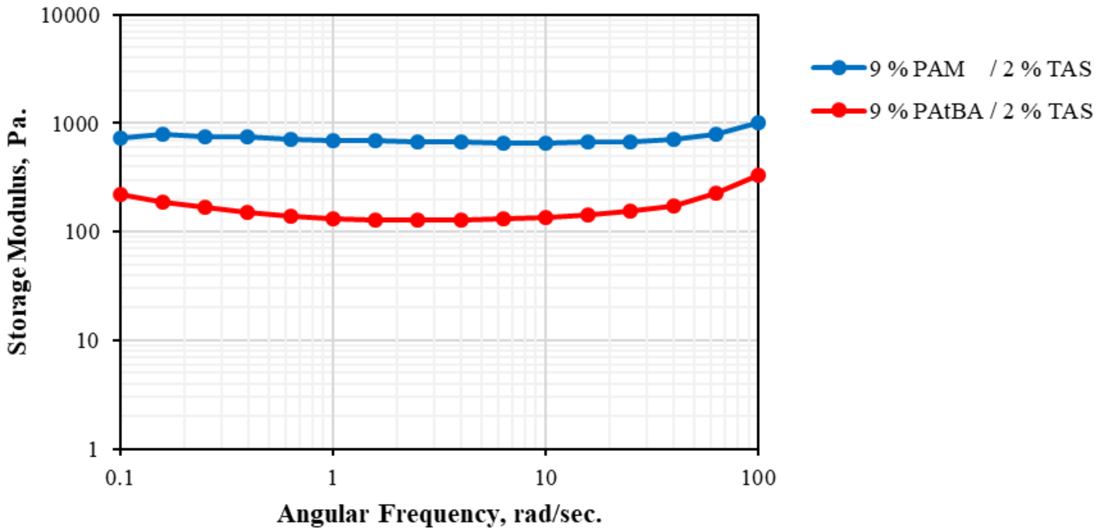


Figure 4.21. Frequency sweep of Triamine silica (TAS) crosslinked systems (a strain of 1 % at 25^{o}C)

4.3.3. Use of Un-functionalized Nanosilica as a Stabilizer

While TAS has succeeded in crosslinking the polymer and produced a gel, it failed, alone, to achieve the same gel strength achieved by PEI as strength values between 1000-2000 Pa were reported for PAM/PEI and PAtBA/PEI systems [26,37,79]. Thus, nanosilica is introduced to the system to enhance both the stability of the particles and the physical strength of the gel. At low NS concentrations, settling behavior was not much affected whereas the addition of 2 wt. % nanosilica has completely inhibited the settling and strengthened the composed gel. Sydansk [24] developed an alphabetic coding system from “A” to “J” to evaluate the gel strength based on the bottle test. Table 4.3 shows the Sydansk code of different gels formed after crosslinking 9 wt. % PAM by TAS at various concentrations before and after adding nanosilica.

Table 4.3. Sydansk code of the formed gels using TAS only to crosslink PAM and silica settling

	Polymer System	Sydansk Code	Silica Settling
1	9 % PAM / 0.1 % TAS	A	No
2	9 % PAM / 0.5 % TAS	B	No
3	9 % PAM / 1 % TAS	C	Yes
4	9 % PAM / 2 % TAS	E	Yes
5	9 % PAM / 0.5 % NS / 2 % TAS	F	Yes

6	9 % PAM / 2 % NS / 2 % TAS	I	No

Adding nanosilica has improved the gel strength of the PAM/TAS system as shown in Figure 4.22. It was clear that nanosilica has prevented the settling of TAS. The high storage modulus of 1901 Pa was achieved upon the addition of 1 wt. % NS compared to 1542 and 1868 Pa for 1.5 and 2 wt. % NS, respectively. However, the gel strength has sharply increased when more nanosilica was added with the highest value at 9014 Pa which is about 374 % greater compared to the storage modulus at 1 wt. % NS and about 13 times stronger than the gel formed without nanosilica at the same polymer/TAS concentrations. More importantly, the gel produced using TAS crosslinker only was able to achieve more than four times the strength of conventional PAM/PEI system.

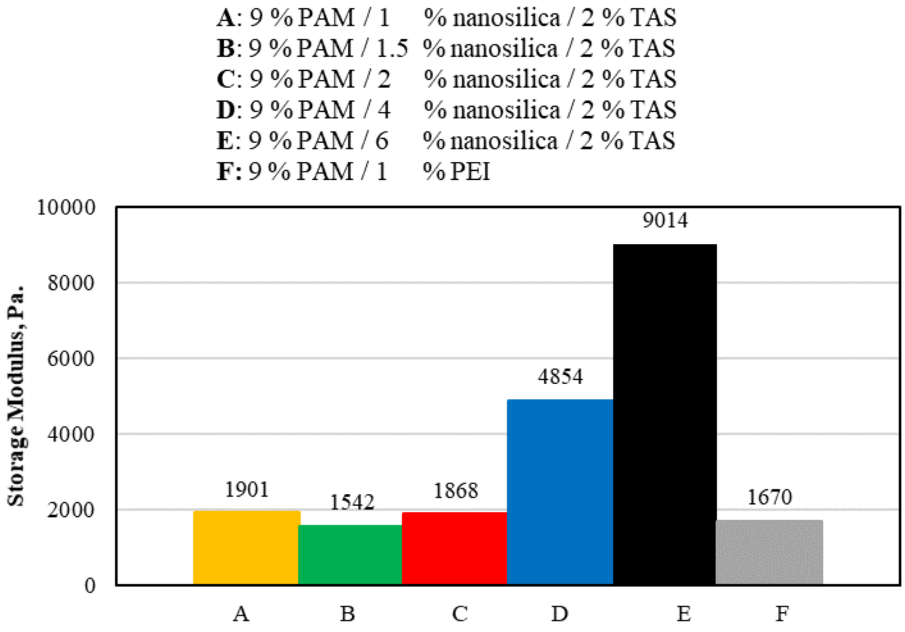


Figure 4.22. Effect of adding 50 nm silica at different concentrations on the gel strength of 9 wt. % polyacrylamide (PAM) crosslinked by 2 wt. % Triamine silica (TAS)

The increase in gel strength after adding nanosilica can be explained by the adsorption of PAM onto the surface of nanosilica by the silanol group and carboxyl via hydrogen bonding [19,124]. However, the decrease in storage modulus at low concentrations suggests that the interaction between NS and PAM has slightly inhibited the crosslinking reaction with TAS which leads to a weaker gel. This observation is related to the free volume between polymer chains created by the addition of solid particles (reduces storage modulus (G´) since it eases the mobility of polymer chains) versus the reinforcement effect due to the addition of a solid. The free volume effect dominates at very low solid concentrations. Our explanation for the initial drop in modulus is that after a certain limit, the effect of physical reinforcement overcomes this effect which results in an increase in the gel strength upon the addition of more NS. Similar observations were reported earlier when low concentrations of carbon nanotube (CNT) or organoclays were added to polyolefins [140,141].

4.3.4. Multiple Crosslinked System (PEI + TAS)

A system of both PEI and TAS crosslinkers has been examined with different ratios of crosslinkers keeping the total amount of crosslinkers to be 1 wt. % to assess the compatibility of TAS/PEI. Figure 4.23 shows the effect of using TAS as a crosslinker to decrease the percent of PEI in the formulation. The increase in the percentage of TAS results in weak gels because the amount of amine in the solution was less in the functionalized silica compared to the case when high MW PEI was used. However, using a PEI/TAS multiple crosslinking system with a ratio of 9:1 provides higher storage modulus compared to the system with 1 wt. % PEI crosslinker. This is likely a consequence of the reinforcement effect of the silica which surpassed the decrease in the crosslinking sites.

