

SYNTHESIS AND CHARACTERIZATION OF SELF-BREAKING TEMPORARY GEL-
POLY(VINYL ALCOHOL)-SUCCINIC ACID WITH CHROMIUM (III) CROSSLINKER AS
A NOVEL HYDRAULIC FRACTURING FLUID

A Thesis

by

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MASTER OF SCIENCE

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ABSTRACT

Hydraulic fracturing is high pressure injection of fracturing fluid, in order to hydraulically crack open the rock in the area around the wellbore. The fracturing fluid used enters the created fractures and essentially propagates fractures away from the wellbore when fluid pressure is greater than the fracture pressure. Hydraulic fracturing fluids must include thickeners to increase its viscosity, and breakers that degrade consequential fracturing fluid and filter cake on fracture faces in order to avoid formation damage and regain fracture conductivity.

The purpose of this research is to detail the development of a self-breaking temporary polymer gel system as a hydraulic fracturing fluid, Poly(vinyl alcohol)-Succinic Acid (PVA-SA) + Cr³⁺, without addition of internal breakers. First, PVA-SA is synthesized by the reaction of PVA [poly(vinyl alcohol)] with SA (succinic anhydride) in Dimethylformamide (DMF), and then slightly crosslinked with N, N'-Dicyclohexylcarbodiimide (DCC), catalyzed by 4-Dimethylaminopyridine (DMAP) to produce PVA-SA-X; this is to increase its molecular weight, prior to being crosslinked with a Cr³⁺ crosslinker to produce PVA-SA-X gel. Second, PVA-SA and PVA-SA-X gel are characterized through rheological measurements, and analyzed for concentration change response, temperature change response, and shear change response. Both PVA-SA and PVA-SA-X gel prove to be shear-thinning fluids capable of proppant suspendability and transport in conventional and unconventional hydraulic fracturing treatments, respectively, due to its elevated viscosity, and solid-like and water-like behavior. Finally, the degradation of PVA-SA-X and PVA-SA-X gel is tested without any internal breakers at different temperatures, proving that at high temperatures of 95°C, low concentrations of this polymer

system is capable of self-breaking, minimizing formation and proppant-pack damage, post-hydraulic fracture treatment.

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NOMENCLATURE

bpm	Barrels Per Minute
Cr[III], Cr ³⁺	Chromium (III) Crosslinker
DCC	N,N'-dicyclohexylcarbodiimide
DI	Deionized Water
DMAP	4-(Dimethyl amino)pyridine
DMF	N,N-Dimethylformamide
G'	Storage Modulus
G''	Loss Modulus
mL	Milliliter
MW	Molecular Weight
NaOH	Sodium Hydroxide
pH	Negative logarithm of the solution hydrogen ion activity
ppga	Pounds Per Gallon Added
ppm	Parts Per Million
pptg	Parts Per Thousand Gallon
PVA	Poly(vinyl alcohol)
PVA-SA	Poly(vinyl alcohol)-Succinic Acid
PVA-SA-X	Poly(vinyl alcohol)-Succinic Acid Crosslinked with DCC
PVA-SA-X Gel	Poly(vinyl alcohol)-Succinic Acid Crosslinked with DCC and Cr ³⁺ crosslinker
RPM	Rotations Per Minute

SA

Succinic Anhydride

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CHAPTER I

INTRODUCTION

The purpose of hydraulic fracturing is to stimulate production via networks of conductive fractures around the wellbore. With conductivity being proportional to both proppant-pack permeability and fracture width, hydraulic fracture stimulation aims to increase conductivity majorly via the latter variable (Davies & Kuiper, 1988). Ultimately, the hydrocarbon producing surface area is increased. Hydraulic fracturing can be performed in both vertical and horizontal wells, making undeveloped, tight, and unconventional reservoirs economically feasible (Barati & Liang, 2014). The first fracturing fluid type, used in the 1940s, was an oil-based fluid consisting of gelled hydrocarbons. The very first hydraulic fracturing process occurred in 1947, on the Hugoton field in Kansas (Clark, 1949). It was just a simple, vertical, 2-wing well fracture. Nowadays, one can perform multiple stages of hydraulic fractures. When oil-based fracturing fluids posed some environmental and safety concerns in the 1950s, more environmentally friendly water-based fracturing fluids were developed (Veatch, Moschovidis, & Fast, 1989). They proved to be cost effective and safe (Li, Al-Muntasheri, & Liang, 2016).

