ENHANCING THE PERFORMANCE OF HYDRAULIC FRACTURING FLUIDS USING SINGLE AND DUAL CROSSLINKERS

A Dissertation

by

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ABSTRACT

Hydraulic fracturing has become a common practice in the petroleum industry. Polymers are the main components of fracturing fluids, but high polymer loadings can leave more residue after the treatment. Therefore, crosslinkers are used to improve the properties of polymers and reduce the damage through use of lower concentration of polymers. Various systems have been developed to obtain a suitable crosslinked polymer for the treatment. Boron, zirconium, and titanium are usually used in the industry to crosslink guar gum polymer; however, each system has its own strengths and weaknesses. One of the factors that affect the gel performance is the type of ligands attached to the zirconium. Thus, two Zr crosslinkers with almost the same concentration of Zr can display different performances if the ligand attached to Zr is not the same. Therefore, this study aims to investigate the effect of ligand types attached to Zr on the performance of CMHPG crosslinked with Zr-based crosslinkers with three different ligands.

Moreover, aluminum-lactate crosslinker was examined in this study as an alternative to available crosslinkers like boron and zirconium to address their limitations such as temperature, pH, and shear sensitivity.

In the next phase of this study, to achieve a broader range of applications, Al-Zr dual crosslinker was studied and its performance was compared against the commercially available Zr-B crosslinker.

Extensive lab research is a key to a successful field treatment, and these results indicate that fracturing fluids are complex. In the case of Zr-based crosslinkers, ligand type is one of the important factors in determining the final properties of fracturing fluids. The shortcomings of both Al and Zr crosslinkers were addressed through the new Al-Zr dual crosslinker.

DEDICATION

This dissertation is dedicated to myself, as there is nothing stronger than self-love. I also dedicate this dissertation to my family and friends. This dissertation is also dedicated to my advisor, Hisham A. Nasr-El-Din for all his support toward both my personal and professional life, and to my father, Jamshid Sokhanvarian who has always been wise enough to direct me to reach all my potential.

I also dedicate this dissertation to my loving companion in life, Homayoon Shobeiri. This journey could not have been accomplish without his continuous love and support.

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Thanks also go to my friends and colleagues for all their help, and especially Ms. Gia Alexander for proofreading my work. Their help is truly appreciated.

I am greatly thankful to my mother Narges Moghispour for all her love and encouragement in my life. I truly owe my rational and emotional growth to my wonderful father, Jamshid Sokhanvarian, and I do not know if I ever can pay him back in any way. Finally, my sincere gratitude goes to my dearest friend, companion in life, and my husband, Homayoon Shobeiri for his unswerving support and his continuous inspiration toward my academic goals.

CONTRIBUTORS AND FUNDING SOURCES

Contributors

This work was supervised by a dissertation committee consisting of Professor Hisham A. Nasr-El-Din [advisor], Dr. Jerome J. Schubert, Dr. Sara Abedi of the Department of Petroleum Engineering and Professor Mahmoud M. El-Halwagi of the Department of Chemical Engineering.

All work for the dissertation was completed by the student, under the advisement of Hisham A. Nasr-El-Din of the Department of Petroleum Engineering.

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NOMENCLATURE

b = the intercept of fluid loss graph, cm^3

C_w = leakoff coefficient, $ft/min^{0.5}$

m = the slope of fluid loss graph, $cm^3/min^{0.5}$

S_p = spurt loss, gal/ft^2

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CHAPTER I

INTRODUCTION[*]

Hydraulic fracturing treatments were first performed in 1947 to stimulate the Hugoton gas field. From that time, fracturing techniques have been improving. Hydraulic fracturing is an important means to produce hydrocarbons from unconventional reservoirs at an economic rate. Fracturing fluids are key components of any fracturing treatment, and must be capable of opening up the fractures and transporting the proppants to the fracture (Gidley et al. 1989, Economides 2000, Harris et al. 2008, Loveless et al. 2011). Polymers are the main components of fracturing fluids, but high polymer loading can result in more gel residue after the treatment. In addition, lower productivity corresponds to higher polymer loadings (Lei and Clark 2007; Guo et al. 2012). Therefore, breaking the gel is important, and breakers are needed to clean up the fracture pack after the treatment. However, sometimes the residual polymer can damage the fracture pack as the polymer is not broken completely due to uneven distribution of breakers. The efficiency of clean up jobs depends on several factors, and understanding these factors is very important in achieving a successful treatment (Barati et al. 2008). Therefore, a formulation with a lower polymer loading is beneficial, and among guar derivatives, CMHPG **(Fig. I 1**) offers the least amount of residue due to unbroken gel (Rae and di Lullo 1996; Putzig 2012; Hu et al. 2015).

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The addition of crosslinkers to polymers improve the properties of fracturing fluids, resulting in less damage and cost. Crosslinkers are soluble metal complex solutions and divided to reversible and irreversible categories. Boron, zirconium, and titanium are usually used in the industry to crosslink guar gum polymer (Demkowicz 2001). Each crosslinker poses its own strengths and weaknesses. Some of the shortcomings of boron-based crosslinkers are temperature, pH, and reversibility due to pressure. Metallic crosslinkers are introduced to address the limitations associated with boron-based crosslinkers. Zirconium crosslinkers are a good choice in high temperature and pressure wells. However, one of the shortcomings associated with the commercially available Zr crosslinkers is the fast viscosity buildup at high pH (Demkowicz 2001; England and Parris 2010, 2011; Putzig 2012). Moreover, as Zr-based crosslinkers are shear-sensitive, ligands were introduced to delay the crosslinking until the fluid passes the high shear environments (perforations) (Rae and di Lullo1996; Hu et al. 2015). It should be noted that the type of ligand attached to Zr can determine the final rheological performances if all other components are the same (Moorhouse et al. 1998; Mirakyan et al. 2009; Kalgaonkar and Patil 2012; Hu et al. 2015). In addition to utilizing ligands, adding another crosslinker to Zr-based crosslinkers is an approach to achieving a broader range of applications and addressing the shortcomings of Zr-based crosslinkers. Dual crosslinkers (Zr-B) have been developed (Yaritz et al. 1997) and their field applications were successful (Driweesh et al. 2013; Rahim et al. 2013). However, this dual crosslinker is associated with pH limitation as it only works at a pH of 10, agreeing with the range of 8-12 mentioned in the literature (Rae and di Lullo 1996; Yaritz et al. 1997).

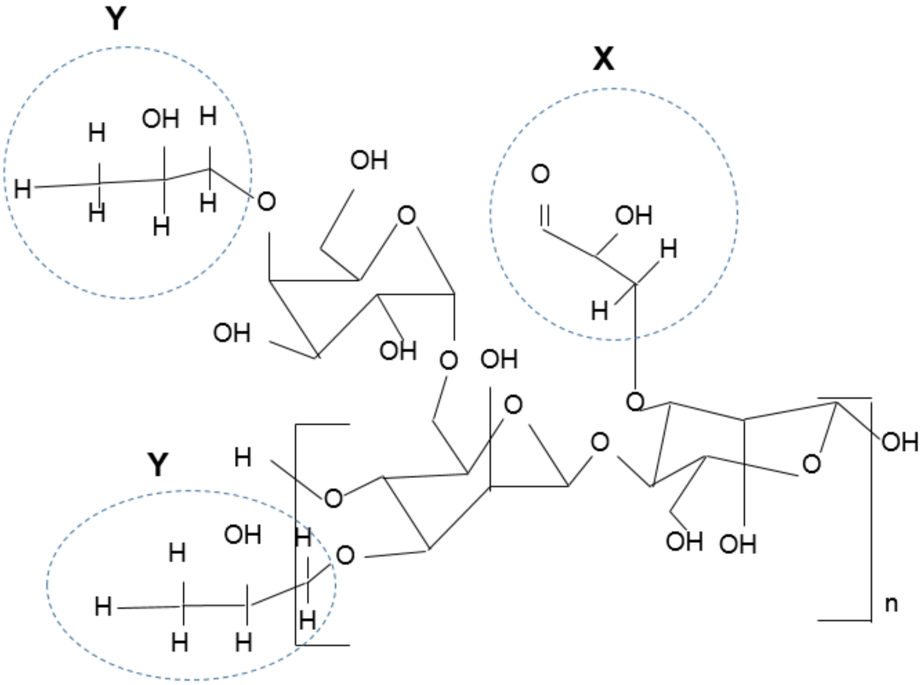

Figure I 1— Chemical structure of carboxymethylhydroxypropyl guar (CMHPG). (Bunger et al. 2013). X (carboxymethyl) and Y (hudroxypropyl) can vary based on degree of substitution (DS).

Crosslinkers that are limited to a specific range of pH impose limitations in field treatment. For instance, smectite is sensitive to pH and can swell in high pH environments (Gupta et al. 2008). In addition, frac pack treatments with deep matrix invasion can lead to permeability reduction (Harry et al. 1999; Gdansky 2002; Gupta et al. 2008). Therefore, a crosslinker which functions at a low pH as well as a high pH is beneficial.

Fluid leakoff is an important evaluation for fracturing fluids as it can affect the fracture geometry, closure time, final distribution of proppants in fractures, and the fluid efficiency. In addition, less fluid loss is needed, decreasing the pumping cost and formation damage (Gidley et al. 1989; Gupta et al. 2008).

Proppant suspension capability of gels is also crucial as it should be able to transfer the proppants into the fracture creating pathways that will remain open. Proppant transport is related to fracturing fluid viscosity at shear rates of 10 to 100 s^{-1} (existing shear rates inside the fracture during pumping) based on Stokes’ law (Hu et al. 2015). Moreover, looking only at steady shear viscosity is not enough; elasticity, which is representative of the network structure of crosslinked polymer should also be considered in evaluating the proppant suspension capability of a gel (Goel et al. 2002; Harris et al. 2008; Gomaa et al. 2015; Hu et al. 2015).

CHAPTER II

OBJECTIVES

To the best of the authors' knowledge, no literature has discussed the effect of different ligands and how the strength of ligands affect the performance of fracturing fluids crosslinked with Zr in detail. Furthermore, Al-Muntasheri (2014) in the critical review of hydraulic fracturing fluid concluded that the advancements on Zr-based crosslinkers are limited. Also, the Al-Zr crosslinker in the present study is a dual crosslinker that has not been studied before.

Therefore, the objectives of the present study are to: (1) Investigate the effect of ligand type on viscosity of crosslinked CMHPG with three zirconium-based crosslinkers at shear rates of 10 and 170 s^{-1} over a temperature range of 80 to 250°F, (2) Address the immediate viscosity buildup at high pH by examining the aluminum-zirconium-based dual crosslinker, (3) Overcome the limitation of pH associated with Zr-B crosslinker by introducing Al-Zr crosslinker, which is functional at a pH of 3.8 and 10.8.

To investigate the deliverability of these objectives, laboratory tests were conducted to study: steady shear viscosity measurements, API RP 39 guidelines to assess the fracturing fluid, shear recovery capabilities, proppant-settling properties, and the leakoff rate of gels formed.

CHAPTER III

EXPERIMENTAL STUDIES[*]

Materials

Three zirconium, one aluminum-zirconium, and one zirconium-boron-based crosslinkers were provided by a service company. The metal and ligand types of all of the crosslinkers are given in **Tables III 1 and 2**. Boron and aluminum were used to prepare dual cross-linker systems, which were present as lactates. Two buffers (pH of 3.8 and 10.8) were used to adjust the pH before adding the crosslinkers to the polymer solutions. Furthermore, fluids having 15 to 25 PPTG (pound per thousand gallons) polymer concentration can be used in place of 30 to 40 PPTG (Harris and Walters 2000). In this study, 20 PPTG CMHPG was used to investigate the potential use of low polymer loading fracturing fluid. CMHPG powder, provided by a service company was used to prepare 20 PPTG polymer solutions. DI water of resistivity greater than 18.2 MΩ.cm at 77°F was used to prepare all polymer solutions. Two wt% KCl is added to the base fluid in hydraulic fracturing treatments as a temporary clay stabilizer. KCl solutions works better than organic clay stabilizers, which are typically quaternary amine compounds (Bunger et al. 2013).

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Crosslinker (#)	Metal type	Metal concentration (wt%)			Activity (wt%)	pH	Density (g/cm^3)	Ligand type
		Zr	Al	B				
1	zirconium	5.2-5.8	-	-	30.7	9.6	1.286	lactate
2	zirconium	5.4	-	-	37.9	9.4	1.288	lactate and triethanolamine
3	zirconium-boron	5.6	-	1.5	27.2	7.7	1.311	lactate
4	zirconium	5.7	-	-	35.7	11.4	1.258	lactate and propylene glycol
5	aluminum- zirconium	2.5	3.5	-	39.5	3.0	1.282	lactate

Table III 1— Properties and compositions of five crosslinkers. pH and density were measured at 75°F.

Metal type	Metal concentration (wt%)	Activity (wt%)	pH	Density (g/cm^3)	Ligand type
aluminum	6.5	53.7	3.5	1.289	lactate

Table III 2— Properties and compositions of aluminum crosslinker. pH and density were measured at 75°F.

Methods

1. Below are the steps used to prepare a crosslinked polymer:
2. 1. 20 g KCl was added to 1,000 g DI water.
3. 2. A vortex was generated without air bubbles, then 2.4 g of the CMHPG polymer powder was added slowly to the shoulder of the vortex.
4. 3. The solution was mixed for 30 (±1) minutes using an overhead three-bladed mixer at 620 rpm.
5. 4. The crosslinker was added to the polymer solutions after the addition of a suitable buffer to adjust the pH to a desired value (3.8 or 10.8).
6. 5. The pH was measured after the addition of a buffer to ensure the desired pH was achieved.
7. 6. The solution was mixed for a few seconds and 52 cm^3 of it was transferred to the sample cup of the rotational viscometer with bob B5.

8. 7. To measure G’ and G’’, bob HB5 was used, and the solution volume needed was 65 cm^3.

The performance of the crosslinked polymers was evaluated based on varying shear rates and temperatures. For all of the tests at high temperatures, the heating oil bath of viscometer was preheated to a desired temperature of 140, 250, or 300°F before conducting the experiment. It took 36-39 minutes for the sample to reach the desired temperature. Two dynamic methods (steady shear viscosity and oscillatory measurements) were used to determine the rheological properties. Furthermore, the proppant settling and leakoff tests were conducted in a static mode on the crosslinked polymers.

Experimental Studies

Steady Shear Viscosity

The viscosity of crosslinked polymers and the impact of shear rate and temperature were assessed using an HP/HT rotational rheometer. Both rotor (R1) and bob (B5) were Hastelloy C. The sizes of the rotor and bob followed API PR 39 standards. The instrument used in the present study integrates a direct drive between the bob shaft and the torque transducer, preventing the momentum of inertia errors. The machine had the repeatability of ± 0.05% of full scale range or better. The effect of shear rate on viscosity was investigated at 10 and 170 s^{-1}. The waiting time for each measurement was 60 seconds. Using a nitrogen source, 400 psi was applied for all the tests at temperatures equal or greater than 140°F.

Viscosity Measurement Based on American Petroleum Institute (API RP 39)

API RP 39 recommends determining the rheological properties through constants shearing of the fluid at 100 s-1 followed by shear ramps of 75, 50, 25, 50, 75, and 100 s^{-1} every 30 minutes.

Proppant Settling: Dynamic (indirect) method

The dynamic or indirect method does not include any proppants and is called Dynamic Oscillatory (DOS). An HP/HT rotational rheometer was used with a hollow bob (HB5) (**Fig. III 1**) to measure viscoelastic properties of crosslinked polymers. The instrument used in the present study did not utilize the magnetic coupling, and instead, recorded the measurements directly inside the pressure vessel. This obtained accurate measurements in a pressurized environment, which provided the capability of measuring G' and G'' under pressure. The network structure of the fluid can be understood through examining the frequency dependence of G' and G'' in the linear viscoelastic region of the crosslinked polymer (Prudhomme et al. 1985; Knoll and Prudhomme 1987; Loveless et al. 2011). A stress sweep test was conducted and confirmed the amplitude value of 5% was within the linear viscoelastic region. Therefore, a sinusoidal amplitude of 5% and a pressure of 400 psi were applied through all the oscillatory tests.

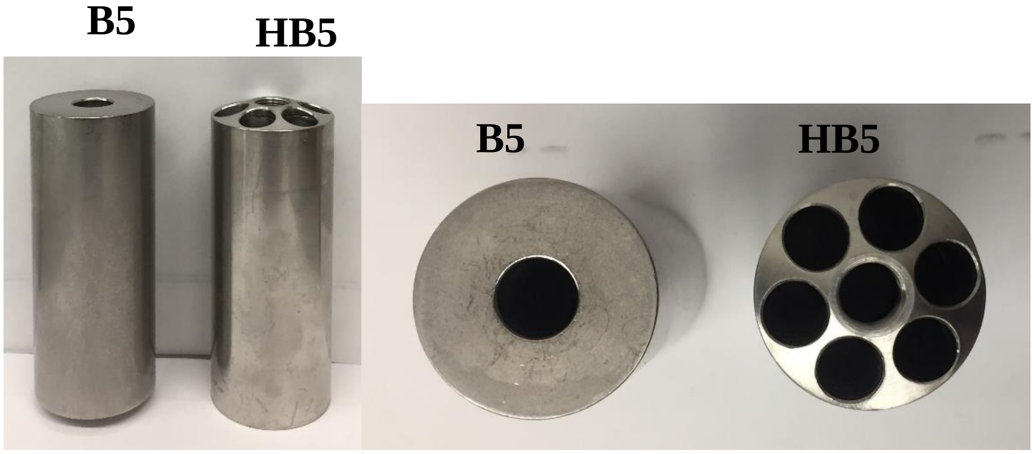

Figure III 1— Bob B5 and HB5 used in conducting steady shear viscosity and oscillatory measurements, respectively

Static (direct) method

In the direct (static) method, 4 lbm/gal of a 40/70-mesh Ottawa sand with the apparent specific gravity of 2.65 was used throughout the tests. The settling tests were conducted for the five crosslinkers. The slurry for each crosslinker was conducted as follows:

1. 20 PPTG CMHPG solution was prepared, and a buffer was added to it such that the pH was 10.8.
2. 4 lbm/gal proppant was added to the polymer solution (step 1) while it was mixing, followed by the addition of crosslinker.
3. Immediately, the slurry (polymer + crosslinker + proppant) was transferred to a 100 cm^3 glass cylinder and moved into the preheated HP/HT visual cell, and the settling of the proppants was monitored visually as a function of time. The settling tests at 140 or 230°Fwere conducted using an HP/HT visual cell (Al Moajil and Nasr-El-Din 2014), which was pre-heated to the desired temperature before each experiment, and a nitrogen source was used to pressurize the system to 300 psi.

Static Leakoff Tests

The fluid loss experiments were conducted using an HP/HT filter press, which is functional up to 2,000 psi and 500°F, to determine the leakoff coefficients and spurt losses. Bandera sandstone disks with the mineralogy presented in **Table III 3** (porosity and permeability range 13-19 vol% and 4-12 md, respectively) and with the specification of 2.5 in. diameter and 1 in. thickness, were used. Anew disk was used in each leakoff experiment. The experimental procedures were followed based on the guidelines of API RP 39, which calls for applying a differential pressure of 1,000 psi. However, the core was cracked at 1,000 and 500 psi pressure differential. Therefore, 300 psi pressure differential was applied. After preparing the crosslinked polymer solution, it was immediately transferred to the filter press cell, and the cell was preheated to 140°F for 15 minutes. The stem valve was opened to the atmosphere and the filtrate volume was collected and recorded every two minutes for a total of 35 minutes.

Mineral	Grey Berea Sandstone	Bandera Sandstone
	Concentration, wt%	
Quartz	86	57
Plagioclase	0	12
K-feldspar	3	0
Calcite	2	0
Dolomite	1	16
Kaolinite	5	3
Illite	1	10
Chlorite	2	1

Table III 3— Mineralogy of Grey Berea and Bandera cores used in the static leakoff and coreflood tests.

Coreflood Tests

The schematic of coreflood setup is shown in **Fig. III 2**. A 6 in. length and 1.5 in. diameter Grey Berea and Bandera sandstone cores with a determined mineralogy (Table 2) were used. The core was dried at 220°F for four hours and its weight was measured. Then the core was saturated in 5 wt% KCl under vacuum for four hours and its weight was recorded. The pore volume of the core was calculated from the dried and saturated weight of the core, and the density of the brine (1.029 g/cm^3 at 75°F). 1,500 psi overburden pressure was used, and a back pressure of 1,100 psi was applied to keep the CO_2 in solution. The core holder was placed inside the oven to provide a uniform heating environment. The core effluent sample was collected every quarter PV after half a PV of the gel was injected. The injection of brine followed by 2 PV of the gel was continued until the core effluent samples became colorless and pressure drop was stabilized.

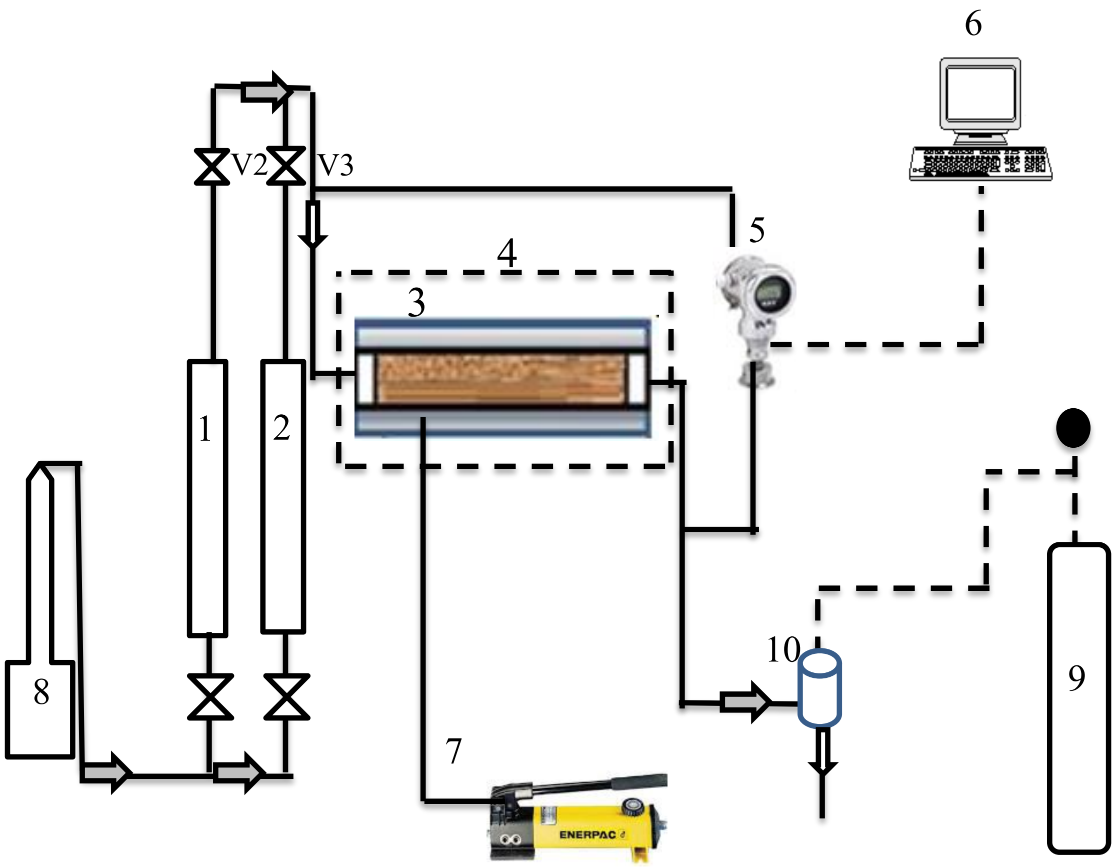

Figure III 2— The schematic of coreflood. 1 and 2: accumulator for 5 wt% KCl and crosslinked polymer, 3: core holder, 4: oven, 5: pressure transducer, 6: computer (lab view software), 7: over burden pressure, 8: syringe pump, 9: nitrogen cylinder, 10: back pressure regulator.