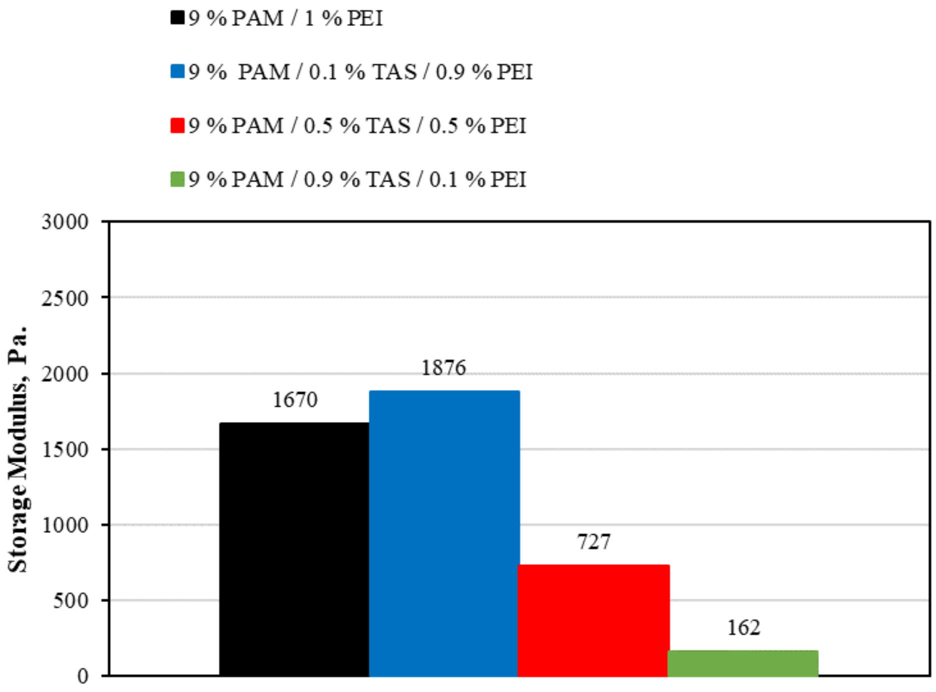


Figure 4.23. Gel strength of 9 wt. % polyacrylamide (PAM) with various concentrations of polyethyleneimine (PEI) /Triamine silica (TAS) at a frequency of 10 Hz, 1 % strain and temperature of 25°C

The frequency sweep test (Figure 4.24) illustrates that frequency has an insignificant effect on the mature gels. This observation is important for field applications since gels that are sensitive to dynamic loads could break easily and reduce gel stability. The stability of

PAM/PEI/TAS system has been investigated by measuring the storage modulus of 9 wt. % PAM crosslinked with PEI with a total weight of crosslinkers (PEI+TAS) of 1 wt.%. PEI was used at various ratios (0.1, 0.5 and 0.9 wt. %) has with the balance being TAS (0.9,0.5 and 0.1 wt. %).

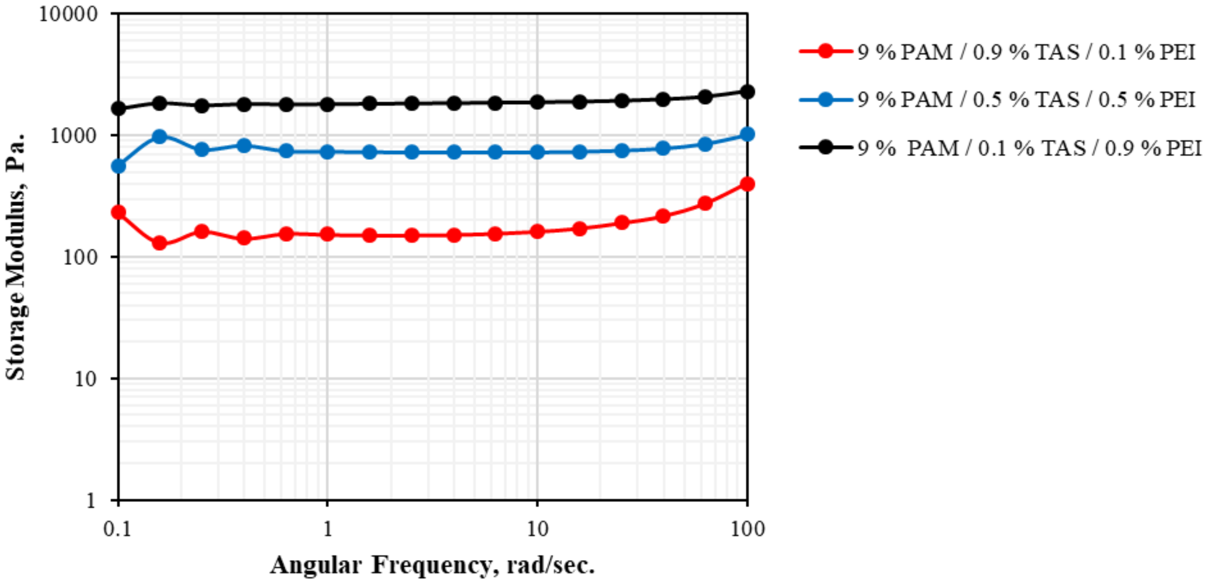


Figure 4.24. Frequency sweep on mature gels of 9 wt. % polyacrylamide (PAM) with different ratios of polyethyleneimine (PEI) / Triamine silica (TAS) at 1 % strain and 25^{o}C

Figure 4.25 depicts that adding TAS has improved the gel strength compared to the base fluid. Hence, introducing the functionalized silica to PAM/PEI solutions enhances the performance of the crosslinking due to the addition of amine functional groups. No gel was detected when only 0.1 wt. % PEI was used to crosslink 9 wt. % PAM because there were no sufficient amine molecules to crosslink with the carboxyl groups in PAM. However, addition 0.9 wt. % of TAS has reinforced the three-dimension structure of base fluid causing an increase of gel strength to 162 Pa.

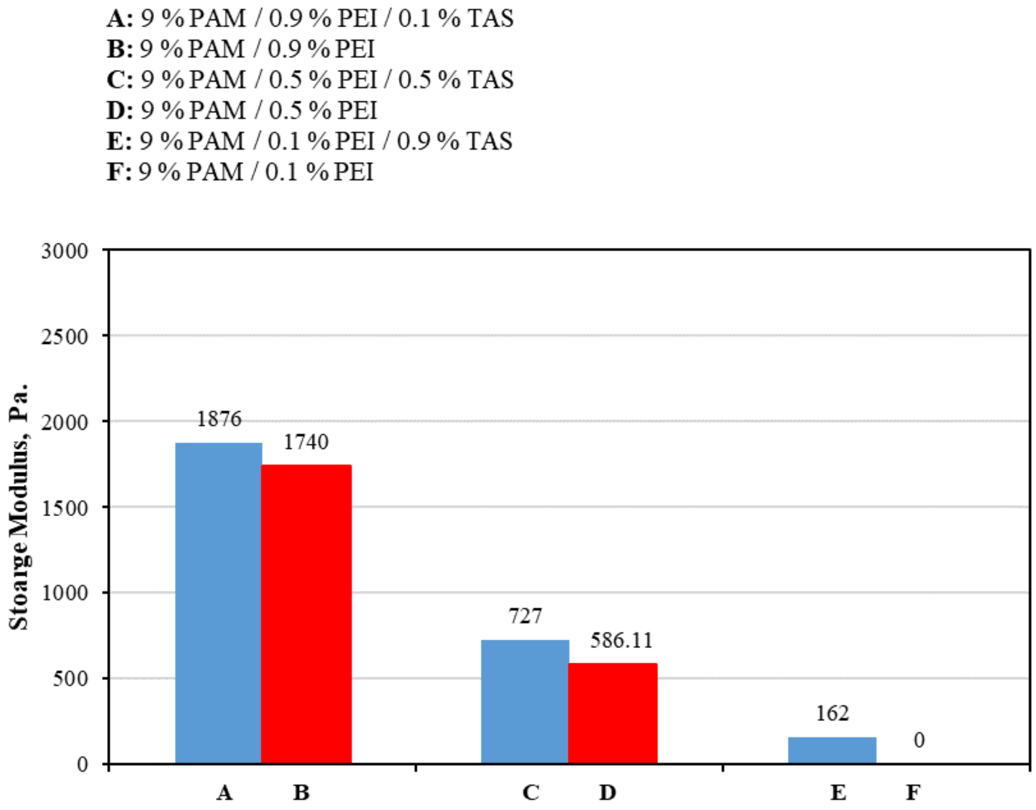


Figure 4.25. Comparing the gel strength of polyacrylamide (PAM) / polyethyleneimine (PEI) systems with and without adding Triamine silica (TAS)

