MIXED CMHPG AND SYNTHETIC POLYMER HYDRAULIC FRACTURING

FLUID FOR HIGH-TEMPERATURE APPLICATIONS

A Thesis

by

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ABSTRACT

Recent interest in deep low permeability formations demands growth in high-temperature hydraulic fracturing technologies. Conventional guar systems break down above 300°F and require higher polymer loadings to maintain thermal stability. Synthetic polymers designed for high-temperature utilize specialty monomers that are expensive. Individually, both these polymers are lacking in either performance or price. However, when these polymers are combined, they exhibit a synergistic interaction and produce a higher viscosity and better thermal stability than the individual polymer systems.

Polymer solutions were prepared at a concentration of 20, 30 and 40 lb/1,000 gal, were crosslinked with a zirconium crosslinker, and broken with sodium bromate oxidizer, at 300°F. Testing was carried out in a HP/HT rheometer for viscosity, elasticity, salt influence, thermal stability, and breaking. A HP/HT see-through cell and an aging cell were used for visual assessment of proppant settling, and broken polymer residue respectively.

Results show that the 20, 30 and 40 lb/1,000 gal mixed polymer fracturing fluid generates a stable crosslinked viscosity at 300°F and 100 s^{-1}. Mixture containing 1:2, 1:1, and 2:1 (CMHPG: Synthetic) exhibit the most improvement in viscosity at 20, 30 and 40 lb/1,000 gal mixed polymer fracturing fluids, respectively. Results also show that synthetic polymer adds thermal stability while CMHPG improves the peak viscosity of the mix. The two polymers create a shared crosslinking network that enables reduced polymer loading applications. Moreover, the polymer mixture fracturing fluid exhibits

good tunable delayed crosslinking, is able to carry proppant effectively at high temperature, and shows a controlled clean break with an oxidizer.

Extensive experiments were pursued to evaluate the developed high temperature mixed polymer system for the first time. This mixture exhibits a positive interaction between the polysaccharide and polyacrylamide families and generates excellent thermal stability. Mixed polymer systems are a viable solution to combat the challenges currently faced in the industry such as the need to increase high temperature stability, high salt tolerance, and reduce the polymer loading used. Polymer mixture technology can potentially reduce material cost, simplify field operation, and reduce damage to the proppant pack and formation.

DEDICATION

This work is dedicated to my parents, sisters, brother, friends, loved ones and those who continuously support me through life.

ACKNOWLEDGEMENTS

CONTRIBUTORS AND FUNDING SOURCES

NOMENCLATURE

#	lb/1,000 gal
AA	Acrylic acid
AM	Acrylamide
AMPS	2-Acrylamido-2-methylpropane sulfonic acid
CMHPG	Carboxymethyl hydroxypropyl guar
G'	Elastic/storage modulus
G''	Viscous/loss modulus
Gpt	Gallons per thousand gallons
HPG	Hydroxypropyl guar
MBI	Monoborate ions
MW	Molecular weight
pKa	Acidity constant/ acid ionization constant
ppt/pptg	pounds per thousand gallons
TDS	Total dissolved solid

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1. INTRODUCTION

1.1 Hydraulic Fracturing

Hydraulic fracturing is a technique used to enhance production from wells with low permeability formations. During hydraulic fracturing treatments, fluids are pumped at high rates and enough pressure to fracture the rock. A successful hydraulic fracturing fluid requires the ability to generate sufficient viscosity, remain stable, carry proppant into the fracture for the duration of the treatment, and break significantly at the end of the job to reduce damage and allow flow back.

1.2 CMHPG

Carboxymethyl hydroxypropyl Guar (CMHPG) is a negatively charged polysaccharide based biopolymer that is produced by treating guar with both propylene oxide and chloroacetic acid, **Fig. 1**. Guar is derivatized to CMHPG to reduce impurities, increase pH tolerance and improve temperature stability. These properties enable CMHPG to work as an excellent polymer for fracturing fluids in a variety of formations. Although CMHPG has many advantages, it still has shortcomings regarding thermal stability and salt resistance limits.
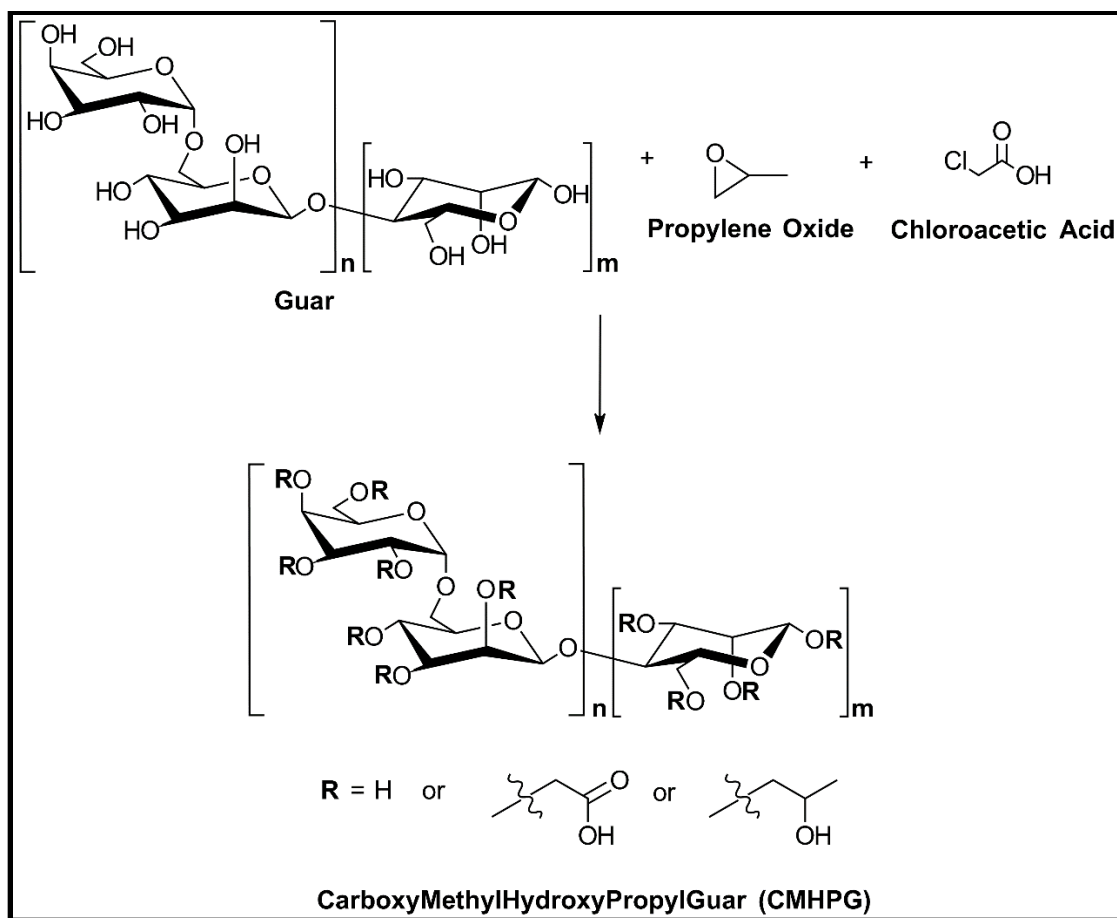
Fig. 1 – Derivatization of Guar to CMHPG.

Thermal stability in polysaccharides depends on two types of bonds. First, crosslinking bonds between the polymers and the crosslinker. Second, the glycosidic bonds between monomers in the polymer. Polysaccharide glycosidic (acetal) linkages are susceptible to degradation through hydrolysis at high temperature (Picout et al., 2001; Vega-Cantu et al., 2006; Weaver et al., 2003). High-temperature stabilizers, oxygen scavengers, and pH buffers are typically added to improve the thermal stability of polysaccharides.

1.3 Synthetic Polymers

Synthetic polymers used in the oil industry are mainly composed of a polyacrylamide backbone and acrylate side groups. Synthetic polymers can be used as an alternative to biopolymers for hydraulic fracturing fluid applications. They can be manufactured cheaper than biopolymers, have a higher molecular weight range (1-20MM), and contain low residue when broken. However, due to the long single strand backbone structure, they are susceptible to severe shear degradation (Maerker 1975). Also, synthetic polymers in the oil and gas industry are generally polyelectrolytes that have low salt tolerance.

Unlike biopolymers where secondary chemicals are added to compensate for their disadvantages, synthetic polymers can be modified with specific monomers during production to compensate for their flaws. Typical successful high-temperature synthetic polymers tested for hydraulic fracturing fluids can contain polyacrylamide-acrylate-AMPS (Funkhouser and Norman 2003; 2006; Holtsclaw and Funkhouser 2010) or polyacrylamide-AMPS-vinyl phosphonate (Gupta and Carman 2011). AMPS adds thermal stability and slight salt tolerance while acrylic acid or vinyl phosphonate contribute mainly in the crosslinking. Unsurprisingly, the enhancement of the polymer properties comes at the expense of higher cost.

1.4 Crosslinkers

Charged polymers such as CMHPG and synthetic polymers face difficulties crosslinking in the presence of borate ions. Borate crosslinkers generate monoborate ions (MBI) in solution, which predominantly form 1:1 complexes with cis-diols, but can also

form 2:1 complexes, that crosslink the polymer to increase the viscosity, as shown in **Fig. 2** (Prud'homme et al. 1989; Harris 1993). However, since CMHPG loses some properly configured hydroxyl groups during the derivation reaction, it may not crosslink using borate ions. Additionally, CMHPG and synthetic polymers are both negatively charged and therefore exhibit repulsion when mixed. This repulsion reduces overlapping between polymer chains, to the extent that borate crosslinking does not occur easily. Cationic salts and additives such as surfactants can be used to reduce this repulsion and enhance chain overlap to promote crosslinking in the presence of borate ions (Parris et al. 2010).
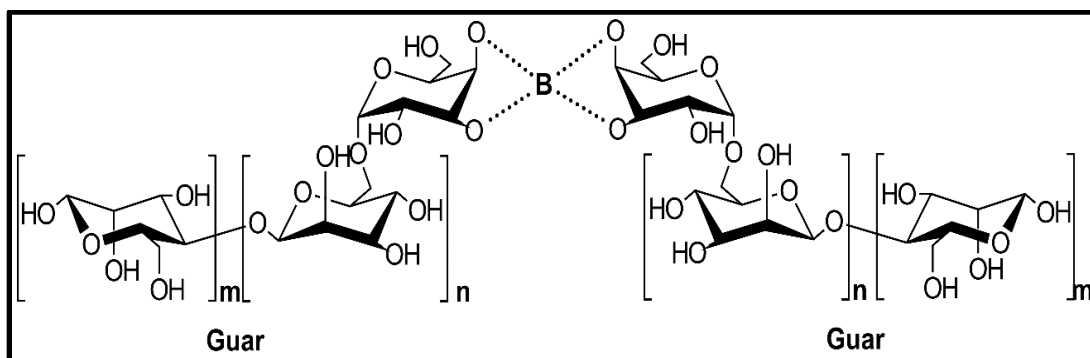
Fig. 2 – Crosslinking of Guar through MBI.

To crosslink charged polymers strong bonds are required. Metallic crosslinkers such as Ti, Zr, Hf, Ni, and Al are often used to crosslink charged polymers. Hurnaus and Plank (2015a and 2015b) studied the crosslinking of guar and derivatives through ITC, DLS, rheology, and TEM. They showed that the crosslinking of zirconium and titanium crosslinkers is due to the generation of metal nanoparticles at specific solution conditions. **Fig. 3** shows how the nanoparticles may connect the polymers and create the 3d crosslinked network. Metallic crosslinkers such as zirconium and titanium provide a stable bond with CMHPG and synthetic polymers. However, they do not re-heal, so a properly

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selected ligand must be used to control the release of zirconium and generation of nanoparticles in solution to prevent severe early shear degradation (Harry et al. 1997; Moorhouse et al. 1998; Harry et al. 1999; Sokhanvarian et al. 2016).
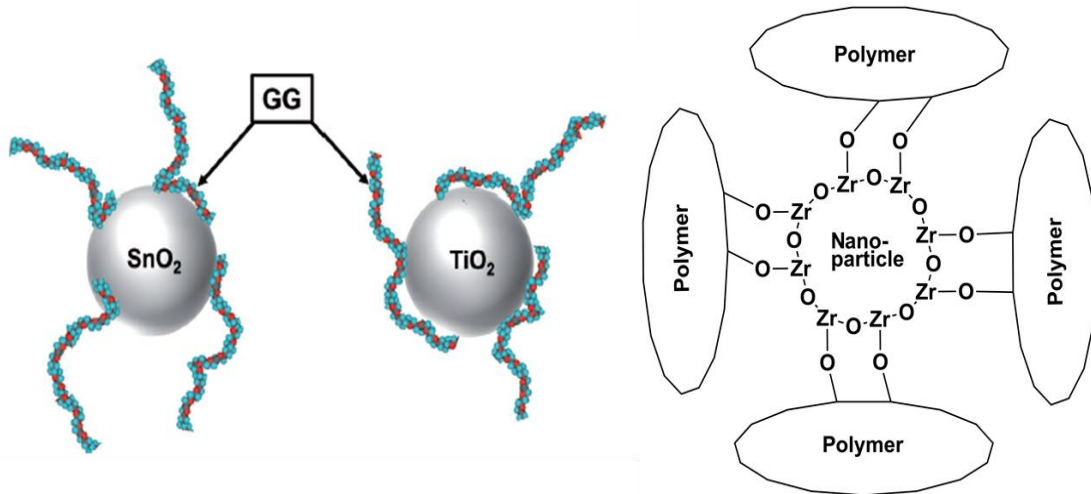
Fig. 3 - Crosslinking of guar and derivatives through metallic crosslinkers (adapted from Kramer et al. 1987; Harry et al. 1999; Harnaus and plank, 2016).

1.5 Breakers

At the end of the hydraulic fracturing treatment, it is necessary to break the polymer solution to reduce formation damage and allow maximum flow back of used fluids. This can be achieved using breakers such as oxidizers and enzymes. Effective oxidizers include ammonium persulfate, sodium bromate, and sodium hypochlorite (Funkhouser and Norman 2003). These oxidizers break polymers by cleaving the polymer acetyl linkage or the crosslinking bond (Economides and Nolte 2000). Persulfates are used at low temperature (<250°F), and bromate oxidizers are used at higher temperatures (>250°F) (Gall and Raible 1985; Al-Muntasheri 2014). Sodium hypochlorite is also used at high temperatures but has limited applications due to environmental considerations

(Albonicao et al. 2007). However, oxidizers can also cause unexpected damage in the treatment. They can corrode the tubular, break other polymer additives such as clay stabilizers, and can cause precipitation of elemental sulfur in sour environments (Almubarak et al. 2015). Enzymes are more selective and can be used as an environmentally friendly and non-damaging way to break polymers. They are traditionally used to breakdown biopolymers that contain long chain sugar backbones on which the enzymes attack. Recent studies have also shown that polyacrylamide based synthetic polymers can be broken down using enzymes such as Asparaginase (Gupta 2012). The disadvantages of using enzymes include higher costs compared to oxidizers as well as their requirement for specific operating conditions.

1.6 Fracturing Fluid Challenges

Various fracturing treatments are conducted every year. However, there is always a need for improvement. Many fracturing fluid challenges are being addressed recently. Such challenges include the use of alternative water sources (Almubarak et al. 2016; Li et al. 2016a and 2016b), high-temperature stability (Prakash et al. 2014), and reduced polymer loading (Feng et al. 2017). Polymer mixture synergy is a potential technology that can provide an alternative solution to many of these issues. This work aims to show some of the synergetic combinations, potential improvements, and challenges to the newly developed CMHPG/Synthetic polymer mixture fracturing fluid.

2. EXPERIMENTAL METHODS

2.1 Materials

An adjustable RPM blender with a 1.2L glass jar was used to mix the fluids. The synthetic polymer used was provided in emulsion form (30 wt.% active), and was used as received. The main monomers consist of acrylamide and acrylic acid and 2-Acrylamido-2-methylpropane sulfonic acid (AMPS) as illustrated in **Fig. 4**. Sodium bromate powder, CMHPG, and zirconium lactate and propylene glycol crosslinker (5.7 wt. % ZrO_2) were provided by a service company and were used as received. Acetic acid was provided at 99 wt.% and used as received. Houston tap water (<500 ppm) was used to mix all the systems.
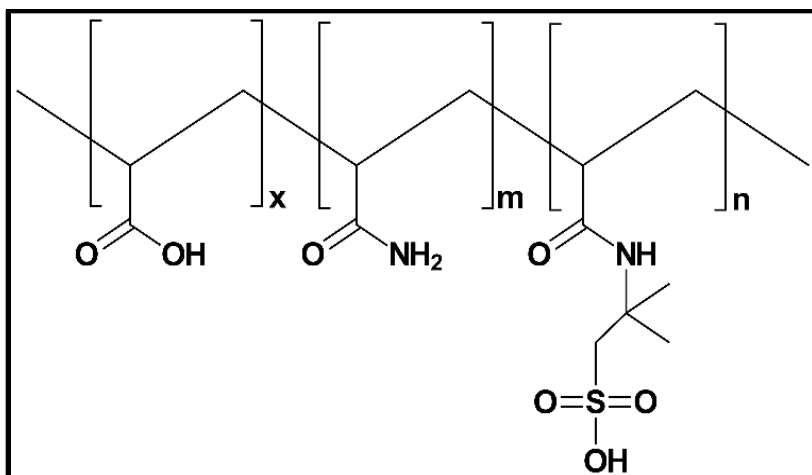
Fig. 4 – Synthetic polymer composition (AA-AM-AMPS).

2.2 Fracturing Fluid Preparation

The fluids were mixed and used the same day, for that reason, no biocide was used. Also, no surfactants, HT stabilizers or crosslinking delay agents were used. This was to enable a direct evaluation of the polymer to polymer interactions in the mixture without the influence of additives. A mixture of 40 lb/1,000 gal synthetic polymer base gel was

prepared by adding 6.4 ml of the synthetic polymer (16 gpt) to 400ml of tap water in a warring blender under rapid agitation (800+RPM) for 15 seconds to ensure inversion of the emulsion. Subsequently, the mixer speed was reduced to 200-400 RPM to generate a small vortex and was mixed for 15 minutes. 40 lb/1,000 gal CMHPG base gel was prepared by adding 3.84g of polymer to 800 ml of tap water in a warring blender maintaining a good vortex for 30 minutes (200-800 RPM). The solutions were kept in beakers for a few hours to allow the release of trapped air bubbles and full hydration of the polymers. The solutions were also centrifuged to remove small air bubbles when necessary at a speed of 500 RPM for 1 minute.

To prepare the CMHPG and synthetic polymer mixture solutions, a total of 250ml of the hydrated fluids were measured using a graduated cylinder at 1:1, 1:2, and 2:1 ratio. They were later transferred to the blender and mixed at low shear (200-400 RPM) for 10 minutes. The pH of the solution was then adjusted by adding an appropriate amount of acetic acid. Sodium bromate live breaker was then added as required. Zirconium crosslinker was added last and mixed thoroughly for 30 seconds.

2.3 HP/HT Viscometer

An HP/HT viscometer was used to measure the apparent viscosity of the gelling samples under different shear rates and temperature. The viscometer utilized R1/B5 bob and rotor combinations which require a sample volume of 52 cm^3. The viscometer uses an electric jacket for heating; a temperature sensor is mounted on the stator/bob to control sample temperature. A pressure of 350-500 psi was applied with nitrogen gas to prevent boiling and evaporation of the sample.