CHAPTER IV

ZIRCONIUM-BASED AND ALUMINUM-ZIRCONIUM CROSSLINKERS*

Effect of Ligand Type Attached to Zirconium

The crosslinking reaction happens through the replacement of at least two of the ligands attached to Zr by the functional groups (OH and COOH) attached to the polymer backbone (**Fig. IV 1**). One of the main factors, which affects the rate of the viscosity development, is the strength of the bonds between Zr and the ligand. If the ligand forms a strong complex with Zr, then the rate of the viscosity development is slow (Putzig and St. Clair 2007).

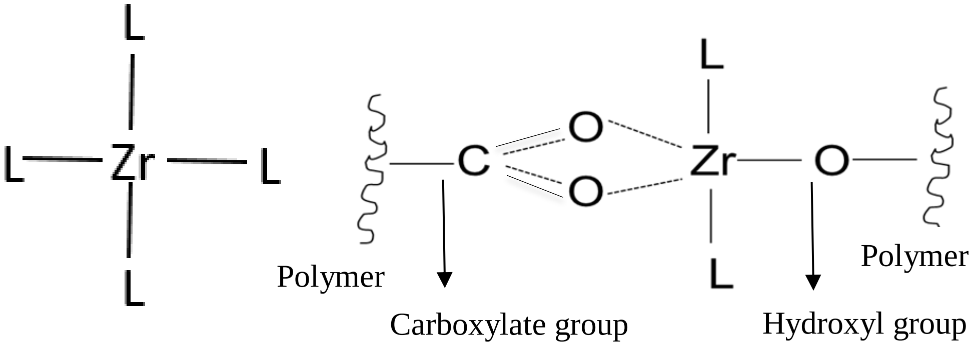

Figure IV 1— Exchange reaction between Zr and at least two functional groups of the polymer (Putzig and St. Clair 2007).

In the absence of a strong ligand, OH^- group forms around Zr in aqueous solutions due to hydrolysis of Zr and a cyclic form dominants. However, Zr dimers, a better candidate for

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crosslinking in the case of strong ligand like chelant is available. Therefore, ligands prevent polymerization of Zr and the dominant species will be Zr (ligand) $_4$, which slightly polymerize to form Zr dimers: Zr$_2$ (ligand)$_6$ at high pH. Another factor affecting the formation of either Zr dimer or cyclic form is the concentration of Zr ligand. The lower concentration of zirconium lactate showed the presence of tetramer, while dimer was dominant in the concentrated solutions of zirconium lactate (Rose et al. 2001; Rose et al. 2003). In addition, as zirconium is prone to hydrolysis and readily polymerizes (Demkowicz 2001), less polymerization leads to the availability of more zirconium sites to bond with the polymer chains. In this study, the concentration of zirconium was almost the same in all three of the crosslinkers. However, the type of ligand was not the same. For example, crosslinker 1 contained only lactate, whereas crosslinker 2 included both lactate and triethanolamine, and crosslinker 4 had lactate and propylene glycol as the ligand.

Figs. IV 2 to **4** show the viscosity of 20 PPTG CMHPG crosslinked with crosslinkers 1, 2, and 4 at shear rate of 10 s^{-1} and 80, 140, and 230°F, respectively. Several points can be interpreted from the latter figures, and it can be seen that the ligand type affects the rate of viscosity development and the performance of crosslinked polymers.

- The crosslinking reaction, or the rate at which the ligand releases Zr, increases with raising the temperature from 80 to 140 and 230°F. Up to 140°F, there is a delay to reach the peak viscosity, where there is no time lag to reach the peak viscosity at 230°F.
- Crosslinker 2 offers the slowest viscosity development because it has the strongest ligand attached to Zr. There are different functional groups in the ligand, which can contribute to forma Zr-complex, and among all groups, alcohol forms the strongest

bond and complex with Zr (Demkowicz 2001). Therefore, the latter can be the reason of more delay in the viscosity buildup in the case of crosslinker 2 at 80 and 140°F (Figs. IV 2 and 3). Crosslinker 2 has four alcohol groups (three from triethanolamine (TEA) and one from lactate). Crosslinker 2 offers the slowest viscosity development and the reason can be that it has the strongest ligand attached to Zr. There are different groups in the ligand, which can contribute to form a Zr-complex, and among all groups, alcohol forms the strongest bond and complex with Zr (Demkowicz 2001). Therefore, the latter can be the reason of more delay in viscosity buildup in the case of crosslinker 2 at 80 and 140°F (Figs. IV 2 and 3). Crosslinker 2 has four alcohol groups (three from triethanolamine (TEA) and one from lactate).

- Lactate (as a ligand) is temperature activated (Harris and Heath 2007), which can be seen by looking at crosslinker 1 at 80 and 140°F. At 80°F (Fig. 2), crosslinker 1, which has only lactate, shows a delay to reach the peak viscosity, but at 140°F (Fig. 3), the crosslinking occurred immediately.
- Fig. IV 4 shows that the viscosity of crosslinkers approached a constant value at 230°F.

The results of this study show that both a weak or very strong ligand can be unfavorable, especially at high shear rates. Furthermore, it should be noted that trying to solve the shear sensitivity of zirconium crosslinkers through the addition of a ligand to delay the crosslinking reaction can cause no peak viscosity situation at high shear rates if the ligand is very strong (in the case of crosslinker 2) or in other words the gelation process will be very slow. The hypothetical reason behind the low viscosity at 170 s^{-1} and 140°F (**Fig. IV 5**) in the case of crosslinker 2 is the slower crosslinking reaction, which enables the agglomeration to break under high shear before becoming very large (Chauveteau et al. 2001). Fig. IV 5 shows that crosslinker 4 has a stronger ligand than crosslinker 1 but weaker than crosslinker 2, is the best choice at high shear rates. Because the viscosity should be at least 100 cp at 170 s^{-1} (Bunger et al. 2013), both crosslinkers 1 and 4 are well above the requirement. Crosslinker 4 provided a much higher viscosity than crosslinker 1. In addition to steady shear viscosity measurements, API RP 39 was followed to evaluate the performance of crosslinkers 2 and 4 (**Fig. IV 6**), and the results agree with the steady shear viscosity tests that crosslinker 4 is a better choice than crosslinker 2. Fig. IV 6 shows that the ligand type can affect the shear recovery capability of Zr-based crosslinkers, as crosslinker 2 with a strong ligand led to unrecoverable viscosity after removing constant shearing at 100 s^{-1}. Crosslinker 4 having a weaker ligand than crosslinker 2 resulted in a more shear tolerant fluid. The shear sequence and temperature profile are shown in **Fig IV 7**. It is worth noting that Moorhouse et al. (1998) showed that 40 pptg CMHPG crosslinked with Zr crosslinkers with different ligands performed significantly different and they also showed that the ratio of ligand to Zr was very important.

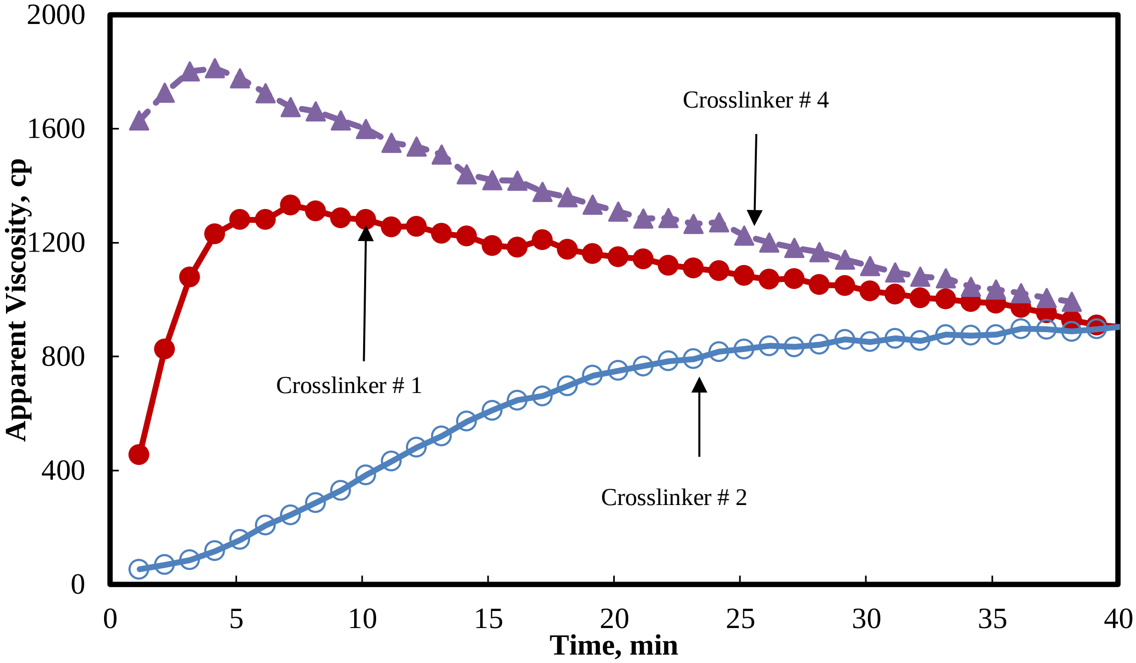

Figure IV 2—Viscosity of 20 PPTG CMHPG crosslinked with three Zr-based crosslinkers at 80°F and 10 s^{-1}. Crosslinker 2 has the strongest ligand attached to Zr leads to a slower viscosity development. 1.7 gpt of crosslinker was used. Initial pH was 3.8. No breaker was added.

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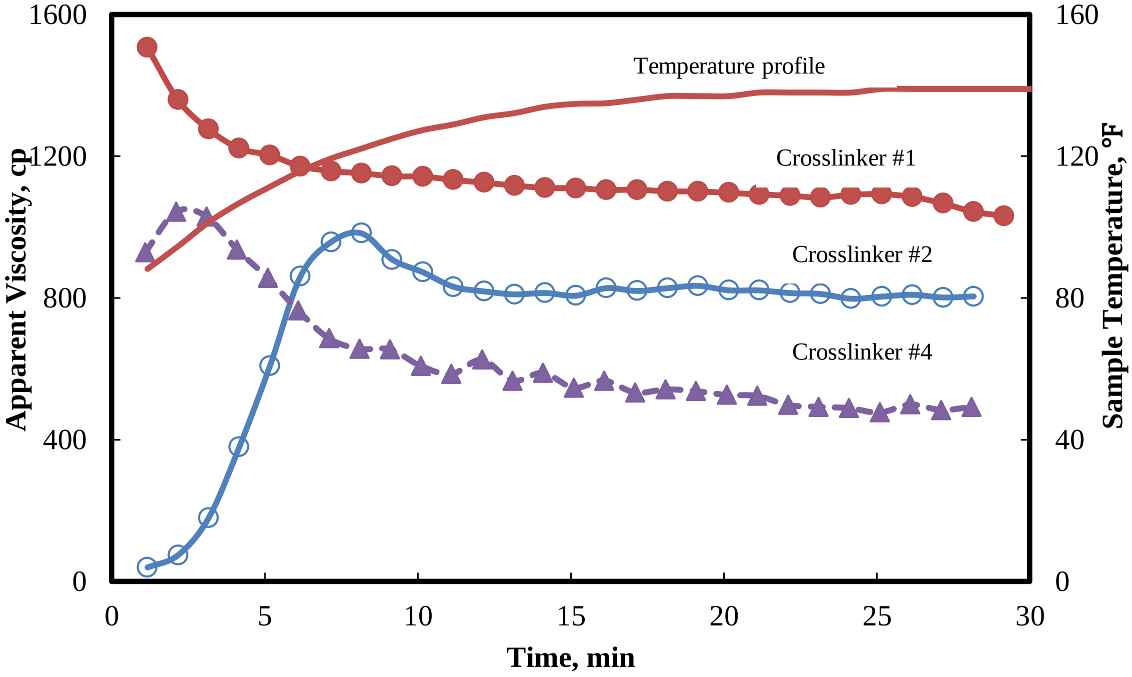


Figure IV 3— Viscosity of 20 PPTG CMHPG crosslinked with three Zr-based crosslinkers at 140°F and 10 s-1. Crosslinker 2 has the strongest ligand attached to Zr leads to a slowest viscosity development compared to crosslinker 1 and 4. The bond between the ligand (lactate) and Zr is weak compared to the other two crosslinkers and can be seen that there is no delay in viscosity in the case of crosslinker 1 having lactate as a ligand. 1.7 gpt of crosslinker was used. Initial pH was 3.8. No breaker was added.

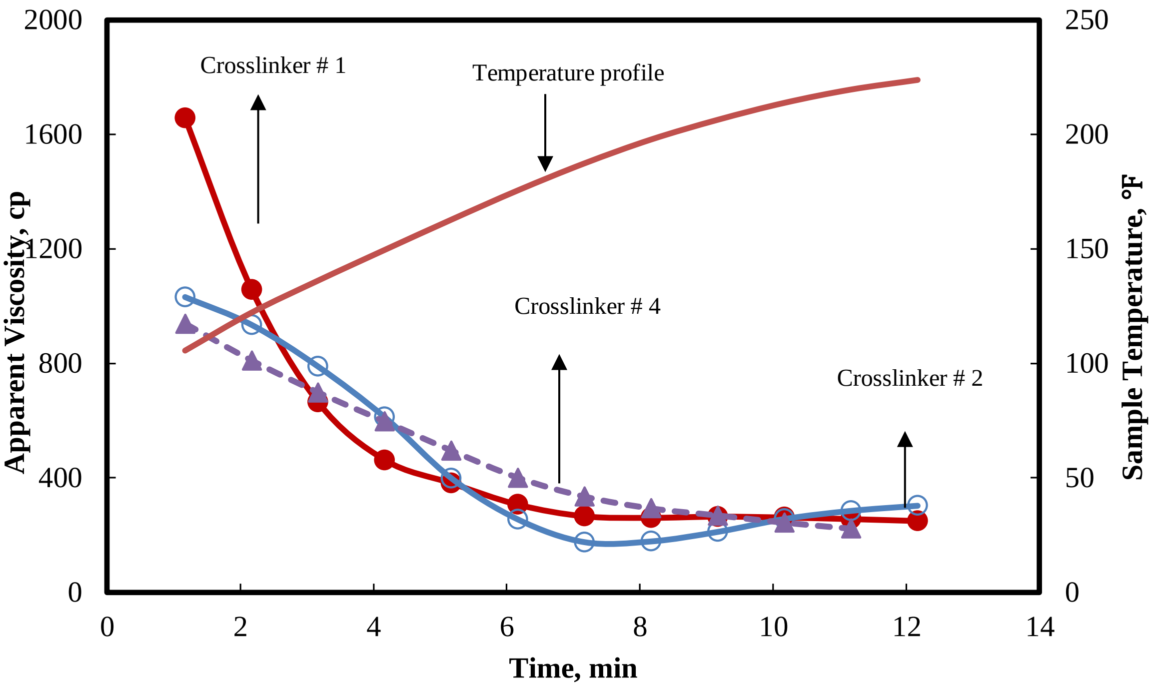


Figure IV 4— Viscosity of 20 PPTG CMHPG crosslinked with three Zr-based crosslinkers at 230°F and 10 s-1. Increasing the temperature from 140 to 230°F accelerated the crosslinking reaction for all three crosslinkers.

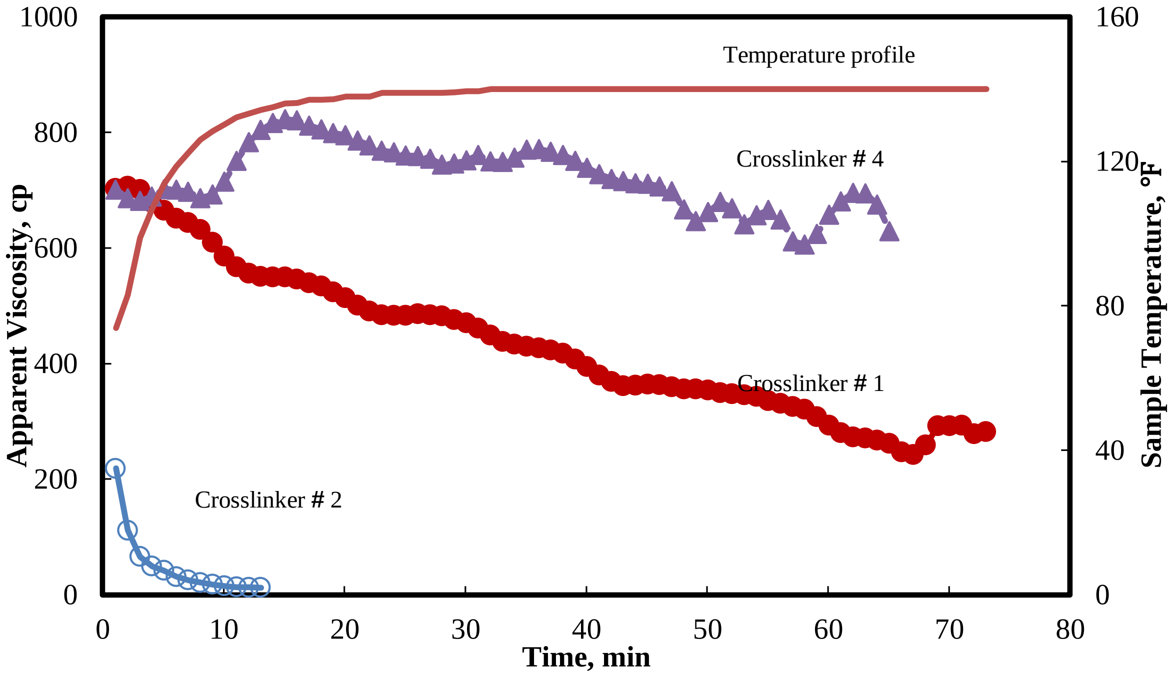


Figure IV 5— 20 PPTG CMHPG crosslinked with three zirconium crosslinkers (1.7 gpt) at a shear rate of 170 s-1 at 140°F. No breaker was added. Initial pH was 3.8. Viscosity drop in the case of crosslinker 2 can be due to a slow crosslinking reaction, which cause the agglomeration to break under high shear.

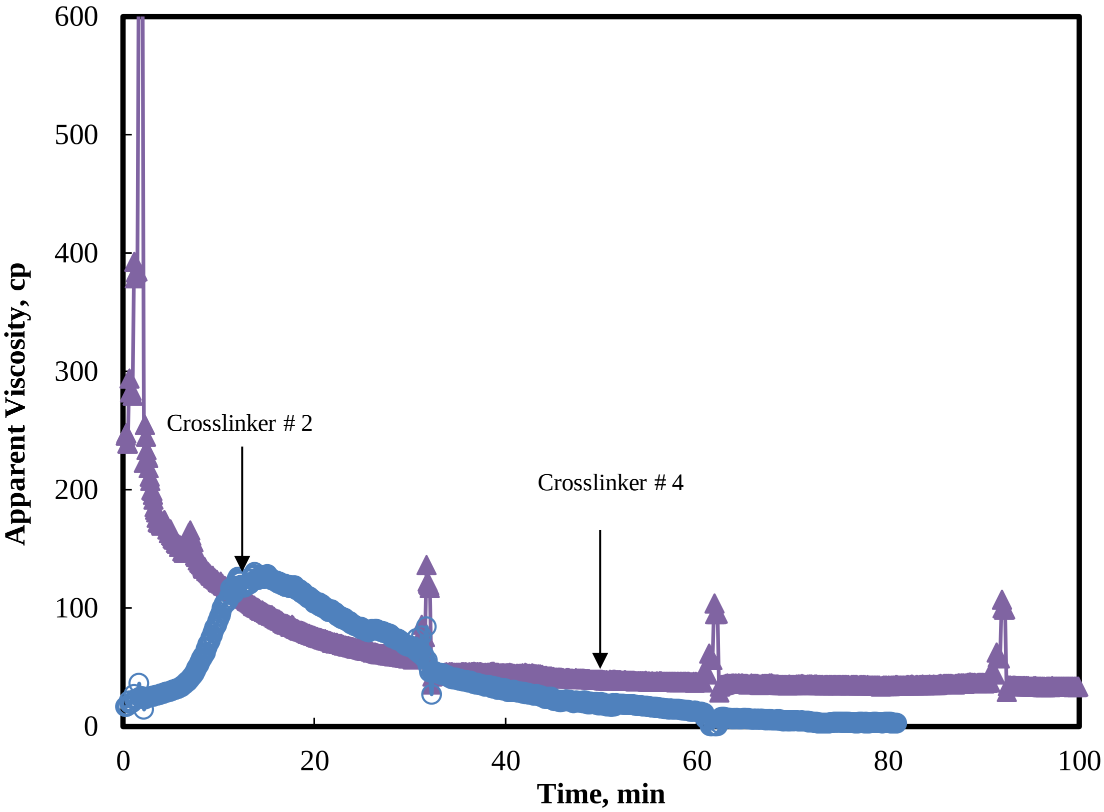


Figure IV 6— Viscosity profile of 20 PPTG CMHPG crosslinked with 1.7 gpt Zr-based crosslinkers at 140°F. No breaker was added. Initial pH was 3.8. The effect of ligand type on shear recoverability of Zr-based crosslinekrs after the removal of initial shearing at 100 s^{-1} can be seen.