The storage modulus is an indicator of the gel strength. Accordingly, high storage modulus points out for strong gel which can withstand high pressure in the formation. High gel strength is very useful in conformance control applications such as water shutoff, fracture sealing to prevent loss circulation and for wellbore strengthening. The full crosslinking takes place after approximately 75 minutes so the injection time should be short to avoid gelation inside the wellbore. The developed formulation is suitable for fracture sealing and plugging of low and high permeability (> 6 mD) as long as the pore throat size is higher than 40 µm to avoid filtration of TAS.

4.3.5. Gel Compatibility With Seawater

The evaluation of the performance of the gel in saline water is important to account for field applications. The salinity of seawater in the region is considered in this study as Gulf water has high salinity compared to other seas [142]. The use of seawater has decreased the storage modulus of PAM/PEI, prepared in deionized water, by about one third because of the effect of salts on PAM chain. Using seawater with PAM/PEI revealed similar trend in previous studies [37,73]. Moreover, the addition of 1 wt. % of the chelating agent Ethylene diamine tetraacetic acid (EDTA) is evaluated as it has been proved to be good for scale prevention in systems with high salinities [121]. Figure 4.26 reveals that EDTA is compatible with the developed system, however, the gel strength is slightly lower than EDTA-free deionized water gel. Increasing EDTA concentration up to 3 wt. % decreased gel strength. This behavior can be attributed to the competing effect between chelating agent and the functionalized silica to bond with PAM and the presence of Na^+ in the EDTA structure which might hinder the crosslinking process [92,143,144].

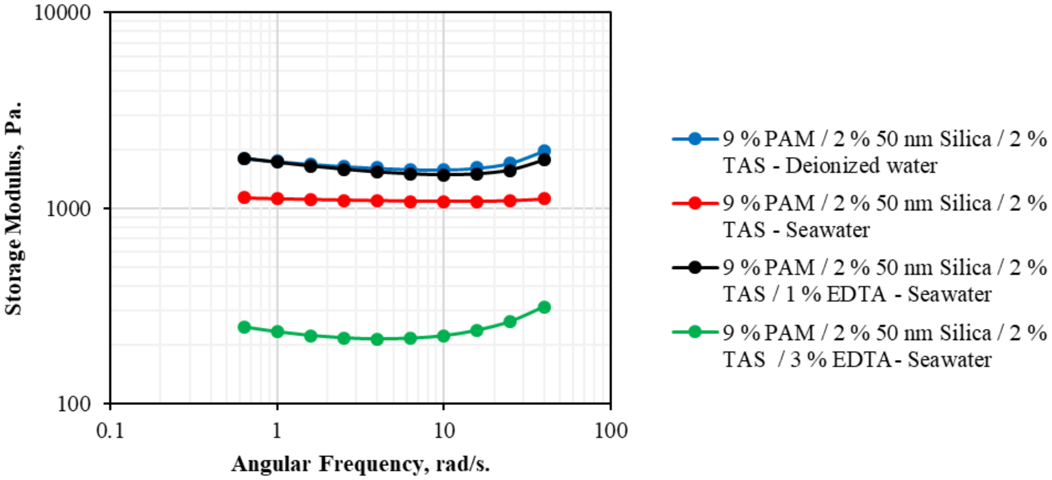


Figure 4.26. Frequency sweep tests of 9 % polyacrylamide (PAM) crosslinked by 2 % Triamine silica (TAS) combined with 2 % of 50 nm silica prepared using deionized water, seawater and seawater with 1 % sodium- Ethylene diamine tetraacetic acid (Na_4EDTA)

4.3.6. Conclusions

In this study, a new triamine functionalized silica (> 40 µm) has been successfully used with PAM and PAtBA as a crosslinker to replace or reduce the amount of PEI for conformance control in high temperature reservoirs. Gel performance has been investigated in both fresh and seawater. Based on the obtained results, the following conclusions can be drawn:

1. The use of 2 wt. % of Triamine functionalized silica has achieved crosslinking of PAM and PAtBA and formed a flowing gel on Sydansk coding system at 130°C, however, settling of silica has been observed which is attributed to the large size of silica.

2. The addition of low concentration (1 – 2 wt. %) of 50 nm nonfunctionalized silica has stabilized TAS, prevented the settling, and consequently resulted in a stronger reinforced gel.
3. The increase in the concentration of nanosilica in the developed formulation has enhanced the strength of the formed gels by more than 4 times.
4. The new formulation is compatible with saline water, which could provide higher storage moduli compared to solutions prepared with PAM/PEI in fresh water.
5. The use of 1 % of EDTA chelating agent can reduce formation damage caused by calcium sulfate precipitation, which is associated with the use of seawater, without affecting the gel strength.

4.4. Part D: Investigation of inorganic Aluminum-based crosslinkers with polyacrylamide

4.4.1. Introduction

Although the research on aluminum as a crosslinking agent for in-situ water shut-off treatments is limited, it has been extensively investigated in Colloidal Dispersion Gel (CDG) systems. CDGs are systems with low polymers and crosslinker concentration, used for in-depth treatments and enhanced oil recovery, that produce a viscous flowing gel after crosslinking [145]. Aluminum citrate is the most common crosslinker in CDGs where its ability in penetrating porous media and reducing permeability has been proven [146–148]. PAM/Al-Citrate CDG system has also been successfully applied in more than 30 cases in Asia, North America, and Latin America [149]. Nevertheless, Aluminum has rarely been used to produce a rigid gel.

Based on the physical stability of the system as well as the rheological performance, different types of aluminum-based crosslinkers are screened and investigated in this study. While Cai and Huang (2001) claimed that PAM / Al-Citrate system is only stable at low pH and low temperature conditions [150], this paper presents an investigation on PAM / Aluminum systems with different associated ligands, namely; Acetate, Amino-Acetate, Nitrate, and Lactate to examine their tolerance towards the change in the surrounding environment. Previous studies have focused on evaluating the gelation performance of such systems. Given that inorganic crosslinkers are poorly soluble in aqueous solutions, hence physical stability is an essential parameter that defines the completion of gelation reaction. The objectives of this study are to (i) Investigate the ability of the different screened aluminum crosslinkers to produce a strong gel, (ii) Evaluate the physical and thermal stability of the polymer / inorganic colloidal systems, and (iii) Asses the rheological and viscoelastic behavior of the mature gels.