Viscosity measurements were performed under different shear rates to simulate the flow of the fracturing fluid through production tubular, perforations and inside the created fracture. The API RP 39 schedule was followed, where the majority shear rate schedule was set to 100 s^{-1} with short shear ramps between 25 and 100 s^{-1}. The heater temperature was preheated to 150°F for the 300°F tests and to 200°F for the 400°F. This was done to ensure quick and consistent heating profiles. The schedule temperature was set to 300°F, and the fluid took 10-15 minutes to reach test temperature.

Hydration and shear stability tests were conducted at room temperature. An appropriate amount of polymer powder or emulsion was added to water, and the resulting viscosity was measured at 100 and 300 RPM (170 and 511 s^{-1}).

The dynamic viscoelastic properties of the fluid were measured using a hollow B5 bob in oscillatory testing mode. Approximate samples of 60-62 cm^3 were used in these tests. Amplitude and strain sweeps were conducted and both values were determined to be appropriate at 5%. The samples were preheated for 1 hour at 300°F before testing to ensure full crosslinking. Modulus measurements were conducted at 300°F and 350-500 psi. The schedule included a full frequency sweep from 1-5 Hz. No higher frequencies were tested because the concern with proppant settling was limited to static or low-frequency conditions.

2.4 HP/HT Aging Cell

Fracture fluid breaking and proppant settling were evaluated using HP/HT aging cell. The breaker was mixed in the fracturing fluid samples as described in the preparation section (10 ppt breaker for each sample). Each sample was placed in 200 ml glass bottles

in the HP/HT aging cell. Glass bottles were used to prevent direct contact with metal in the aging cell. The aging cell was pressurized to 500 psi and heated to 300°F in an oven for 24 hours. Pictures were taken to evaluate the remaining residue after breaking the polymers.

Proppant settling tests were also carried out in the HP/HT aging cell using a similar procedure mentioned above. However, the heating time was reduced to 1 hour in order to fully crosslink the fluid while minimizing thermal degradation of the fluid. After removing the sample and ensuring the formation of a lip, 4ppt of 40/70 proppant was thoroughly stirred in 100 cm^3 crosslinked fluid sample.

2.5 HP/HT See-Through Cell

HP/HT see-through cell was utilized to visualize proppant settling at reservoir conditions. Samples prepared from the HP/HT aging cell section were transferred to the HP/HT see-through cell. The cell was then pressurized to 500 psi using nitrogen, and heated to 300°F. To monitor the proppant settling rate, a timer was started as soon as the temperature reached 300°F. A similar procedure was conducted in a graduated cylinder at room temperature (77°F). Pictures were taken to show the proppant suspension level at both room temperature and HP/HT setup.

3. RESULTS

3.1 Polymer Hydration

The first step is to evaluate the polymer hydration properties for 20, 30 and 40 lb/1,000 gal CMHPG and synthetic polymer solutions. If the polymers do not hydrate fast enough, the fluids will not meet the expected viscosity and cause delays in the treatment, which will results in more expenses. **Fig. 5** shows that CMHPG and synthetic polymer both achieve full hydration within 5 minutes.
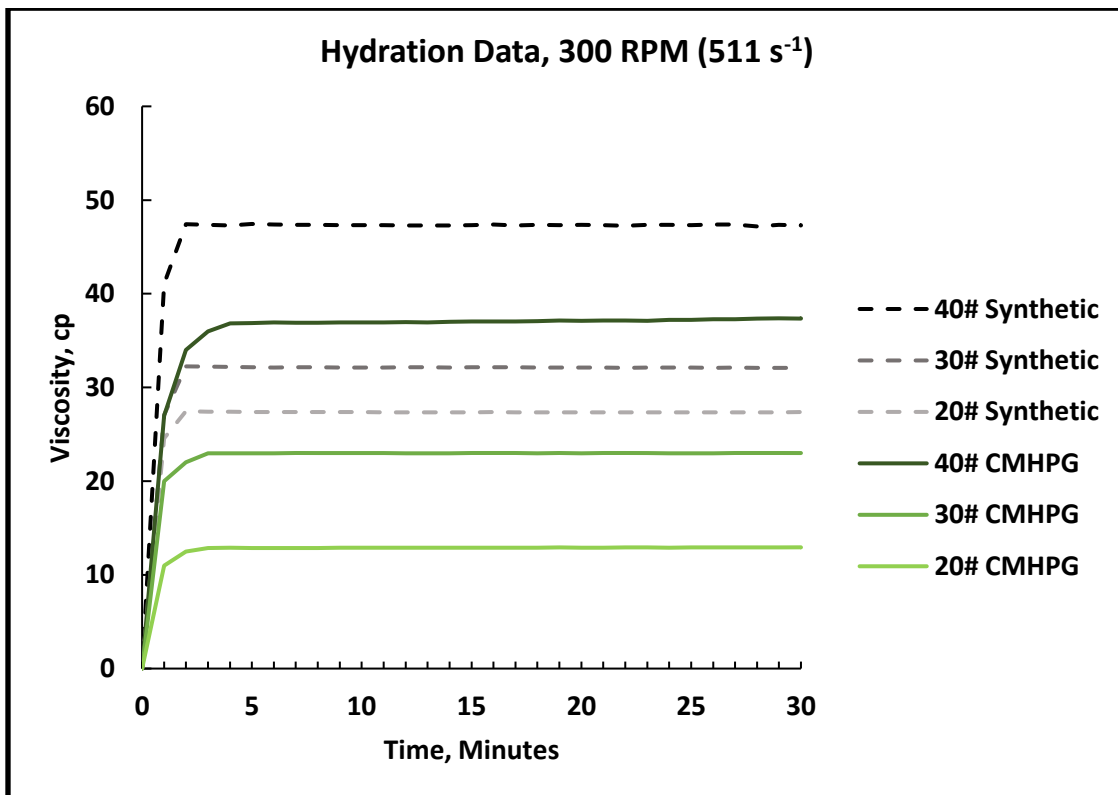
Fig. 5 – Measured viscosity of hydrated 20, 30, and 40 lb/1,000 gal CMHPG and synthetic polymer at 77°F.

3.2 Mixed Polymer Ratio

Following hydration evaluation, mixed polymer linear viscosity is studied. **Fig. 6** shows 40 lb/1,000 gal mixed polymer solution viscosity results at 100 and 300 RPM. The

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graph illustrates that a mixture of 1:2 and 1:1 (CMHPG: Synthetic) observe synergy. Based on these results, ratios of 2:1, 1:1, and 1:2 (CMHPG: Synthetic) are chosen for crosslinking viscosity tests.
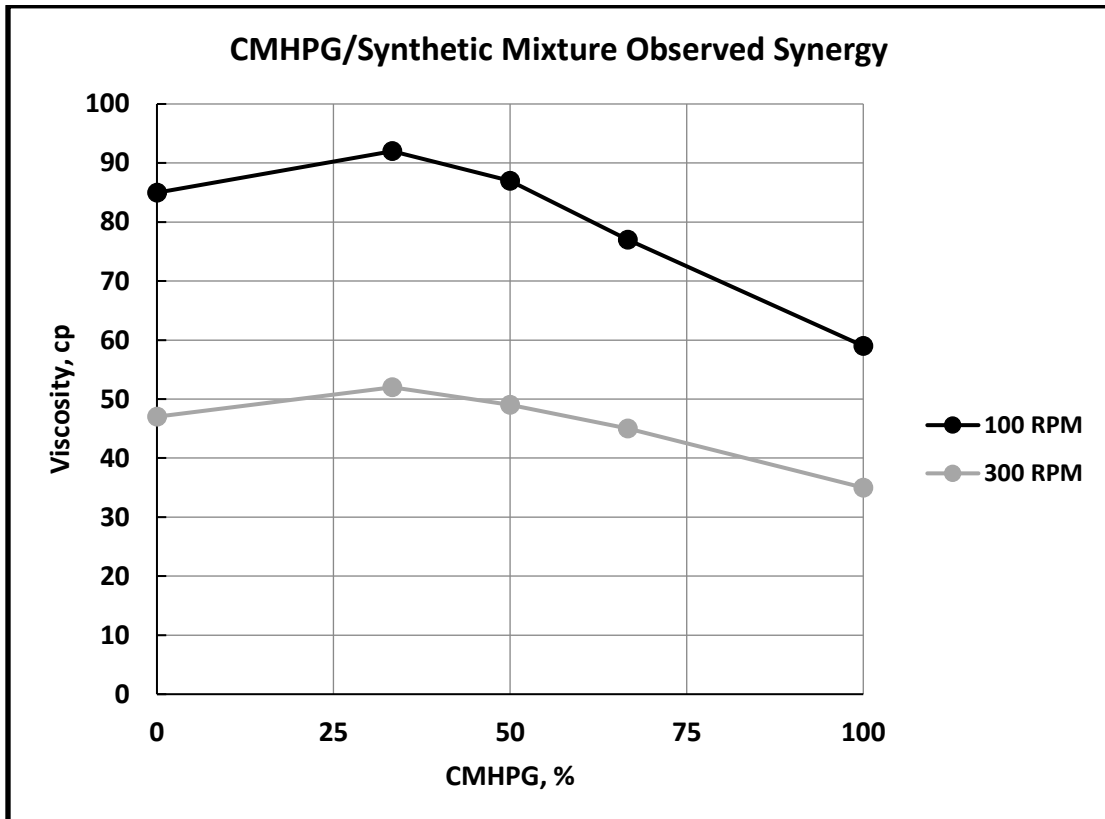
Fig. 6 – Measured viscosity of hydrated 40 lb/1,000 gal CMHPG/synthetic polymer mixture at 77°F.

3.3 Crosslinking pH

Each polymer has a proper crosslinking pH that depends on the chemistry of the side groups. **Fig. 7** shows that the synthetic polymer is unable to generate sufficient viscosity at a pH of 7 and 10. On the other hand, at a pH of 5, synthetic polymer crosslinked shows high and stable viscosity.
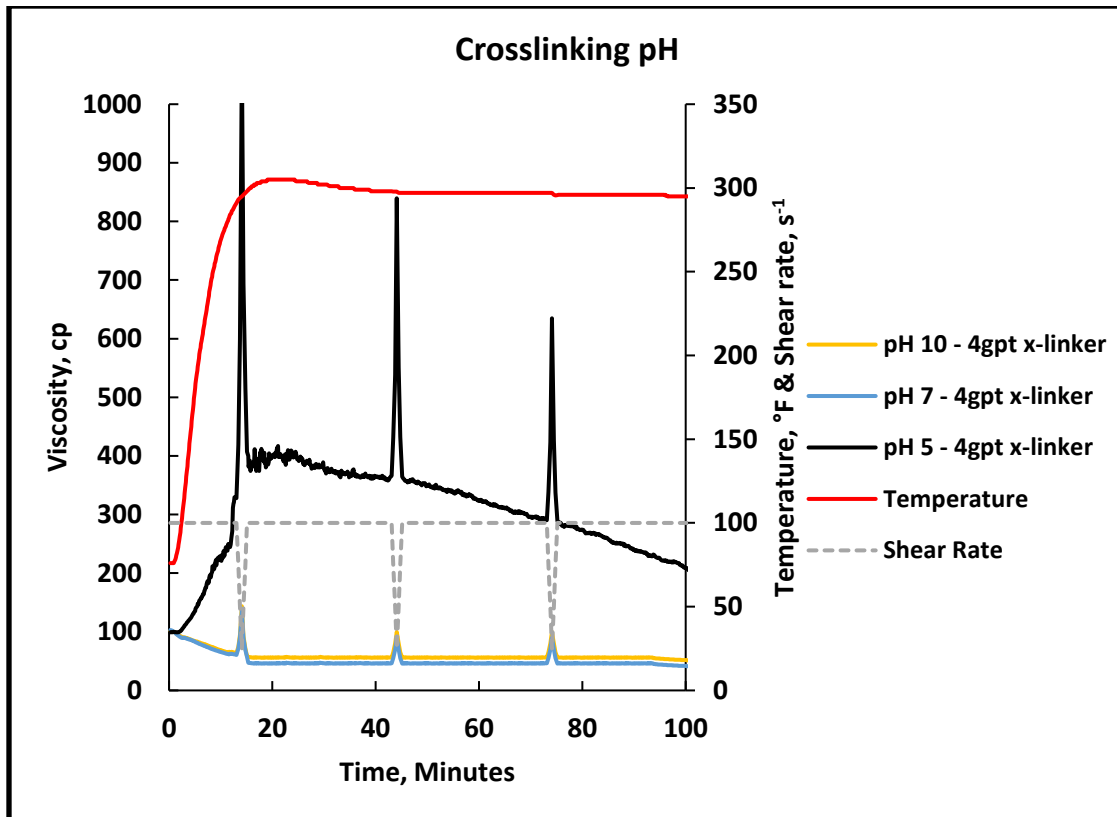
Fig. 7 –Measured viscosity of 40 lb/1,000 gal synthetic polymer with 4 gpt crosslinker at pH 5, 7, 10 and 300°F.

3.4 Crosslinker Concentration

Crosslinker concentration is studied to determine the concentration at which over-crosslinking occurs for each polymer. **Fig. 8** shows test results of 40 lb/1,000 gal CMHPG crosslinked with 1-5 gpt crosslinker. CMHPG crosslinked viscosity improves from 1-4 gpt crosslinker and decreases at 5 gpt. The decrease in viscosity at 5 gpt is due to over-crosslinking the polymer at these conditions. In general, CMHPG crosslinked viscosity did not perform well at pH 5 and 300°F.

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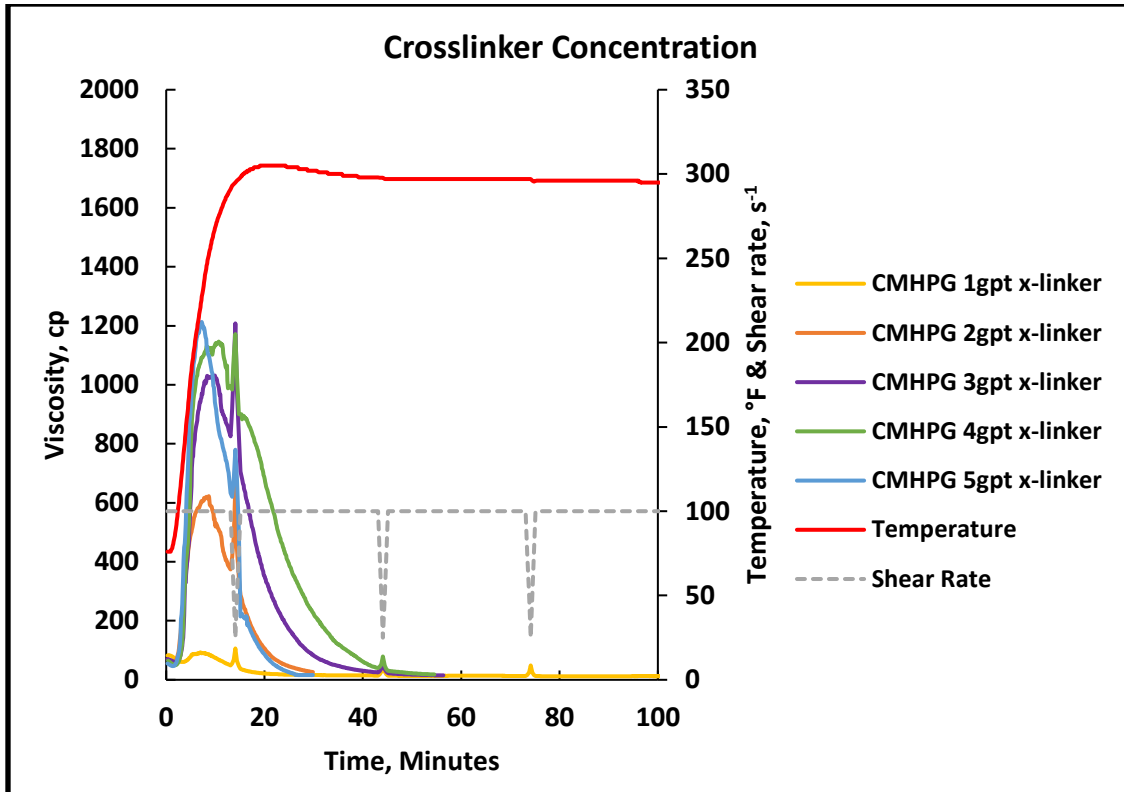
Fig. 8 – Measured viscosity of 40 lb/1,000 gal CMHPG crosslinked with 1-5 gpt crosslinker at pH 5 and 300°F.

Fig. 9 evaluates the crosslinking of 40 lb/1,000 gal synthetic polymer crosslinked with 1-8 gpt crosslinker. The synthetic polymer exhibits very weak crosslinking at concentrations between 1-3 gpt crosslinker. On the other hand, the synthetic polymer viscosity strengthens at 4 gpt and is best at 6 gpt. A further increase in crosslinker concentration does not generate significant additional viscosity. Based on the CMHPG and Synthetic polymer crosslinking trends, the mixture crosslinker concentration limit is highly related to CMHPG's crosslinking limit. A conservative 4 gpt crosslinker concentration is chosen to carry out the intial polymer mixture fracturing fluid tests.

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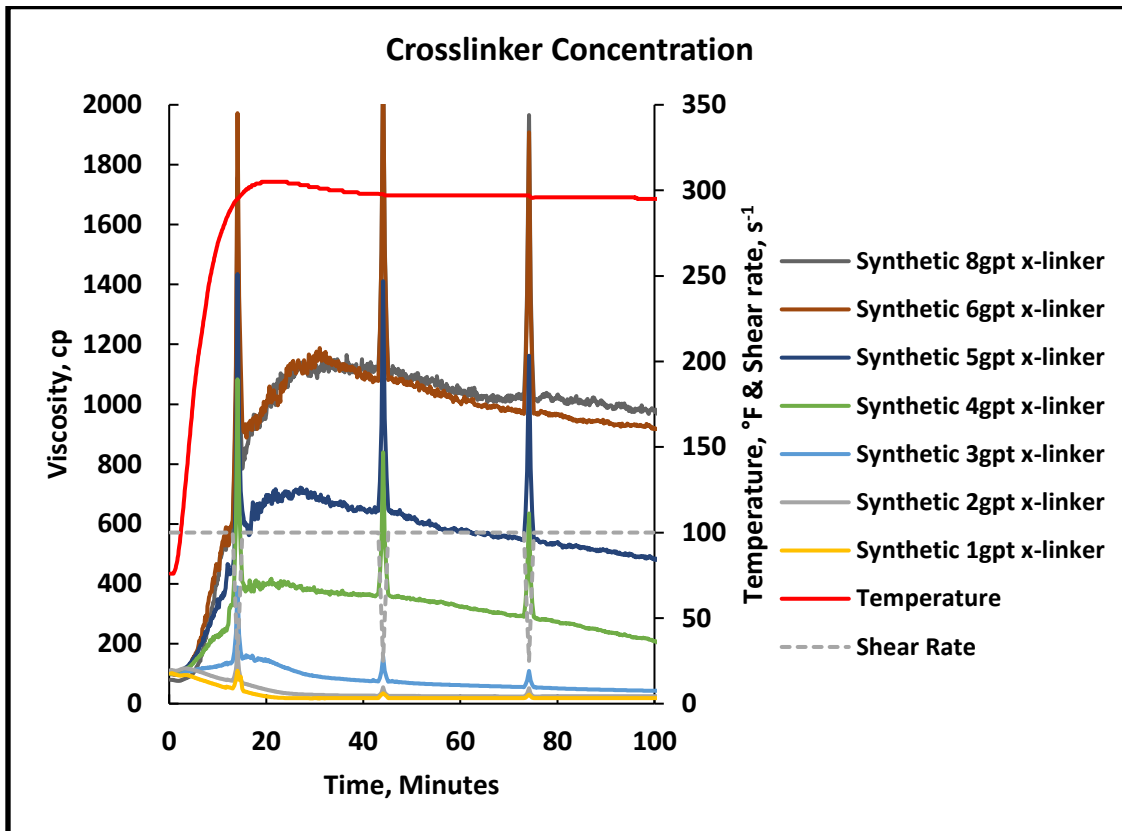
Fig. 9 – Measured viscosity of 40 lb/1,000 gal synthetic polymer crosslinked with 1-8 gpt crosslinker at pH 5 and 300°F.