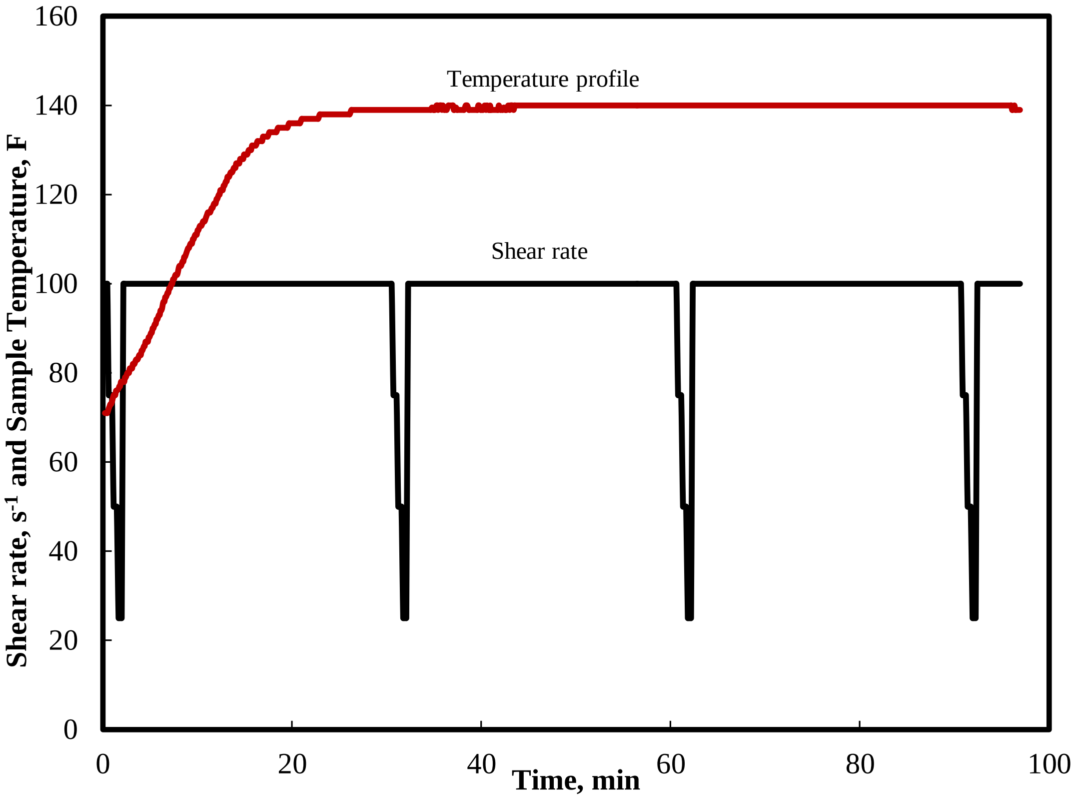


Figure IV 7— API RP 39 sequence and temperature profile used for the results of Fig. 6a.

Current Shortcomings of Zr and B Crosslinkers: No Delay in Gelation Process at High pH

One of the favorable applications of crosslinkers is their ability to control and delay the crosslinking reaction to reduce the frictional pressure and to prevent the gel from shearing during pumping. Furthermore, the lack of delay in crosslinking at high pH is one of the shortcomings in commercially available Zr-based crosslinkers (Putzig 2012). To address the latter limitation, two crosslinkers were combined to overcome one's weakness through the other one's strength. Furthermore, previous research showed that dual crosslinkers of boron-zirconium showed promising results (Rae and di Lullo 1998; Rahim et al. 2013).

Aluminum resides in the same group as boron in the periodic table. As such, they share properties that make their application suitable in fracturing applications under certain specific conditions, such as high shear rates (Sokhanvarian et al. 2015). Broader ranges of application are possible by combining two metallic crosslinkers, and in this study, this new dual crosslinker consisting of aluminum and zirconium was developed to address the fast crosslinking at high pH (10.8). **Fig. IV 8** shows that there is almost 9 to 10 minutes delay in forming a fully three-dimensional network structure at a pH of 10.8, 170 s^{-1}, and 140°F, which is in a favorable time window of 3 to 8 minutes (Putzig 2012). The Al-Zr crosslinker in the present study also works at low pH (3.8). **Fig. IV 9** shows the viscosity at 140, 250, and 300°F. Increasing the temperature to 250°F shortens the time it takes to reach the peak viscosity. At 300°F, there is almost no delay to reach the peak viscosity. It is also clear that the viscosity is above 100 cp, which is the acceptable at 170 s^{-1} (Bunger et al. 2013).

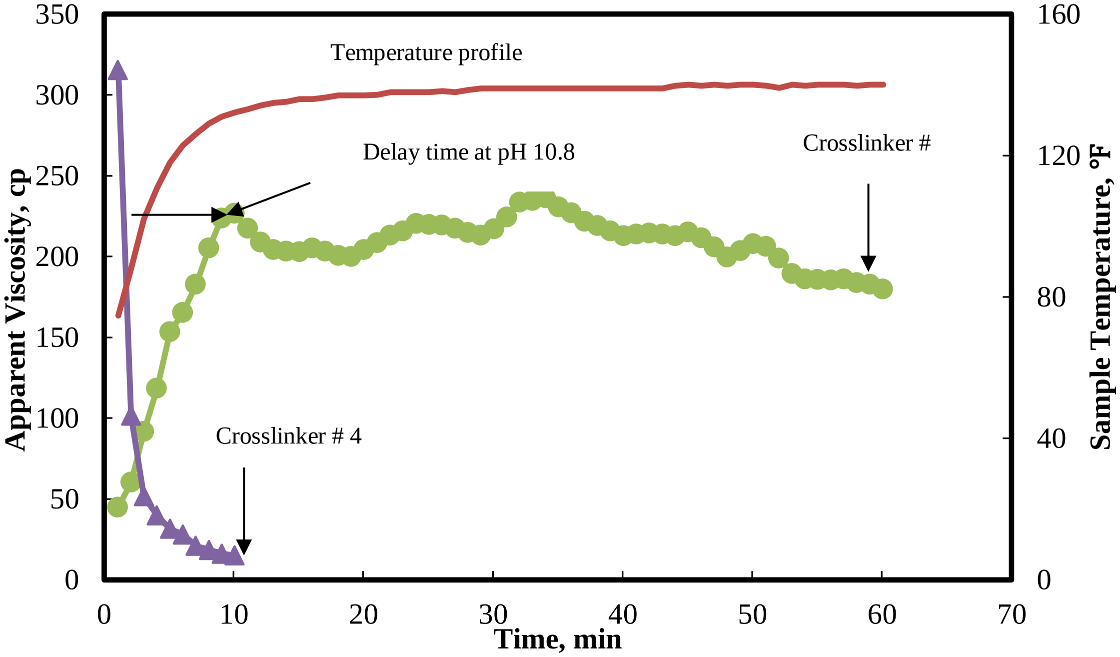


Figure IV 8— 20 PPTG CMHPG crosslinked with 1.7 gpt crosslinkers 4 and 5 at a shear rate of 170 s-1 and 140°F at high pH (10.8). No breaker was added. Immediate viscosity buildup at high pH is a shortcoming of Zr-based crosslinkers (crosslinker # 4), which can be addressed through Al-Zr crosslinker # 5.

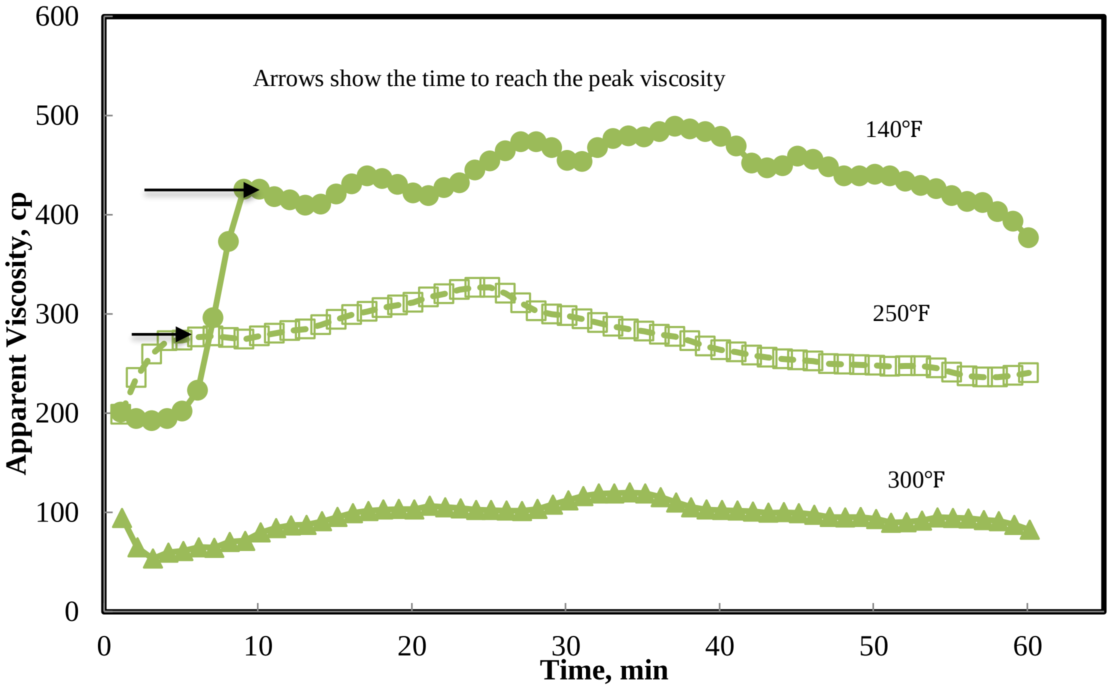


Figure IV 9—Effect of temperature on the viscosity profile of 20 PPTG CMHPG crosslinked with 1.7 gpt crosslinker # 5 at a shear rate of 170 s-1. No breaker was added. Initial pH was 3.8.

Lack of Shear Recovery

The effect of shear history was investigated on one of the zirconium-based crosslinkers, as it is known that the viscosity of gels with Zr crosslinkers do not recover after the shear rate is removed. The CMHPG polymer crosslinked with crosslinker 4 was tested under a shear ramp of 10 to 1,000 s^{-1} and then from 1,000 to 10 s^{-1} at 80°F. The viscosity was not fully recovered, and this confirms the irreversible nature of zirconium-based crosslinkers. However, the same shear sweep test was conducted on CMHPG crosslinked with an Al-Zr based dual crosslinker (crosslinker 5), and the gel almost recovered its viscosity after reverting from high to low shear rates (**Figs. IV 10 and 11**). The Al-Zr crosslinker in the present study is a favorable choice compared to Zr-based crosslinkers for fracturing applications, as it can retain its viscosity after exposing to high shear rates (during pumping, especially at perforations) (Al-Muntasheri 2014).

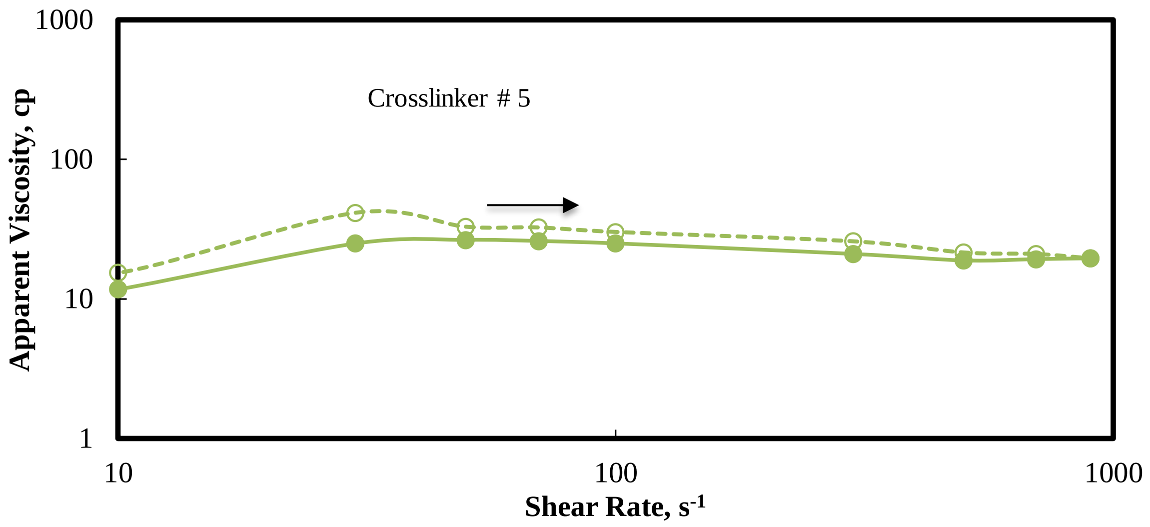


Figure IV 10—Effect of shear history on viscosity recovery of 20 PPTG CMHPG crosslinked with 1.7 gpt of crosslinker# 4 at 80°F. Initial pH was 3.8. Shear recovery is a limitation of Zr-based crosslinkers that can be improved and addressed with Al-Zr crosslinker in the present study.

Figs. IV 12 and **13** show that by raising the temperature to 140°F, the viscosity recovery for the Al-Zr dual crosslinker decreased compared to the test at 80°F, however, the viscosity loss after experiencing shear is significantly lower than Zr crosslinker (crosslinker # 4).

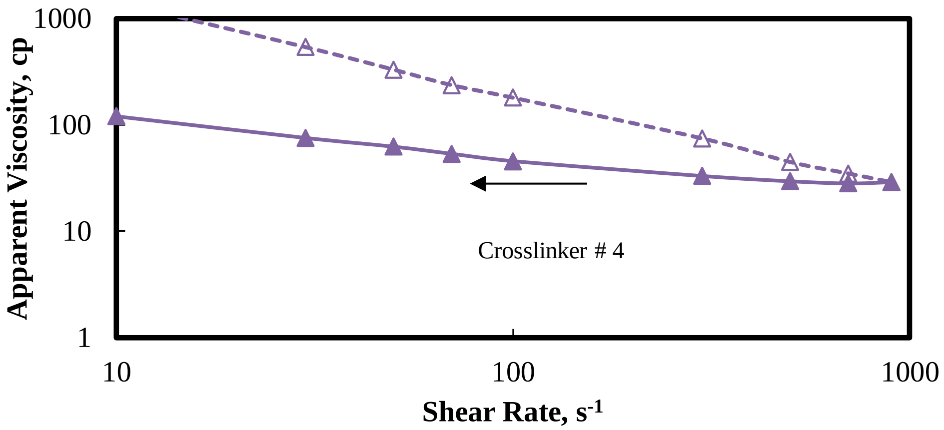


Figure IV 11—Effect of shear history on viscosity recovery of 20 PPTG CMHPG crosslinked with 1.7 gpt of crosslinker # 5 (Al-Zr) at 80°F. Initial pH was 3.8. Shear recovery is a limitation of Zr-based crosslinkers that can be improved and addressed with Al-Zr crosslinker in the present study.

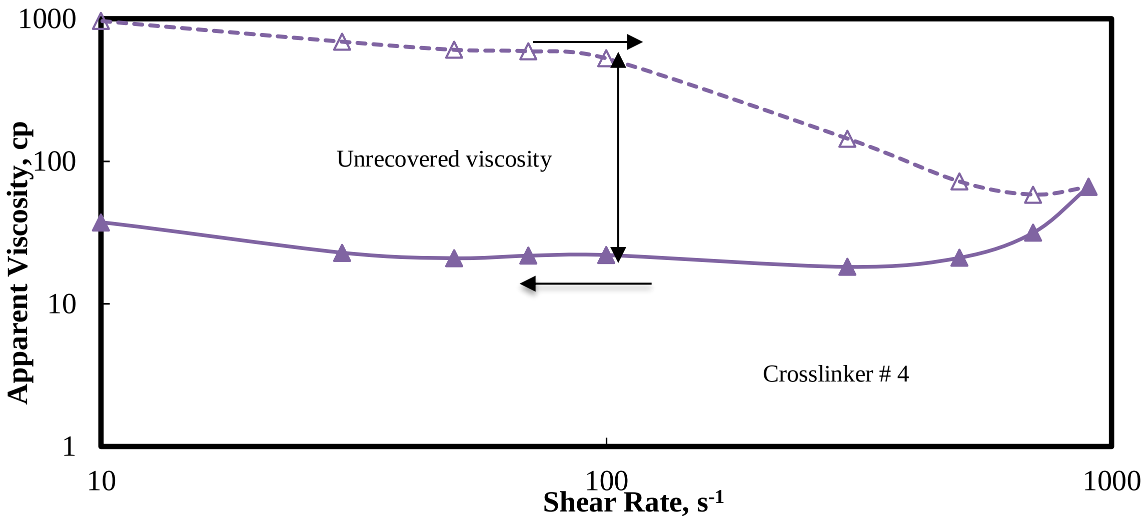


Figure IV 12—Effect of shear history on viscosity recovery of CMHPG (20 PPTG) crosslinked with 1.7 gpt of crosslinker # 4 at 140°F. Initial pH was 3.8. The area inside the loop is unrecovered viscosity, which is a limitation of Zr-based crosslinkers that can be improved and addressed with Al-Zr crosslinker in the present study.

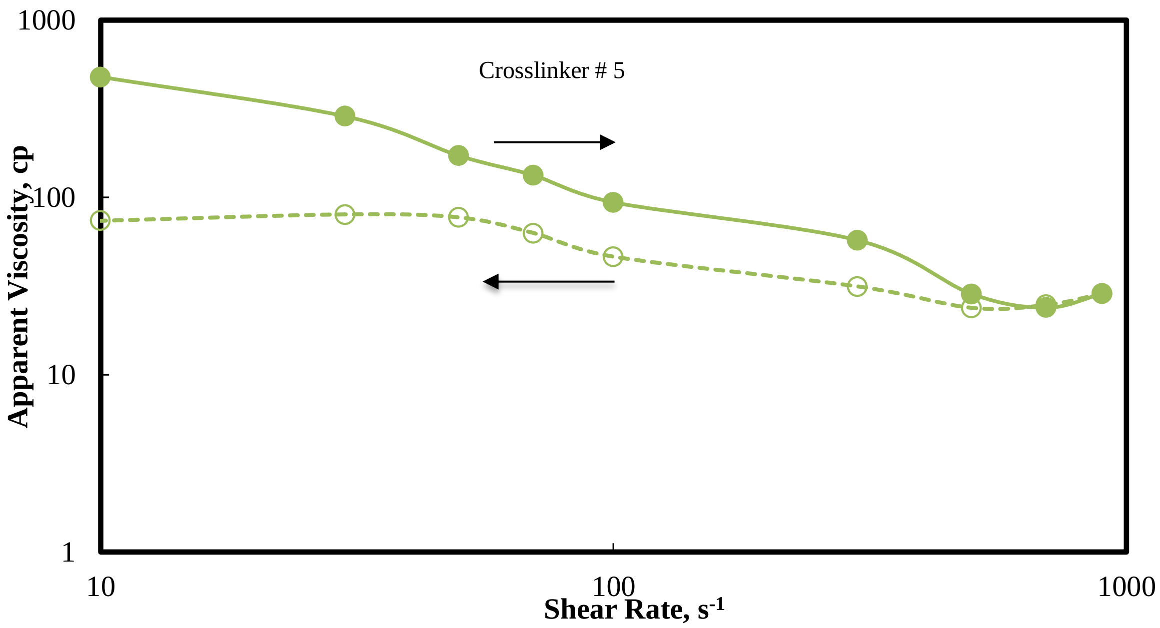


Figure IV 13 —Effect of shear history on viscosity recovery of CMHPG (20 PPTG) crosslinked with 1.7 gpt of crosslinker # 5 (Al-Zr) at 140°F. Initial pH was 3.8.

Zirconium-Boron Crosslinker VS. Zirconium-Aluminum

The performance of Zr-B crosslinker is compared to Al-Zr crosslinker through steady shear viscosity and oscillatory measurements. These two crosslinkers have the same ligand (lactate); however, the concentration of Zr (metallic crosslinker) is higher in Zr-B crosslinker than Zr-Al crosslinker. Therefore, the higher viscosity of CMHPG crosslinked with Al-Zr at 170 s^{-1} may be due to higher concentration of Al compared to Zr in Al-Zr crosslinker (**Fig. IV 14**). These results indicate that the concentration ratio of Zr/B and Zr/Al plays a significant role in determining the final performance of the dual crosslinker. Viscosity measurements based on API RP 39 were conducted for CMHPG crosslinked with Al-Zr and Zr-B (**Fig. IV 15**) and show that for the CMHPG crosslinked with Zr-B, after the initial shearing at 100 s^{-1}, the viscosity decreased and did not recover to initial viscosity after the shear is removed. Alternatively, for the CMHPG crosslinked with the Al-Zr, the viscosity was retained throughout the test. The shear sequence and temperature profile are shown in **Fig IV 16**. Dynamic oscillatory measurements can provide the crossover point at which the elastic and viscous modulii intersects implying the material stores as much energy elastically as it loses viscously. **Figs. IV 17** and **18** show the viscous and storage modulii responses for 20 PPTG CMHPG crosslinked with the Zr-B and Al-Zr crosslinkers, respectively. Fig. IV 18 shows that the fluid having Al-Zr as a crosslinker behaves like a fluid up to the frequency of 0.4 rad/s, and then moves toward a solid-like behavior (more elastic). The performance of CMHPG crosslinked with the Zr-B crosslinker was more elastic as G’ is higher than G’’ over the whole frequency range in this test (Fig. IV 17).

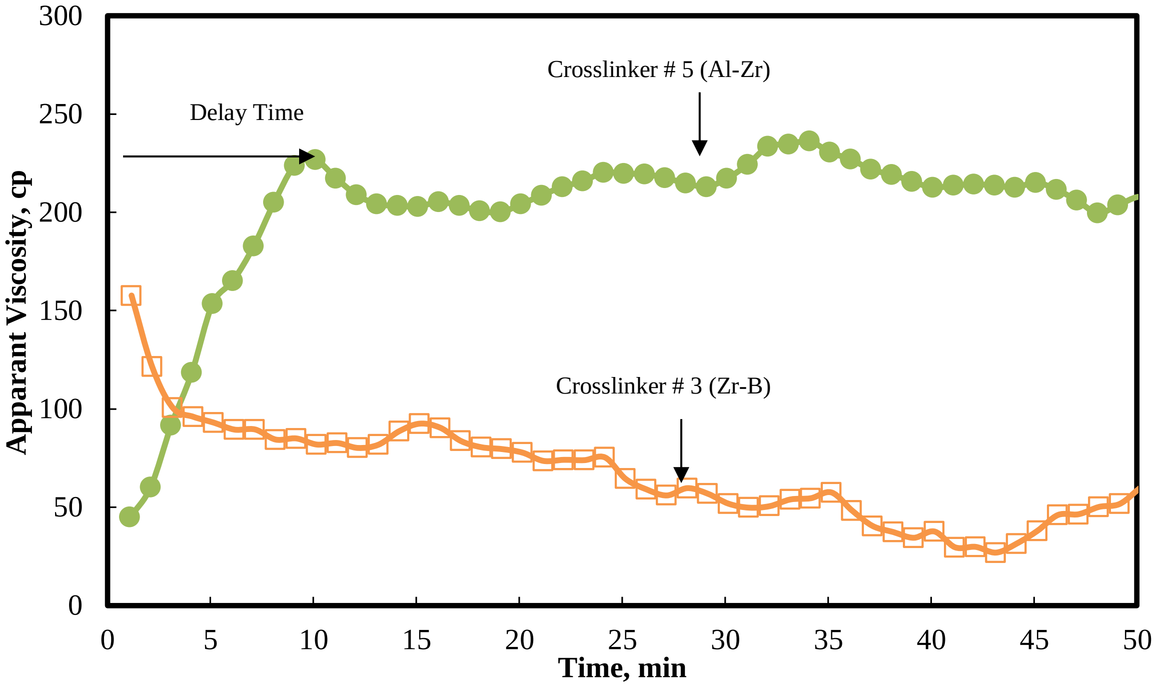


Figure IV 14—Comparison of viscosity profile at 170 s-1 and 140°F using 1.7 gpt Al-Zr and Zr-B crosslinkers. 20 PPTG CMHPG was used. No breaker was added. Initial pH was 10.8. The initial viscosity for 20 PPTG CMHPG crosslinked with B-Zr is higher but Al-Zr maintains a higher viscosity than Zr-B at 170 s^{-1}.