4.4.2. Effect of Crosslinker Concentration

Screening process of the chosen aluminum based crosslinkers starts by varying the polymer to crosslinker ratio. In the current study, PAM’s concentration is fixed at 9% to benchmark with previous studies where PAM was crosslinked with the organic crosslinker PEI, and the inorganic crosslinker chromium acetate using the same polymer concentration [19,151]. Figure 4.27 illustrates the final gel strength of the produced gels with the different crosslinkers as a function of concentration at a fixed temperature of 75 ^oC without pH modifications. Aluminum Lactate was screened out as it failed to crosslink with PAM where no gel is produced when a concentration of up to 5% was used at varying acidic conditions between 2.1 to 11.3 and temperatures between 25 to 100 ^oC. Moreover, mixing PAM with AlNt produced a rapid strong gel, which made it difficult to be transferred to the test tube. Therefore, 1 wt% ammonium chloride has been used with all AlNt experiments throughout the study to slow down the reaction as it has been previously reported to be an effective retarder [47]. The change in the storage modulus (~ 300 Pa), for both AlAc and AlNt, was insignificant after 3 wt%. Hence, this concentration has been used as the optimum concentration in this investigations. Yet, Al-AmAc failed to produce a gel at concentrations of less than 3 wt; the storage modulus kept increasing in the range between 3 to 5 wt% reaching a maximum value of 125 Pa, where the concentration of 5 wt% was considered as the optimum.

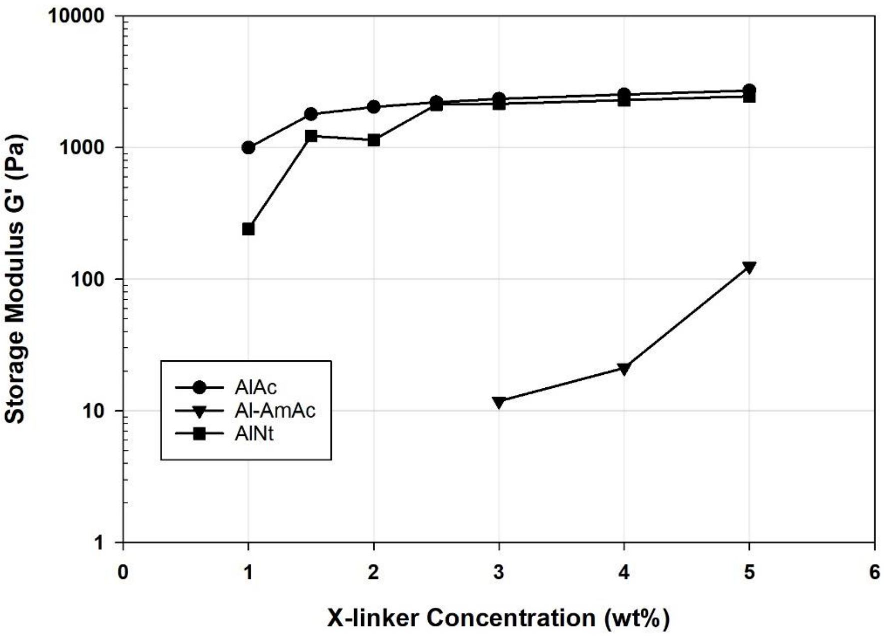


Figure 4.27 Storage modulus of the mature gel as a function of the storage modulus

4.4.3. Effect of pH

Acidity of the system is a key parameter that controls the gelation process in crosslinkable polymeric systems. The gelation can be very fast at some conditions to produce a rapid gel while it fails to produce a gel at some other conditions. Among the three-screened crosslinkers, two of them exhibited a colloidal behavior: *AlAc* and *Al-AmAc,* where the physical stability and the suspension of the system affects the degree of success. On the other side, *AlNt* is soluble in aqueous media, within the studied range of parameters, where the degree of suspension is not an issue. The stability of both colloidal crosslinkers in aqueous solutions was studied through zeta potential (Figure 4.28). For *AlAc*, it is clear that the stability decreases at higher pH conditions. *Al-AmAc,* however, showed the least stability in the pH range between 8 to 10.

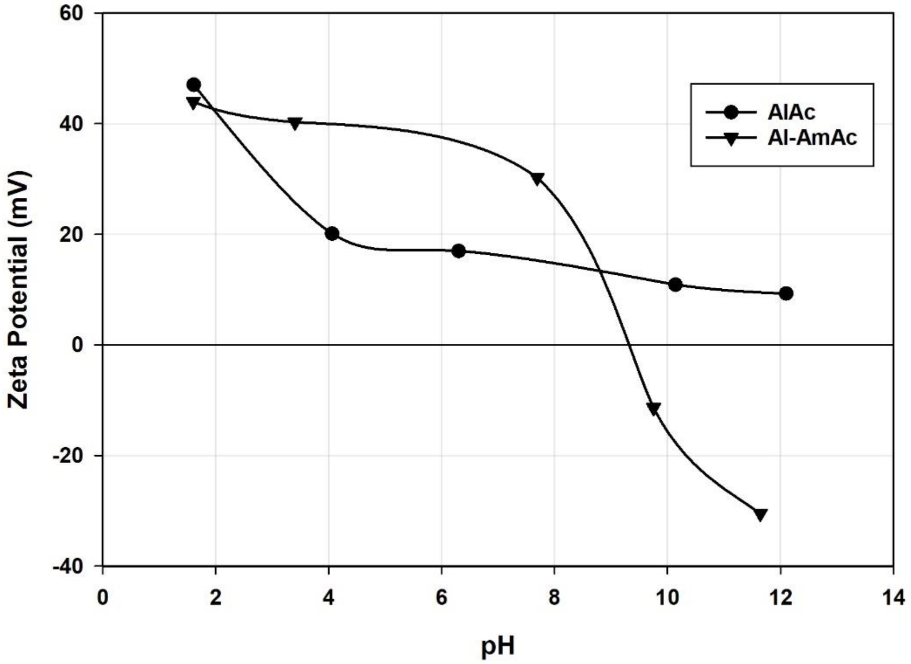


Figure 4.28 Zeta Potential of the colloidal crosslinkers

The settling behavior of the gelants crosslinked with colloidal crosslinkers (*AlAc and Al-AmAc*) came in alignment with the zeta potential results as more separation was observed at higher pH conditions. Moreover, the both gelants reach a pH value where no more gel is produced due to the high settling rate; reducing the contact time between the polymer and the crosslinker. The sole system in both *AlAc* and *Al-AmAc* failed to produce a gel at pH conditions of more than 6.2 and 8.7, respectively. This behavior can be attributed to be resulting from two combined effects; the first is that the crosslinking reaction rate decreases with the increase in pH, unlike the behavior of chromium acetate which exhibited a higher crosslinking rate in the high pH range [35]. The other effect is because the stability of such particles decrease in the alkaline conditions where the settling rate becomes faster; allowing less contact time between the polymer and the crosslinker. To test this theory, Nanosilica (NS) was added to the system in an attempt to increase the stability of the colloidal system and decrease the settling rate, since NS succeeded to provide the stability of another colloidal crosslinker in a previous study [152]. As presented in Table 4.4**,** NS succeeded in physically stabilizing these systems where a gel was produced at conditions where gel was not producible in the absence of NS. In addition, it has successfully decreased the separation phase at the lower pH conditions. Hence, the results provide evidence that the destabilization of the system is a main factor that leads to the failure of inorganic colloidal particles to crosslink PAM.