3.5 Crosslinked Mixed Polymer Viscosity

Fig. 10 presents 40 lb/1,000 gal mixed fracturing fluid results with 4 gpt crosslinker concentration at pH 5 and 300°F. It shows that all polymer mixtures surpass the performance of the individual polymer fracturing fluid with the 2:1 (CMHPG: Synthetic) fluids exhibiting the highest viscosity. Also, 2:1 crosslinked mixture shows a steep decrease in viscosity over time, whereas higher synthetic polymer ratios in the mix exhibit a more gradual decrease in viscosity.
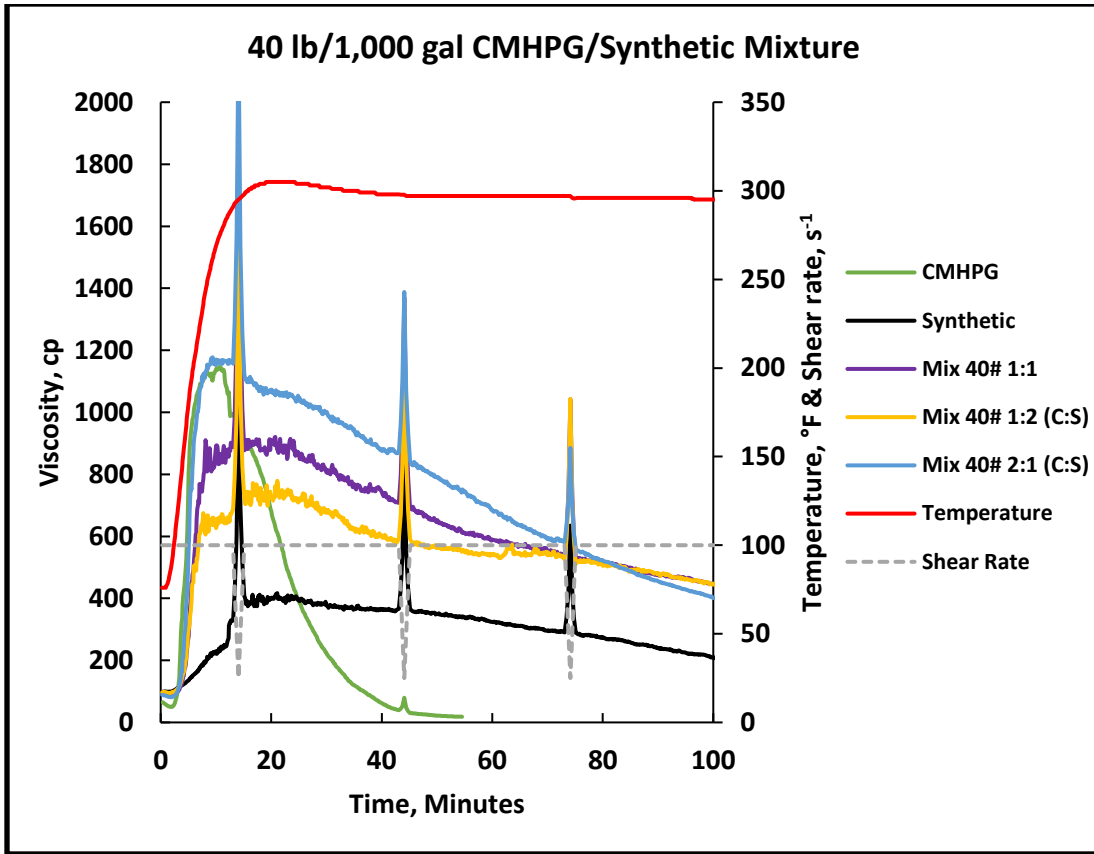
Fig. 10 – Measured viscosity of 40 lb/1,000 gal mixed polymer with 4 gpt crosslinker at pH 5 and 300°F.

Fig. 11 shows 30 lb/1,000 gal mixed fracturing fluid results with 4 gpt crosslinker concentration at pH 5 and 300°F. Similar to the 40 lb/1,000 gal mixed polymer results, the 30 lb/1,000 gal mixture fluids outperform the individual crosslinked polymer fracturing fluid viscosity. At 30 lb/1,000 gal the 1:1 (CMHPG: Synthetic) crosslinked polymer mixture fluid show highest viscosity. Also, the peak viscosity of all mixture fluids surpasses the peak viscosity of the individual CMHPG based fracturing fluid.

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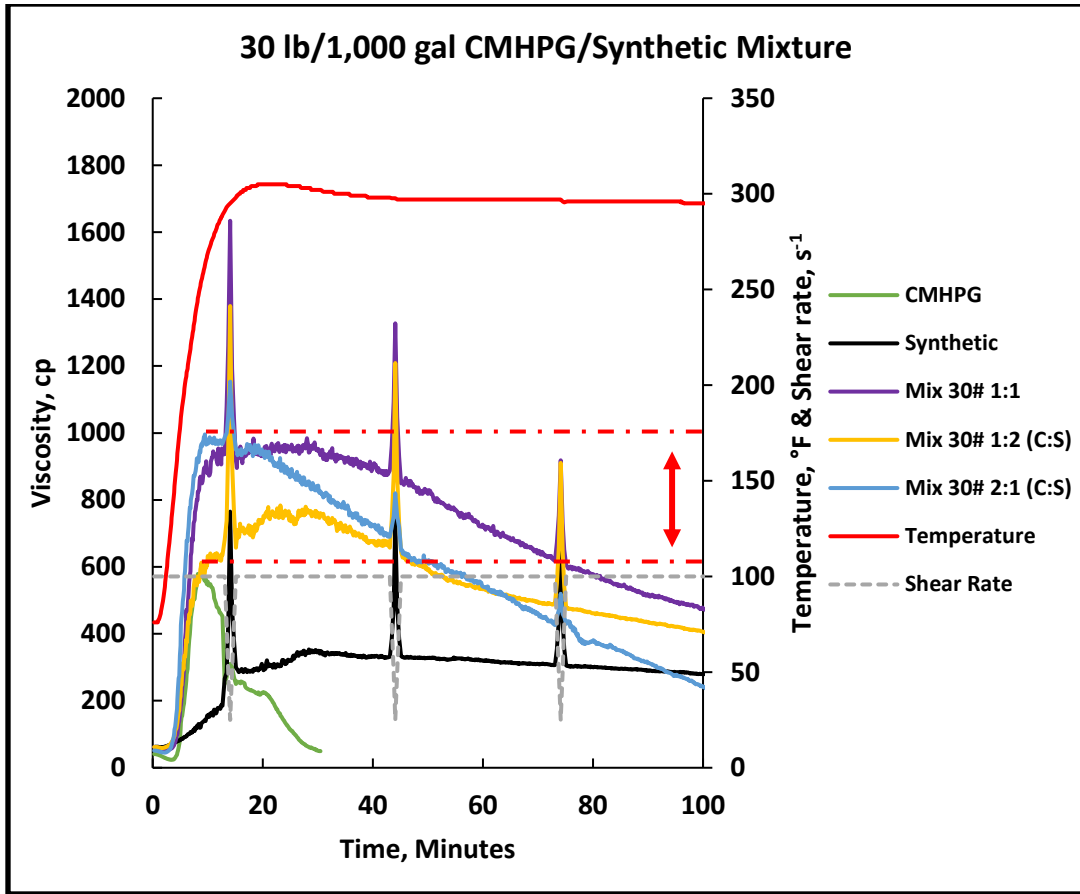
Fig. 11 – Measured viscosity of 30 lb/1,000 gal mixed polymer with 4 gpt crosslinker at pH 5 and 300°F.

Fig. 12 illustrates 20 lb/1,000 gal mixed fracturing fluid results with 4 gpt crosslinker concentration at pH 5 and 300°F. The 1:2 (CMHPG: Synthetic) crosslinked fluid generates the highest viscosity. At this low total polymer concentration, synthetic polymer has more influence than CMHPG on the performance of the mixture. Also, individual CMHPG fracturing fluid and 2:1 (CMHPG: Synthetic) mixture fracturing fluid show the least viscosity and thermal stability.
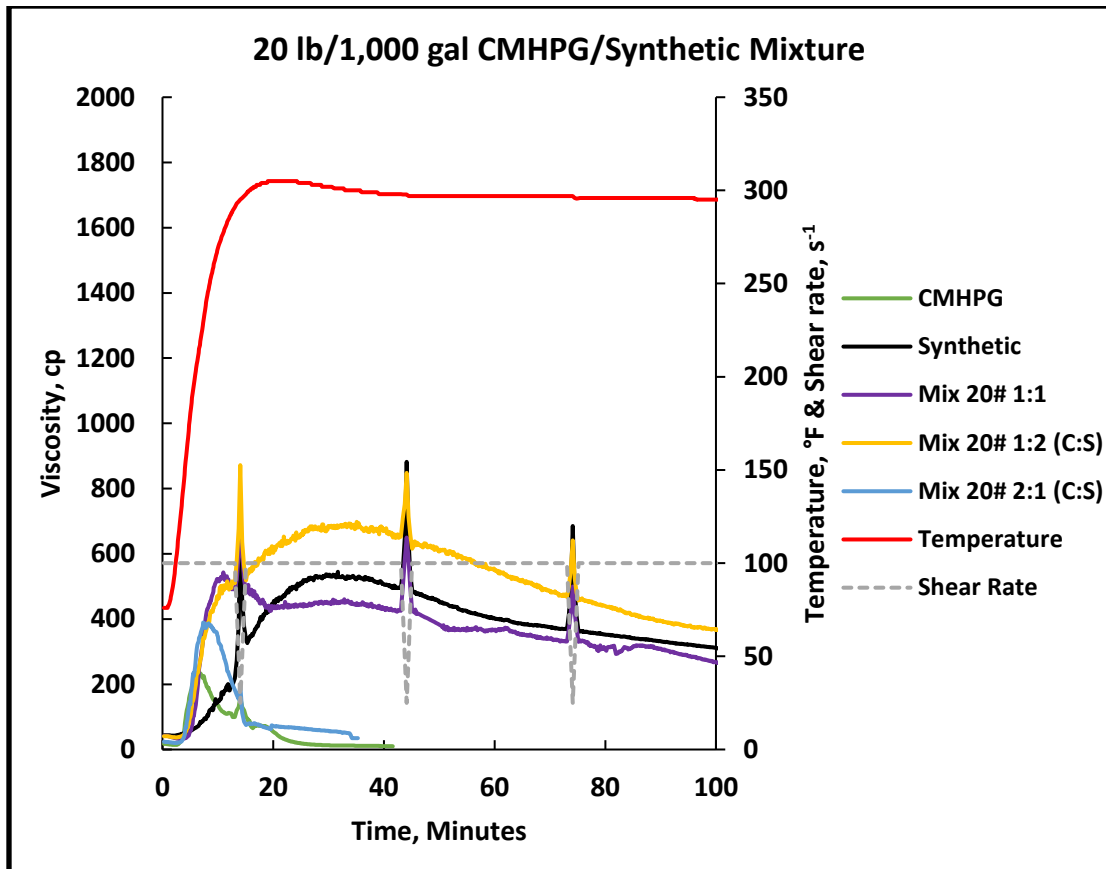
Fig. 12 – Measured viscosity of 20 lb/1,000 gal mixed polymer with 4 gpt crosslinker at pH 5 and 300°F.

Fig. 13 depicts a comparison of the best performing mixed polymer fracturing fluid ratios at different polymer loadings with 4 gpt crosslinker concentration at pH 5 and 300°F. The graph illustrates that the best-performing fluids regarding viscosity and thermal stability are at a ratio of 2:1 (CMHPG: Synthetic) at 40 lb/1,000 gal, 1:1 (CMHPG: Synthetic) at 30 lb/1,000 gal, and 1:2 (CMHPG: Synthetic) at 20 lb/1,000 gal. The influence of crosslinker to polymer ratios and thermal stability of used polymers are discussed later.
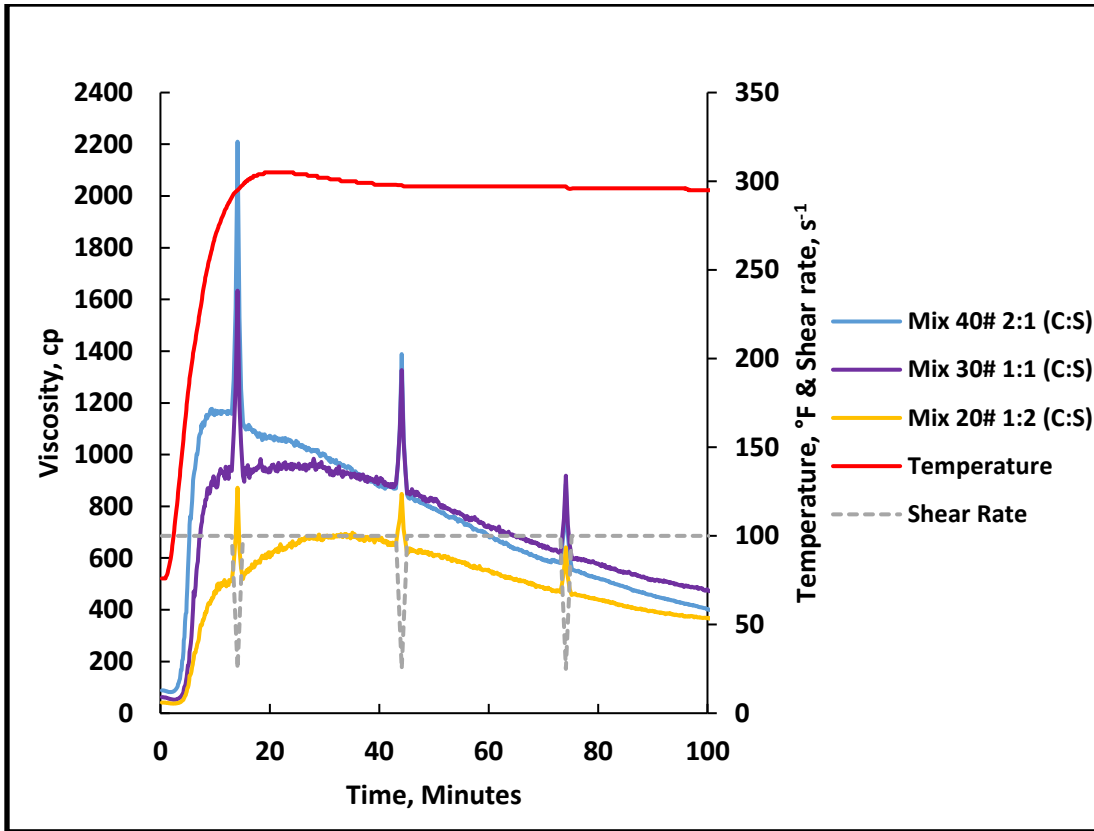
Fig. 13 – Summary of the highest crosslinked viscosity and thermal stability mixtures with 4 gpt crosslinker at pH 5 and 300°F.

3.6 Elasticity and Viscous Modulus

Fig. 14 shows the elastic modulus measurements for 20, 30, and 40 lb/1,000 gal 1:1 (CMHPG: Synthetic) mixed polymer fluid crosslinked with 4 gpt crosslinker at pH 5 and 300°F. These results show that the mixed polymer fracturing fluid elastic modulus are high and stable. The results indicate that the polymer mix of 30 lb/1,000 gal fluid has the highest elasticity followed by the polymer mix of 40 and then 20 lb/1,000 gal fluids. The fluids show a high and stable elastic value at both low and high-frequency values.
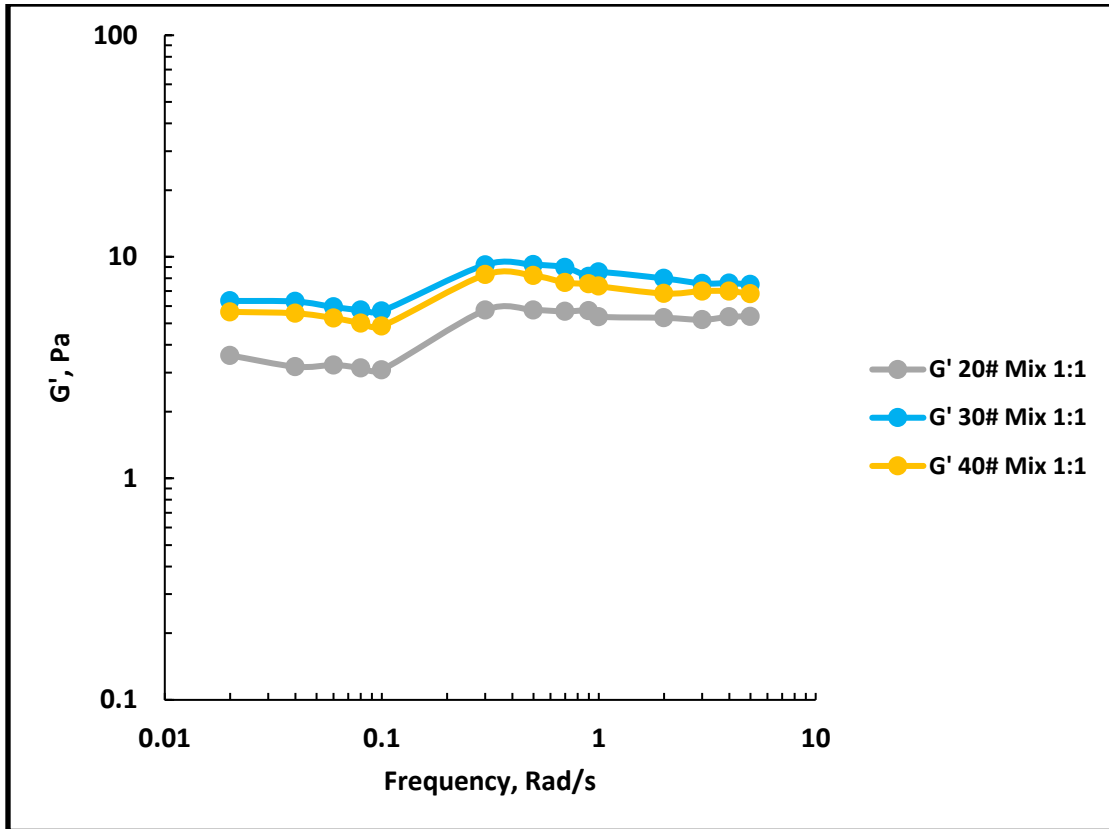
Fig. 14 - Elastic modulus measurements of 20, 30 and 40 lb/1,000 gal 1:1 (CMHPG: Synthetic) polymer mixture with 4 gpt crosslinker at pH 5 and 300°F.