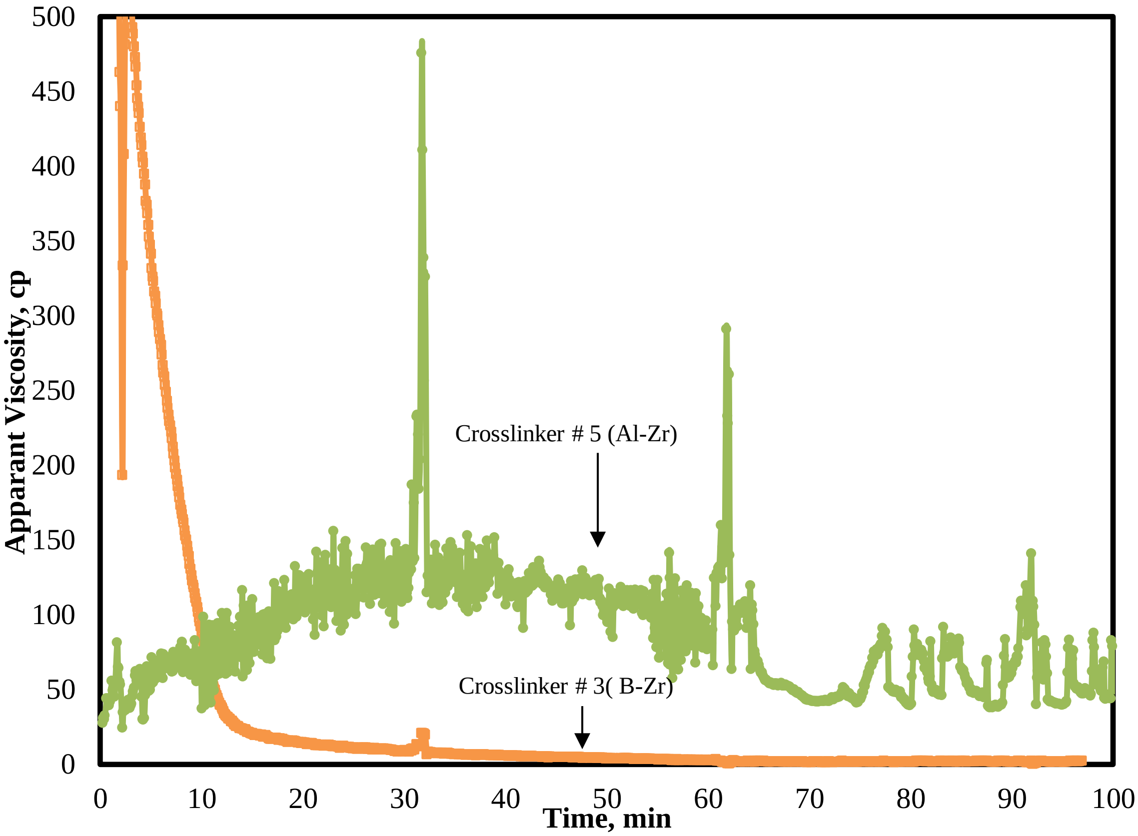


Figure IV 15— Viscosity profile of 20 PPTG CMHPG crosslinked with 1.7 gpt Al-Zr and Zr-B crosslinkers at 140°F. No breaker was added. Initial pH was 3.8. The viscosity did not recover for CMHPG crosslinked with Zr-B after the initial shearing at 100 s^{-1}.

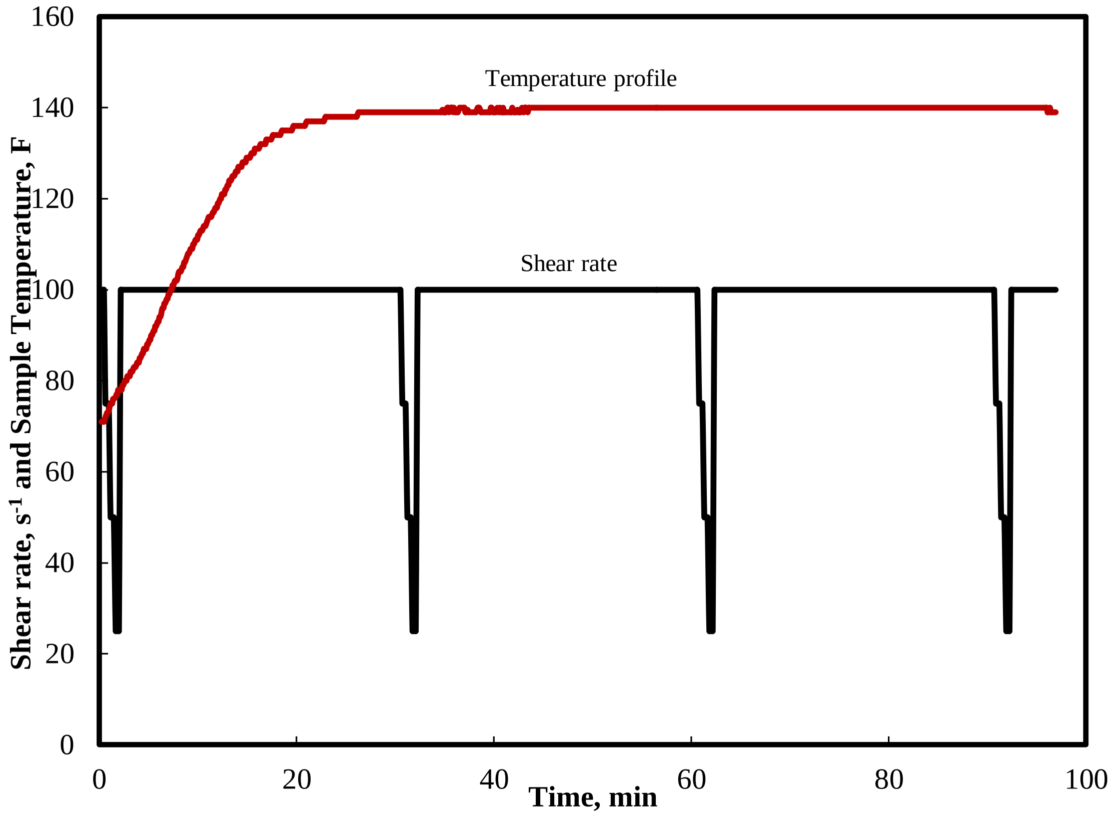


Figure IV 16— API RP 39 sequence and temperature profile used for the results of Fig. 10b.

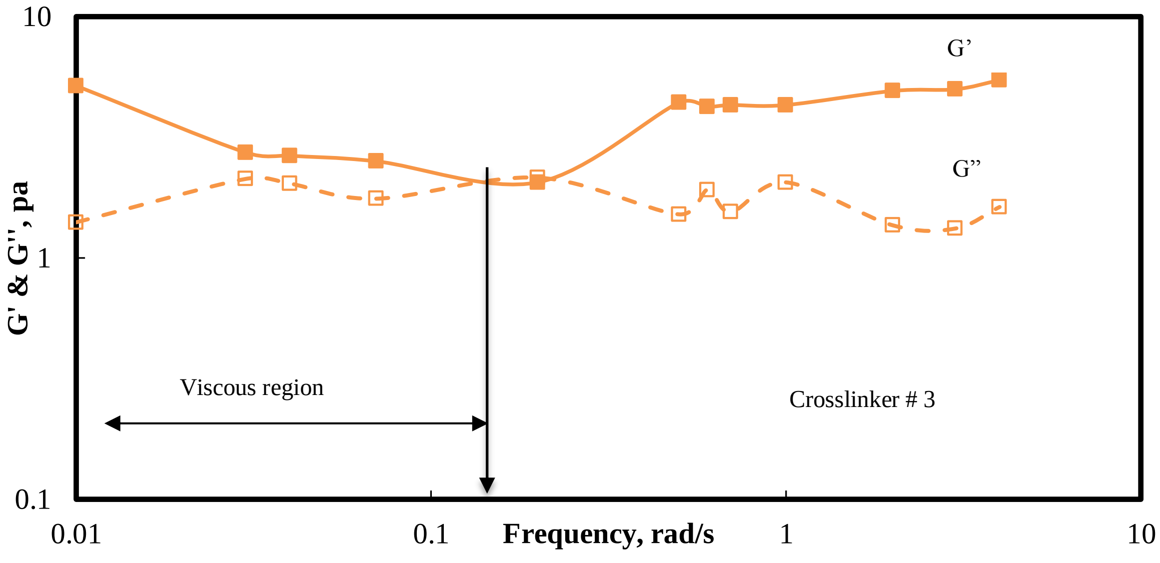


Figure IV 17— 20 PPTG CMHPG crosslinked with Crosslinkers # 3 at 5% strain at 80°F (crossover point: 0.2, 2.153). No breaker was added. Bob HB5 was used. Initial pH was 10.8. The faster the relaxation time, the sooner proppant will settle.

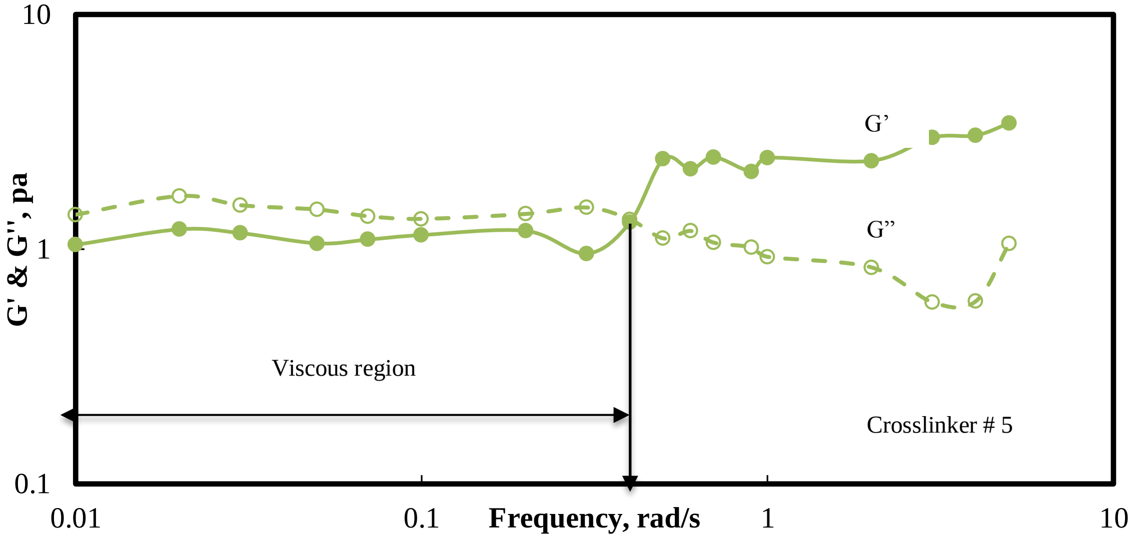


Figure IV 18— 20 PPTG CMHPG crosslinked with Crosslinkers # 5 at 5% strain at 80°F (crossover point: 0.4, 1.344). No breaker was added. Bob HB5 was used. Initial pH was 10.8. The faster the relaxation time, the sooner proppant will settle.

Settling Tendency of Proppants: Measurements of G’ and G’’

Effect of Ligand Type on Proppant Transport

DOS is a non-destructive method to analyze the network structure and viscoelastic behavior of a crosslinked polymer. The three-dimensional structure is not represented in steady shear viscosity measurements that its purpose is to simulate the field and pump process. The imposed motion on the fracturing fluid is sinusoidal and unidirectional in DOS and steady shear viscosity measurements, respectively. In the DOS technique, the results can be divided into two parts: in-phase and out-phase components, which are the representatives of storage (G’) and loss (G’’) moduli, respectively.

The crosslinker concentration is one of the factors that can affect the elastic modulus response of a crosslinked polymer. **Fig. IV 19** shows that the elastic modulus is highest at 1.7 gpt of crosslinker 2. The use of 1.9 gpt crosslinker resulted in a smaller elasticity, which is due to overcrosslinking the polymer (Goel and Subhash 2001). The independency of G’ at low frequencies in Fig. IV 19 is an indication of a three-dimensional structure of the crosslinked polymer. The elastic modulus becomes independent of frequency as the stress in the gel structure cannot relax over any time scale (Prudhomme et al. 1985; Knoll and Prudhomme 1987).

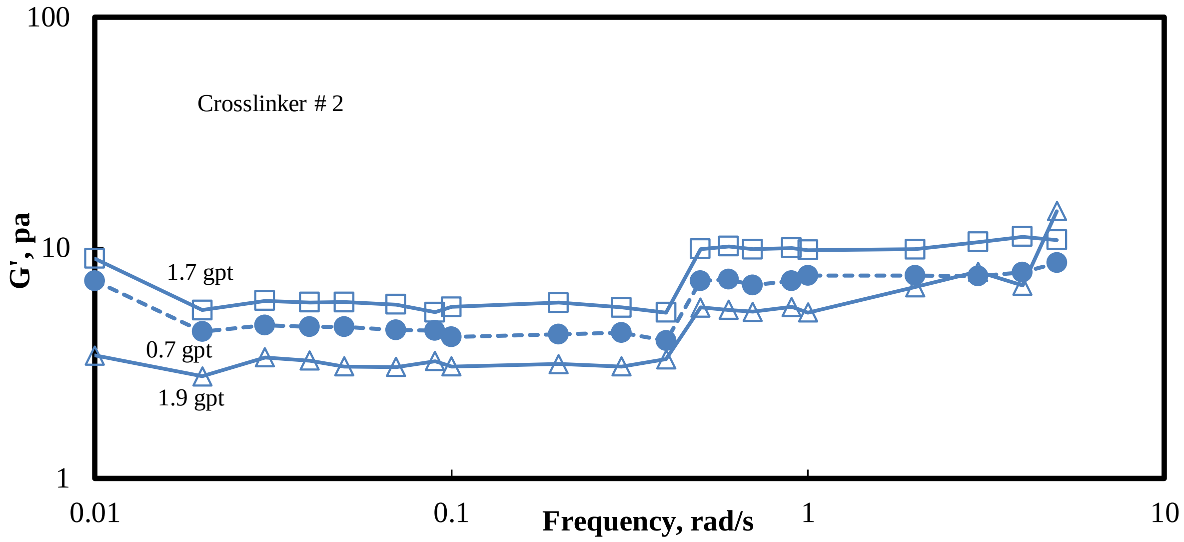


Figure IV 19— 20 PPTG CMHPG crosslinked with different concentrations of crosslinker # 2 at 5% strain at 80°F. No breaker was added. Initial pH was 10.8. The right concentration of crosslinker leads to highest elastic modulus.

Figs. IV 20 and **21** show the viscous and storage modulii for 20 PTTG CMHPG crosslinked with Zr-based crosslinkers 2 and 4, respectively. The strain was 5% and temperature was 80°F. Crosslinker 2 contains TEA and lactate, and crosslinker 4 has a weaker ligand (propylene glycol and lactate) attached to Zr. The crossover point is where the fluid stores as much energy elastically as it loses viscously. The crossover point also is called relaxation time, which is the inverse of frequency. It can indicate the proppant settling velocity in the fracture fluid. The crossover points for crosslinkers 2 and 4 are at 0.4 and 0.03 rad/s, respectively. Therefore, these results show that crosslinker 4 is a better choice than crosslinker 2 for proppant transfer purposes, as the proppant will settle sooner in the case of crosslinker 2 due to the faster relaxation time.

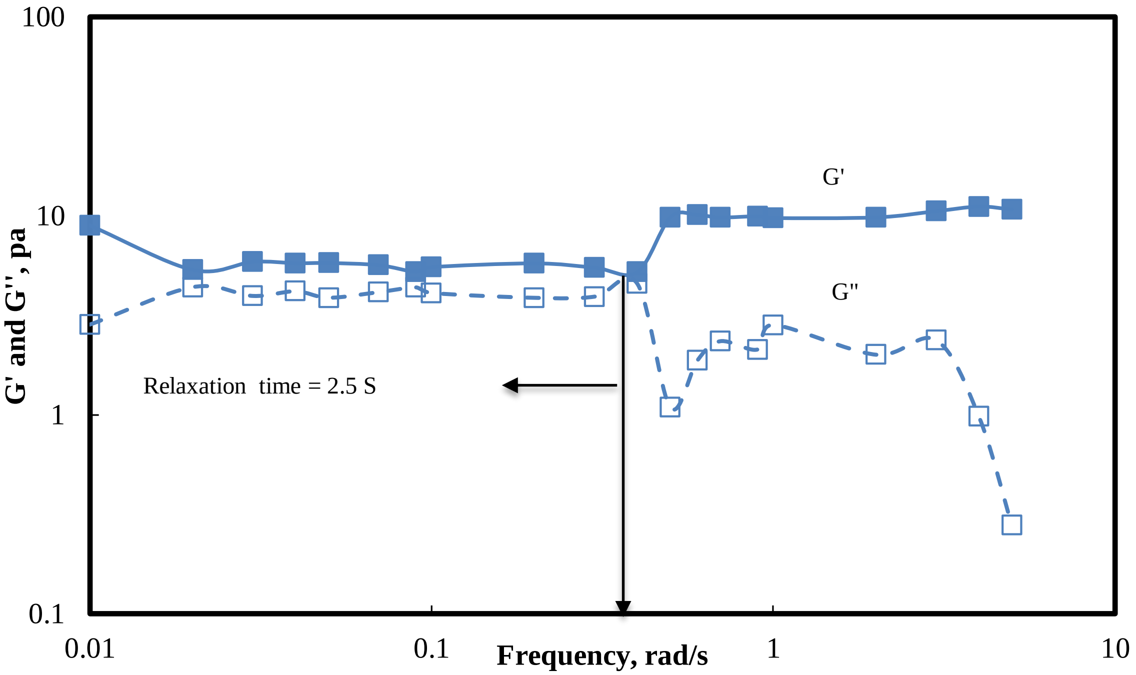


Figure IV 20— G' and G'' responses for 20 PPTG CMHPG crosslinked with 1.7 gpt of crosslinker # 2 at 5% strain at 80°F (Crossover point: 0.4, 4.573). Initial pH was 10.8. Faster relaxation time is indicative of earlier proppant settling.

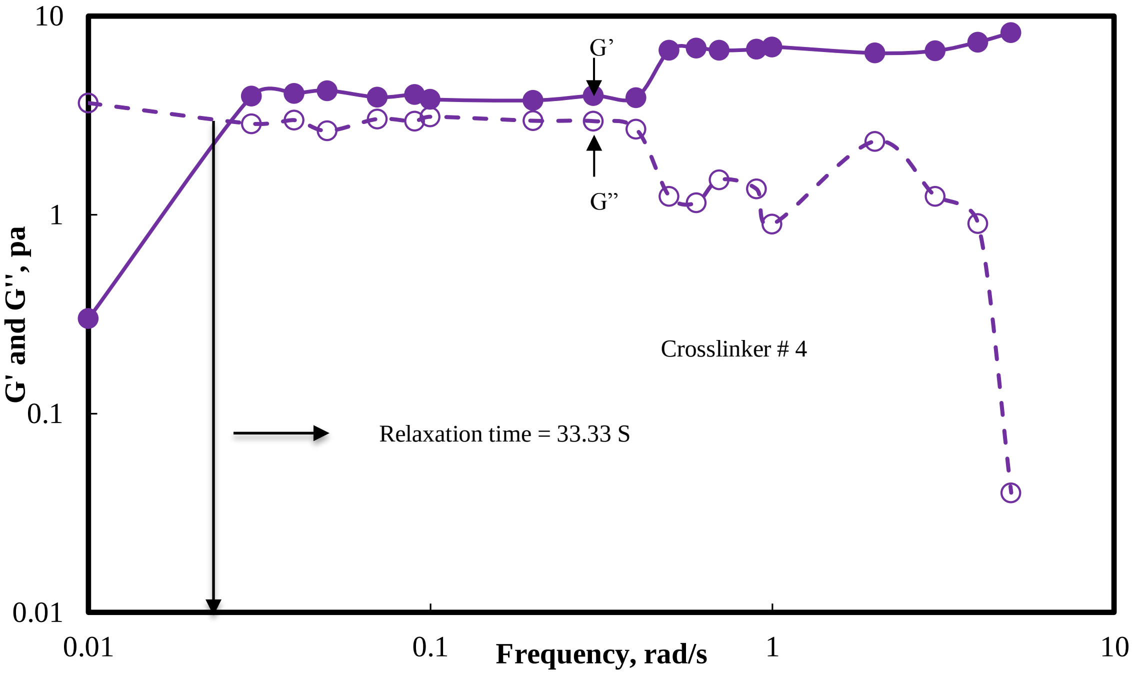


Figure IV 21— G' and G'' responses for 20 PPTG CMHPG crosslinked with 1.7 gpt of crosslinker # 4 at 5% strain at 80°F (Crossover point: 0.03, 2.874), Initial pH was 10.8. Faster relaxation time is indicative of earlier proppant settling.

Proppant Suspension Experiments Using Ottawa Sand as Proppants

In hydraulic fracture treatments, the appropriate placement of proppants into the fracture is a crucial parameter for a successful treatment. Furthermore, enough vertical settling velocity leads to a maximum horizontal distance in the fractures (Harris et al. 2005). All of the tests were conducted at 80, 140, and 230°F using a 4 lbm/gal of 40/70-mesh Ottawa sand.

The process of the static settling test as a function of time is shown for crosslinker 2 at 80 and 140°F in **Figs. IV 22** and **23**, respectively. **Fig. IV 24** shows the level of proppant suspension for 20 PPTG CMHPG crosslinked with each of 5 crosslinkers examined in the present study. It is obvious from Fig. IV 24 that there is a plateau and then decrease (proppants start to settle), which can be attributed to the polymer becoming relaxed after being in a static mode for a long period of time (Harris et al. 2005). Proppant settling occurs sooner for crosslinker 2 compared to crosslinker 4, which agrees with the shorter relaxation time for crosslinker 2 obtained from G' and G'' measurement in the last section (Figs. IV 20 and 21).