Table 4.4 Degree of suspension in the systems crosslinked with colloidal crosslinkers at different pH conditions

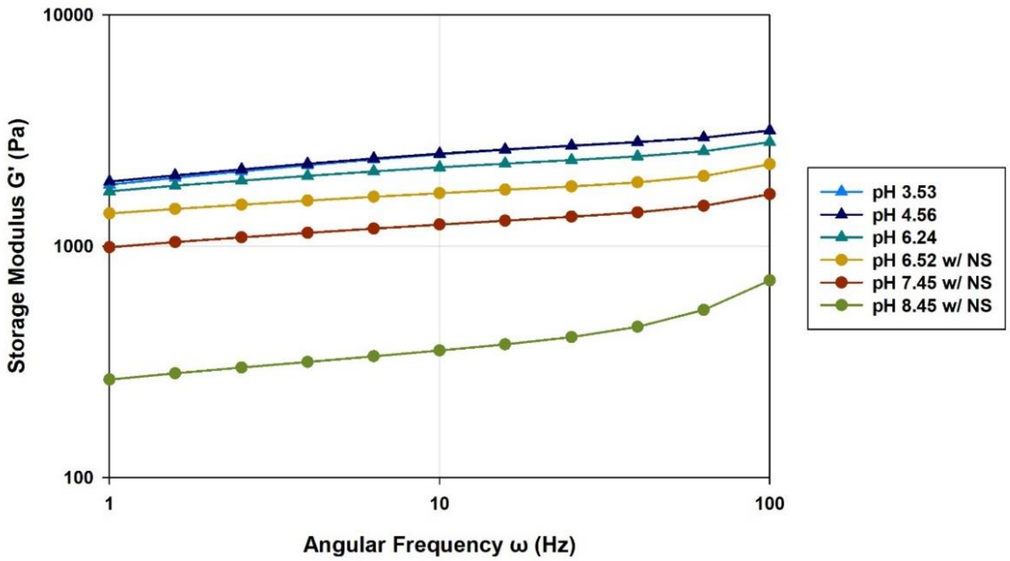
System	pH	Separation Phase % (sole system)	Separation Phase % (with NS)	Notes
PAM 9 wt% + AlAc 3 wt%	2.0 ± 0.5	0%	0%	Rapid Gel
	4.0 ± 0.5	18.4%	12.17%	More stability with NS
	6.0 ± 0.5	20.8%	15.7%	More stability with NS
	8.0 ± 0.5	100%	30.8%	No gel without NS
	10.0 ± 0.5	100%	100%	No gel
PAM 9 wt% + Al-AmAc 5 wt %	2.0 ± 0.5	0%	0%	Rapid Gel
	4.0 ± 0.5	0%	0%	Rapid Gel
	6.0 ± 0.5	0%	0%	Stable with and without NS
	8.0 ± 0.5	23%	0%	More stability with NS
	10.0 ± 0.5	100%	7.2%	No gel without NS

Figure 4.29 shows the viscoelastic behavior for the systems crosslinked with *AlAc* and *Al-AmAc*, where the sole systems are plotted with triangles and the systems with NS are plotted with circular points. Both systems behaved in a similar manner where the high decrease in acidity produce a rapid gel and no gel is produced at high pH conditions. Moreover, the separation phase was observed to increase as the pH increases. Therefore, a conclusion can be drawn that the gelation rate decreases with the decrease of pH for these two colloidal

crosslinkers. The strengthening effect of NS can also be observed in the PAM / Al-AmAc as higher strength was attained at similar pH conditions.

Even with the addition of ammonium chloride as a retarder, *AlNt* had a very narrow window of controllable gelation. The solution remained viscous at the region between 2.8 to 3.2 where increasing the pH more than that produces a rapid gel while the system does not produce a gel, even at elevated temperatures, when the pH is decreased below that range. Figure 4.30 summarizes the behavior of all the examined gelant systems in the whole pH range. Contrary to the behavior of chromium acetate, *AlAc* and *Al-AmAc* showed an increase in the gelation time with the increase in pH, where the system forms a rapid gel at low pH conditions. Consequently, aluminum based crosslinkers can be superior in the presence of acid gases (such as H_2S and CO_2), which were proved to limit the application of chromium acetate and weakens the gel produced [14].

a) PAM 9 wt% - AlAc 3 wt%



b) PAM 9 wt% - Al-AmAc 5 wt%

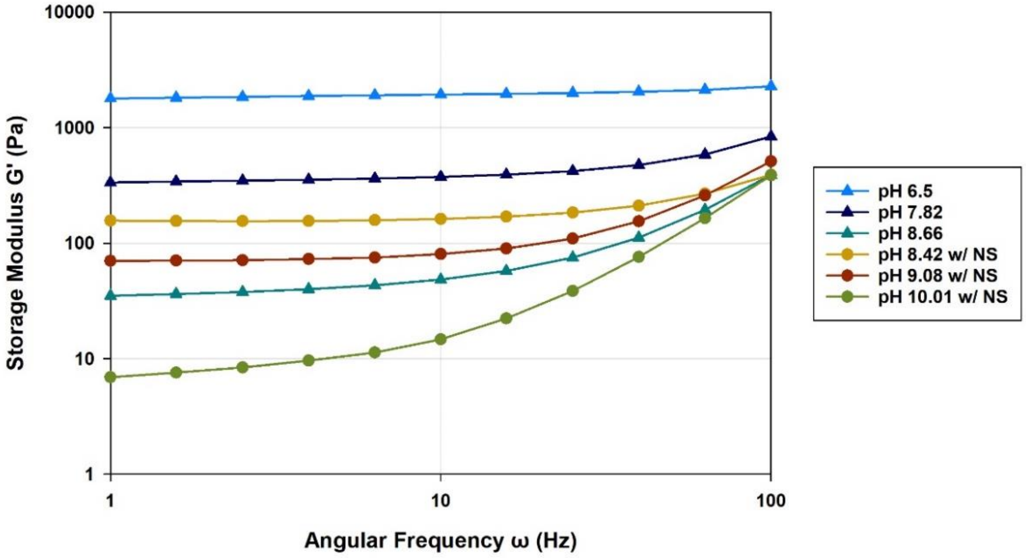


Figure 4.29 Frequency Sweep of PAM crosslinked with a) AlAc b) Al-AmAc at varying pH conditions

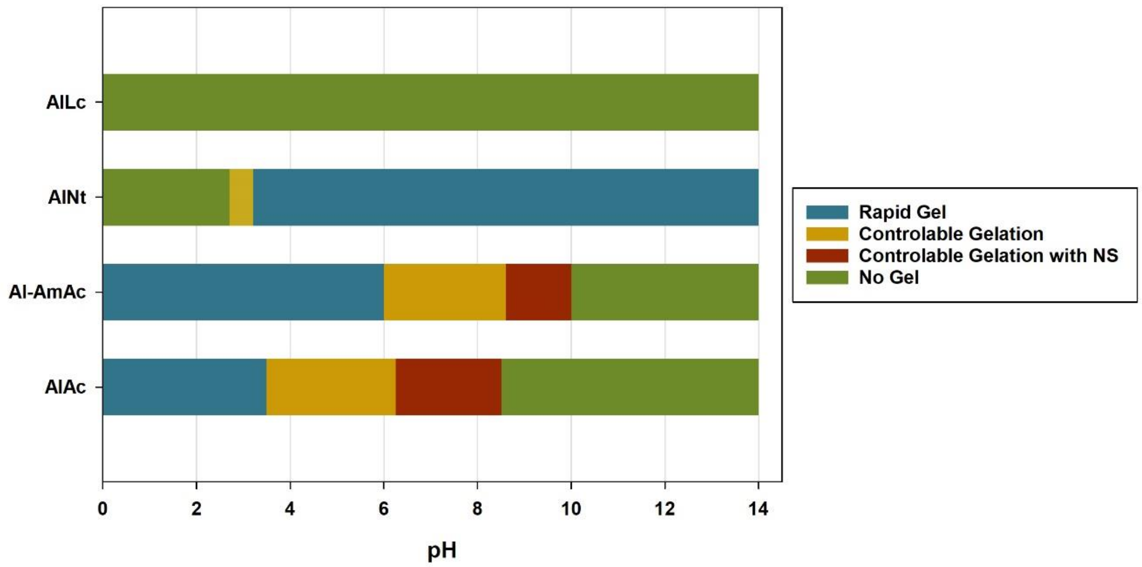


Figure 4.30 Behavior of the different aluminum-based-crosslinked-polyacrylamide at the whole pH range

4.4.4. Effect of aging temperature and thermal stability

Temperature plays an important role in the gelation process. The effect of temperature on the equilibrium gel strength is described in Figure 4.31 in the range between 25 to 100 ^{o}C representing most of the oil reservoirs. The effect of temperature on the gelation system is complex as it can be an interaction of several consequences. On the one hand, the increase in the temperature is known to increase the crosslinking rate [70], which will hinder the particles from further settling leading to more crosslinking intensity. On the other hand, polyacrylamide exhibits a thermal-thinning behavior [153], suggesting that the settling velocity of the colloids will increase with temperature. Furthermore, degree of hydrolysis in PAM was found to increase at elevated temperature; causing more amide groups to turn into carboxylates [154]. While some researchers described the carboxylate groups as the crosslinking sites [35]; the increase in temperature can increase the crosslinking density in the bulk of the system. Moreover, thermal stresses in general are known to weaken the strength of materials. Therefore, the combined effect of all the above led to the behavior shown in Figure 4.31. The strength of *AlAc* system had a directly proportional relation with temperature within the studied scale, while both *AlNt* and *Al-AmAc* had a polynomial-behavior where a peak was reached followed by a decrease in the strength. Similar polynomial-like behavior was reported for PAM/Chromium-Acetate gelant in the literature [70].