Components of a hydraulic fracturing fluid typically include thickeners, propping agents, and breakers. Other additives include friction reducers to reduce the friction generated as the fluid is pumped down the well tubulars, fluid loss additives to minimize leak-off in high permeable areas, scale inhibitors to prevent the formation of carbonate and sulfate scales, clay stabilizers to prevent fines migration or clay particle swelling when exposed to water-based fluids, and many more (Montgomery, 2013). These additives make up to 2% of the fracturing

fluid. They each serve a specific, engineered role, as they function to fulfill different purposes for different fracturing jobs, while maintaining the integrity of the fluid and formation.

1.1 Thickeners

Thickeners (or gelling agents) are responsible for increasing the viscosity of fracturing fluids in order to improve proppant transport, increase fracture width so it can accept higher proppant concentration, reduce fluid loss to improve fluid efficiency, and reduce friction pressure. They include guar and its derivatives, viscoelastic surfactants, and foams.

1.2 Guar and Its Derivatives

Guar, originally grown in India and Pakistan, is a natural, branched polysaccharide, used for fracturing. Its desirable rheological properties, economic feasibility, and hydration ease make it a favorable biopolymer in the oil and gas industry. Common guar derivatives include hydroxypropyl guar (HPG), carboxymethyl guar (CMG), and carboxymethyl hydroxypropyl guar (CMHPG), however, guar is the most common. Botanically known as *Cyamopsis tetragonoloba*, this natural galactomannan gum is of the legume family. In 2012, approximately 25,000 tons of guar was used per month at \$7.83/lb in the USA (Beckwith, 2012). Crosslinkers typically associated with guar include complexes of boron (B^{3+}), titanium (Ti^{4+}), and zirconium (Zr^{4+}), however, it is most stable with a sodium thiosulfate stabilizer (Walker, Shuchart, Yaritz, & Norman, 1995). The chemical structure of guar consists of a straight chain of D-mannose units, linked together by beta (1-4) glycoside linkages; almost every alternate mannose unit has a D-galactose unit, joined by an alpha (1-6) glycoside linkage (Chudzikowski, 1971). Guar can be readily crosslinked at the cis-hydroxyl groups and broken at the acetyl linkages. Once broken, however, guar leaves behind 6% - 10% insoluble residue, which can cause significant damage to

the formation and/or the proppant pack. In response, chemically modified guar was created to alter the molecular structure of guar and reduce this insoluble residue. HPG is a product of guar modified with propylene oxide, while CMP or CMHPG is guar modified with monochloroacetic acid. For extreme conditions such as harsh temperatures and high salinity, guar alternatives such as carboxymethylcellulose (CMC) and carboxymethylhydroxyethylcellulose (CMHEC) crosslinked with metal based agents are used. These polymers are typically transported to the field in dry powder form, which hydrate when mixed with an aqueous solution, forming a viscous gel. (Barati & Liang, 2014) (Walker, Shuchart, Yaritz, & Norman, 1995)

1.3 Viscoelastic Surfactants (VES)

Viscoelastic surfactants are polymer-free and sometimes, breaker-free solutions that decrease in viscosity with increasing shear rate, and leave minimal to no residue. VES consists of hydrophobic and hydrophilic groups that are arranged to shield non-polar groups. Their association of anionic, cationic, or zwitterionic surfactant molecules contribute to increased fluid viscosity (Smith & Montgomery, 2015). Viscosity increases via rod-like micelle-formation, with increasing concentration forming a mesh of entangled, rod-like micelles. These rod-like micelles are broken into smaller, spherical micelles when exposed to organic and hydrophobic fluids like oil and gas (Gandossi, 2013). Resultantly, breakers are not typically added to VES systems, however in some cases, internal breakers are added to improve fracture conductivity. Disadvantages include no wall-building characteristic, enabling a high fluid leak-off volume, higher cost, and lower stability at elevated temperatures. (Barati & Liang, 2014) (Gandossi, 2013) (Smith & Montgomery, 2015)

1.4 Foams

Foams are systems consisting of large gas fractions (carbon dioxide or nitrogen), surfactant (a foaming agent), and small volumetric water fractions. Mainly used in tight to ultra-tight formations containing high contents of clay, they reduce damage due to capillary pressure, permeability discontinuities, and invaded fluids (Barati & Liang, 2014). Advantages include limited amount of water invading the matrix, improved conductivity recovery, and minimal sensitive clay-related effects. Disadvantages include operationally handling gas onsite, increased costs, and associated energy losses due to friction when increasing pumping capacity and horsepower requirements (Edrisi & Kam, 2012).