The effect of temperature was also tested for both crosslinkers 2 and 4 at 140 and 230°F, and again the results confirm the better performance of crosslinker 4 (**Figs. IV 25** and **26**). It should be noted that the proppant settling did not change for crosslinker 4 as the temperature increased from 80 to 140 and 230°F.

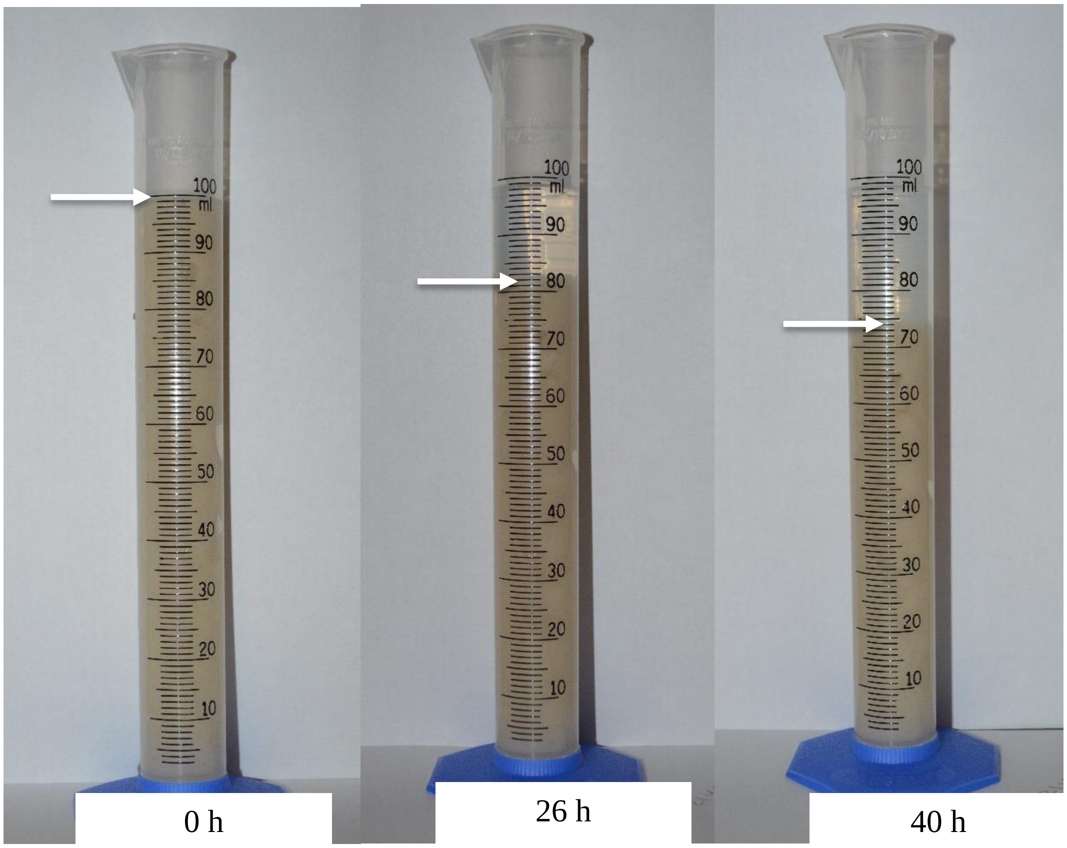
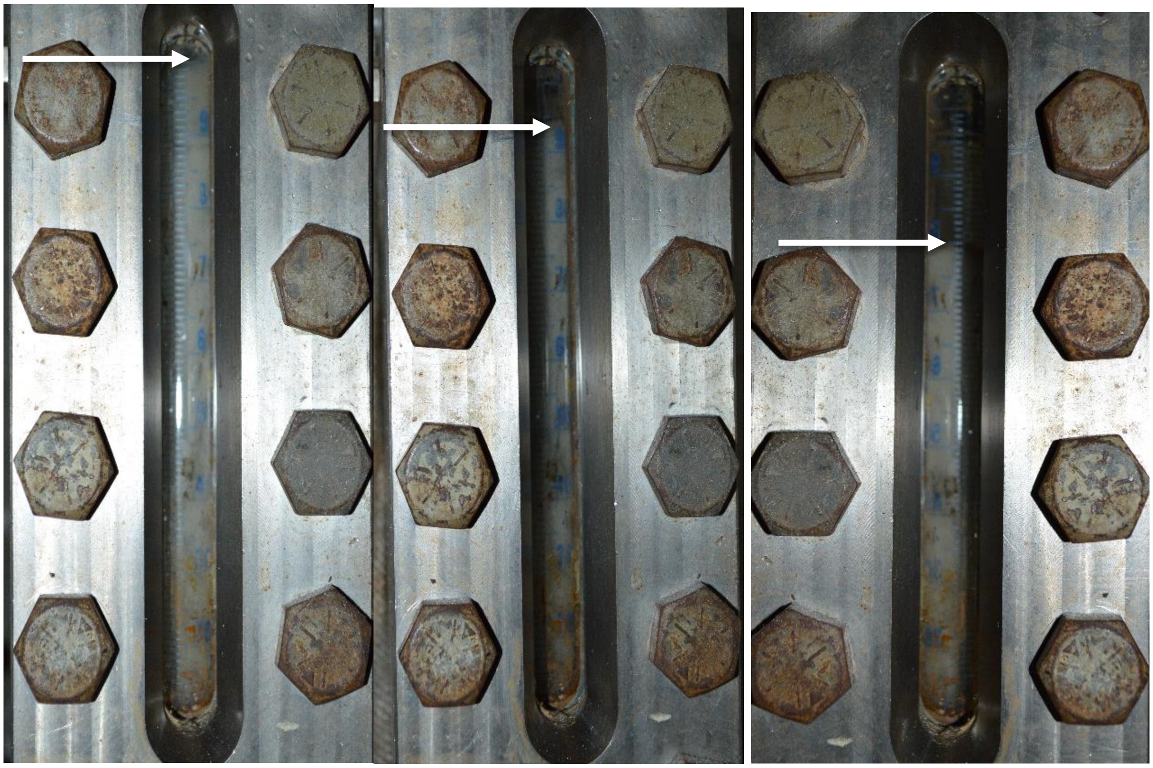


Figure IV 22— Static settling test for 20 PPTG CMHPG crosslinked with crosslinker # 2 (1.7 gpt) using 4 lbm/gal 40/70-mesh Ottawa sand at 80°F. Initial pH was 10.8. The arrow shows the level of suspension in the graduated cylinder.



0 h 3 h 20 h

Figure IV 23— Static settling test for 20 PPTG CMHPG crosslinked with crosslinker # 2 (1.7 gpt) using 4 lbm/gal 40/70-mesh Ottawa sand at 140°F. Initial pH was 10.8. The arrow shows the level of suspension in the graduated cylinder.

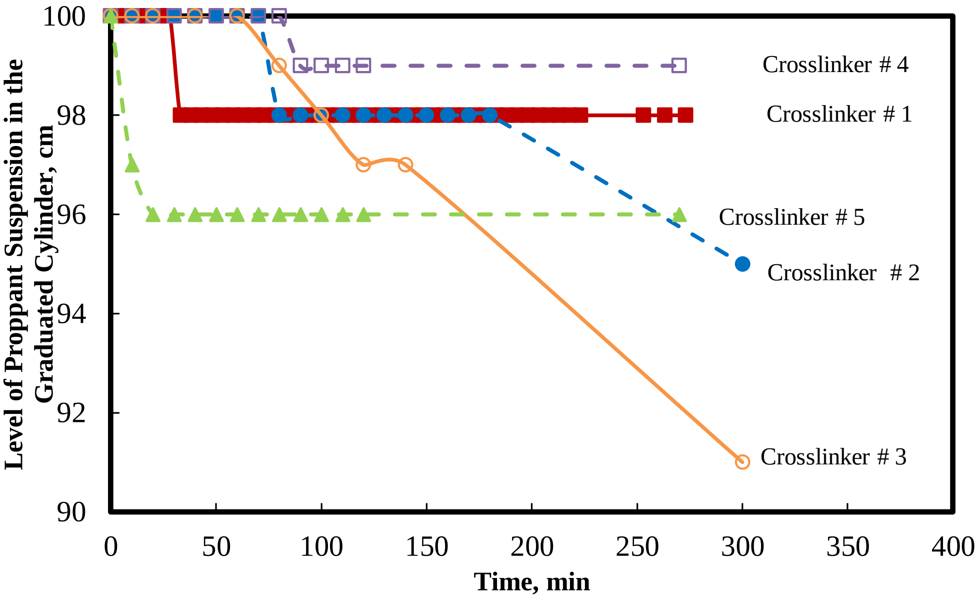


Figure IV 24— Static settling test for 20 PPTG CMHPG crosslinked with different crosslinkers (1.7 gpt) using 4 lbm/gal 40/70-mesh Ottawa sand at 80°F. Initial pH was 10.8.

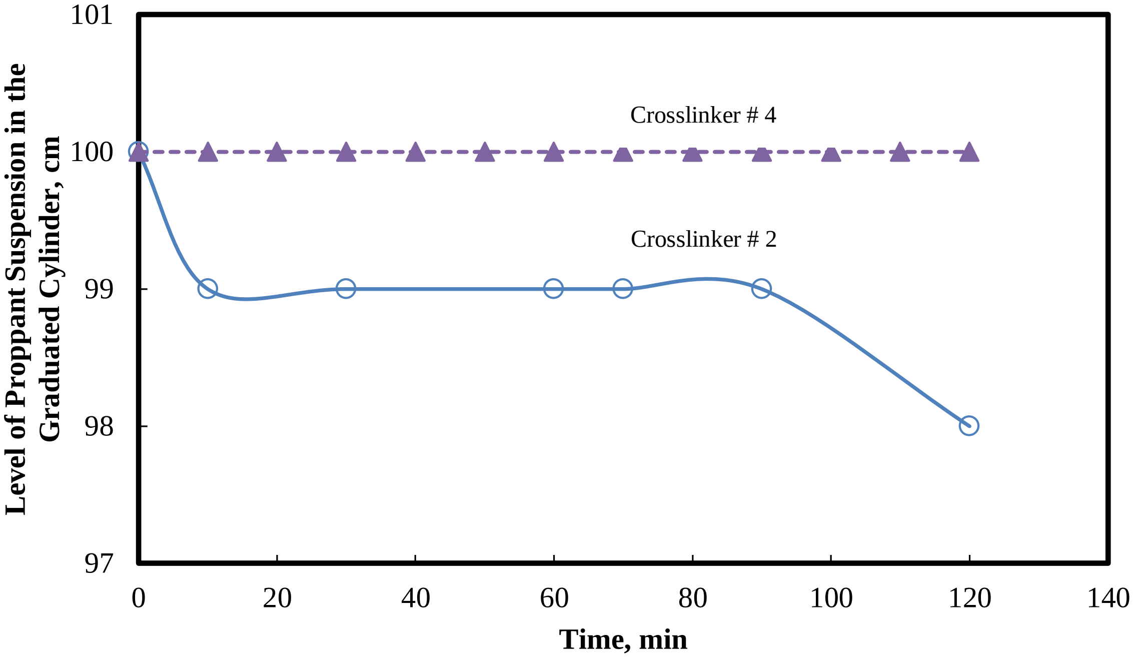


Figure IV 25— Static settling test for 20 PPTG CMHPG crosslinked with zirconium-based crosslinkers 2 and 4 (1.7 gpt) using 4 lbm/gal 40/70-mesh Ottawa sand 140°F. Initial pH was 10.8. Crosslinker 4 is a better choice.

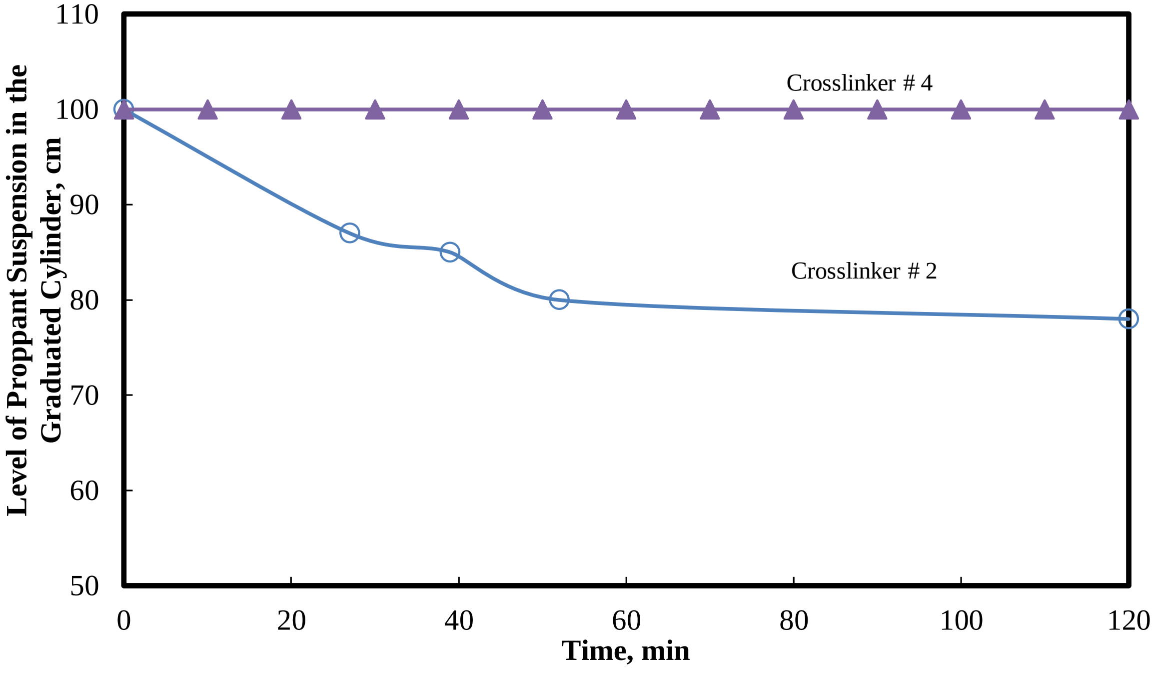


Figure IV 26— Static settling test for 20 PPTG CMHPG crosslinked with zirconium-based crosslinkers 2 and 4 (1.7 gpt) using 4 lbm/gal 40/70-mesh Ottawa sand 230°F. Initial pH was 10.8. Crosslinker 4 is a better choice.

Fluid Loss

Fluid leakoff into the formation is always a concern, especially for the fracturing fluids with low polymer loadings. The filtration rate is high before forming the filter cake, and then it decreases. As the fluid leaksoff into the formation, the proppant concentration will increase in the fracture, which can stop the fracture propagation. Furthermore, fluid loss is one of the most important parameters in fracture treatment design. The leakoff coefficient (C_w) and the spurt loss (S_p) can be used to characterize the fluid loss (Harris 1988; Dawson et al. 1998; Economides 2000; Gupta et al. 2008). These variables can be determined according to Eqs. 1 and 2 by Economides (2000).

$$C_w = \frac{0.0164m}{A} \quad (1)$$

$$S_p = \frac{24.4b}{A} \quad (2)$$

where m ($cm^3/min^{0.5}$) and b are the slope and the intercept of the fluid loss graph (**Fig. IV 27**), respectively, A is the cross-sectional area of the core (cm^2) used in the leakoff test, C_w

(ft/min$^{0.5}$) is the leakoff coefficient, and S_p (gal/ft^2) is the spurt loss.

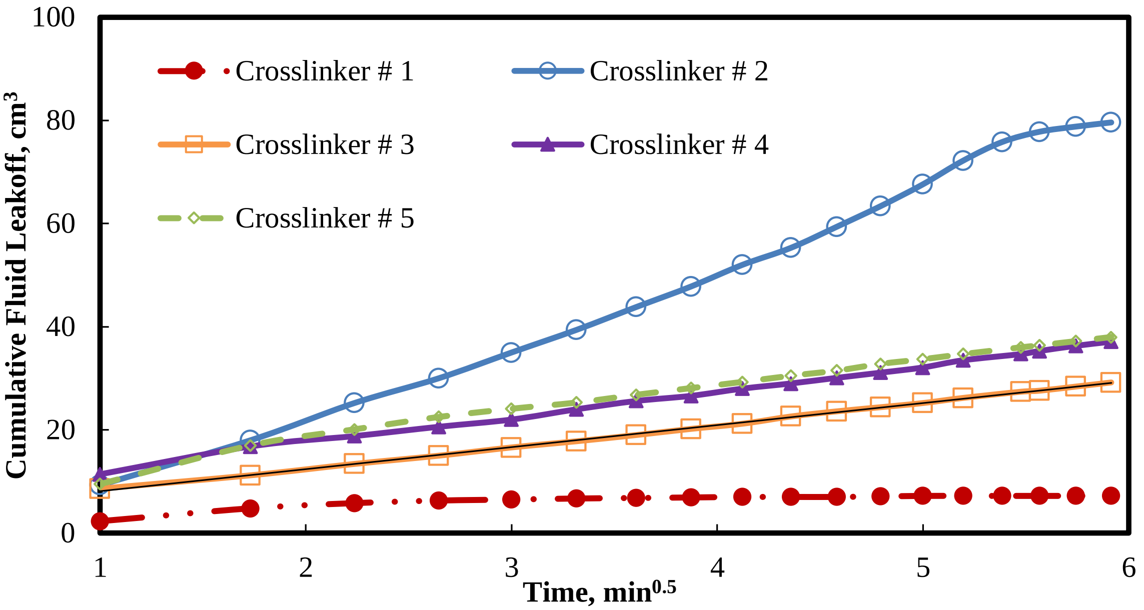


Figure IV 27— Fluid loss data using all five crosslinkers examined in the present study obtained from the static leakoff test at the differential pressure of 300 psi at 140°F. 20 PPTG CMHPG, 1.7 gpt of crosslinkers were used. Initial pH was 10.8. Linear regression was obtained from the first 6 points of data.

Fig. IV 27 is a graph of the cumulative filtrate volume as a function of the square root of time for 20 PPTG CMHPG crosslinked with each crosslinker examined in the present study. The crosslinkers that were used in this study were three zirconium-based (1, 2 and 4), one zirconium-boron-based (crosslinker 3), and one aluminum-zirconium-based (crosslinker 5) crosslinkers. The leakoff coefficients and spurt losses are given in **Table IV 1**. The leakoff coefficients in an increasing order are as follows: 1 > 3 > 4 > 5 > 2. Crosslinker 2 had a leakoff rate and spurt loss higher than recommended by Davies et al. (1991) and is not accepted. All of the formed filter cakes were measured using a caliper, and they were very thin and uniform ($< 1\ mm$). To find the experimental errors, the leakoff test was repeated for crosslinker 3 (**Table IV 2**), and the standard deviation was 0.00015 ft/min$^{0.5}$.

The results agree with findings by Dawson et al. (1998) that the fracturing fluid with low polymer loading can have acceptable leakoff rates. The leakoff results are in agreement with the findings of Reyes et al. (2015).

Crosslinker #	Crosslinker concentration (gpt)	Bandera core porosity (%)	Leakoff coefficient (ft/min$^{0.5}$)	Spurt loss (gal/ft^2)
1	1.7	19.5	0.0013	0.0009
2	1.7	13.8	0.0075	0.057
3	1.7	19.6	0.0022	0.029
4	1.7	18.7	0.0026	0.055
5	1.7	14.8	0.0027	0.006

Table IV 1— Leakoff results using 20 PPTG CMHPG crosslinked with crosslinkers # 1 to 5 at 300 psi differential pressure and 140°F. The maximum allowable leakoff coefficients and spurt loss are 0.003 ft/min$^{0.5}$ and 0.05 gal/ft^2 (Davies et al. 1991).

Crosslinker #	Crosslinker concentration (gpt)	Bandera core porosity (%)	Leakoff coefficient	Spurt loss (gal/ft^2)
3	1.7	19.6	0.0022	0.029
3	1.7	19.5	0.0024	0.017
3	1.7	19.3	0.0028	0.016
3	1.7	19.3	0.0029	0.007

Table IV 2— Reproducibility of leakoff tests results conducted at 300 psi and 140°F.

Conclusions

Three zirconium-based, one zirconium-boron-based, and one aluminum-zirconium-based crosslinkers were used to form CMHPG-crosslinked polymers. The proppant transfer and leakoff experiments were conducted for 20 PPTG crosslinked CMHPG. The conclusions below are based on the results and findings of the present study:

1. Ligand type is a very important parameter affecting the performance of Zr-based hydraulic fracturing fluids. A very strong ligand may lead to agglomeration breakage under high shear before they become bigger, especially in the case of crosslinker 2.
2. Crosslinker 4 is a better option among Zr-based crosslinkers examined in this study. Lactate and propylene glycol (crosslinker 4) is a better choice of ligand compared to

lactate (crosslinker 1) or lactate and triethanol amine (crosslinker 2).

3. Delay in the crosslinking reaction at high pH (10.8) is a shortcoming of current Zr-based crosslinkers, which was addressed through the new dual crosslinker (Al-Zr).
4. The lack of shear recovery of Zr crosslinkers can be addressed through combining Zr and Al crosslinkers.
5. The Al-Zr crosslinker maintained a higher viscosity at high shear rates, and showed a better shear recovery than B-Zr crosslinker. The reason may be due to the higher concentration of Zr (irreversible crosslinking characteristics) in the Zr-B crosslinker than in the Al-Zr crosslink.

CHAPTERV

EVALUATION OF AL-LACATTE AS AN ALTERNATIVE CROSSLINKERS FOR HYDRAULIC FRACTURING TREATMENTS*

Introduction

Hydraulic fracturing treatments were first performed in 1947 to stimulate the Hugoton gas field. From that time, fracturing techniques have been improving. Hydraulic fracturing is an important means to produce from unconventional reservoirs at an economic rate. Fracturing fluid is one of the key components of any fracturing treatment, and it must be capable of opening up the fractures and transporting the proppants to the fracture (Gidley et al. 1989, Economides 2000, Harris et al. 2008, Loveless et al. 2011). Water-soluble polymers have been used to increase fluid viscosity in well treatments. Guar derivatives are more expensive compared to the standard guar; however, there are fewer insoluble materials associated with them. Among all of the guar derivatives, CMHPG (**Fig. V 1**) produces the least amount of residue due to unbroken gel (Rae and di Lullo 1996; Putzig 2012; Hu et al. 2015).