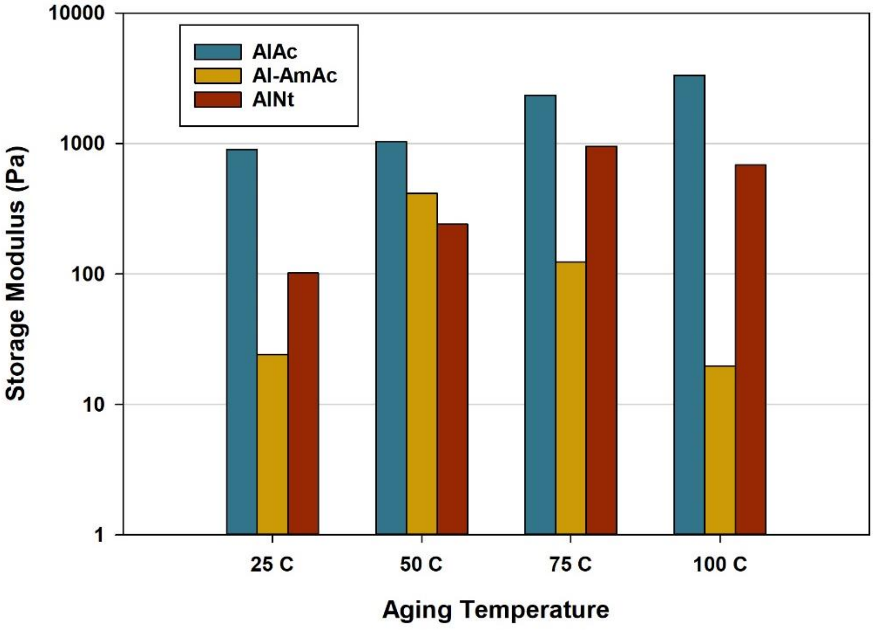


Figure 4.31 Effect of aging temperature on the final gel strength

To better understand the thermal stability of the systems, thermogravimetric analysis was carried out for the screened crosslinkers (Figure 4.32). *AlAc* and *Al-AmAc* revealed a good thermal stability to a temperature of up to 105 ^{o}C. Weight loss of less than 10% was observed in both systems, which is mostly can be attributed to the loss of moisture content. On the contrary, *AlNt* showed a poor behavior where around 67% of the net weight was lost by exposing it to a temperature of 105 ^{o}C. *AlNt* holds nine water molecules per each molecule of aluminum nitrate ($Al(NO_3)_3 \cdot 9H_2O$) naturally. However, calculating the water content reveals that it only accounts for around 43% of the net mass in the system. The remaining lost 24% can be explained by the chemical properties of the compound. *AlNt* has a melting point and a boiling point of 72.8 ^{o}C and 135 ^{o}C, respectively. Thus, at a temperature of 105 ^{o}C, *AlNt* has some vapor pressure that is swept away by the purging nitrogen gas leading to continuous decrease in the net weight. As a resultant of this behavior, although the gel samples crosslinked with *AlNt* produced a good strength, it was observed that some syneresis started to develop after only 24 hours of aging. Therefore, *AlNt* can only produce a stable gel at low-temperature reservoirs.

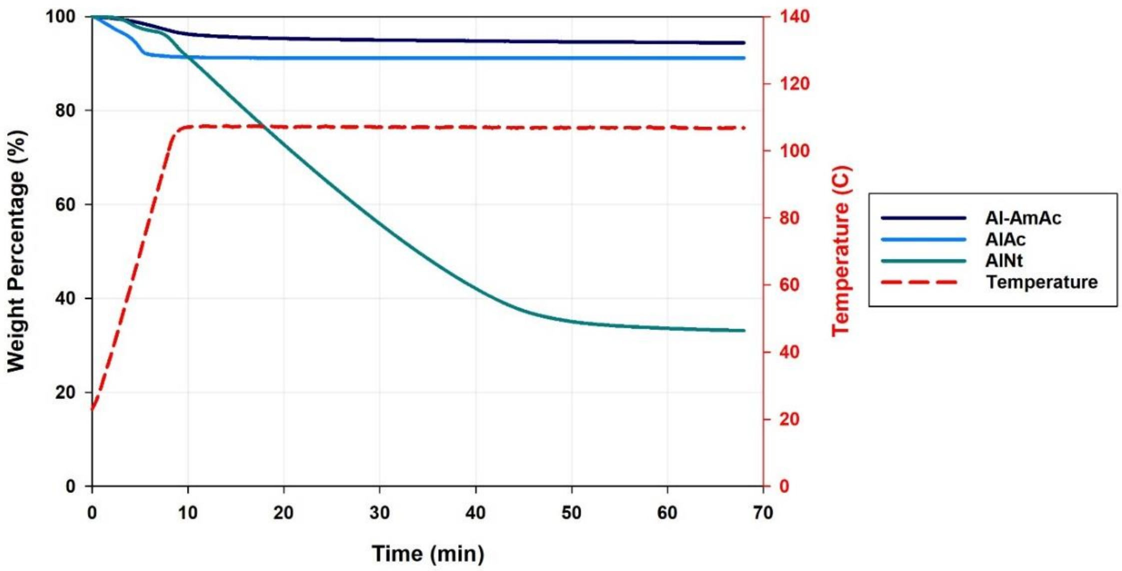


Figure 4.32 Thermogravimetric analysis for the screened crosslinkers

4.4.5. Effect of salinity

In some oil reservoirs, especially in the offshore, access to the fresh water may be limited. Therefore, it is essential to examine the compatibility of these systems with the salinity content. While the salt content had a positive impact on stabilizing the colloidal system by decreasing the separated phase, generally, it impacted negatively the equilibrium strength of the gel phase (Figure 4.33). The main effect in the saline conditions is believed to be caused by the main polymer chain, not the colloidal crosslinkers. Salts have been reported to have shielding effect on acrylamide chains where the cations are adsorbed negatively-charged carboxylic group leading to a decrease in the available crosslinking sites [155]. Moreover, salts has been speculated to cause the chains of polyacrylamide to shrink and encounter compaction more entanglements [156], hence, the accessibility of the crosslinkers to the crosslinking sites become limited and the probability of reaction decreases according to the *collision theory*. Moreover, it has been reported that the presence of salts has reversed the flocculation process using PAM in clay suspensions suggesting that salts gives a better stability in the system similar to the behavior of aluminum showed in Figure 4.33 [157].