Fig. 15 presents the viscous modulus values for 20, 30, and 40 lb/1,000 gal 1:1 (CMHPG: Synthetic) mixed polymer fluid crosslinked with 4 gpt crosslinker at pH 5 and 300°F. The results indicate that the 30 lb/1,000 gal crosslinked polymer mix fluid has the highest viscous modulus followed by 40 and then 20 lb/1,000 gal fluids. The viscous modulus measurements decrease with higher frequency.
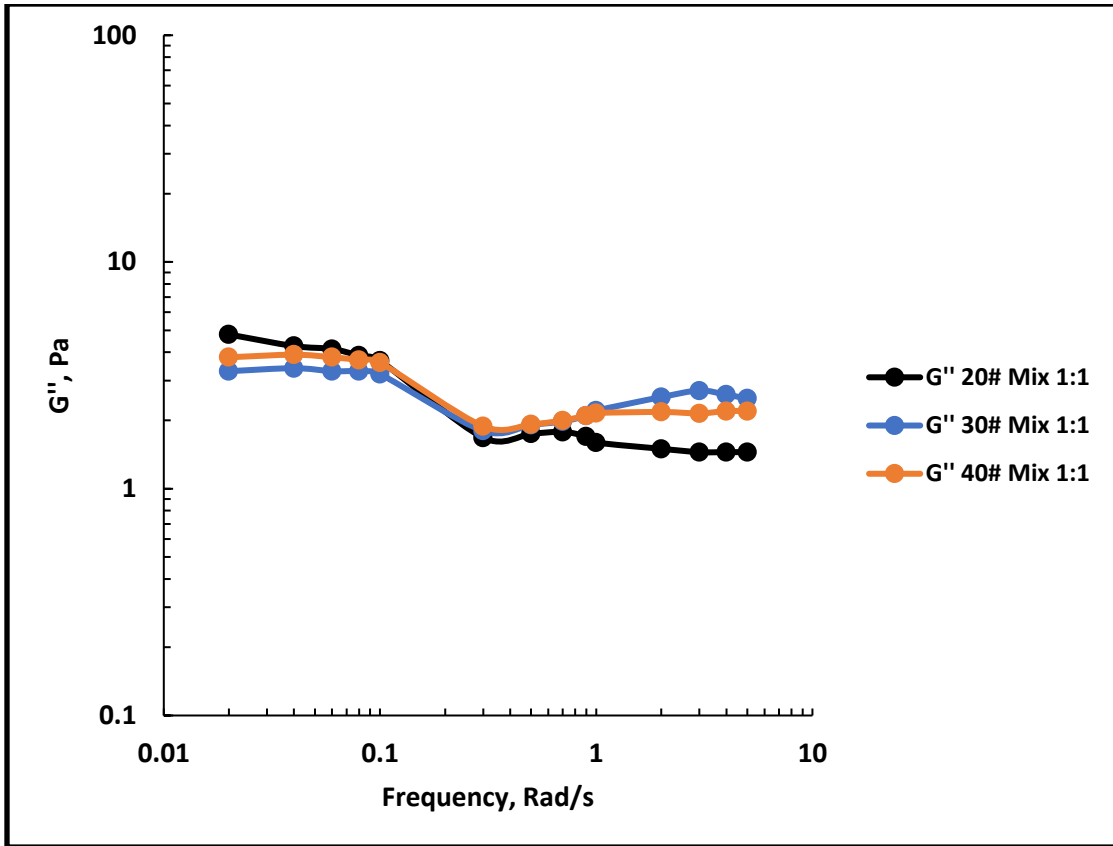
Fig. 15 - Viscous modulus measurements of 20, 30 and 40 lb/1,000 gal 1:1 (CMHPG: Synthetic) polymer mixture with 4 gpt crosslinker at pH 5 and 300°F.

3.7 Proppant Settling

Fig. 16 shows HP/HT see-through cell proppant settling test results for 40 lb/1,000 gal mixed polymer ratios of 2:1, 1:1 and 1:2 (CMHPG: Synthetic) at 300°F. The results show that all tested systems can suspend proppant in static conditions at 300°F. The polymer mixture crosslinked fluids show good proppant suspension properties with almost no loss in proppant suspension level for several hours.
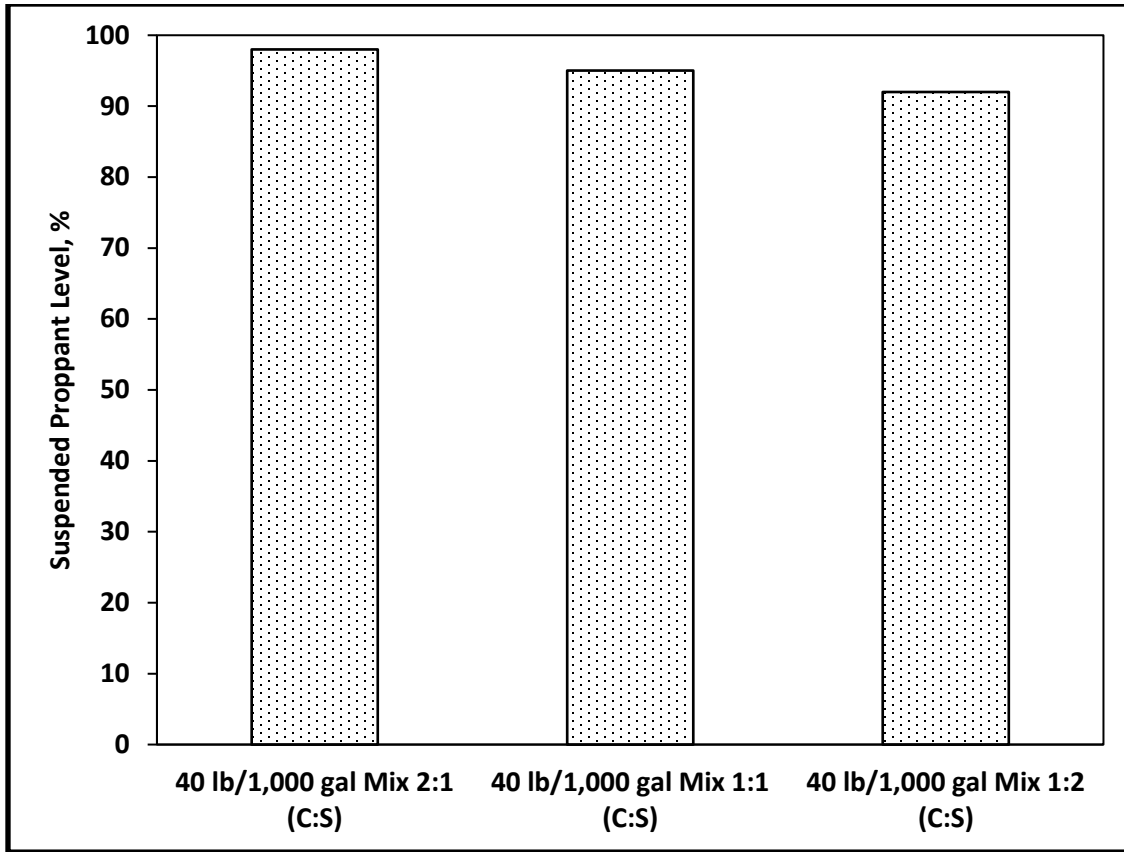
Fig. 16 – Proppant settling HP/HT see-through cell tests for 40 lb/1,000 gal mixed polymer with 4 gpt crosslinker at pH 5 and 300°F for 2 hours.

3.8 Crosslinked Mixed Polymer Breaking

Fig. 17 presents the breaker tests for 40 lb/1,000 gal 2:1 and 1:1 (CMHPG: Synthetic) polymer mixture with 4 gpt crosslinker at pH 5 and 300°F. The fluids are broken using a sodium bromate oxidizer at 5 and 10 ppt (lb/1,000 gal). Sodium bromate can break the mixed polymer fracturing fluid, and the break is controllable. The fracturing fluids final fluid viscosity values are low (<20 cp) at the end of the 2-hour test, **Fig. 18**.
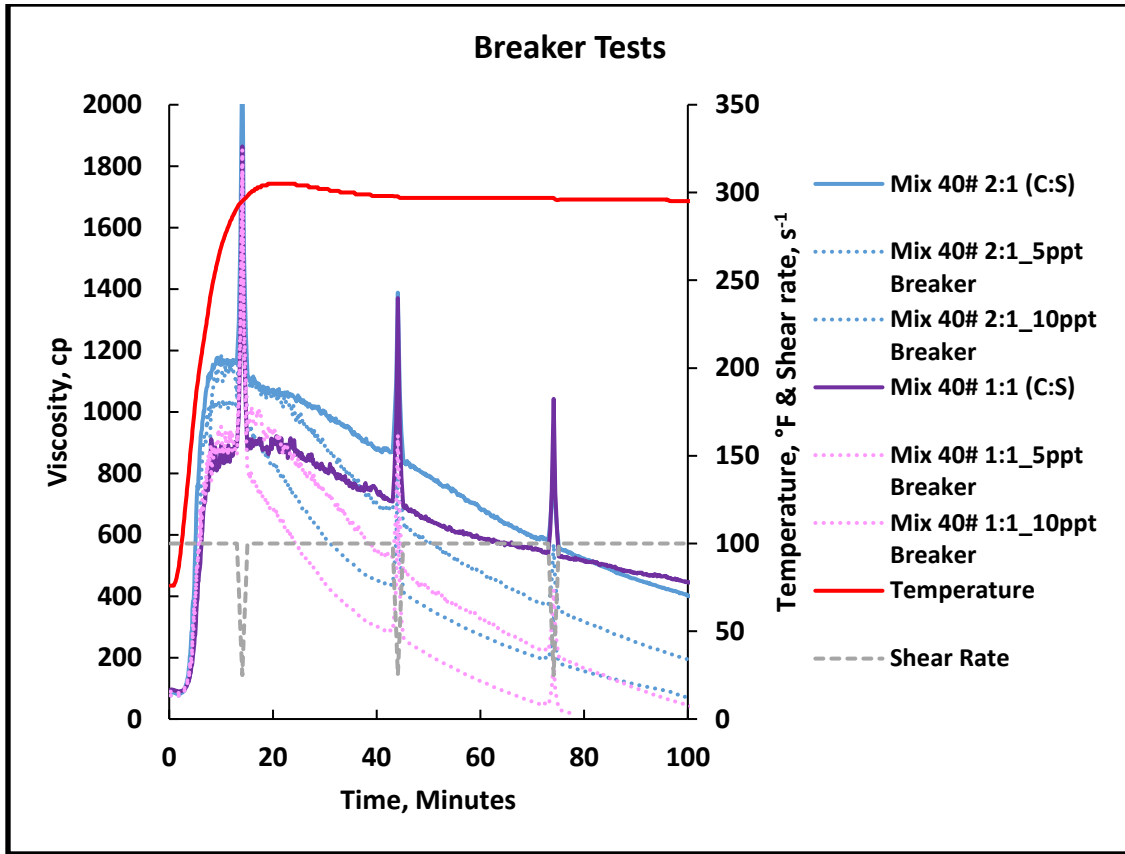
Fig. 17 – Measured viscosity of 40 lb/1,000 gal mixed polymer with 4 gpt crosslinker and sodium bromate oxidizer at pH 5 and 300°F.

Fig. 18 – Effluent from 40 lb/1,000 gal 1:1 (CMHPG: Synthetic) polymer mixture fracturing fluid using 10 ppt bromate oxidizer at 300°F.

4. DISCUSSION

4.1 Polymer Hydration

The synthetic polymer is particularly easy to hydrate because it is manufactured in a pre-hydrated emulsion form. Also, the synthetic polymer emulsion contains surfactants that help in inverting the emulsion to aid the hydration process.

4.2 Crosslinking pH

The synthetic polymer contains acrylic acid, which has a pKa of around 4.2. Due to this property, it is deprotonated and capable of crosslinking at a pH above 4.2. Although the synthetic polymer also contains AMPS, which has a lower pKa of 1.7, previous work has shown that AMPS does not contribute directly in the crosslinking (Sigale and Omari, 1997). Crosslinking does not occur at high pH due to several factors that could not be included in this study. In brief, factors such as molecular weight distribution, polymer configuration, polymer charge, generation of ZrO_2 nanoparticles in solution, and type of ligand used can all contribute to crosslinking at different pH values.

4.3 Crosslinking Performance

From **Figs. 8** CMHPG exhibits a delayed crosslinking behavior at low pH. In addition, **Fig. 9** shows that the synthetic polymer crosslinking is delayed longer than CMHPG. The delay in crosslinking both polymers is a function of the Zirconium crosslinker ligand release rate, molecular weight, and polymer crosslinking site distribution. Delay and performance between same compositions of synthetic polymers can significantly vary due to these factors. A general observation of **Figs. 8** and **9**

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demonstrate that the synthetic polymer can handle higher concentrations of crosslinker and works best at these high concentrations.

4.4 Thermal Stability

Crosslinked fracturing fluid thermal stability depends on many chemical and physical factors. Chemically, crosslinker to polymer bonds, monomer to monomer bonds, and dissolved oxygen in solution can influence thermal stability. In addition, the physical aspect includes understanding the influence of the polymer architecture, bulkiness, damping, branching and crosslinking density on thermal stability.

Fig. 19 shows the influence of 300°F on the crosslinking viscosity of 15, 20, 30 and 40 lb/1,000 gal CMHPG. At high temperature, the polymer chains vibrate, and at low polymer concentration, the vibrations are more pronounced. These vibrations weaken the polymer chains and can influence the thermal stability. To minimize chain vibrations, a well-connected crosslinking polymer network is required. Also, CMHPG at pH 5 is not fully deprotonated which minimizes crosslinking points and reduces the total negative charge on the polymer. This allows oxygen radicals to easily reach and attack the polymer backbone at high temperatures. An attack on the polymer backbone causes the polymer to break easily and lose significant viscosity. This thermal stability analysis explains the steep decline in measured viscosity in mixtures with high CMHPG polymer ratio.
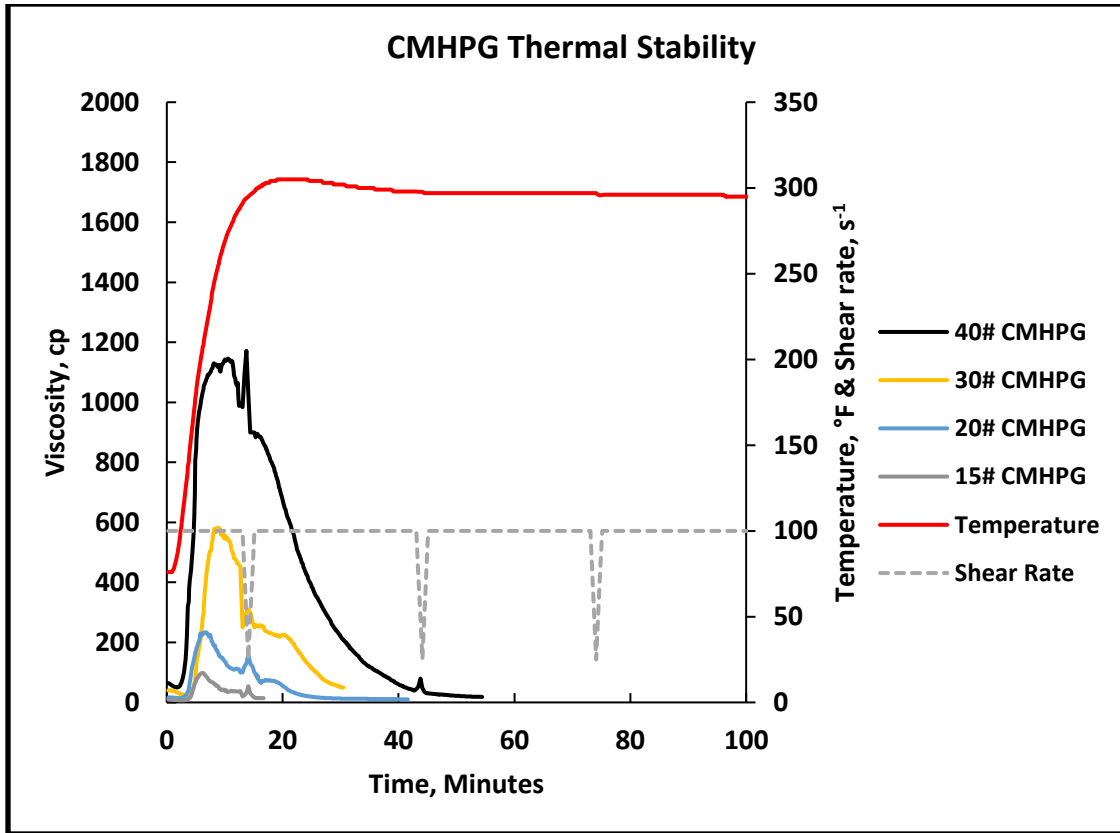
Fig. 19 – Measured viscosity of 15, 20, 30, and 40 lb/ 1,000 gal crosslinked CMHPG with 4 gpt crosslinker at pH 5 and 300°F.

An example of this point is shown in **Fig. 20** which compares the performance of 2:1 (CMHPG: Synthetic) mixed polymer fracturing fluid systems at 20, 30 and 40 lb/1,000 gal. The graph shows that the 30, and 40 lb/1,000 gal systems perform well compared to the 20 lb/1,000 gal mixture fracturing fluid. A pronounced viscosity slope decline is seen, which is due to weak thermal stability because the ratio of CMHPG is high in these mixtures. The failure of the 20 lb/1,000 gal mixture is largely due to thermal instability of CMHPG polymer at this concentration, pH 5, and 300°F. Also, the polymers at low concentration are not sufficiently overlapped to induce crosslinking viscosity.

Fig. 20 – Measured viscosity of 20, 30, and 40 lb/ 1,000 gal 2:1 (CMHPG: Synthetic) mixed polymer with 4 gpt crosslinker at pH 5 and 300°F.

Fig. 21 shows the performance of 15, 20, 30, and 40 lb/1,000 gal synthetic polymer fracturing fluid at 300°F. Synthetic polymer used in this study contains AMPS monomers which serve to enhance temperature stability. AMPS monomer is deprotonated at pH 5, and a negative sulfonate molecule is located several carbon atoms away from the polymer backbone (**Fig. 4**). These conditions can enhance polymer thermal stability by shielding salts, and repelling oxygen radicals away from the main polymer chain. Also, AMPS adds stiffness to the polymer, which increases thermal stability and shear resistance (Jamshidi and Rabiee 2014). Therefore we observe a less severe viscosity slope decline in mixtures with a high synthetic polymer ratio.

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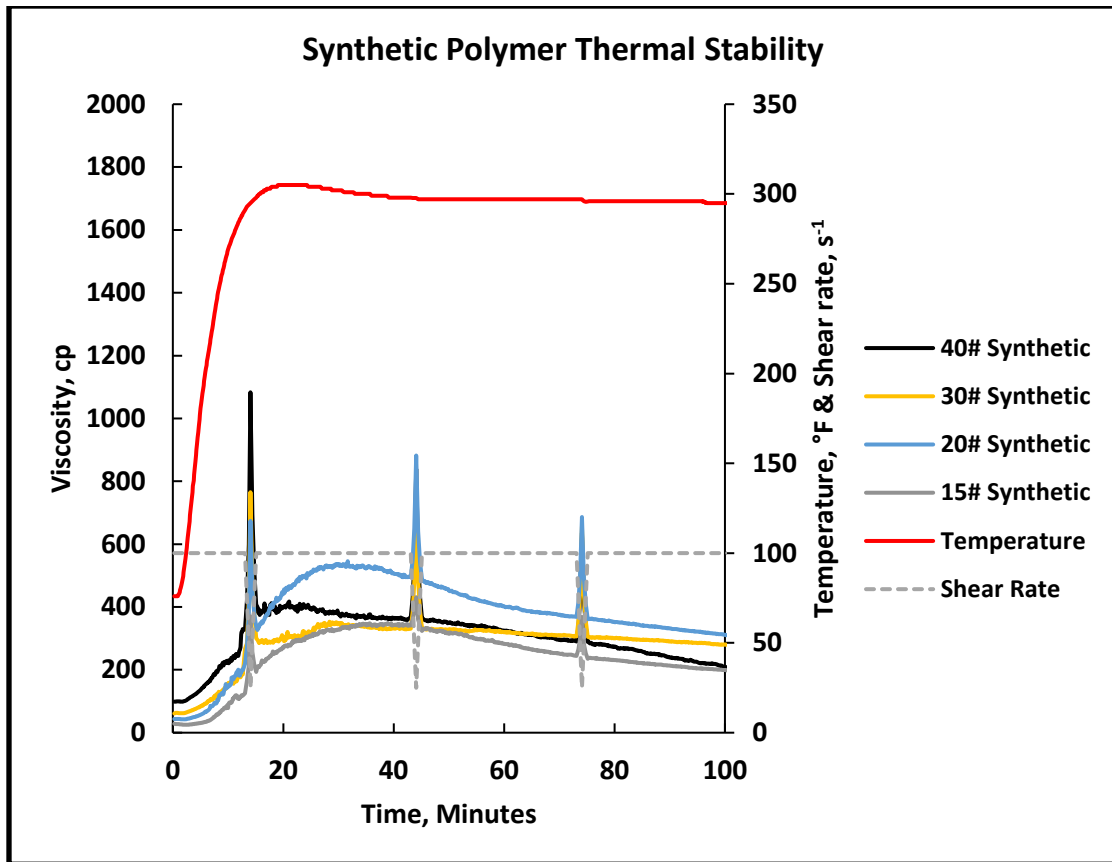
Fig. 21 – Measure viscosity of 15, 20, 30, and 40 lb/ 1,000 gal crosslinked synthetic polymer viscosity with 4 gpt crosslinker at pH 5 and 300°F.