1.5 Propping Agents

Proppants are propping agents usually applied to form a thin layer between fracture faces to prop open the fractures at the end of a fracturing job. Ideally, proppant characteristics include low density, high resistance to fracture compression, resistance to acid degradation, and the ability to maintain high formation permeability at the respective formation pressures. Proppants come in a wide range of sizes with densities ranging from nearly buoyant up to 1.75 g/cm^3 , and up to 2.59 g/cm^3 , for unconventional and conventional fracturing purposes, respectively (Liang, Sayed, Al-Muntasheri, Chang, & Li, 2016). The most common proppant used is ~85% proppant with 20/40 mesh. Other proppant types include high-strength such as sintered bauxite and zirconium oxide (which can withstand closure stresses up to 16,000 psi), intermediate-strength proppant (which can withstand closure stresses up to 10,000 psi) resin-coated sand, and ceramic proppant (Liang, Sayed, Al-Muntasheri, Chang, & Li, 2016).

Sintered bauxite spheres with silica are typical proppant materials, ranging from 0.02-0.3 microns in size. Coated proppant are used to prevent subsequent flow back. The coating usually contains a tackifying agent meant to glue the particles within the fracture when under pressure. Ceramic particle proppants have a density less than 2.2 g/cm^3 . Its outer shell can be composed of metal oxide, with an inner content of mineral particulates, silicon carbide, and binder. Proppants are transported into the fractures by fracturing fluids that also include polymers and gels. Research has shown that metal crosslinked fracture fluids have better proppant transport characteristics than non-crosslinked fluids. Slickwater, for example, have the least proppant transport efficiency which is why it requires high velocity (at least 60 bpm) to prevent proppant settling near wellbore or collecting at the fracture bottom, limiting its effective height. Slickwater typically contains 0.25-1 ppga of proppant. (Barati & Liang, 2014) (Fink, 2015) (Li, Al-Muntasheri, & Liang, 2016)

1.6 Breakers

Breakers are necessary to breakdown a solution's viscosity and molecular weight post-fracturing, to ensure that maximum well production can be achieved. Ideally, breakers are to be only activated once pumping stops. There are two main breaker systems, oxidative breakers and enzyme breakers, and both are pH and temperature sensitive. Mechanistically, breakers degrade polymer chains by cleaving the acetyl linkages in the polymer backbone.

Common oxidizers include ammonium persulfate, sodium persulfate, and potassium persulfate. These persulfates produce free oxygen radicals at temperatures greater than 125°F , which attach to the polymer backbone, and break it into its consecutive sugars. However, oxidizers negatively impact equipment and the environment. Enzymes are easy-to-handle,

environmentally benign, protein molecules with the capability to slice specific polymer backbone structures. They are miscible with the fracturing fluid and not as easily consumed as oxidizers. However, enzymes are very sensitive to pH and temperature.

Unfortunately, degradation via oxidative or enzymatic means may occur too quickly at high temperatures, lowering the fracturing fluid viscosity before it reaches the target zone. Hence, an encapsulated breaker system delays the breaking of the fluid at high temperature applications. Encapsulated breakers incorporate high concentrations of breaker in a water-resistant, semi-permeable coating, preventing premature loss of fluid properties, and is gradually released into the formation. Encapsulated breakers control the release rate of the breaker by the crushing pressure of the fracture when it closes on the capsule, osmotic rupture, or by diffusion of the breaker chemical. (Barati & Liang, 2014) (Fink, 2015)