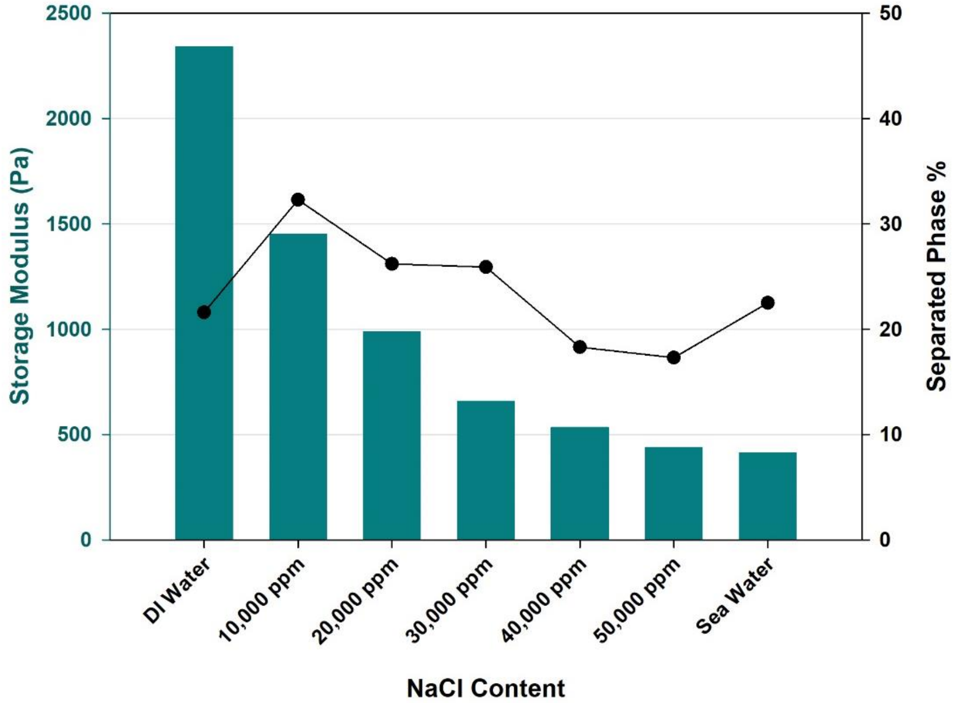


Figure 4.33 Salinity Effect on the gelation and stability of PAM/AlAc gelant

4.4.6. Gelation time

The course of gelation is shown in Figure 4.34 for PAM/*AlAc* system. The experiment was designed to mimic the injection process where the temperature was increased at a rate of 1 ^{o}C/min and the pressure was kept at 500 psi [38]. The gelation time is described as the time where the storage and loss modulus become equals where the solid-like behavior dominates beyond that point. The gelation time for the PAM/*AlAc* without pH modifications (4.1 pH) is around 50 minutes making it suitable for near-wellbore treatments. After 5 hours of exposing the sample to a temperature of 75 ^{o}C, the storage modulus was still increasing at a very low rate. While the bottle test for the same sample reveals the equilibrium storage modulus after 24 hours of aging is around 2340 Pa, compared to 1025 Pa after 5 hour as presented in Figure 4.34. This can be attributed to the slow rate of conversion as the system approaches the equilibrium where the crosslinking is not 100% complete after 5 hours. Moreover, the samples from the test tubes where measured at ambient conditions where the thermal stresses where released, which may have resulted in a higher strength. Figure 4.34 also provides evidence of the reversed pH triggering where the slight increase of pH from 4.1 to 4.6 delayed the gelation from 50 to 80 minutes.

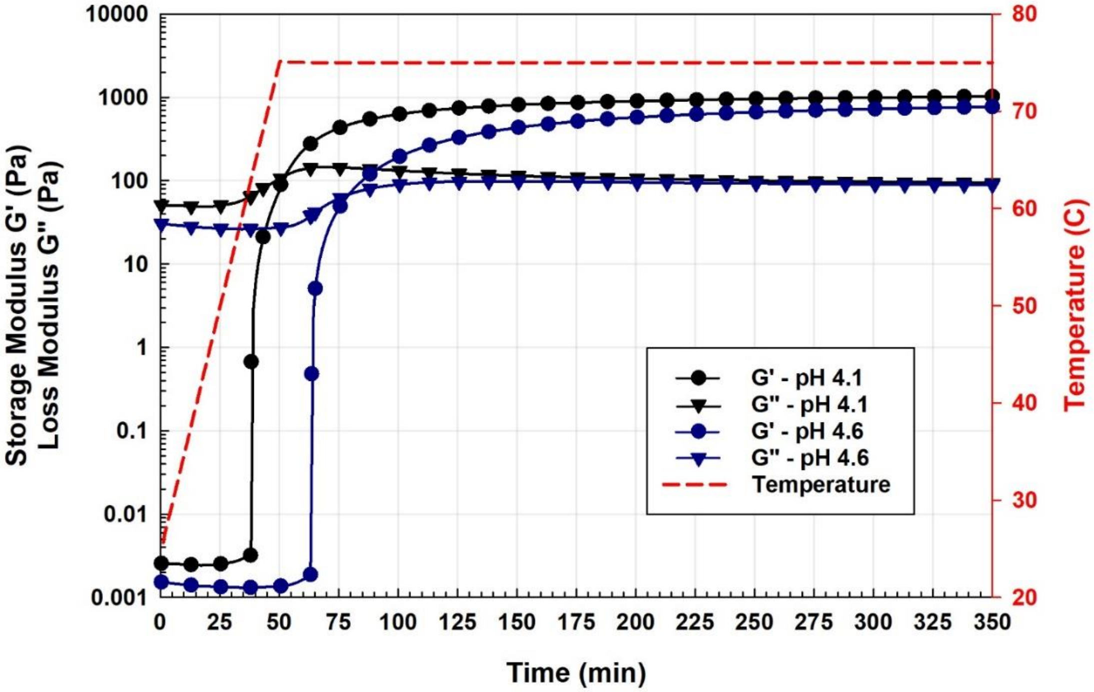


Figure 4.34 Gelation profile of PAM/*AlAc* system

4.4.7. Crosslinking mechanisms

SEM imaging was used to understand the nature of the colloids-polymer interaction on the micro level (Figure 4.35). The images shows the uniform distribution of the particles throughout the sample revealing the importance of physical stability for such systems. The 3D structure shows the behavior of polymer chains where they took the shape of sheets wrapping around the colloidal particles that provides the crosslinking.

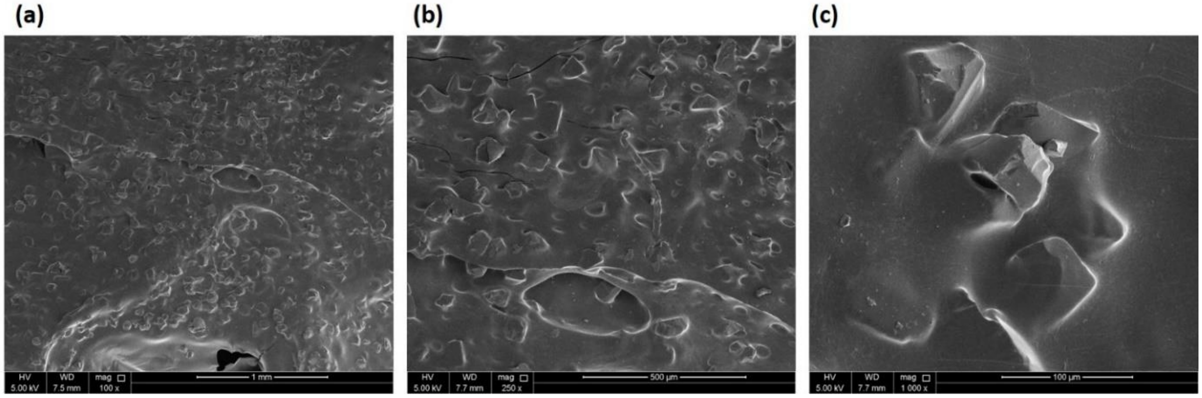


Figure 4.35 SEM images of PAM/AlAc colloidal gel at a scale of a) 1 mm b) 500 µm c) 100 µm

Similar to the other inorganic crosslinkers, it is believed that the crosslinking between aluminum colloidal crosslinkers and PAM is to be through coordination bonds. Moreover, the outcome of screening the different aluminum-based crosslinkers implies the highly dependence of the associated ligands on the gelation behavior. The presence of acetate functional group in both *AlAc* and *Al-AmAc* slowed down the crosslinking as the similarity between acetate and the carboxylic group on PAM shifted the equilibrium and had a retardation effect.