To further analyze thermal stability, a high-temperature sodium thiosulfate stabilizer is added to CMHPG. Sodium thiosulfate HT stabilizer was added at the recommended concentrations of 0.5 and 1 gpt (50% and 100%) per 5 lb/1,000 gal of CMHPG fracturing fluid at 300°F. **Fig. 22** compares the performance of the addition of these additions to the 40 lb/1,000 gal polymer mixture fracturing fluid.

The addition of sodium thiosulfate to CMHPG does not perform as well as the polymer mixture fracturing fluid. This is because the high-temperature stabilizer contained salts that influence CMHPG greatly at this low pH and weakly deprotonated state. This

indicates that the presence of a synthetic polymer outperforms the use of sodium thiosulfate in stabilizing polymers at pH 5 and high temperatures. Sodium thiosulfate enhances thermal stability through scavenging oxygen. On the other hand, a synthetic polymer containing AMPS acts as a stabilizer through repelling oxygen radicals and adding stiffness to the polymer. The presence of AMPS eliminates the need for additional stabilizers in the polymer mixture fracturing fluid system, and adds sufficient thermal stability at 300°F.
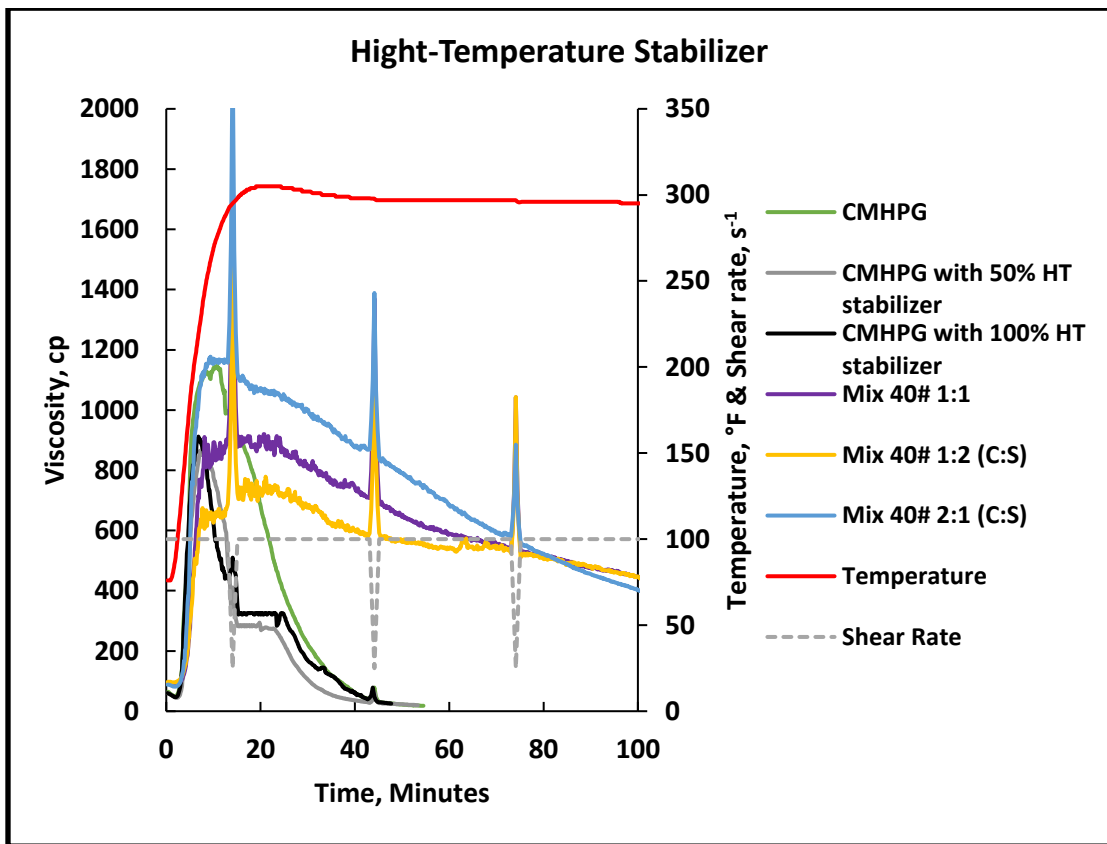
Fig. 22 – Measured viscosity of 40 lb/1,000 fluids with 4 gpt crosslinker at pH 5 and 300°F to evaluate the use of HT stabilizer.

Additionally, **Fig. 23** depicts the results of 30 lb/1,000 gal polymer mixture fracturing fluid comparison with sodium thiosulfate stabilizer. It shows that the addition

of AMPS containing synthetic polymer produces a more thermally stable fluid, which eliminates the need for HT stabilizers and has higher viscosity performance than the individual polymer crosslinked fracturing fluids.
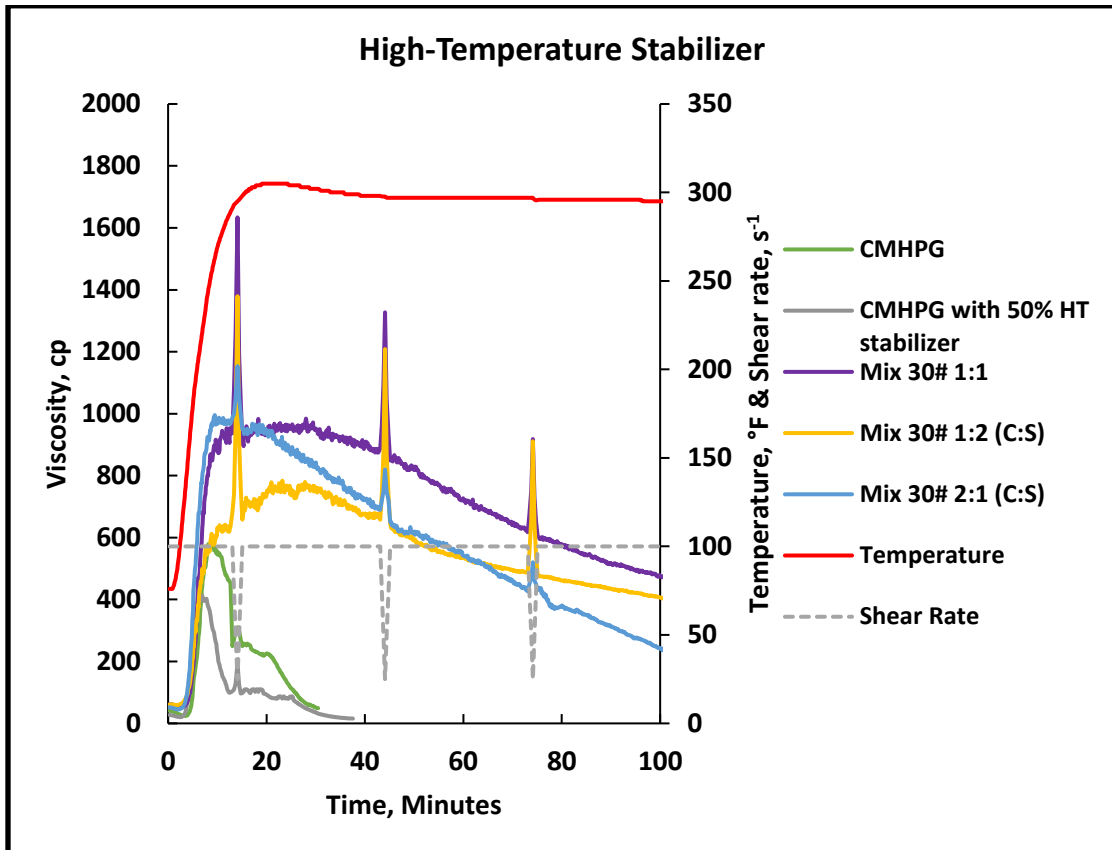
Fig. 23 - Measured viscosity of 30 lb/1,000 fluids with 4 gpt crosslinker at pH 5 and 300°F to evaluate the use of HT stabilizer.

4.5 Crosslinker to Polymer Ratio

In the results section (**Fig. 8**), a mixture of 30 lb/1,000 gal 1:1 (CMHPG: Synthetic) shows a very similar viscosity to 40 lb/1,000 gal 2:1 (CMHPG: Synthetic) under the same conditions. We also notice an enhancement in peak viscosity when comparing the mixtures to individual CMHPG in **Figs. 6** and **7**. In an effort to better understand these

results, the crosslinker to polymer ratio is studied. **Fig. 24** shows the effect of increasing

the crosslinker concentration from 4 gpt to 5 gpt for 40 lb/1,000 gal at 2:1 polymer mixture

ratio. The results show that the crosslinking viscosity performance is enhanced. Moreover,

the 2:1 mixture crosslinked peak viscosity surpasses the maximum viscosity of the

individual crosslinked CMHPG polymer. However, we notice that the 2:1 steep viscosity

slope decline did not change for a higher crosslinker to polymer ratio. This indicates that

the slope of the 2:1 mix is directly related to CMHPG thermal stability and not likely

influenced by polymer to crosslinker ratio.

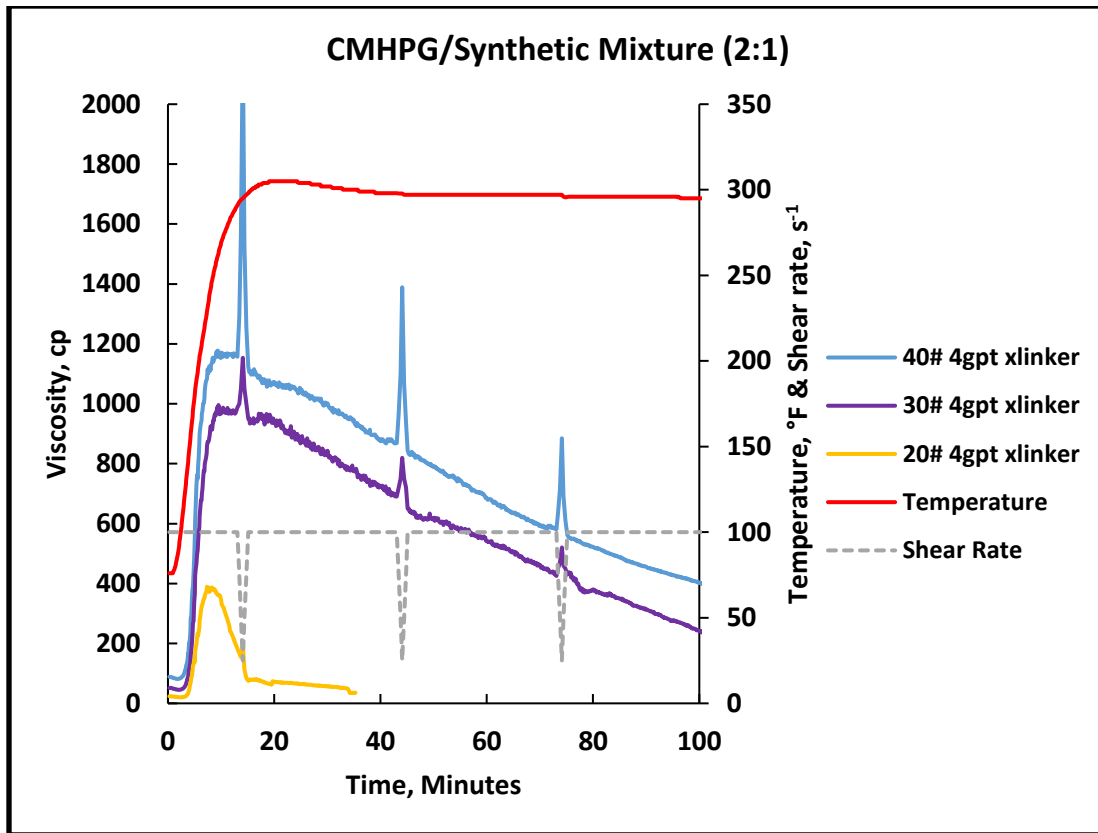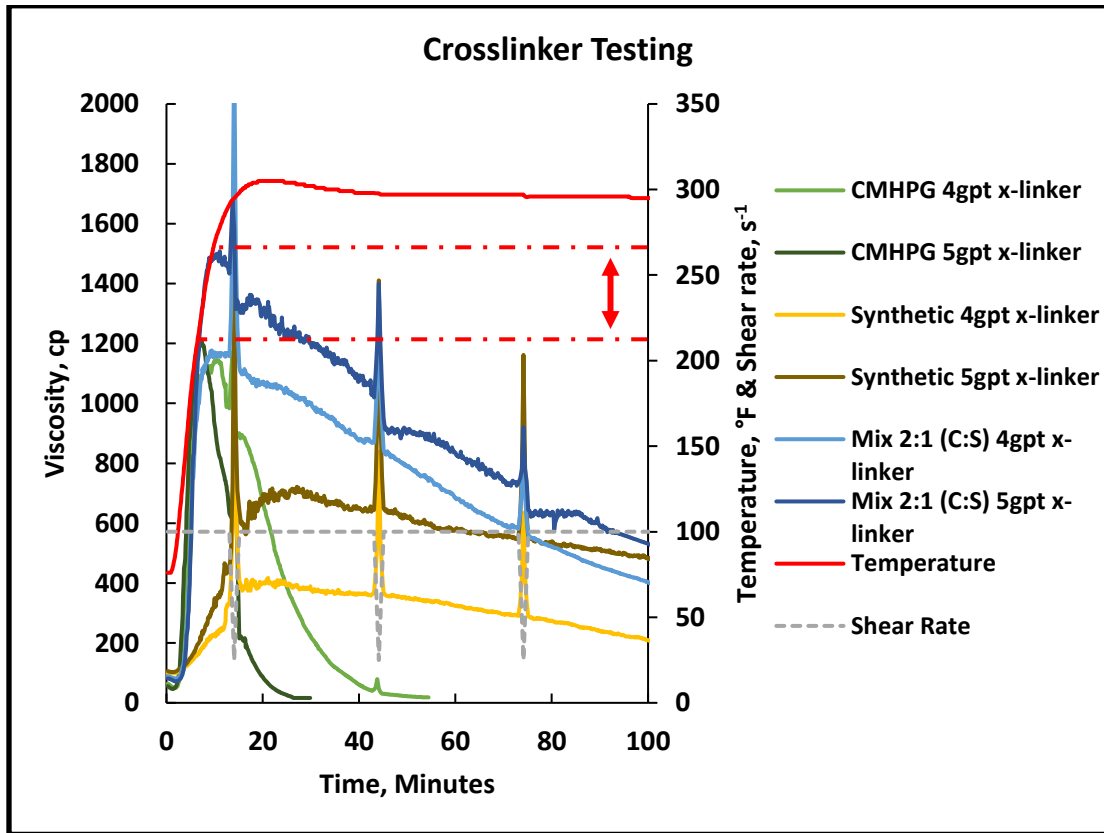**Fig. 24 – Measured viscosity of 40 lb/ 1,000 gal 2:1 (CMHPG: Synthetic) mixed polymer with 4-5 gpt crosslinker at pH 5 and 300°F.**

Similarly, the 2:1 30 lb/1,000 gal polymer mixture was investigated. **Fig. 25** shows the influence of the crosslinker concentration on the performance of the 30 lb/1,000 gal 2:1 mixed polymer crosslinked fluid. The results indicate that 4 gpt crosslinker concentration generates a more stable viscosity than the 3 and 5 gpt crosslinker concentrations. The 3 gpt crosslinker concentration shows enhancement in thermal stability without enhancing peak viscosity. The 5 gpt crosslinker concentration shows enhancement in peak viscosity. However, this induced over-crosslinking of the polymer mixture.
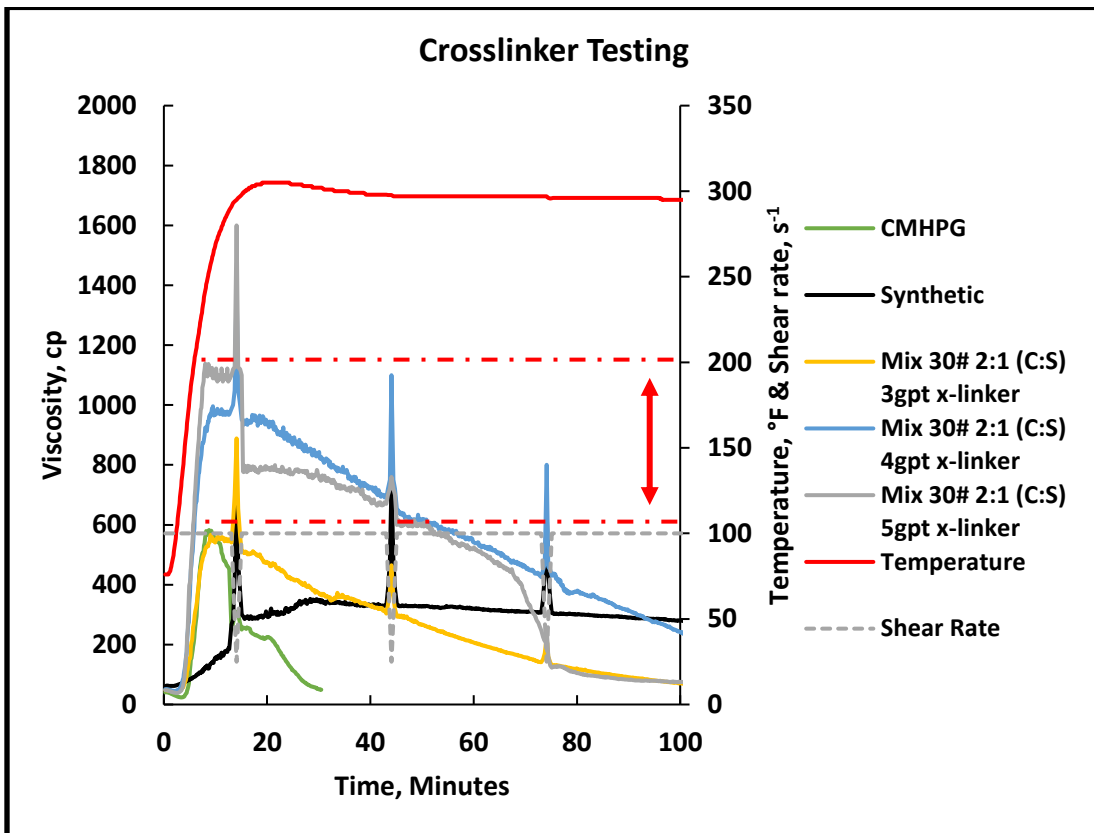
Fig. 25 - Measured viscosity of 30 lb/ 1,000 gal 2:1 (CMHPG: Synthetic) mixed polymer with 3-5 gpt crosslinker at pH 5 and 300°F.