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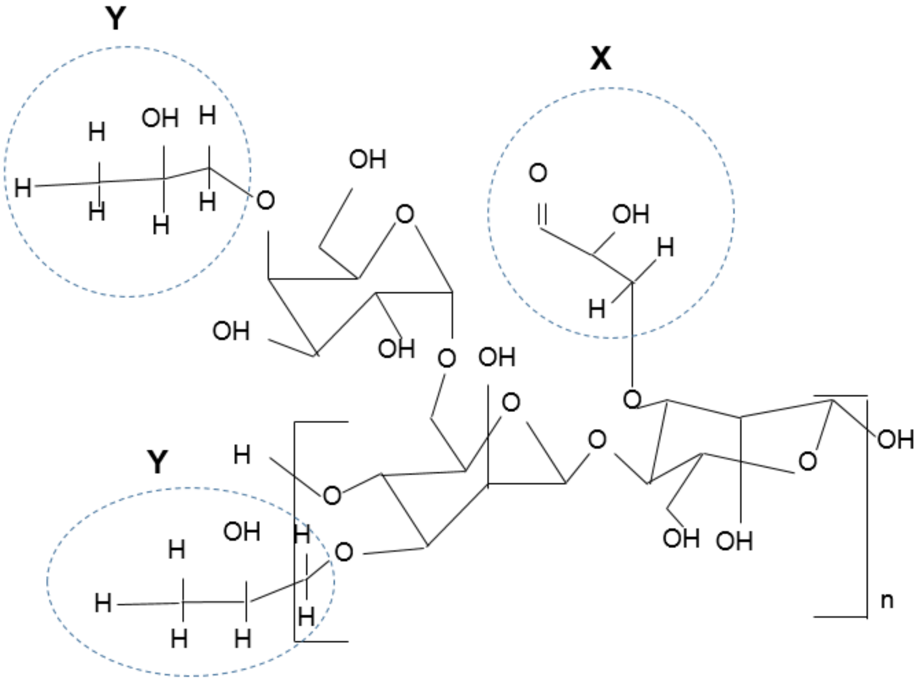

Figure V 1— Chemical structure of carboxymethylhydroxypropyl guar (CMHPG). (Bunger et al. 2013). X (carboxymethyl) and Y (hydroxypropyl) can vary based on the degree of substitution (DS). n is the number of repetition.

Crosslinkers are added to polymer solutions to improve their properties and to avoid introducing more damage and cost through increasing the polymer load (Lei and Clark 2007; Guo et al. 2012). A favorably formed crosslinked polymer is a dependent on choices among different factors. Variations in the crosslinker concentration, polymer type, and even source, which the components of fracturing fluids are provided from, can lead to huge differences in rheological performance of the treatment fluid (Harry et al. 1999). A good candidate is one in which its viscosity can be controlled. Some factors that govern the final viscosity of a crosslinked polymer are concentration of the crosslinker and pH. A crosslinker that is functional under a broad range of pH is very useful as for instance some clays are sensitive to pH, and they can swell in high pH environment (Gupta et al. 2008).

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Crosslinkers are soluble metal complex solutions, which are categorized into two types: reversible and irreversible, and crosslinking reaction occurs through permanent or transient bonds. Boron, titanium, and zirconium, are commonly used (Demkowicz 2001). Each crosslinker poses its own challenges and shows some benefits. Limitations of temperature and pH are associated with borate (reversible) crosslinkers, and recently it is shown that the viscosity of crosslinked polymers using boron is pressure sensitive (England and Parris 2010&2011). Therefore, metallic crosslinkers are developed to overcome these weaknesses. Metallic crosslinkers like zirconium are among the irreversible crosslinkers. One of the shortcomings of zirconium crosslinkers is their instability at high shear rates (Hu et al. 2015). The motivation of developing Al crosslinker in the present study arises from the fact that aluminum resides in the same group as boron in the periodic table, and they share properties that make their application suitable in crosslinked polymers under certain specific conditions such as high shear rates. However, Al is not commonly used (Bunger et al. 2013). Crosslinking using Al can occur at a pH of up to 4.5 or in the transition region near 9.5. Moreover, other researchers have reported that Al-based crosslinkers are functional only at low pH (Borchardt and Yen 1989; Rae and Di Lullo 1996; Economides 2000). Aluminum ions were used to crosslink CMHPG and it was shown that higher degree of molar substitution of hydroxypropyl groups (MS level) resulted in increase in viscosity of Al-CMHPG gels (Kramer et al. 1987). Shah and Watters (1986) showed a few results on 60 pptg CMHPG crosslinked with Al-based crosslinker (aluminate), and concluded instability of this gel at 250°F after 30 minutes. In a patent by Horton et al. (1993), the use of Al-based crosslinker and CMHPG for hydraulic fracturing application was proposed. However, most of the studies available in the literature are based on aluminum chemistry for reducing the water permeability applications (Dovan and Hutchins 1987; McKown and Rothenberger 1993; Smith 1995; Stavland and Carlsen 1996; Ranganathan et al. 1998; Al-Assi et al. 2009; Spildo et al. 2010).

Breakers are used to clean up the formation after the treatment. However, there are some limitations such as sometimes the breakers cannot distribute evenly to completely break the polymer and the residual polymer can damage the fracture pack. Therefore, it is very important to understand the main elements influencing the cleanup process and addressing those concerns (Barati et al. 2008). Fluid loss to the formation has always been a concern, especially in the case of treatment fluid formulations with low polymer loadings. The fluid leakoff rate affects the fracture geometry, closure time, final distribution of proppants in the fracture, and fluid efficiency. Furthermore, low leakoff rates decrease pumping cost and preventing formation damage (Gidley et al. 1989, Gupta et al. 2008).

Successful fracturing fluid provides enough viscosity to carry proppants as well as enough net pressure for fracture height growth (Gupta et al. 2008). The latter is based on the conventional theory, however, there are different scenarios that are said to be responsible for proppant transport. The conventional theory, which is based on Stokes' law, relates the proppant suspension to the viscosity of the fracturing fluid at 10 to 100 s^{-1} (existing shear rates inside the fracture during pumping) (Hu et al. 2015). Another rheological property of a crosslinked polymer that is responsible for proppant transport is elasticity as it represents the network structure of the crosslinked polymer and is not reflected in the steady shear viscosity measurements (Goel et al. 2002; Harris et al. 2008; Hu et al. 2015).

To the best of the authors' knowledge, there is not detailed study about CMHPG crosslinked with aluminum lactate in the literature for hydraulic fracturing treatments. Therefore, the objectives of this study are to: (1) investigate the performance of a new Al-based crosslinker to form a stable gel with CMHPG at high temperatures and shear rates at pH of 3.8 and 10.8 (2) determine the leakoff rates and proppant settling using Al-CMHPG, and (3) Assess the effect of residual polymer on the permeability of Grey Berea and Bandera sandstone cores.

To investigate the deliverability of these objectives, laboratory tests were conducted to study: steady shear viscosity measurements, proppant-settling properties, coreflood performance, and the leakoff rate of the crosslinked polymers formed.

Impact of Crosslinker Concentration on the Viscosity of Aluminum Crosslinked CMHPG

Fig. V 2 shows the viscosity profile for 20 pptg CMHPG containing different concentrations of Al-based crosslinker at a shear rate of 10 s^{-1} and a temperature ramp. The optimum concentration of the crosslinker for 20 pptg polymer solution is 1 gpt, and Fig. V 2 confirms that a higher or lower concentration of crosslinker than 1 gpt results in a crosslinked polymer with a lower viscosity. Lower viscosity is achieved with higher concentrations of crosslinker than optimum concentrations, and the reason can be attributed to syneresis and faster crosslinking rate. Syneresis happens when the network structure of the crosslinked polymer collapses and results in polymer deposition (Economides 2000).

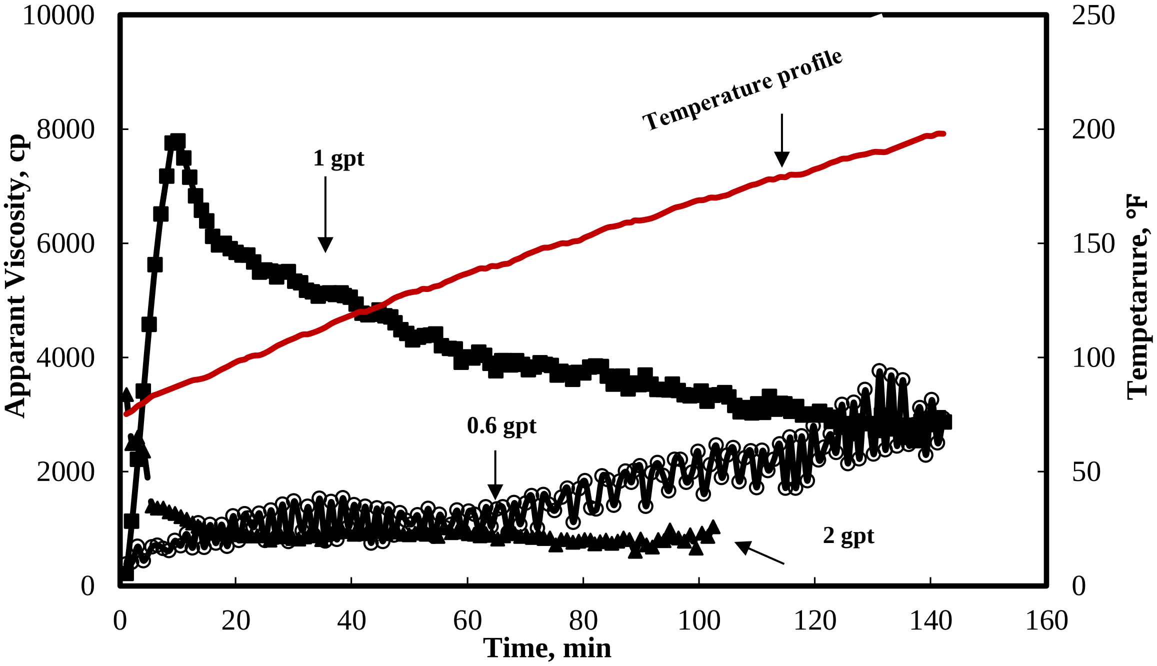


Figure V 2— 20 pptg CMHPG crosslinked with different concentrations of the crosslinker at shear rate of 10 s-1- temperature ramp. No breaker was added. Initial pH was 10.8. Lower and higher concentrations of crosslinker than 1 gpt resulted in lower viscosity.

Investigating the Effect of Constant Shearing on Aluminum-Crosslinked CMHPG at High Temperatures

The steady shear viscosity test is one of the most useful and practical method to determine whether the fracturing fluid is capable of carrying proppant into the fracture or not. The optimum concentration of the crosslinker at a shear rate of 10 s^{-1} was found to be 1 gpt. However, the results of this section of the study indicated that at a shear rate of 170 s^{-1}, higher viscosity can be achieved if the crosslinker loading is increased to 1.4 gpt **(Fig. V 3).** Both concentrations resulted in an acceptable viscosity, however, a delay in viscosity buildup can

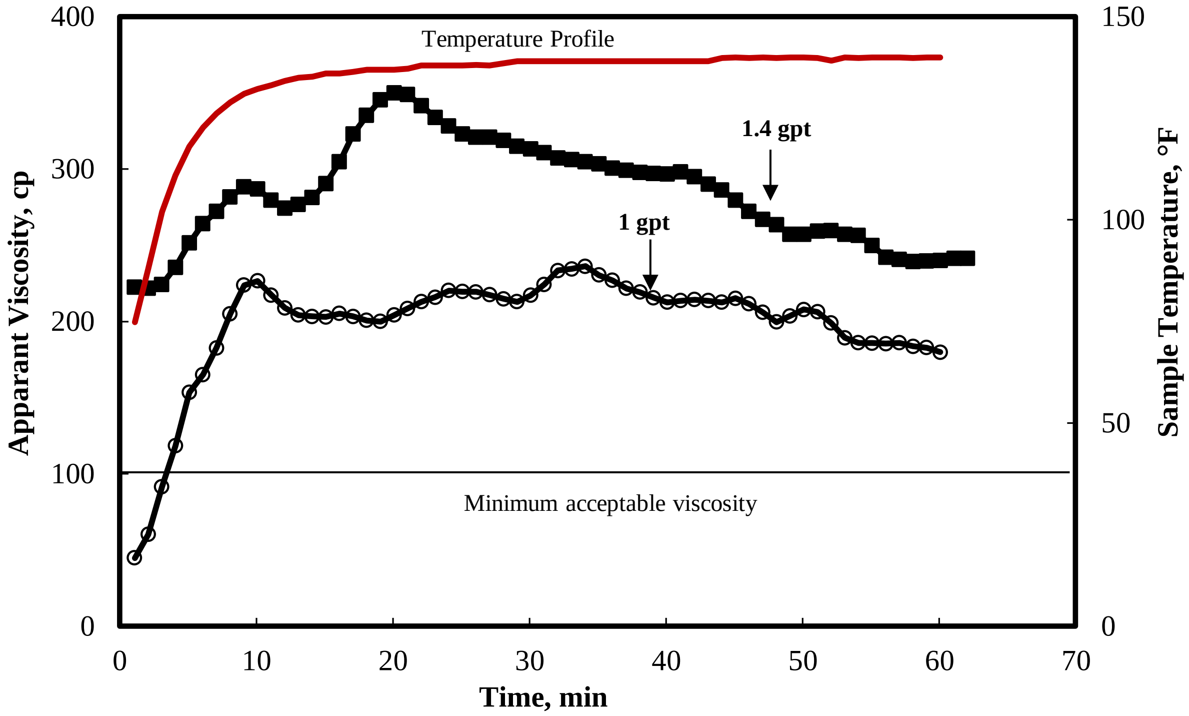


Figure V 3— The comparison between different concentrations of the crosslinker and 20 pptg CMHPG at a shear rate of 170 s-1 at 140°F. No breaker was added. Initial pH was 10.8. Both concentrations of crosslinker led to acceptable viscosity but using 1 gpt, a delay in viscosity buildup can be achieved.

be achieved using 1 gpt A-based crosslinker. The latter shows that the fracturing fluid can be optimized to meet specific requirements.

The effect of temperature was studied by raising it to 250°F, at which the viscosity profile showed negligible changes from that at 140°F and remained above 100 cp, which is the acceptable viscosity (Bunger et al. 2013) after 1 hour of shearing at 170 s^{-1}. The latter indicates that unlike the previous Al-based crosslinkers that were reported to be functional up to 150-230°F (Gidley et al. 1989; Rae and Di Lullo 1996; Economides 2000), the Al-based crosslinker in the present study is capable of forming a viscous and stable gel at high shear rates and temperatures **(Fig. V 4).**

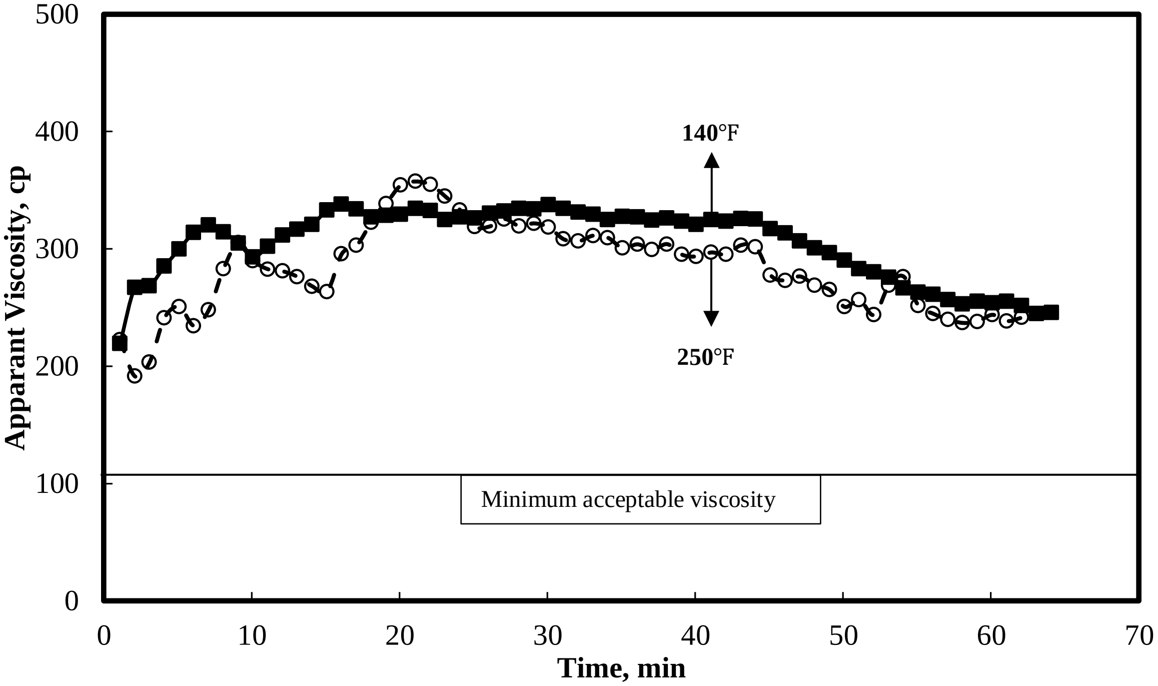


Figure V 4— The viscosity profile at 140 and 250°F using 1.4 gpt of the crosslinker with 20 pptg CMHPG at a shear rate of 170 s-1- initial pH 10.8. No breaker was added.

-

API Methodology in Evaluating the Viscosity Profile of Crosslinked CMHPG

The API method calls for initial shearing at 100 s^{-1} and then following by shear ramps of 100, 75, 50, 25, 50, and 75 every 30 minutes. The latter sequence can investigate the shear ramp effect on the viscosity profile of the crosslinked polymer. **Figs. V 5** and **6** shows the viscosity profile of 20 pptg CMHPG crosslinked with 1.4 gpt Al crosslinker at 140 and 250°F, respectively at initial pH of 3.8. It can be concluded that the polymer crosslinked with the Al crosslinker in this study can recover its viscosity after a shear ramp effect. Shear sensitivity is a shortcoming of metal crosslinkers like Zr, which can be addressed through Al crosslinker in this study. More oscillation can be seen for the viscosity profile at 140°F compared to 250°F. At 140°F, the gelation is slower so there is time for agglomerates to break and form again before becoming too large where at 250°F the crosslinking is faster and oscillation is less (Chauveteau et al. 2001).

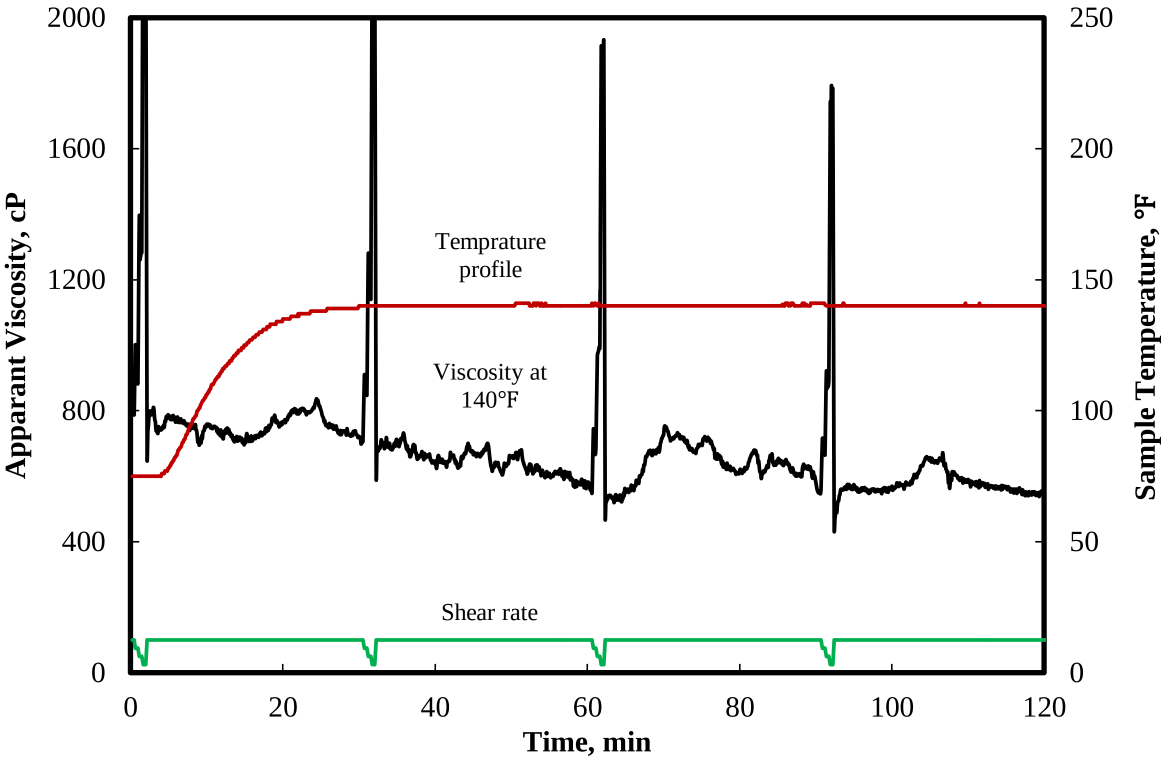


Figure V 5— Viscosity profile of CMHPG crosslinked with 1.4 gpt Al crosslinker based on API guidelines at 140°F- initial pH 3.8. No breaker was added. The graph shows that the crosslinked polymer has shear recovery abilities.

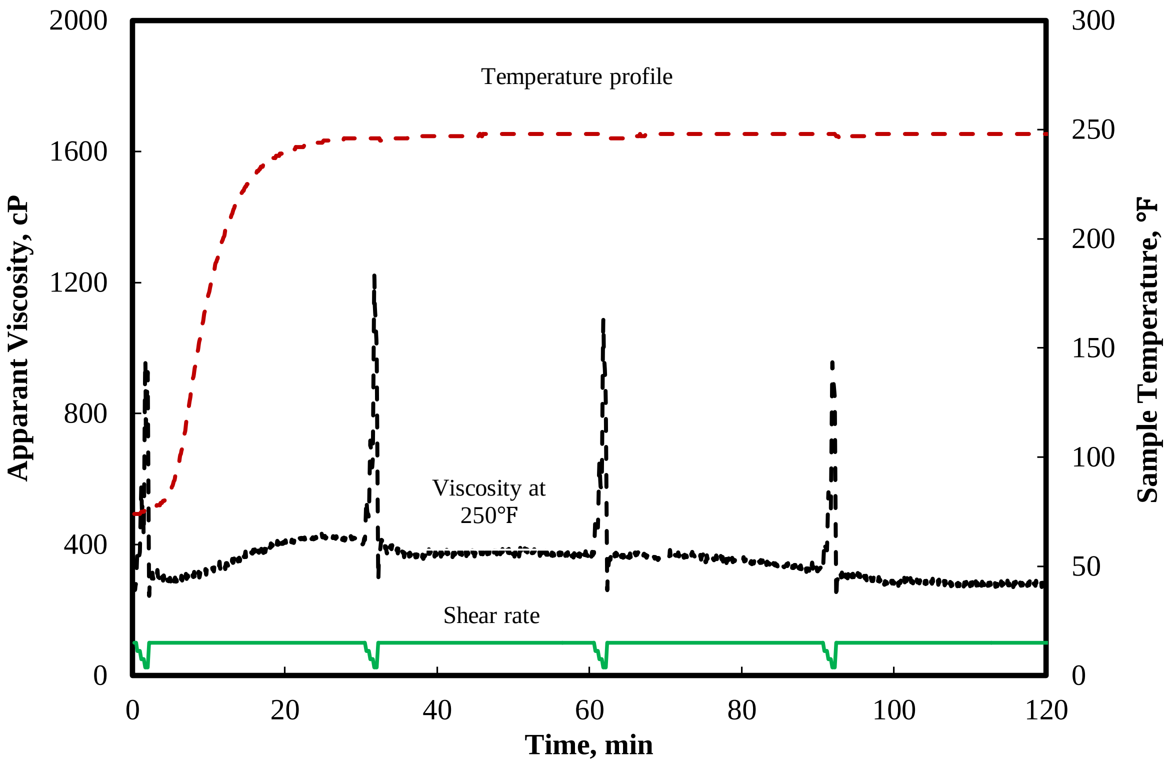


Figure V 6— Viscosity profile of CMHPG crosslinked with 1.4 gpt Al crosslinker based on API guidelines at 250°F- initial pH 3.8. No breaker was added. The graph shows that the crosslinked polymer has shear recovery abilities.