4.4.8. Aluminum-Based Crosslinkers vs Other Crosslinkers

Evaluated the new proposed crosslinkers would be incomplete without benchmarking with the currently available crosslinkers commercially. The screening process in this study nominates *AlAc* as the best aluminum-based crosslinker as it provided the strongest gel, has a good thermal and physical stability, and has a wide range of applicability. PEI, from part A, and chromium acetate from a recent study will be used to benchmark *AlAc* as a crosslinker [151]. Compared to PEI, *AlAc* prospered in terms of gel strength where a storage modulus of up to 2340 Pa was achieved in the unmodified system compared to 1670 Pa achieved by PEI using the same polymer concentration. *AlAc* has also provided a better strength compared to PAtBA/Chromim-Acetate system that had a gel strength of 1283 Pa. Thus, aluminum crosslinkers can be an environment-friendly alternative to replace chromium acetate for water shut-off applications.

4.4.9. Conclusions

In conclusion, this study examines the ability of different Aluminum-based crosslinkers to provide a strong gel to be used for water shut-off applications. Four different ligand associated to aluminum were investigated, namely: Acetate, AminoAcetate, Nitrate, and Lactate. The findings of this study can be summarized as:

1. All the examined crosslinkers were able to crosslink PAM to produce an inflowing gel, except Aluminum-Lactate.
2. Both *AlAc* and *Al-AmAc* forms a colloidal system in the aqueous solutions, while *AlNt* is soluable in water.
3. *AlNt* has a very narrow pH window of applicability between 2.8 to 3.2 where increasing the pH more produces a rapid gel while the system fails to produce a gel when the pH is reduced to below that range.
4. *AlAc* and *Al-AmAc* responds differently to the change in pH compared to the conventional crosslinkers where the gelation rate decreases with the increase in pH.

5. *AlAc* has the widest pH window of applicability where it can crosslink PAM in the range between 3.5 to 8.5 with the help of nanosilica to provide a better stability for the colloids in the aqueous solution.
6. *AlAc*, which was nominated as the best crosslinker among the screened ones, showed some compatibility with the saline conditions as gel was produced even at very high salinities. Nevertheless, the salinity compromises the strength of the gel as it was reduced by 82% from freshwater to seawater.
7. The system of PAM/*AlAc* has a gelation time of around 50 minutes at a temperature of 75 ^{o}C, making it suitable for near-wellbore plugging, while the gelation was delayed to 80 minutes when the pH was increased from 4.1 to 4.6.
8. PAM/*AlAc* system produced a comparable gel strength to the conventional gelants nominating the aluminum-based crosslinkers as a greener replacement to chromium acetate.

Chapter 5: Overall Conclusions and Future Perspectives

This project aimed mainly to provide alternatives and overcome some of the shortcomings of the currently available technologies for gel treatments in oil reservoirs. While polyacrylamide is mostly used polymer in practice, the choice of crosslinker depends highly on the characteristics of the treated reservoir. Generally, polyethyleneimine is used for high temperature reservoirs (>90 ^{o}C) while chromium acetate is the most known inorganic crosslinker for low temperature reservoirs (< 90 ^{o}C). Treatments with polyethyleneimine showed poor performance on the long-run in the very high reservoirs (> 130 ^{o}C). This was attributed to the degrading effect resulting from the cyclic shear and thermal stresses. Also, chromium acetate suffers from toxicity as well as high sensitivity to the acidic conditions and the presence of sour gases (CO_2 AND H_2S). Therefore, this study investigates, in the first part, the effect of using nanosilica of different sized to reinforce and strengthen the final gel strength of PAM/PEI gelant. In the second part, different functionalized silica was screened based on the ability to crosslink PAM where silica serves as a pillar to provide a strong gel, while the attached functional group is responsible for the crosslinking. In the third part, the screened crosslinker from part two, which is the triamine-functionalized silica was comprehensively investigated based on the viscoelastic behavior, stability of the colloidal system, and compatibility with seawater. In the last part, different inorganic crosslinkers that are aluminum-based are screened and investigated to nominate an alternative for chromium acetate. The main conclusions from each part are addressed below.

In the first part, silica nanoparticles with average sizes of 8, 20, 50, and 85 nm are used to reinforce PAM/PEI gelant. The results revealed that the size 50 nm provided the best strengthening effect with the low MW PAM. This came in alignment with the zeta potential tests that showed that the 50 nm silica has the most stability in aqueous solutions. Nevertheless, the size 20 nm provided the best gel strength with the high MW PAM. This was attributed to the hindering of penetration of the larger silica particle in such systems due to the high entanglement of polymers' chains.

In the second part, Triamine, Guanidine, and TAAcONa functionalized silica were screened to crosslink PAM using DSC technique. Both TAAcONa and Guanidine failed to crosslink PAM, nevertheless, Triamine succeeded in doing so. It is believed that triamine functionalized silica (TRI) have the same crosslinking mechanism as PEI due to the similarity in the functional group responsible for crosslinking (Amine). However, the application of the adapted crystallization models on the gelation profiles showed some differences between the two systems. It was revealed that PAM/PEI system is diffusion controlled reaction where the initial formation of gel hinders and slows the rest of the system to crosslink. This effect is believed to be because of the long chains in the crosslinker where the formation of gel limits the accessibility of the PEI functional groups to the crosslinkable sites on PAM's chains. Nevertheless, the diffusion effect is proposed to have the minimum effect in the PAM/TRI system as the initial dispersion of the colloidal system ensures the reachability of the functional groups to the crosslinkable sites at all times.

In the third part, the rheological behavior of the PAM/TRI system is investigated. While the large particles of TRI tends to settle in aqueous solutions, which jeopardized the stability and the strength of the final gel, nanosilica was found to have a stabilizing effect as it hinders TRI particles from settling. PAM/TRI gel achieved a maximum storage modulus of 9014 Pa, which is five times more than the sole PAM/PEI system and almost twice as much as the nanosilica reinforced PAM/PEI system studied in part A. Moreover, the system was shown to be compatible with seawater even in the presence of EDTA chelating agent that is used for scale prevention in oilfields.

In the fourth part, Aluminum Acetate, Aluminum AminoAcetate, Aluminum Nitrate, and Aluminum Lactate. All four crosslinkers, except Aluminum Lactate, succeeded in producing gel with PAM. Nevertheless, Aluminum Nitrate had an uncontrollable gelation time. In addition, slowing the gelation time in Aluminum AminoAcetate system compromises the gel strength. Hence, Aluminum acetate was screened as the best crosslinker where it had a controllable gelation time with a sufficient gel strength. It was tested to be thermally stable in the range from 25 to 100 ^{o}C and controllable gelation in the pH range between 3.5 and 8.5. The gelation of the unmodified system, which had a pH of 4.1, was around 50 minutes. The slight increase of pH to 4.6 delayed the gelation time to 80 minutes. Lastly, PAM/AlAc system has a comparable gel strength to the gel produced by the conventional PEI and chromium acetate.

The developed crosslinkers in this thesis, both the triamine functionalized silica and aluminum acetate, are colloidal particles with micro-sizes. Therefore, applying such formulations in the tight and in the unconventional formations will lead to filtering them out leading to the failure of treatment. Therefore, future work should consider the possibility of producing nano-sized particles for the same crosslinkers. Moreover, one of the main gaps that is not covered in literature is the leaching of gel components into water in the long term. Therefore, the environmental effect of such gel treatments should be addressed in future work.

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