Fig. 26 compares the 1:1 (CMHPG: Synthetic) crosslinked fluid performance at 20, 30 and 40 lb/1,000 gal. One important observation is that the 30 lb/1,000 gal viscosity surpasses the 40 lb/1,000 gal viscosity performance. The improvement is due to the 30 lb/1,000 gal mixture having a higher crosslinker to polymer ratio than the 40 lb/1,000 gal. The influence of crosslink to polymer ratio is highly related to the content of synthetic polymer in the mixtures. As seen previously (**Figs. 17 and 18**), synthetic polymer can handle higher crosslinker concentrations than CMHPG.
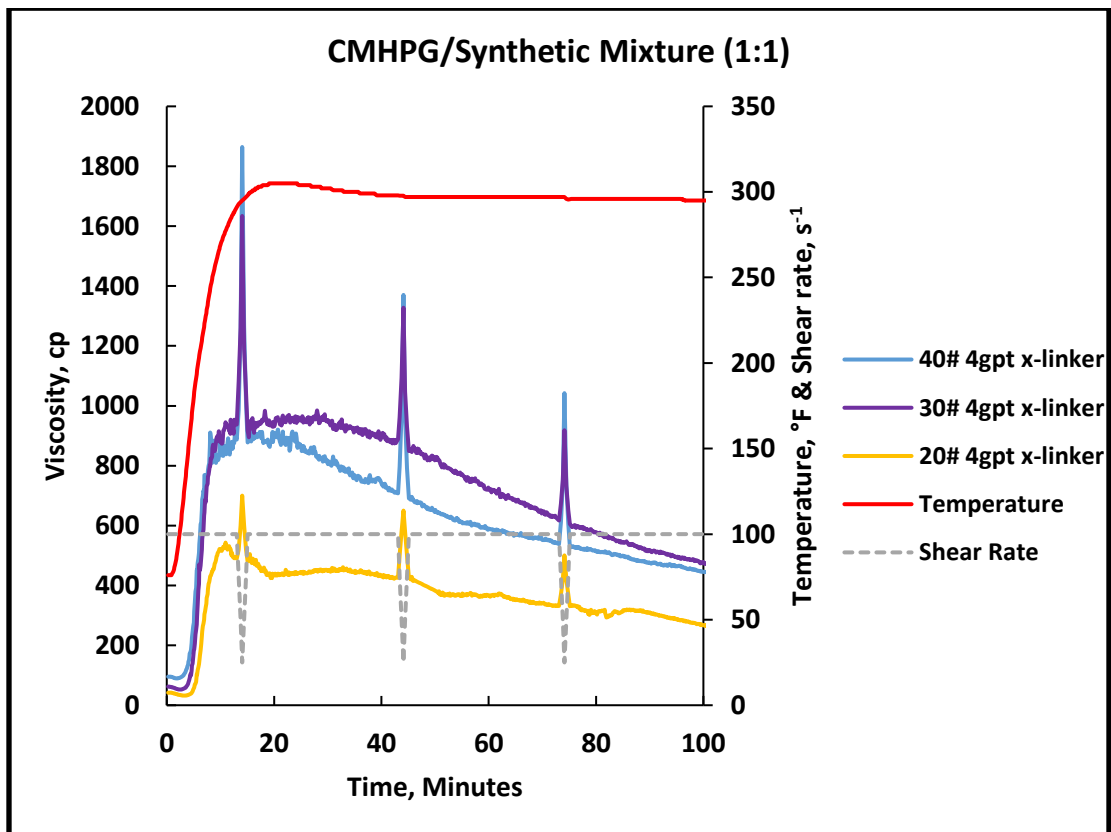
Fig. 26 – Measured viscosity of 20, 30, and 40 lb/ 1,000 gal 1:1 (CMHPG: Synthetic) mixed polymer with 4 gpt crosslinker at pH 5 and 300°F.

Fig. 27 compares the 1:2 mixed polymer ratio across all loadings. The figure indicates that if the crosslinker to polymer ratio is properly adjusted, the 20 lb/ 1,000 gal

can perform as well as the 30 and 40 lb/1,000 gal mixed polymer systems at 300°F. Lowering polymer loading is the main benefit of using polymer mixtures. It can reduce cost, ease operation and reduce damage to the fracture face, proppant pack and inside the formation.
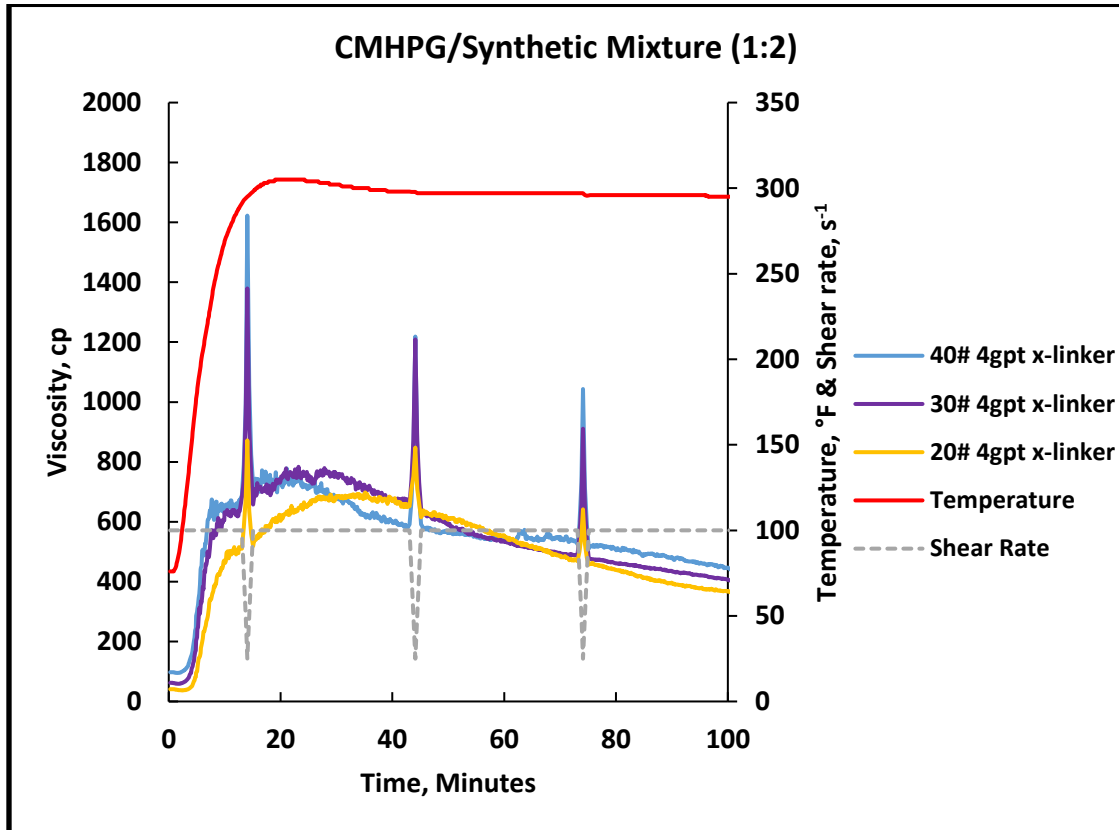
Fig. 27 - Measured viscosity of 20, 30, and 40 lb/ 1,000 gal 1:2 (CMHPG: Synthetic) mixed polymer with 4 gpt crosslinker at pH 5 and 300°F.

4.6 Elastic and Viscous Modulus

Elastic and viscous modulus tests are conducted at 40 lb/1,000 gal with a ratio of 1:1 (CMHPG: Synthetic) to try to understand the properties that each polymer adds to the mix. **Fig. 28** shows the lip behavior of CMHPG, synthetic polymer, at a mixture of 1:1 (CMHPG: Synthetic). The fluids are mixed with 4 gpt crosslinker and heated to 300°F for

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1 hour to ensure complete crosslinking. The figure shows that CMHPG is highly viscous, and can lip very easily with good elastic and viscous visual performance. On the contrary, synthetic polymer is not able to hold a good lip but looks very elastic. The polymer mixture fluid combined properties from both CMHPG and synthetic polymer. It holds a good lip, with excellent visual viscous and elastic performance.
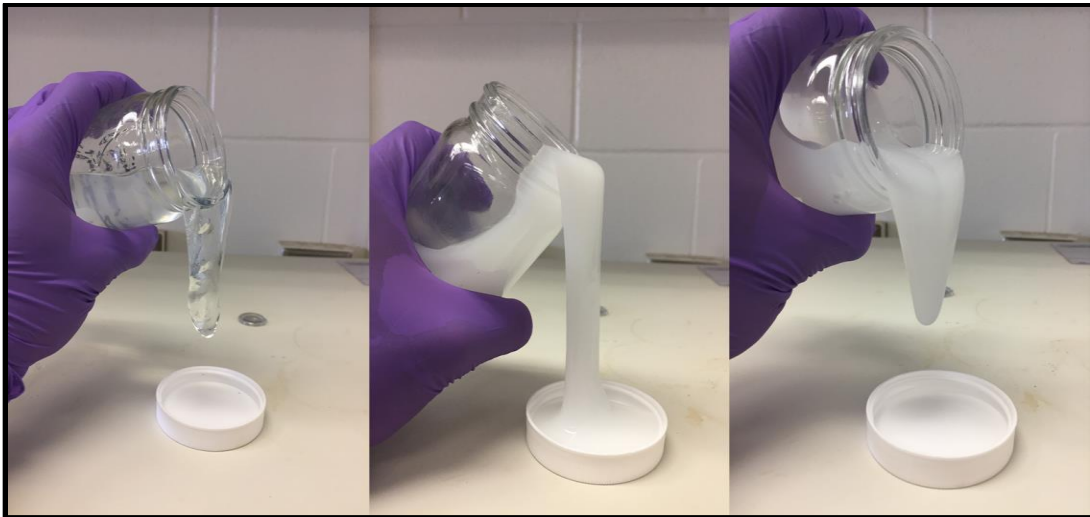
Fig. 28 – 40 lb/1,000 gal CMHPG (left), Synthetic (middle), and 1:1 mix (right), all at 4 gpt crosslinker, heated for 1 hour at 300°F.

The elastic modulus represents the behavior of storing energy. The higher the value, the more energy the polymer can store. A constant G' trend can be related to the formation of the 3D polymer network that is well crosslinked and can suspend proppant fairly well. When the fluid is pumped at high shear rate, it can suspend proppant through high velocity. The important aspect of this study is to analyze low-frequency behavior, where the fluid is fairly static and has no external forces to help suspend the proppant. The fluid must have sufficient energy stored to keep the crosslinked network strong and keep the proppant suspended. The higher the crosslinking density, the higher the elastic

modulus. Therefore polymer loading and crosslinker concentration can have great influence on these properties.

     Fig. 29 shows both the viscous and elastic modulus results for crosslinked 40 lb/1,000 gal CMHPG, synthetic, and 1:1 mix (CMHPG: Synthetic). The elastic behavior of CMHPG is not stable; the values oscillate as the frequency increases. This supports the unstable behavior of crosslinked CMHPG. The elastic behavior of synthetic polymer is more stable and increases as frequency increases. This trend is common because the polymers do not have time to lose the stored energy at high frequency.
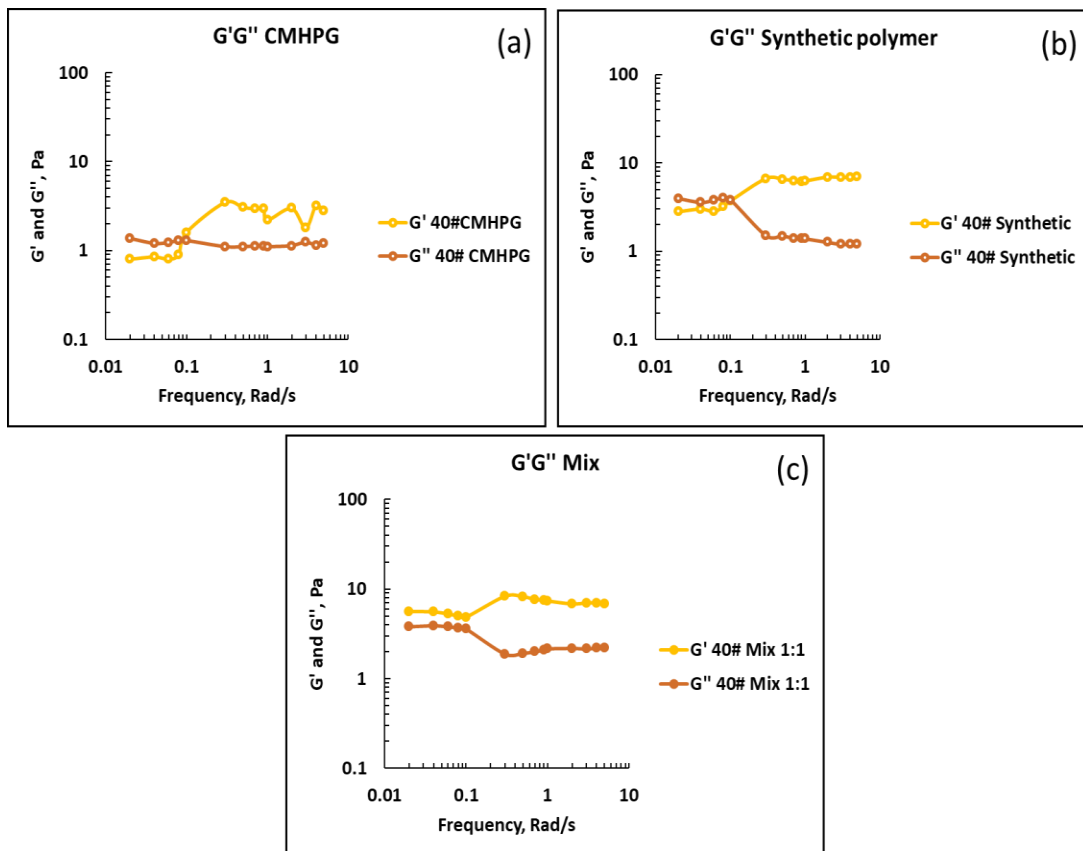
Fig. 29 – G' and G'' measurement of 40 lb/1,000 gal CMHPG (a), Synthetic (b) and 1:1 polymer mix (c), with 4 gpt crosslinker at pH 5 and 300°F.

The viscous modulus represents the ability of polymers to lose energy and deform. It decreases with higher frequency because the polymers do not have time to lose the energy and relax back to the original state. The intersection of G' and G'' is interpreted as the point where proppant will settle. The smaller the intersection frequency, the longer the time it will take for proppant to settle. The 40 lb/1,000 gal mixture fracturing fluid shows good modulus properties, with a dominant and high elastic region throughout the low-frequency range. These properties show good proppant suspension at 40 lb/1,000 gal.

Fig. 30 shows both the viscous and elastic modulus results for crosslinked 30 lb/1,000 gal CMHPG, synthetic, and 1:1 mix (CMHPG: Synthetic). The elastic behavior of CMHPG is high, not stable, and the values still oscillate with large variation as the frequency increases. This instability indicates the possibility of over-crosslinking CMHPG. Similarly to the 40 lb/1,000 gal (**Fig. 29**), the elastic behavior of 30 lb/1,000 gal synthetic polymer is more stable than CMHPG, and the modulus increases as frequency increases.
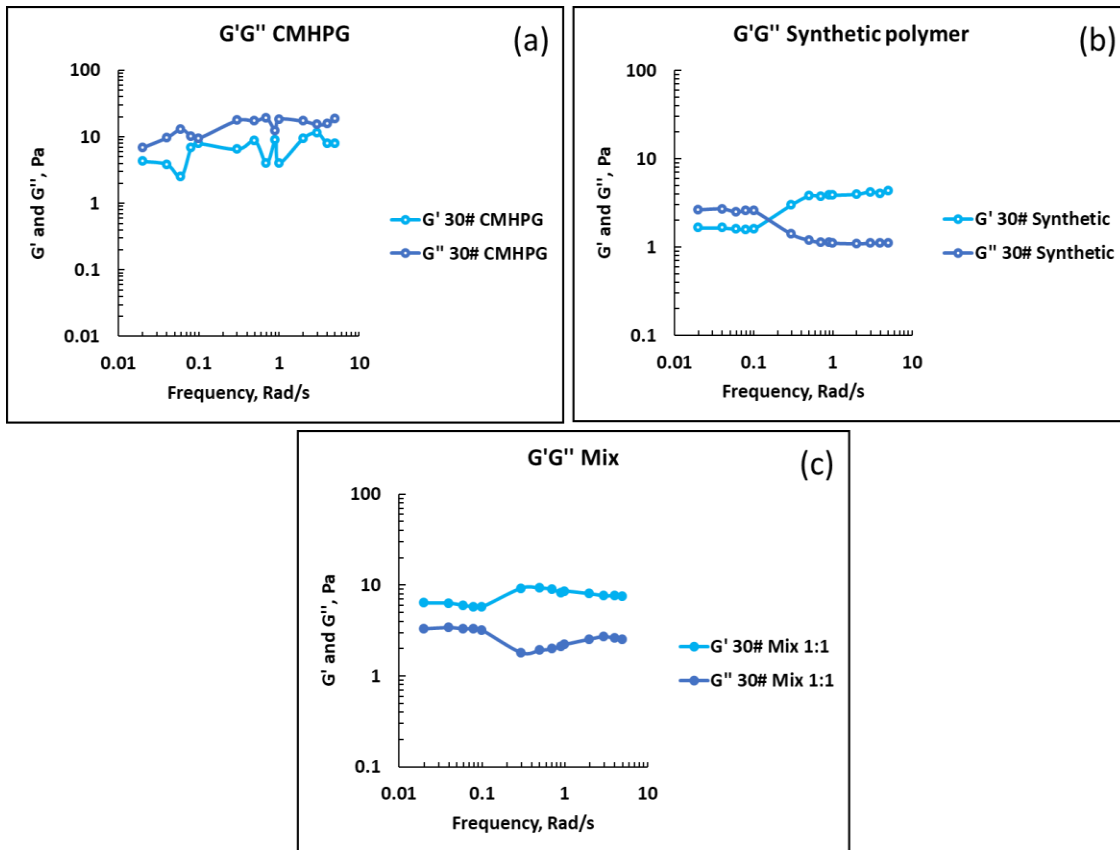
Fig. 30 - G' and G'' measurement of 30 lb/1,000 gal CMHPG (a), Synthetic (b) and 1:1 polymer mix (c), with 4 gpt crosslinker at pH 5 and 300°F.

The viscous modulus is dominant in 30 lb/1,000 gal crosslinked CMHPG, which does not promote good proppant suspension properties. This can also be an indication of over-crosslinking, and that the fluid tends to dissipate energy and irreversibly deform. The 30 lb/1,000 gal mixture fracturing fluid shows the best synergy regarding elastic and viscous properties. The mix exhibits higher modulus properties than the 40 lb/1,000 gal. This is due to having a higher crosslinker to polymer ratio, which allows for excellent proppant suspension.