The Effect of pH on the Performance of the Aluminum Crosslinker at High Shear Rates and Temperatures

Most of the crosslinkers that have been used in industry had high pH ranges (Gupta et al. 2008). Sandstone formations contain some clays that are sensitive to high pH; therefore a crosslinker capable of reacting with the polymer solution at low pH is favorable. Furthermore, a low pH environment is less damaging to sandstone formations with low permeability. On the other hand, the degradation of the crosslinked polymer after the treatment is also important (Ely 1994; Gupta et al. 2008).

Althoug it has been reported that Al crosslinkers were functional at low pH ranges (Rae and Di Lullo 1996, Economides 2000), the new Al-based crosslinker in this study offers applications under low pH (3.8) as well as high pH (10.8) conditions. **Fig. V 7** presents the viscosity of 20 pptg crosslinked CMHPG and it is clear that at low pH there is delay in viscosity build-up compared to high pH condition that makes it usuful in some field applications where a delay is needed to pump the fluid down to the formations. The delay time is almost 8 to 9 minutes, which is in the usfel range mentioned in the literature (Putzig 2007). The potential explanations can be that the difference in the viscosity can arise from the different rate of crosslinking at pH 3.8 and 10.8. At the beginning, at pH 3.8 less Al is available due to its rlease rate compared to pH 10.8 and both viscosity profiles converged to an asympote by time. Furthermore, the available deprotonated carboxylate groups on the polymer backbone are more at higher pH values (Haung et al. 2005).

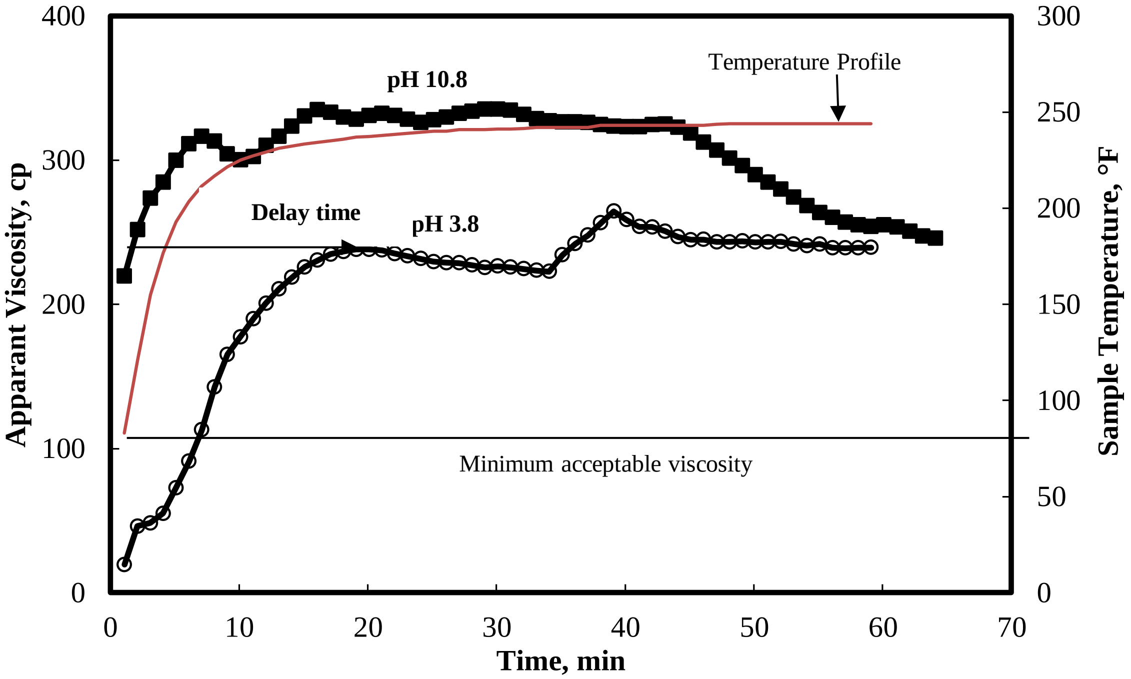


Figure V 7— Comparison between the viscosity profile under high and low pH condition at 250°F using 1.4 gpt of the crosslinker with 20 pptg CMHPG at shear rate of 170 s-1. No breaker was added.

Settling Tendency of Proppants: Indirect Method

DOS is a non-destructive method that is used to study and define the network structure of a crosslinked polymer, while the steady shear viscosity measurements are intended to mimic the field and pump process. The imposed motion on the fracturing fluid is sinusoidal and unidirectional in DOS and steady shear viscosity measurements, respectively. In the DOS technique, the results can be divided into two parts of in-phase and out-phase components, which are the representatives of storage (G') and loss (G'') moduli, respectively. Some insight about the network structure and the state of the fluid can be obtained through the investigation of strain or frequency dependence of G' and G'' in the linear viscoelastic domain of a crosslinked polymer (Prudhomme et al. 1985; Knoll and Prudhomme 1987; Loveless et al. 2011). If one relies only on the steady shear viscosity measurement to assess the proppant transfer ability of a crosslinked polymer, the results may not be accurate. Elasticity represents the network structure of the crosslinked polymer, which is not reflected in the steady-shear viscosity measurements (Goel et al. 2002; Harris et al. 2008; Hu et al. 2015). The inaccurate interpretation if it would be only based on steady shear viscosity is confirmed by measuring G' and G'' of Al crosslinked polymer. **Fig. V 8** shows that, over the whole range of frequency, the viscous modulus is dominant at 80°F. Therefore, the crosslinked polymer may not be successful in carrying proppant. The elastic modulus increased **(Fig. V 9)** by raising the temperature from 80 to 140°F, which indicates temperature dependence of crosslinking reaction as lactate ligands are known to be activated at temperatures greater than about 85°F (Harris and Heath 2007). The storage modulus can be divided into two parts of low and high frequencies. "At low frequencies, both gel and sol polymers are rearranging due to Brownian motion so the measured properties are dominated by the equilibrium elastic deformation of the gel network. Physical entanglements are created and broken quickly compared to the rate of deformation so they do not contribute drag or store elastic energy. At high frequencies the polymer does not have time to rearrange. Physical entanglements persist longer than the oscillation frequency so they physically constrain the polymers, store elastic energy and contribute to viscous dissipation" (Grillet et al. 2012). Moreover, the storage modulus at a higher temperature is larger as a higher temperature forces the crosslinking reaction to completion (Knoll and Prudhomme 1987). The crossover point also is called relaxation time, which is the inverse of frequency. The relaxation time can be representative of proppant settling velocity as the faster the relaxation occur, the sooner the proppant will settle. Figs. V 8 and 9 show that the relaxation time for the crosslinked polymer system at 80 and 140°F are 0.5 and 1.43 s, respectively. The latter finding indicates that the fracturing fluid in the present study based on the current formulation is not capable of proppant suspension at low temperatures, and even at higher temperatures, the relaxation occur significantly sooner comparing to Zr-based crosslinkers in the previous study (Sokhanvarian et al. 2015). Al crosslinkers are reported to create low elasticity (Suddaby 2009), and the latter may be due to the presence of free volume around the crosslinking site, which enables easier and faster movement and disentangelement after the imposed strain (Wolf 2004). It is woth mentioning that McMechan and Shah (1991) studied the static settling of 40 pptg crosslinked CMHPG/Al using 4 lbm/gal 20/40-mesh sand, and the proppant settling was faster comparing other gels crosslinked with borate, antimony, and titanium.

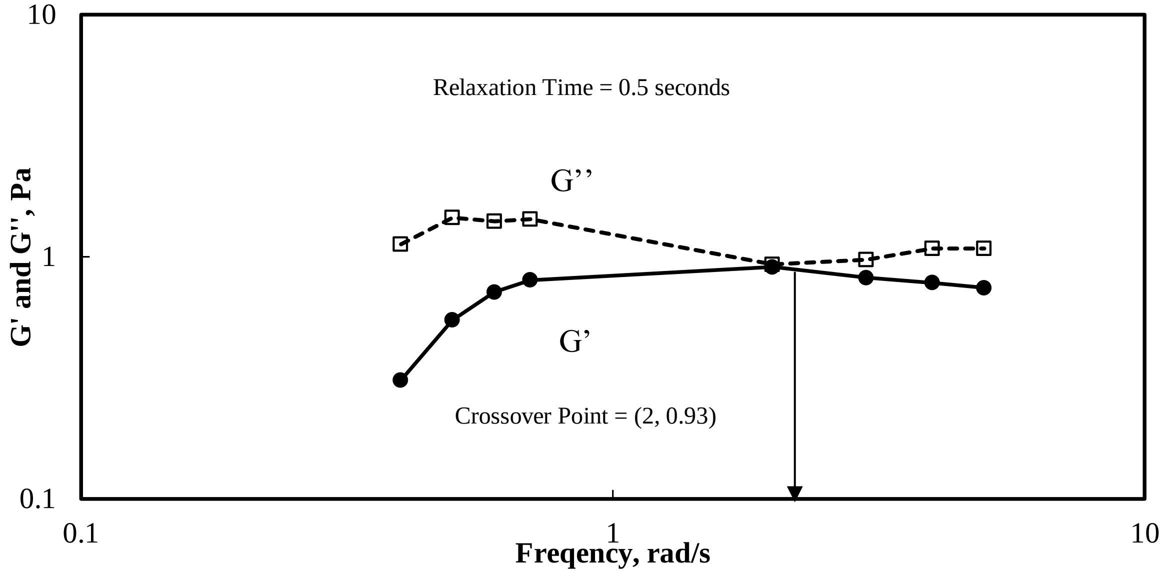


Figure V 8— DOM results for 20 pptg CMHPG crosslinked with 1.4 gpt crosslinker at 5% strain at 80°F. No breaker was added. Initial pH was 10.8. The viscous modulus is dominant.

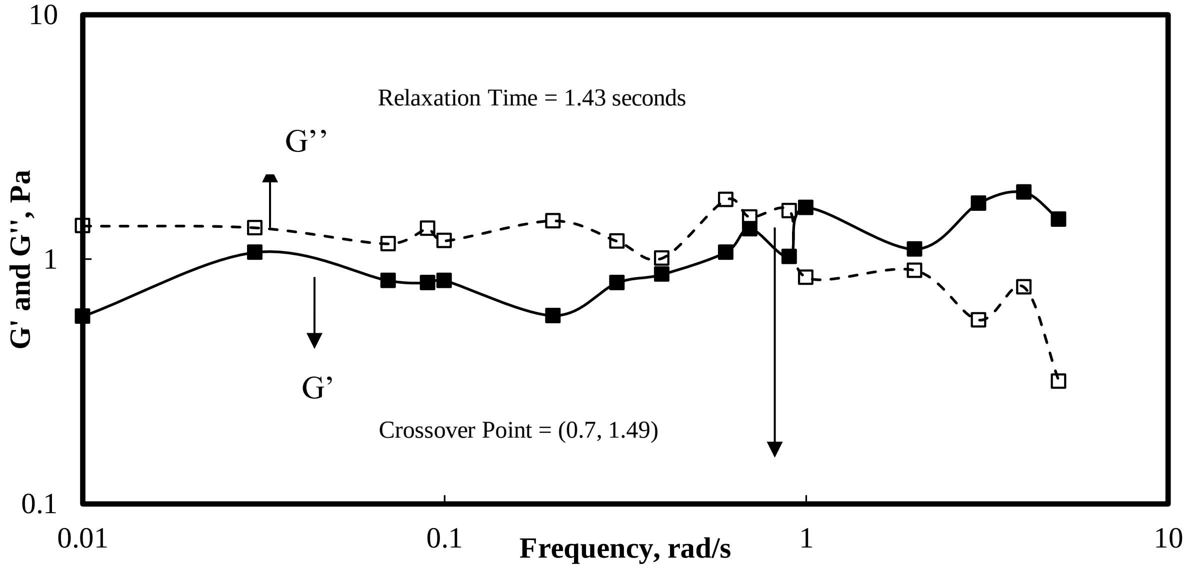


Figure V 9— DOM results for 20 pptg CMHPG crosslinked with 1.4 gpt crosslinker at 5% strain at 140°F. No breaker was added. Initial pH was 10.8. The loss modulus is dominant at low frequencies followed by increasing the storage modulus after the crossover point at 0.7 rad/s.

Direct Method

In hydraulic fracture treatments, the appropriate placement of proppants into the fracture is a crucial parameter for a successful treatment. Furthermore, adequate vertical settling velocity leads to a maximum horizontal distance in the fractures (Harris et al. 2005).

The proppant settling test was conducted at 80°F using 4 lbm/gal of 40/70-mesh Ottawa sand, and the proppant settled in a minute (**Fig. V 10**). This test confirmed the findings from the oscillatory measurements from the previous section that 20 pptg crosslinked CMHPG is not capable of proppant suspension. To address the proppant settling limitations, a second crosslinker (boron or zirconium) was added. The proppant suspension was slightly improved by the addition of boron crosslinker (**Fig. V 11**). Furthermore, in the case of the addition of Zr the crosslinked polymer could suspend the proppant for 2 hours without any settling (**Fig. V 12**).

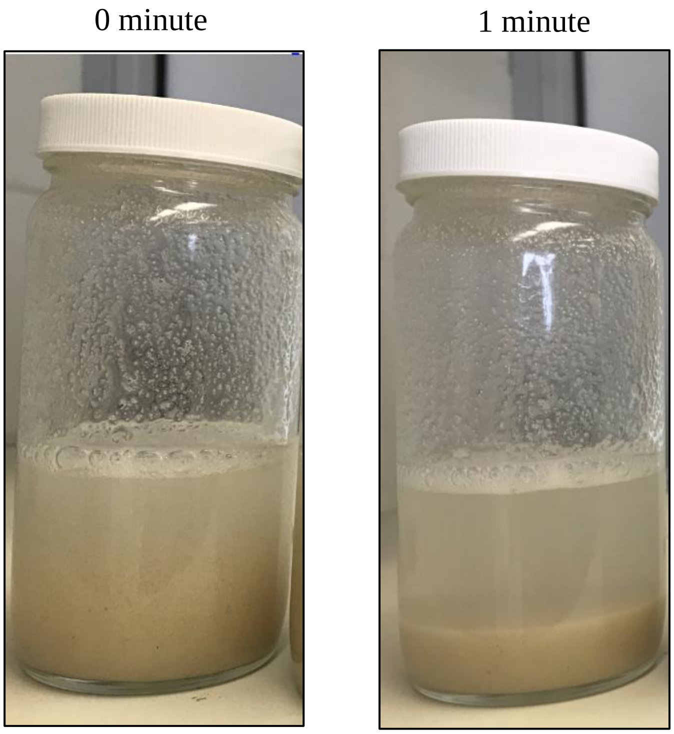
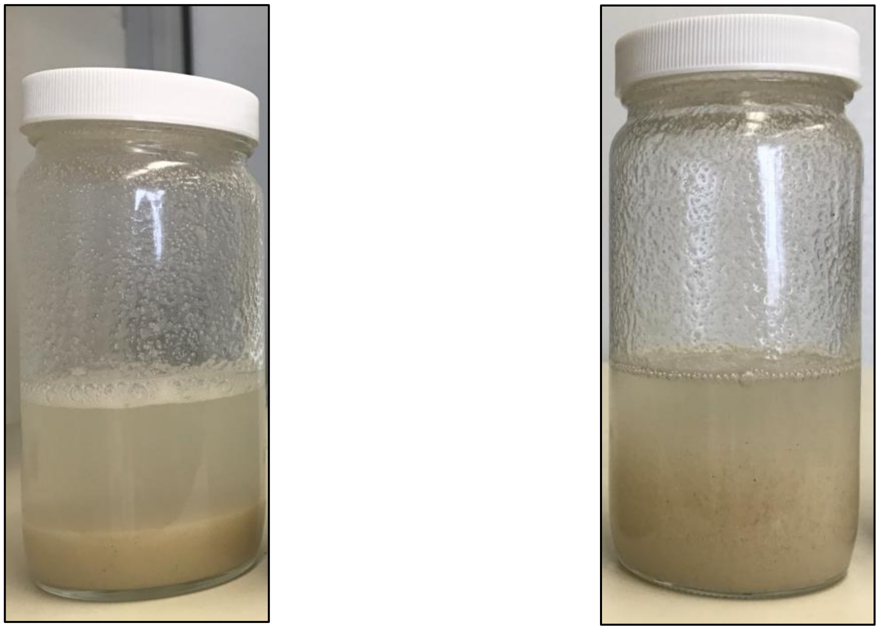


Figure V 10— Proppant settling using 1.4 gpt aluminum lactate and 20 pptg CMHPG at 75°F. All the proppant was settled after 1 minute. 40/70 Ottawa sand particles were used as proppant. No breaker was added. Initial pH was 10.8.



a: 20 pptg CMHPG and 1.4 gpt Al-lactate

b: 20 pptg CMHPG and 1.4 gpt Al-lactate + 1 gpt B

Figure V 11— The proppant settling improved by the addition of boron crosslinker (b). 40/70 Ottawa sand particles were used as proppant. No breaker was added. Initial pH was 10.8.

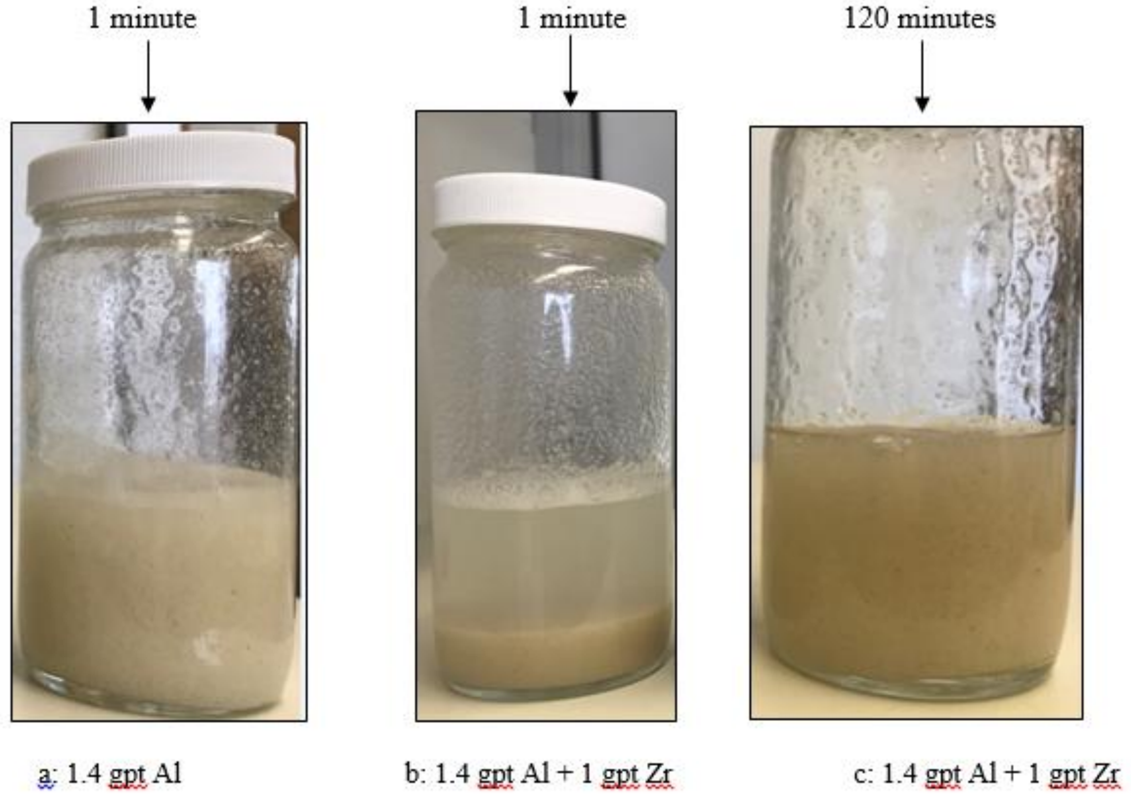


Figure V 12— No proppant settling occurred (c) after the addition of Zr crosslinker to 20 pptg CMHPG crosslinked with Al-lactate at 80°F. 40/70 Ottawa sand particles were used as proppant. No breaker was added. Initial pH was 10.8.

Addressing the Proppant Settling of Al-CMHPG through Increasing the Polymer Concentration

As the objective of the present study is to use Al as a single crosslinker for fracturing treatments, the impact of polymer concentration on proppant settling of Al-CMHPG was investigated. In order to determine the suitable crosslinker concentration, 1, 2, and 3 gpt Al was added to 40 pptg CMHPG and the elastic modulus was measured at 75°F. **Fig. V 13** shows that 1 and 2 gpt resulted in the same elasticity, however, by increasing the Al concentration to 3 gpt the elastic modulus was decreased. The lower elastic modulus at higher concentration of crosslinker can be the indication of over crosslinked gel (Goel and Subhash 2001). **Fig. V 14** shows that 40 pptg CMHPG crosslinked with 1 gpt Al and 4 lbm/gal proppants resulted in 100% proppant suspension.

During the process of addressing the proppant settling, it was found that the type of the solution that is used to adjust the pH of the polymer solution can affect the network structure of Al-CMHPG gel. Two types of solutions were used to adjust the pH (NaOH and carbonated-based solutions). **Fig. V 15** shows a better network structure (higher G') in the case of using the NaOH solution and a lower elastic modulus if a carbonated-based solution was used to adjust the pH. To visualize the results from Fig. 15, each solution (NaOH/carbonated-based) was added to the Al crosslinker. The Al crosslinker remained crystal clear after the addition of NaOH, which indicated that the aluminum is soluble. However, upon the addition of carbonated-based solution to Al crosslinker, bubbles started to form and then the solution turned cloudy and precipitation was occurred. The candidate for crosslinking with CMHPG is Al^{+3}, and the solubility of aluminum in the solution depends strongly on the pH (Dovan and Hutchins 1987). If Al precipitates as solid $Al\,(OH)_3$, then there is no or inefficient crosslinking. Therefore, the lower elasticity in the case of using carbonated-based solution was resulted from the availability of less soluble Al^{+3} to react with the polymer. Aluminum can react with carbonate to form $Al_2\,(CO_3)_3$, and Al-carbonate upon exposure to water can precipitate to solid $Al\,(OH)_3$ (Moody 1991).