Fig. 31 shows both the viscous and elastic modulus results for crosslinked 20 lb/1,000 gal CMHPG, synthetic, and 1:1 mix (CMHPG: Synthetic). The elastic behavior of CMHPG is also not stable; the viscous modulus is dominant in this frequency range. This trend indicates the possibility of over-crosslinking CMHPG. On the other hand, the elastic behavior of 20 lb/1,000 gal crosslinked synthetic polymer is more stable and dominant throughout the frequency range. This is due to the high crosslinker to polymer ratio.
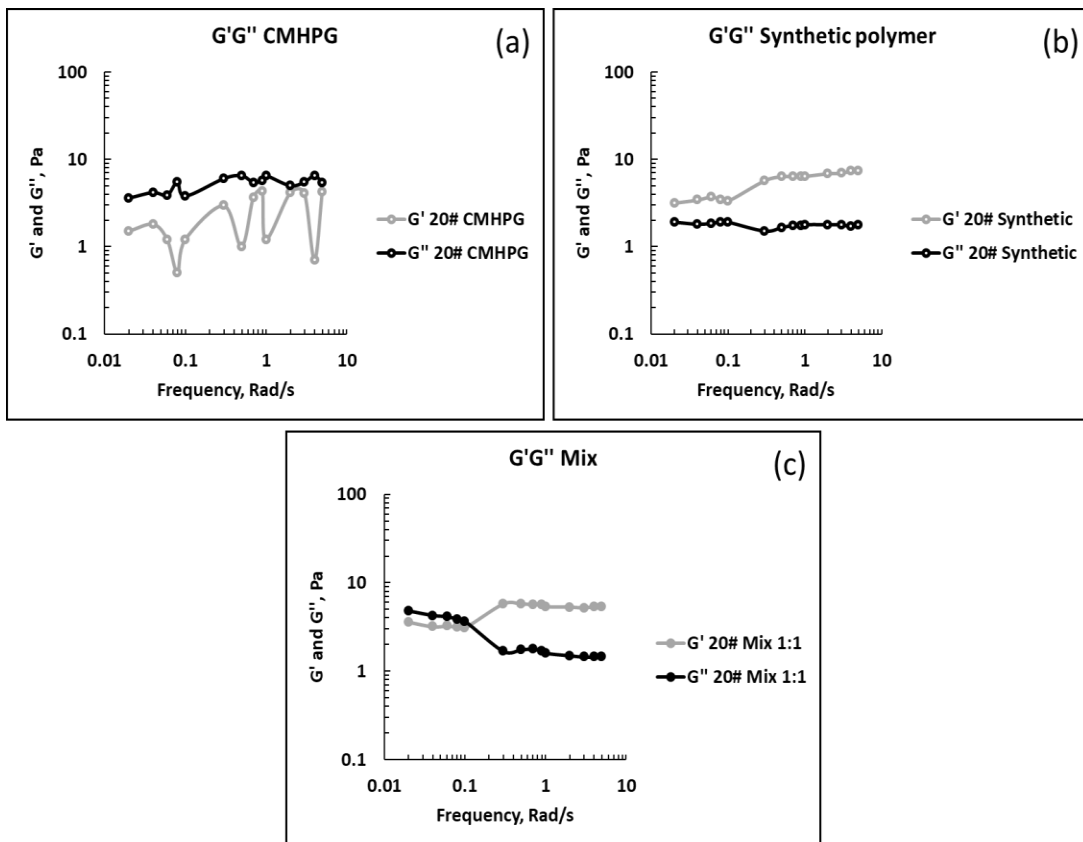
Fig. 31 - G' and G'' measurement of 20 lb/1,000 gal CMHPG (a), Synthetic and 1:1 polymer mix with 4 gpt crosslinker at pH 5 and 300°F.

The 20 lb/1,000 gal mixture at this ratio is weaker than crosslinked synthetic polymer individually. The crossover point did not occur in the individual synthetic polymer system, and it remained in the elastic region for the tested frequency sweep. However, the crossover point between G' and G'' clearly occurs in the polymer mixture results. Maintaining good crosslinking density is difficult with CMHPG at 20 lb/1,000 gal loading. The polymer concentration is low, and it is particularly hard to overlap the polymer sites when the molecular weight of CMHPG is low compared to the synthetic polymer. For this case, CMHPG will face difficulties crosslinking, and this will not promote a good crosslinking network, which results in a lower storage modulus compared to the individual system. Increasing the ratio of synthetic polymer in the mix can generate a higher viscosity at this loading.

Fig. 32 compares the elastic modulus measurements for 20, 30 and 40 lb/1,000 gal crosslinked CMHPG at 300°F. The graph shows that the elastic modulus, in general, is not stable, which is an indication of an unstable crosslinked structure. The unstable crosslinked structure could be due to over-crosslinking. The graph shows that CMHPG has a high elastic modulus at 30 lb/1,000 gal compared to 20 and 40 lb/1,000 gal. This is because it has a high crosslinker to polymer ratio, indicating a high crosslinked polymer density. CMHPG at 20 lb/1,000 gal does not perform as well as the 30 lb/1,000 gal case even though it has a higher crosslinker to polymer ratio. This is because of the low polymer loading. The low loading prevents the system from optimally overlapping and crosslinking as in the 30 lb/1,000 gal case. The 40 lb/1,000 gal shows the least crosslinker to polymer ratio and still performs well regarding elastic modulus. This is because of the higher

polymer loading that promotes overlapping of polymer in solution, which enables the fluid to achieve a strong crosslinking network with low crosslinker concentration.
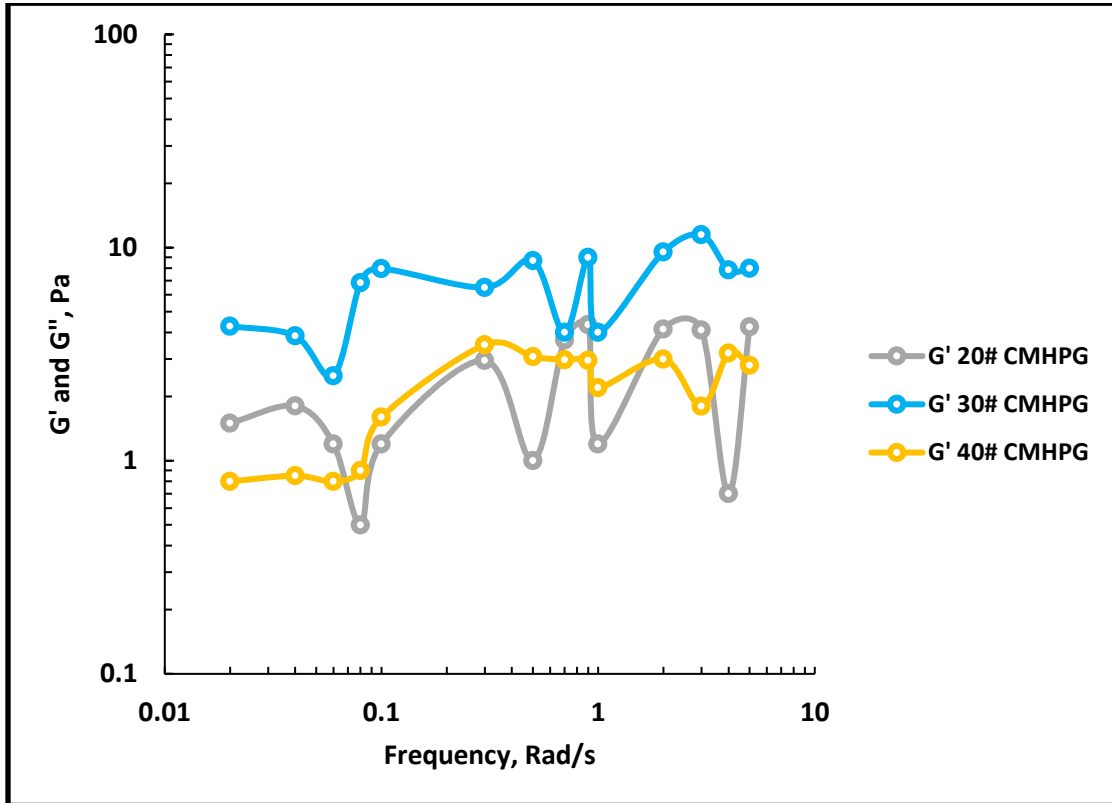
Fig. 32 – Measured elastic modulus of 20, 30 and 40 lb/1,000 gal CMHPG with 4 gpt crosslinker at pH 5 and 300°F.

Fig. 33 compares the elastic modulus of 20, 30 and 40 lb/1,000 gal crosslinked synthetic polymer at 300°F. The graph shows that the elastic modulus, in general, is very stable, which is an indication of a strong 3D crosslinked structure. The graph shows that synthetic polymer has a high elastic modulus at 20 and 40 lb/1,000 gal compared to the 30 lb/1,000 gal case. From the previous discussion, synthetic polymer shows the capability to handle more crosslinker concentration than CMHPG, and works best at higher concentrations. Also, the synthetic polymer is much higher in molecular weight than

CMHPG, allowing the polymer to sufficiently overlap and crosslink at low polymer loadings. Consequently, at 20 lb/1,000 gal, it has a high crosslinker to polymer ratio, indicating a high elasticity and good crosslinking density. Despite the higher crosslinker to polymer ratio at 30 lb/1,000 gal compared to 40 lb/1,000 gal, the elastic modulus at 40 lb/1,000 gal achieves higher values. This is because, at a higher loading, the polymer entangles very well, as seen from the viscosity measurements in the polymer hydration in an earlier section **(Fig. 14)**. The complex entanglement enables the polymer to form a strong crosslinking network with less crosslinker concentration, outperforming the 30 lb/1,000 gal fluid in proppant suspension capabilities.
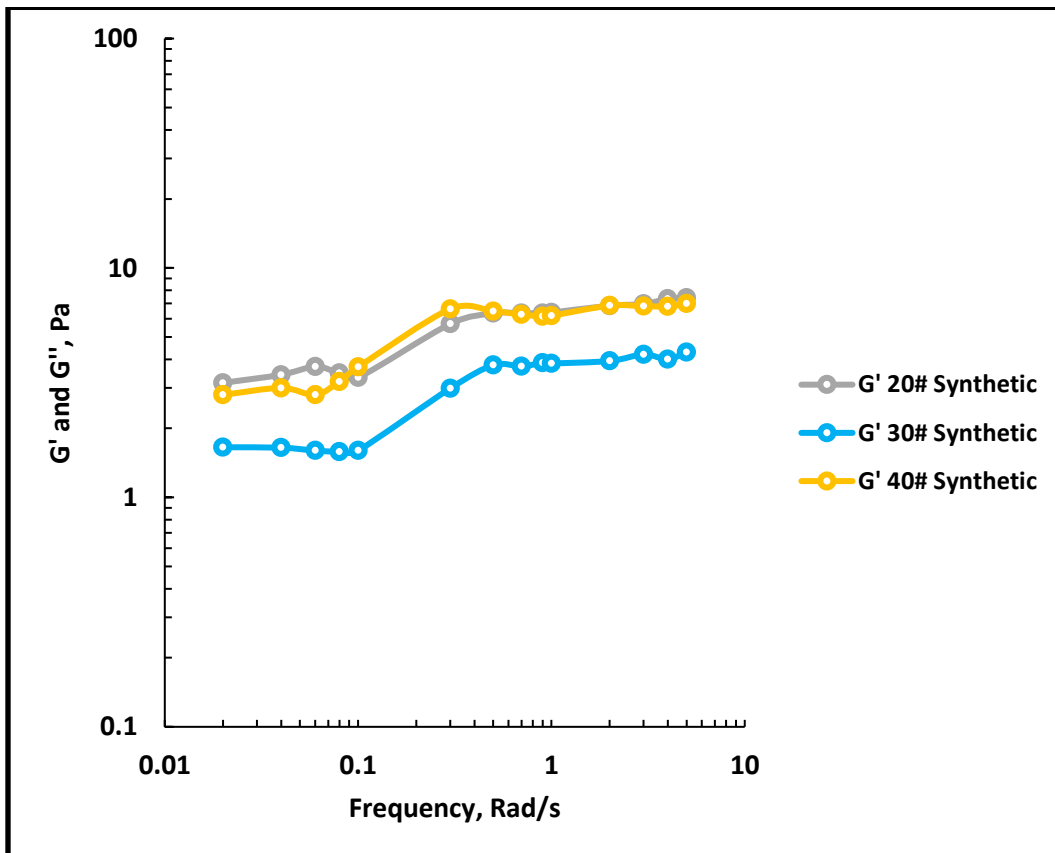
Fig. 33 - Measured elastic modulus of 20, 30 and 40 lb/1,000 gal synthetic polymer with 4 gpt crosslinker at pH 5 and 300°F.

After considering this detailed analysis, we attempt to explain the results (**Fig. 9 and 10**). **Fig. 9 and 10** compare the elastic and viscous modulus of 20, 30 and 40 lb/1,000 gal crosslinked polymer mix 1:1 (CMHPG: Synthetic) at 300°F. **Fig. 9** shows that the elastic modulus, in general, is very stable, which is an indication of the strong 3D crosslinked network that can carry proppant effectively. **Fig. 9 and 10** show that the elastic and viscous modulus at 30 lb/1,000 gal surpasses that for the 20 and 40 lb/1,000 gal cases. This is because of the synergy and proper crosslinker to polymer ratio when both CMHPG and synthetic polymer crosslink in one fluid. The 20 lb/1,000 gal mixture did not perform as well due to the low molecular weight of CMHPG, which prevents sufficient entanglement and results in less crosslinking density. The 40 lb/1,000 gal performs well and can be improved by adding more crosslinker concentration to enhance the crosslinking density and proppant carrying performance.

4.7 Proppant Settling

Proppant settling tests were conducted on 40 lb/1,000 gal polymer mixtures (2:1, 1:1, and 1:2). Polymer mixture fluids were crosslinked at high temperature utilizing the HP/HT aging cell for 1 hour, then loaded with 4 ppt 40/70 mesh Ottawa proppant and tested at both room temperature and high temperature. All polymer mixtures at 40 lb/1,000 gal can suspend proppant successfully at room temperature. This is due to the high elasticity and strong 3D crosslinked network that forms. **Fig. 34** shows proppant settling test for a mixture of 1:1 (CMHPG: Synthetic) at room temperature. The fluid can carry and suspend proppant for over 24 hours at these conditions. A similar behavior occurred with the 2:1 and 1:2 mixtures at these conditions. The tests do not include breakers, and

the fluids are highly viscous with a strong and stable network between the polymers. These properties allow for excellent proppant suspension for long periods of time.

Fig. 34 – Stable proppant suspension of 40 lb/1,000 gal polymer mix 1:1 with 4 gpt crosslinker at pH 5 and 77°F for 24 hours.

Results at room temperature might not perform the same way at high temperature. The HP/HT see-through cell is one way to visualize proppant suspension at high-temperature conditions. The problem with this type of test is visibility. It is very easy to misread the data, especially if a spill occurs inside the cell and stains the glass. Also, this type of proppant test is static and not fully representative of the dynamic behavior downhole.

Fig. 35 shows the 40 lb/1,000 gal polymer mix 2:1, 1:1, and 1:2 (CMHPG: Synthetic) HP/HT see-through cell test results for 2 hour at 300°F. At high temperature, 40 lb/1,000 gal mixtures are very stable, especially under static conditions. All polymer mixtures can suspend over 90% of the proppant at these conditions. This is due to the

highly elastic nature and strong polymer network that forms when the polymer mixture fluids crosslink.
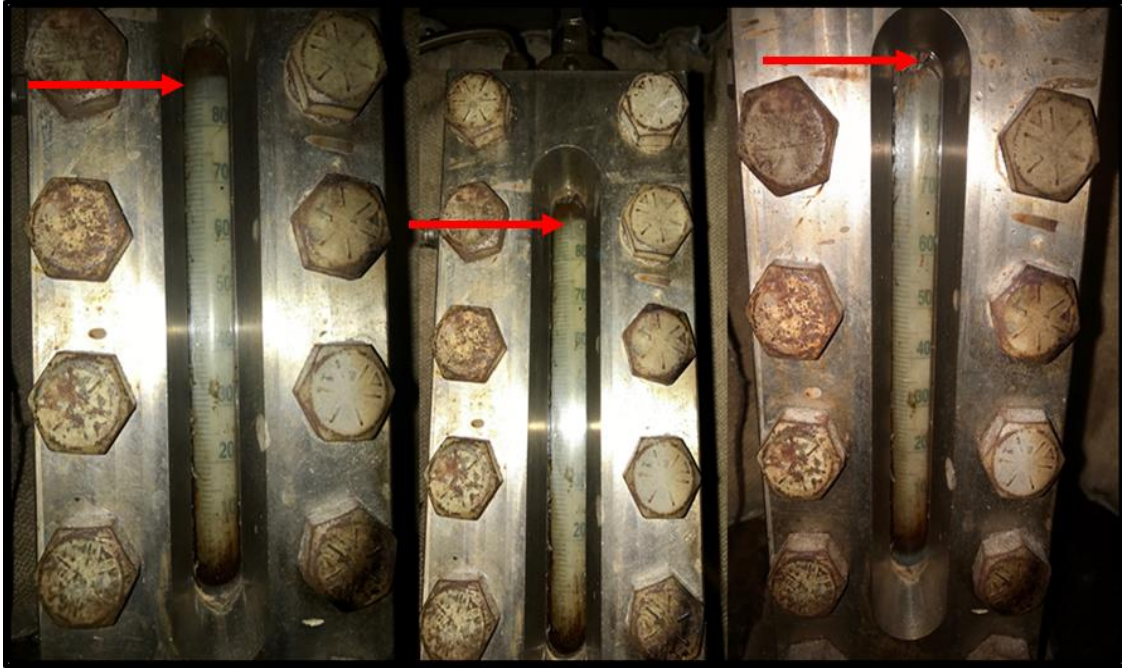
Fig. 35 – Proppant settling of 40 lb/1,000 gal polymer mix (left to right) 2:1, 1:1, and 1:2 (CMHPG: Synthetic) with 4 gpt crosslinker at pH 5 and 300°F for 2 hours.

4.8 Breaking

It is important to control the viscosity of fracturing fluids during field operation. At surface pumping conditions, low viscosity is desired to ease pumping requirements. At 50% to 80% in the tubular, it is desired to crosslink the fluid to generate enough pressure to fracture the rock and to build sufficient viscosity to carry proppant into the fracture preventing a screen-out. At the end of the treatment, the crosslinked polymers need to break to enable flow back. If the fluid does not break completely, it will damage the proppant pack and plug the fracture surface. This will ultimately cause damage to the formation and loss in expected production rates.

Common breakers include salts of persulfates and bromates. At high temperature, some oxidizers can have high reactivity with polymers, which can cause early screen-out of proppant. At 300°F, persulfate oxidizers are extremely reactive, whereas bromate oxidizers are slowly activated. Therefore, bromate would yield a more controlled operation. Because of the low reactivity, higher concentration of bromate are sometimes used to ensure complete break of crosslinked systems. However, large quantities of oxidizers are explosive, so care must be taken to handle them properly in the field.

The polymer mixture breaker tests utilized a HP/HT viscometer and a HP/HT aging cell. The viscometer results show that 40 lb/1,000 gal 1:1 and 2:1 (CMHPG: Synthetic) crosslinked fluid can break to viscosities below 20 cp within 2 hours using the sodium bromate breaker. The fluid came out with a light brown color, and clear with no visible polymer chunks. This visual observation gives a quick indication that the fluid is not severely damaging to the formation. A more in-depth test utilizing core-flooding, fracturing conductivity, and gel permeation chromatography (GPC) measurements is required to understand the impact of the residual broken polymer properly.

A HP/HT aging cell is used to analyze the breaking of the polymer mixture further. It should be noted that breaking the polymer is much easier under a continuous shear environment. However, after the fracturing fluid initiates the fracture and starts propagating, the shear rate is reduced dramatically. The aging cell test is an evaluation of fluid breaking under the worst conditions.

The prepared fluids consisted of 40 lb/1,000 CMHPG, Synthetic and 1:1 (CMHPG: Synthetic) mixture. All samples were mixed with 4 gpt crosslinker and 10 ppt

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sodium bromate oxidizer. **Fig. 36** shows the prepared fracturing fluids initially at 77°F.

Fig. 37 and **Fig. 38** show the final fluids after aging for 24 hours and 72 hours respectively.

Fig. 36 – (Left) 40 lb/1,000 gal CMHPG, (Middle) 1:1 (CMHPG: Synthetic) polymer mix, (Right) Synthetic polymer, mixed with 10 ppt sodium bromate and 4 gpt crosslinker at pH 5 and 77°F, initial.

Fig. 37 – (Left) 40 lb/1,000 gal CMHPG, (Middle) 1:1 (CMHPG: Synthetic) polymer mix, (Right) Synthetic polymer, mixed with 10 ppt sodium bromate and 4 gpt crosslinker at pH 5 and 300°F for 24 hours.

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Fig. 38 – (Left) 40 lb/1,000 gal CMHPG, (Middle) 1:1 (CMHPG: Synthetic) polymer mix, (Right) Synthetic polymer, mixed with 10 ppt sodium bromate and 4 gpt crosslinker at pH 5 and 300°F for 72 hours.

The fracturing fluid samples are completely broken, and no chunks of polymer remain after 24 hours. However, dark brown discoloration is observed in both CMHPG and the 1:1 (CMHPG: Synthetic) mixture. The other set of samples are aged for 72 hours. In this batch, the discoloration is present in all samples and is much darker. The discoloration can be due to a negative interaction between the breaker and the polymers. Additionally, it could be due to excess breaker, **Eq. (1) and (2):**

$$NaBrO_3 \rightarrow NaBr + \frac{3}{2}O_2 \qquad\qquad [Br^-_{(aq)} = Clear] \text{ .... (1)}$$

$$BrO_3^- + 5Br^- + 6H^+ \rightarrow 3Br_2 + 3H_2O \qquad\qquad [Br_{2(l)} = Red/brown] \text{ .... (2)}$$

The breaker used is sodium bromate, which can turn to bromine through side reactions. These reactions can be autocatalytic resulting in higher concentrations of

bromine as time progresses. Bromine is light red/brown at low concentrations, and dark red to dark brown at higher concentrations. **Fig. 39** shows a similar observation from the literature, where dark red discoloration is observed when 5 ppt sodium bromate oxidizer was used at 300°F for 24 hours. The dark discoloration was not found in any other oxidizer used at these conditions.

Fig. 39 – Influence of Breakers, (left to right) enzyme, chlorous acid, sodium bromate, and sodium persulfate with 40 lb/1000 gal CMHPG at 300°F for 24 hours (Almubarak et al. 2015).

To confirm the presence of bromine, samples of the dark-colored broken fluids were taken from the 72 hour tests and sodium thiosulfate added to them, **Eq. (3).** The solutions turned clear, **Fig. 40**. This indicates that the discoloration is indeed bromine.

$$Na_2S_2O_3 + 4Br_2 + 5H_2O \rightarrow Na_2SO_4 + H_2SO_4 + 8HBr \qquad [Br^-_{(aq)} = Clear] .... (3)$$
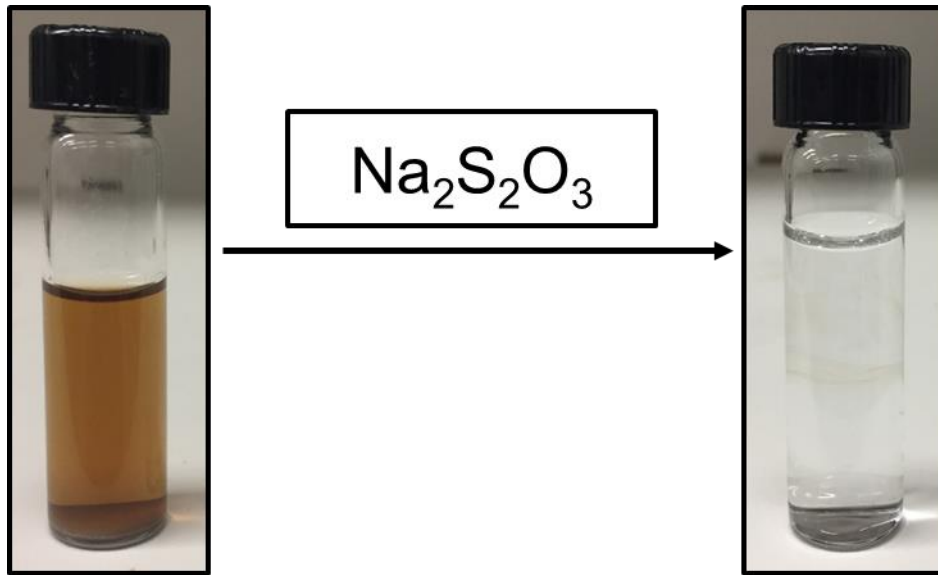
Fig. 40- Confirming the presence of bromine through the addition of sodium thiosulfate.

4.9 Limitations

Based on the previously discussed 40 lb/1,000 gal tests, it was determined that a 5 gpt crosslinker concentration surpasses the performance of 4 gpt crosslinker at a ratio of 2:1 (CMHPG: Synthetic). **Fig. 41** shows the performance of all polymer ratios at 40 lb/1,000 mixed polymers crosslinked fluid at 5 gpt crosslinker concentration. The results show best performance and thermal stability at a ratio of 1:1 (CMHPG: Synthetic).
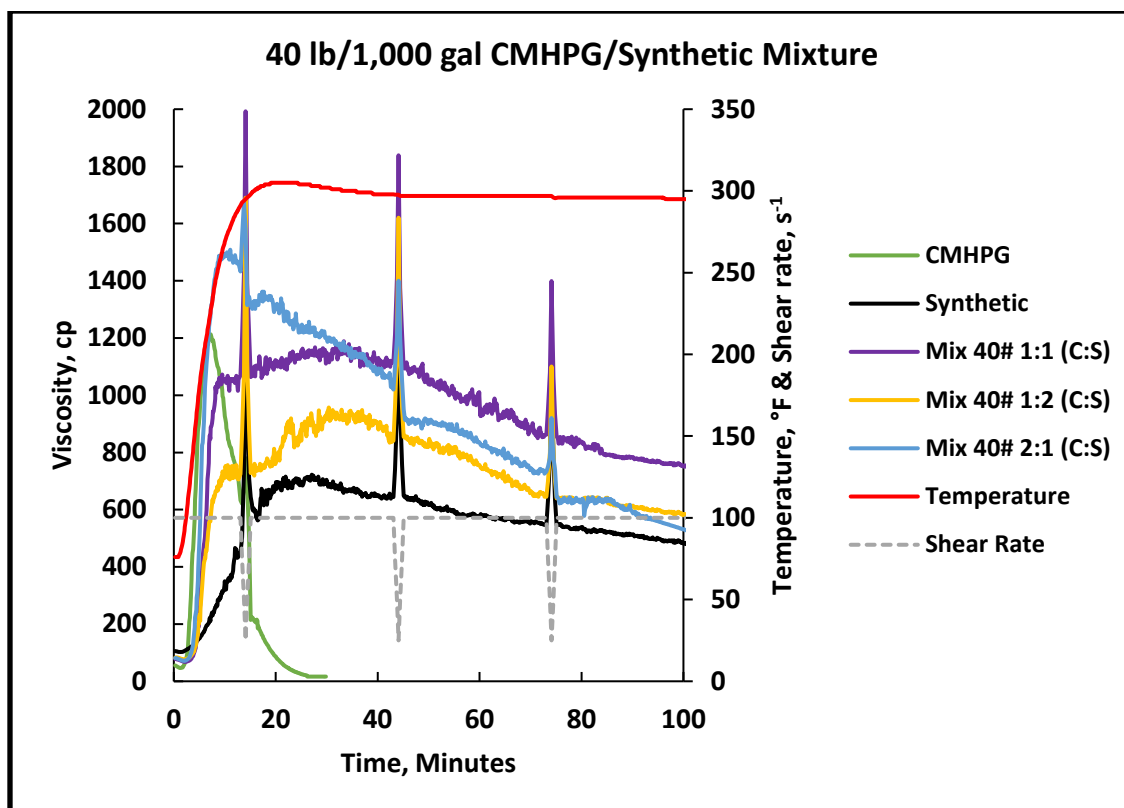
Fig. 41 – Measured viscosity of 40 lb/1,000 gal mixed polymer with 5 gpt crosslinker at pH 5 and 300°F.

The 1:1 (CMHPG: Synthetic) polymer mixture underwent more testing to determine the behavior at extremely high-temperature conditions (400°F). **Fig. 42** shows that the fluid lost viscosity rapidly as soon as the temperature reached 350-375°F. As mentioned previously, an AMPS containing synthetic polymer can enhance thermal stability by repelling oxygen away from the mixed polymer structure. However, the major thermal weakness at this temperature is the polymer itself. At 400°F, CMHPG cooks, and the glycosidic bonds between the CMHPG monomers reach the thermal limit and rapidly break. This break completely collapses the 3D network, and the remaining synthetic polymer (at 20 lb/1,000 gal) is unable to maintain a stable viscosity. Also, the initial high

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peak in viscosity can be attributed to the zirconium ligand rapid release of zirconium ions. This is due to the higher preheating settings for the 400°F high-temperature test. The rapid release of crosslinker hinders performance due to uncontrolled crosslinking rate and rapid shearing of the fluid. Each crosslinker has a thermal limit, and choosing the appropriate ligand is important for the release rate of zirconium which ultimately controls the shear performance.
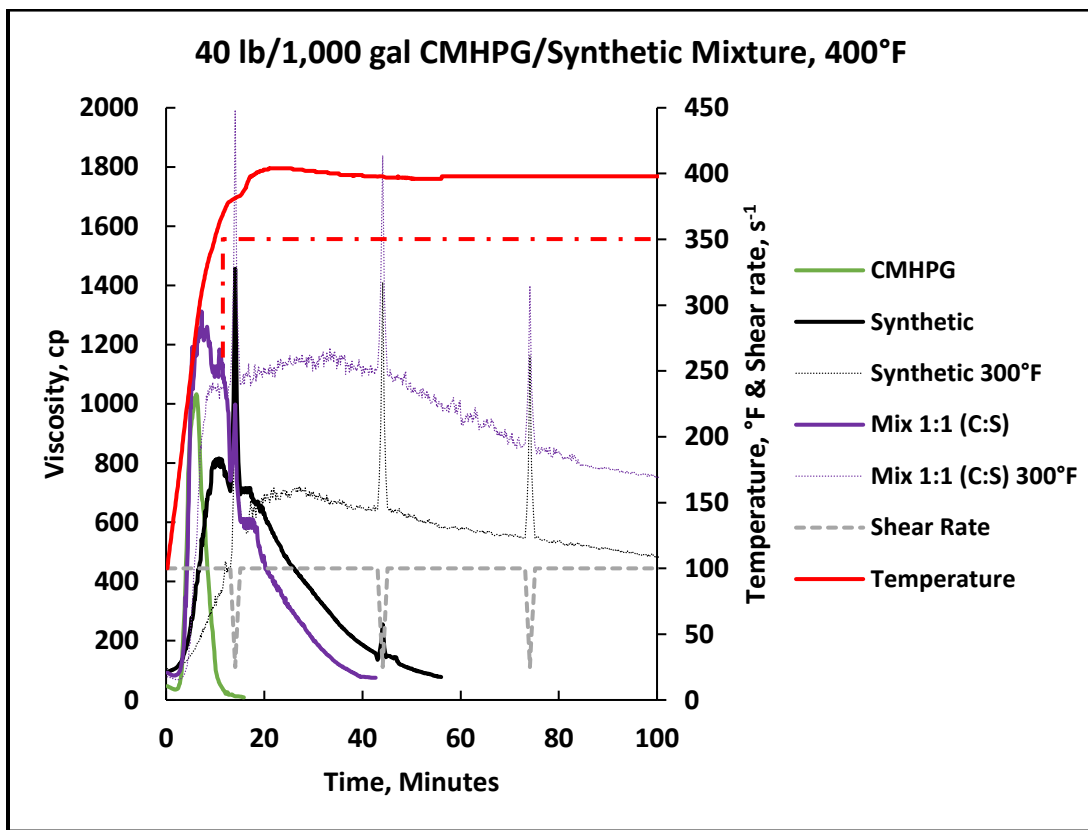
Fig. 42 - Measured viscosity of 40 lb/1,000 gal mixed polymer with 5 gpt crosslinker at pH 5 and 400°F.

CMHPG is relatively functional at high salt concentrations. Also, a synthetic polymer containing AMPS monomer is capable of handling slightly salty water. The next test is to determine the influence of high TDS water on the polymer synergy. **Fig. 43**

depicts the viscosity of crosslinked 40 lb/1,000 gal polymer mixture prepared in synthetic seawater. The synthetic seawater prepared is identical in salt concentration to raw untreated Arabian Gulf seawater.
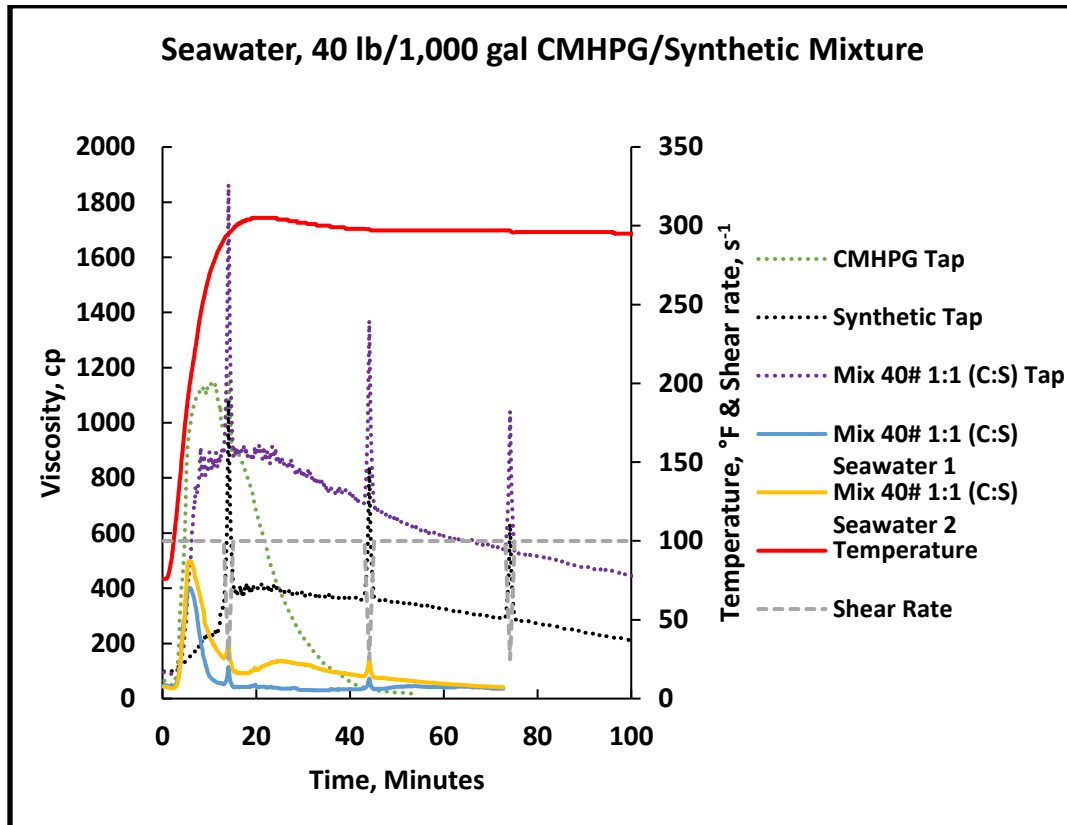
Fig. 43 - Measured viscosity of 40 lb/1,000 gal mixed polymer in seawater with 4 gpt crosslinker at pH 5 and 300°F.

The main concern of this polymer mixture is during the hydration of the polymers. Although CMHPG took a long time to hydrate, it can fully hydrate in synthetic seawater. On the contrary, during the preparation of the synthetic polymer fluid, the polymer coiled and could not hydrate (no visual viscosity increase) due to the high salt content. This prevented the usual preparation method (denoted as seawater 1). A different preparation method was performed (denoted as seawater 2), where CMHPG is fully hydrated, and the

appropriate concentration of synthetic polymer was directly added to the hydrated CMHPG in the mixer. A comparison between the seawater 1 and 2 preparation results is shown in **Fig. 43**. Overall, the synthetic polymers containing acrylic acid side groups are weak against salts. A Higher concentration of AMPS or a different monomer with higher salt resistance must be used to tackle this problem. Unfortunately, the higher concentration of specialty monomers will ultimately raise the cost of this synthetic polymer.

5. FUTURE WORK

This work identified several topics of interest that could be further studied. Work is currently undergoing to determine the nature of synthetic and biopolymer synergy. When the synergy is properly characterized and understood, other polymer mixtures can be developed for applications that require specific properties such as high shear, lower loading, low friction or high salt tolerance.

Unfortunately, high-temperature stabilizers were not tested enough in this work. High-temperature stabilizers are frequently used in the field and are not well understood by operators. There are many recent advances in high-temperature stabilizers. Knowing the different mechanisms to stabilize fluids can help develop more cost-effective recipes.

Moreover, zirconium crosslinkers used in this study were screened in a basic fashion and identified huge differences in performance. A more thorough crosslinker study can help us understand these differences.

AMPS monomer is the most common monomer used in saltwater applications. However, it is expensive, and more work can be done on monomer selection. Specifically, to find cheaper monomers that add salt resistance without hindering the polymer crosslinking ability.

Furthermore, many synthetic polymers with the same monomer composition were screened in this study. It was noted that even though they contain the same monomer composition, the monomer orientation highly influences the delay properties and crosslinking ability. That is why a systematic study of synthetic polymer composition would be beneficial.

Also, breakers were briefly tested and noted discoloration in many samples. An explanation was attempted and was confirmed by previous work on oxidizers. Understanding the breaker-polymer interactions can shed more light on these observations.

Last, although polyacrylamide based synthetic polymers are cheap and perform well, it would be appreciated by the industry to test synthetic polymers that are safer than acrylamide-based polymers. Acrylamide monomers still exist post polymerization, and these monomers are hazardous and can cause illness to the body.

6. SUMMARY AND CONCLUSIONS

CMHPG and synthetic polymer mixtures were extensively tested through viscometry and show enhancement in fracturing fluid properties due to positive interactions between the two polymers. The fortunate event of finding a similar crosslinking pH between the two polymers allows for clear observation of this interaction. The major benefits of this polymer mixture are to enhance thermal stability and lower polymer loading, which potentially reduces material cost, eases field applications, and reduces damage to the formation.

Based on the laboratory results we conclude the following:

- Lower loading can be achieved through polymer synergy.

- Synthetic polymer enhances thermal stability, while CMHPG increases peak viscosity limits of the mix.

- The synergy between synthetic polyacrylamide polymers and CMHPG can be extended to other polymers with a polysaccharide backbone such as guar and HPG.

- The nature of the synergy is obvious at low pH, although it remains applicable at high pH.

- The synergy is not limited to crosslinked fluids; and may also apply to slickwater fracturing, EOR, and drilling fluids.

- Synthetic polymer performance can be very sensitive to composition and polymerization method, QA/QC must be carefully followed.

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