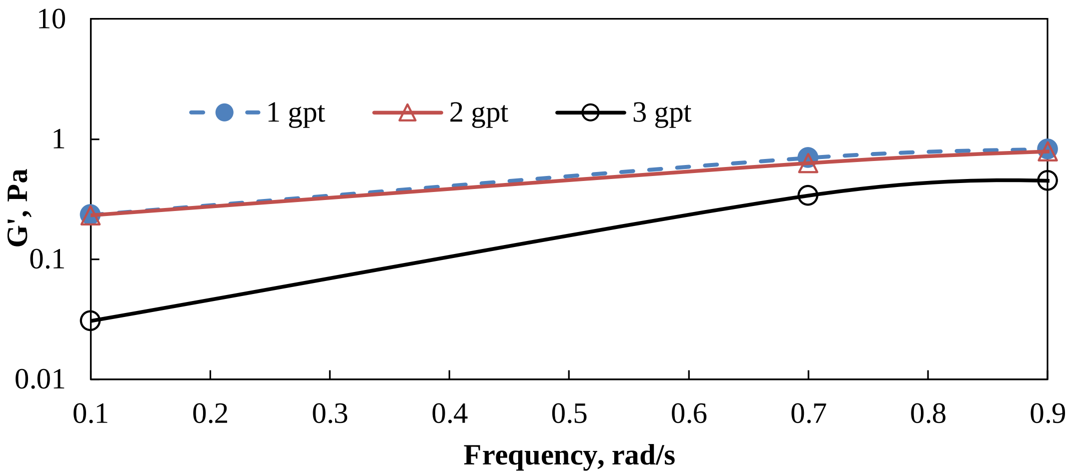


Figure V 13— The elastic modulus of 40 pptg CMHPG crosslinked with different concentrations of Al-lactate crosslinker at 140°F. No breaker was added. Initial pH was 10.8. 3 gpt of Al-lactate crosslinker was resulted in lower elasticity (overcrosslinked gel).

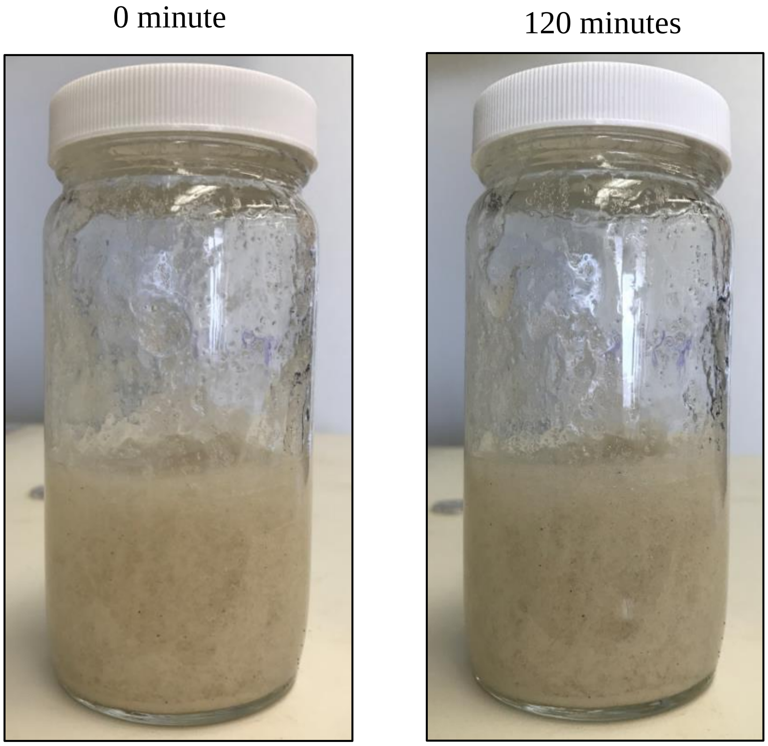


Figure V 14— 40 pptg CMHPG crosslinked with 1 gpt of Al-lactate.No proppant settling was occurred. 40/70 Ottawa sand particles were used as proppant. Initial pH was 10.8. No breaker was added

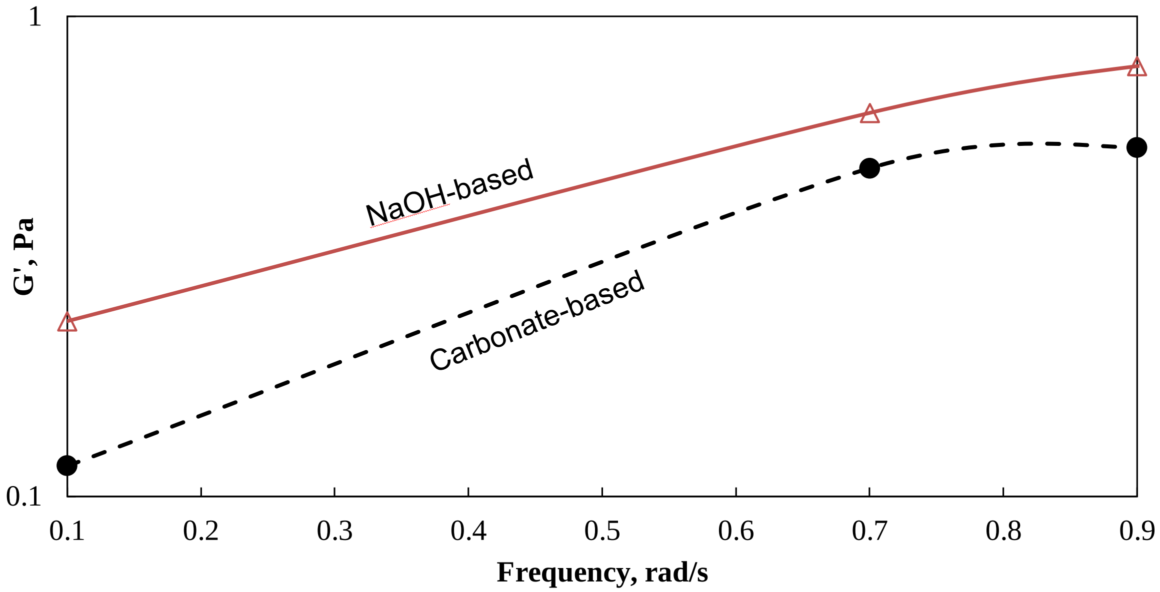


Figure V 15— The elastic modulus for 40 pptg CMHPG crosslinked with 1 gpt Al-lactate crosslinker at 140°F and initial pH of 10.8. No breaker was added. If the solution pH is adjusted using NaOH, a higher G' is achieved.

Static leakoff tests

Fluid loss is one of the shifting parameters in designing the fracture treatments, and it can be characterized through the leakoff coefficients (Cw) and the spurt loss (Sp). Designing a fracture treatment with an aim of a predetermined geometry needs the knowledge of the leakoff rate. The leakoff process includes three phases. The leakoff rate is fast at the beginning before the formation of the external cake, and then it decreases and reaches almost a steady rate (Economides 2000). Therefore it is important that a crosslinked polymer has an acceptable leakoff rates. The leakoff coefficients and the spurt loss was determined according to Eqs. 1 and 2 by Economides (2000).

$$C_w = \frac{0.0164m}{A} \quad \text{......} \quad (1)$$

$$S_p = \frac{24.4b}{A} \quad \text{......} \quad (2)$$

where m ($cm^3/min^{0.5}$) and b are the slope and the intercept of the fluid loss graph **(Fig. V 16)**, respectively, A is the cross-sectional area of the core (cm^2) used in the leakoff test, C_w ($ft/min^{0.5}$) is the leakoff coefficient, and Sp (gal/ft^2) is the spurt loss.

The static leakoff experiment was conducted using 20 pptg CMHPG and 1.4 gpt of the Al crosslinker to investigate the fluid loss of the formed gel. The test was performed under the pressure differential of 300 psi at 140°F.

Some researchers had assumed that a fracturing fluid formulation with a low polymer concentration is not capable of fluid loss control. However, the experimental results showed otherwise, and actually the filter cakes generated by low polymer loadings were thinner and tougher compared to fracturing fluids with high polymer concentrations (Dawson et al. 1998). The results agree with findings by Dawson et al. (1998) that the fracturing fluid with low polymer loading can have acceptable leakoff rates. **Table V 1** gives the leakoff coefficients and spurt losses at 140 and 250°F. The filter cake that was formed **(Fig. V 17)** on the Bandera core was very thin and uniform (< 1 mm). To find the experimental error, the leakoff test was repeated using aluminum crosslinker and the standard deviation was 0.00001 $ft/min^{0.5}$.

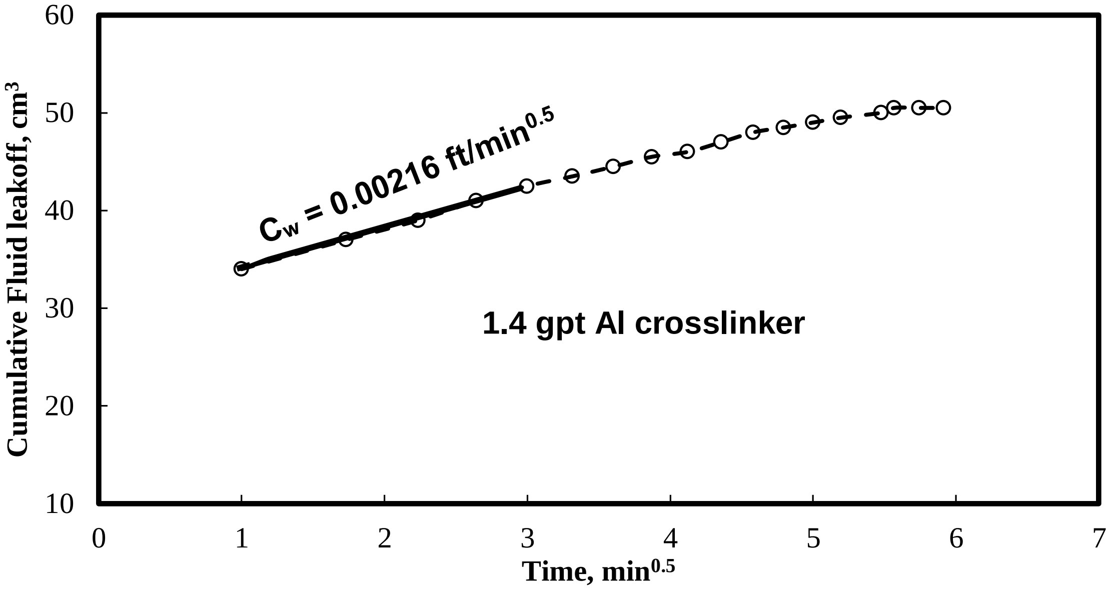


Figure V 16— Fluid loss data obtained from the static leakoff test at the differential pressure of 300 psi and 250°F. No breaker was added. Initial pH was 3.8.

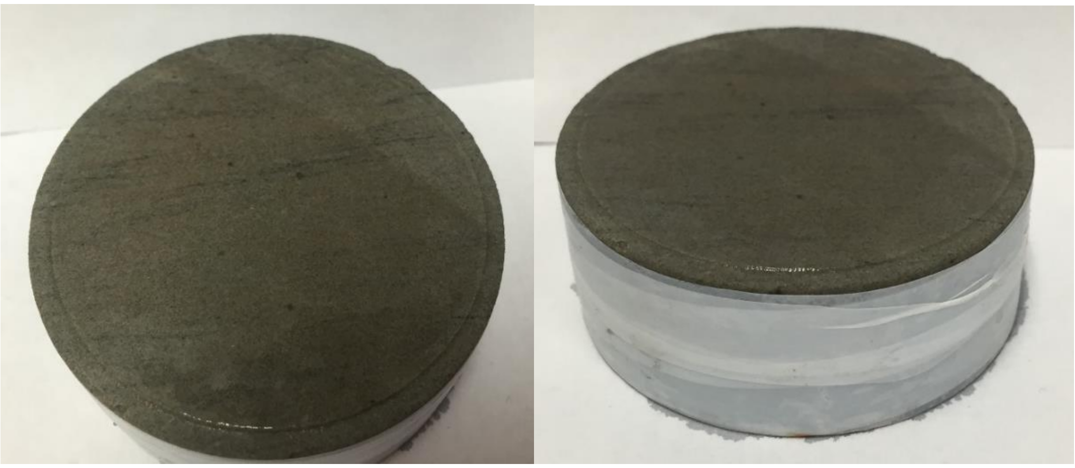


Figure V 17— Thin and uniform filter cake after the static leakoff test at the differential pressure of 300 psi at 250°F. No breaker was added. Initial pH was 3.8.

Temperature (°F)	Bandera core porosity (%)	Leakoff coefficient (ft/min$^{0.5}$)	Spurt loss (gal/ft^2)
140	20.7	0.00007	0.007
250	18.2	0.00216	0.229

Table V 1— Leakoff results using 20 pptg CMHPG crosslinked with 1.4 gpt Al crosslinkers at 300 psi differential pressure. The maximum allowable leakoff coefficients and spurt loss are 0.003 ft/min0.5 and 0.05 gal/ft2 (Davies et al. 1991).

Polymer Residual Effect on the Regained Permeability

To assess the impact of polymer residual on the regain permeability, coreflood experiments were conducted. To measure the initial permeability of the core, 2 wt% KCl was injected in the production direction until the pressure stabilized at 250°F. Then, 2 PV of Al-crosslinked-CMHPG was injected in the injection direction followed by the injection of 2 wt% KCl in the production direction. The brine injection after Al-CMHPG injection was stopped based on two scenarios: (1) the pressure drop was stable and (2) the effluent samples were colorless. **Fig. V 18** shows the graph of pressure drop along the grey Berea core during the intial permability measurement and gel injection, and it is clear that the pressure drop increased as the crosslinked polymer has a higher viscosity compared to brine. In this experiment, 0.2 pptg of ammonium persulfate as a breaker was addded to the gel. In the case of adding the breaker, the Al-CMHPG including the breaker soaked inside the core for two hours and then the core was flushed with brine (2 wt% KCl) to push all the gel out. (Fig. V 18). The regained permability was obtained from the permeability after the tretment devided by the initial permeabiltiy. Two other experiments were conducted using Grey Berea and Bnadera sandstones without the breaker and . The results of the coreflood studies are summerized in **Table V 2**, and it shows that the breaker helped to increase the regained permeability by 10%.

Core type	Porosity (%)	Regained permeability, %	Fluid injected	Temperature, °F
Grey Berea	16.7	31	Al-CMHPG	200
Grey Berea	17.2	41	Al-CMHPG + ammonium persulfate	200
Bandera	17.5	35	Al-CMHPG	250

Table V 2— Regained permeability of sandstone cores with and without using breaker. Ammonium persulfate increased the regained permeability by 10%.

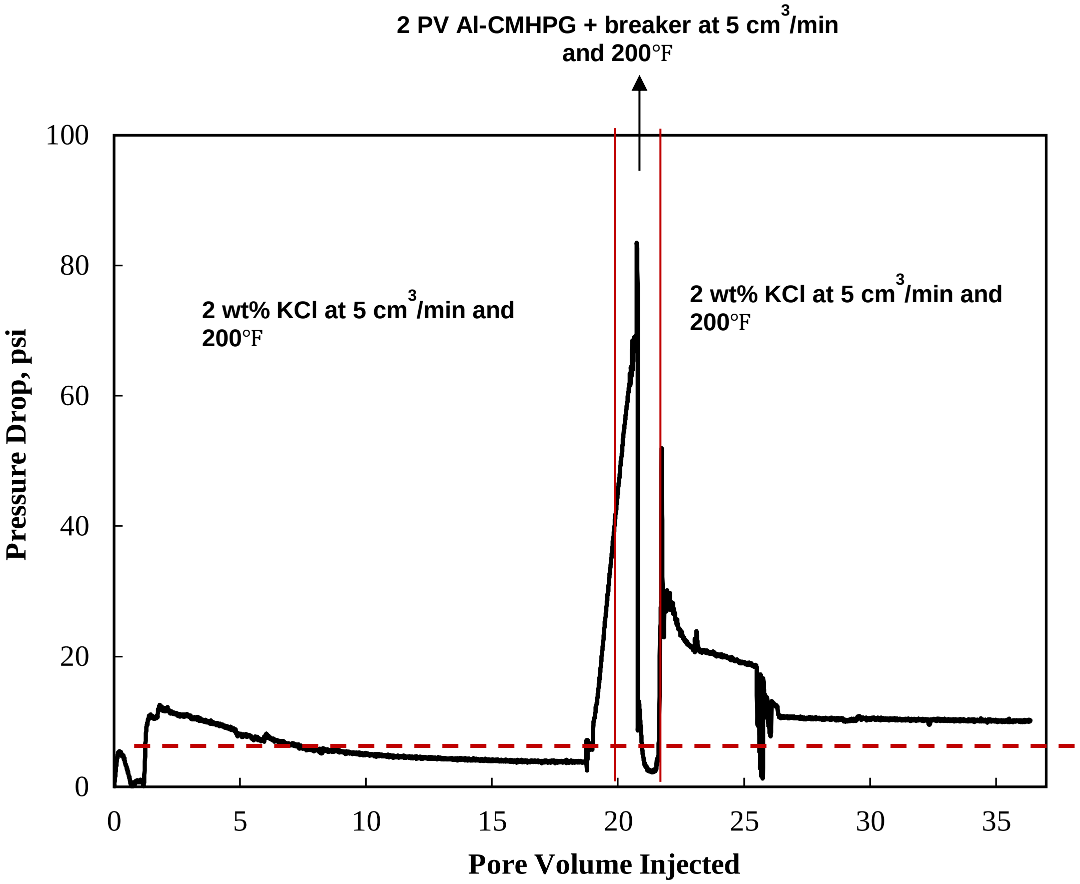


Figure V 18— Initial permeability of the Bandera core and pressure drop along the core during the injection of crosslinked polymer at 250°F. No breaker was added. No breaker was added. Initial pH was 3.8.

Conclusions

Al-lactate has not been studied for fracturing applications and the present study evaluate the ability of a new Al-based crosslinker to form a strong gel using CMHPG and Al crosslinker for high-temperature applications. Based on the results, the following conclusions can be drawn:

1. Aluminum crosslinkers were shear tolerant and formed a gel with high viscosity at high pH (10.8) as well as low pH (3.8) conditions.
2. The leakoff coefficients at 140 and 250°F were very small, but the spurt loss increased significantly at 250°F.
3. The polymer residue caused a 65% reduction in the permeability of Bandera sandstone at 250°F.
4. Ammonium persulfate as a breaker improved the regained permeability of Grey Berea core by 10% at 200°F.
5. High shear rate viscosity measurement is not a good indication of proppant transfer ability as the crosslinked polymer in this study showed high viscosity under shear and temperature, however, lacked enough elasticity to suspend the proppant.
6. The proppant settling of Al-CMHPG was addressed by increasing the polymer concentration from 20 to 40 pptg.
7. Al crosslinker is sensitive to pH and the type of solution for pH adjustment purposes.

This study showed that although 20 pptg Al-CMHPG retained a high viscosity at high shear rate and temperature and it was capable of shear recovery, it was not capable of proppant transfer. The proppant suspension was achieved through raising the polymer concentration. Al crosslinker can be used as an alternative crosslinker to Zr and B-based crosslinkers for hydraulic fracturing treatments.

CHAPTER IV

SUMMARY

In this dissertation, CMHPG was crosslinked with different crosslinkers, and its properties were determined for hydraulic fracturing treatments. The first part of the study focused on the effect of ligand type attached to Zr-based crosslinkers on properties of crosslinked CMHPG. Furthermore, a new dual Al-Zr crosslinker was studied to address the limitations associated with Zr-based crosslinekrs. In the second phase, a new Al-based crosslinker was evaluated as a potential alternative to commercially available crosslinkers. The motivation in the case of each study, the experimental studies conducted, and the results of each study is presented in the next two sections.

Zirconium-based and Aluminum-zirconium Crosslinkers

This study aims to investigate the effect of ligand type attached to zirconium crosslinkers on their final performance as a crosslinker. It is mentioned in the literature that zirconium crosslinkers are shear sensitive, and the latter can be improved through using a ligand. The present study investigated how the type and strength of ligand attached to zirconium affect the final properties of zirconium-crosslinked CMHPG. Three zirconium crosslinkers with different ligand types were studied. Furthermore, Al-Zr crosslinker was investigated to address the fast viscosity buildup at high pH in the case of Zr-based crosslinkers.

Steady shear viscosity measurement, shear ramp, fluid loss, and proppant settling were used to achieve the objectives of this study. It was found that shear sensitivity can be improved significantly if the ligand attached to zirconium is not either very strong or very weak. Lactate and propylene glycol (crosslinker 4) with a medium strength compared to the ligand (lactate) attached to crosslinker 1 and lactate and triethanol amine attached to crosslinker 2 produced the most shear recoverable fracturing fluid. Moreover, crosslinker 4 was a better choice for minimal leakoff and proppant settling purposes. Shear sensitivity of Al-Zr crosslinker was compared against crosslinker 4 (least shear sensitivity), and it was found that the degree of shear recovery is higher for Al-Zr crosslinker. Furthermore, delay in crosslinking at high pH (limitation of Zr-based crosslinkers) can be achieved through Al-Zr crosslinker.

The results of this phase of study can be used to further improve the limitations of Zr-based crosslinkers. The new Al-Zr dual crosslinker also can be used when certain properties cannot be accomplished through Zr-based or Al-based crosslinkers.

Evaluation of a new Aluminum-based Crosslinker for Hydraulic Fracturing Treatments

This phase of study investigated Al-lactate crosslinker for hydraulic fracturing treatments. The most common type of crosslinkers in fracturing treatment are boron-based crosslinkers due to being shear recoverable. However, there are some limitations such as pH, temperature, and pressure associated with boron-based crosslinkers. Aluminum crosslinker was selected as it is in the same group that boron is on the periodic table. The latter means that they share properties that make their application suitable in crosslinked polymers under certain specific conditions such as high shear rates.

Steady shear viscosity measurement, shear ramp, fluid loss, proppant settling, and coreflood were used to assess the possibility of using aluminum crosslinker as an alternative to available crosslinkers. It was found that Al-CMHPG gels are insensitive to shear rate and showed high thermal stability. The leakoff coefficients were minimal at 140 and 250°F, but the spurt loss increased significantly at 250°F. The low elastic modulus for Al-CMHPG confirmed the proppant suspension failure.

The poor proppant settling properties of 20 pptg Al-CMHPG was addressed through increasing the polymer concentration from 20 to 40 pptg. It should be noted that Al-lactate was very sensitive to the type of solution that is used to adjust the pH of fracturing fluid, and if aluminum precipitates as $AlOH_3$, then no or inefficient crosslinking may occur.

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