1.7 Conventional Fracturing

Conventional fracturing require hydraulic fracturing fluids with elevated viscosity necessary for adequate proppant suspendability and transport, adequate fracture width, and minimal leak-off. The viscosity of the fluid can be attributed to a gel (about 20-40 pptg) in fluid, resulting from a reaction between a polymer and metal crosslinker. Guar is the most common polymer used along with monoborate ions ($B(OH)^4^-$) as the crosslinking species. A benefit of a viscous fracturing fluid is its ability to quickly form a layer of filter cake on the fracture face under pressure, minimizing further leak-off into the surrounding formation and causing severe damage, especially to water-sensitive formations. However, viscous fluids in the formation and filter cakes not properly broken at the end of a fracturing job can invade and plug high permeability formations, causing undesirable damage to the reservoir. In response, breakers,

such as oxidizers or encapsulated breakers are typically added. Oxidizers generate free radicals based on thermal decomposition of persulfates, while encapsulated breakers delay the breaking of viscous fluid through controlled release, especially at high temperatures. Disadvantages to this system include premature breaking of the acetal linkages between the mannose groups of guar, before the fracturing fluid is able to properly transport proppant to the target area, and incomplete dissociation of the crosslinked gel, causing further damage to the proppant pack and diminishing conductivity of hydrocarbons through the proppant pack. Hence, it is important that for conventional fracturing, a viscous fracturing fluid capable of breaking down with minimal to no residue post-fracturing, is utilized. (Barati & Liang, 2014)

1.8 Unconventional Fracturing

Development of unconventional reservoirs, such as tight gas, coalbed methane, and shale reservoirs, have increased recently, demanding the advancement of innovative hydraulic fracture designs. They consist of deep and narrow fractures while their conventional counterparts have shallow and wide fractures. The most recent designs have included slickwater, linear gel, or hybrid treatments.

Slickwater treatment, or waterfrac, utilizes large volumes of water with low concentrations (about 10 pptg) of linear gel as friction reducer. As a result, slickwater's viscosity is normally less than 10 cP, which is comparatively lower viscosity than the 50 – 1000 cP viscosity range of conventional fracturing fluids at nominal shear rates from 40-100 s⁻¹ (SPE, 2016). The linear gel or slickening agent, is responsible for reducing the fluid friction within the pipe, reducing the horsepower required to pump the fracturing fluid to the target zone. This allows for greater production flowrates to be achieved, economically (Al-Sarkhi, 2010). Slickwater advantages include lower cost and reduced gel damage within the fracture, compared

to a typical crosslinked fracturing fluid. However, slickwater viscosity is too low to ensure sufficient proppant suspension and transport, which is necessary for formation-wellbore conductivity in a hydraulic fracturing treatment. Following Stoke's Law shown below, the proppant particles settle too quickly, severely limiting the effective fracture length. Assumptions associated with Stoke's Law include the following: static, homogenous fluid; no wall effects; smooth, rigid spherical particle; particles must fall in a laminar settling regime; and no particle-to-particle contact.

Stoke's Law (Daneshy, 1989)

$$V_s = (\rho_p - \rho_f) * \frac{gD^2}{18\mu}$$

Where:

V_s = particle settling velocity

ρ_p = density of the particle

ρ_f = density of the fluid

g = gravitational acceleration

D = diameter of the particle

μ = viscosity of the fluid

Stoke's Law is appropriate for making generalized settling-velocity comparisons of spherical proppants at various fluid viscosities, however it is inadequate in predicting the true transport and deposition of proppant particles in actual hydraulic fracturing treatment.

Secondly, the narrow, pumping, fracture widths generated by slickwater are unable to accommodate higher pumping proppant concentrations, as well as larger-diameter proppants. To help offset this concerns, slickwater is usually pumped at extremely high rates, ranging from 60-100 bpm, and at pump times that can exceed 6 hours. Treating an unconventional well with slickwater will require a slickening agent that can improve its proppant carrying capabilities so that resulting pumping fracture widths are wide enough for better conductivity and ultimate recovery, while maintaining low tubular friction drag for a more efficient production, and ensure breakdown post hydraulic fracturing, restoring proppant pack conductivity. (Barati & Liang, 2014) (Fredd, McConnell, Boney, & England, 2001) (Palisch, Vincent, & Handren, 2010)

CHAPTER II

PROBLEM STATEMENT & PROPOSED THESIS

2.1 Problem Statement

Polymer gels are the most commonly used hydraulic fracturing fluids. Research has proven that guar gel usually results in insoluble residue left post-gel degradation, potentially causing formation damage (Nasr-El-Din, Al-Mohammed, Al-Fuwaires, & Al-Aamri, 2007). To minimize the potential damage to the formation rock and proppant pack, breakers must be added to break the polymer gels down. When mixing polymer gels with breakers, premature or incomplete breaking is a potential issue as it lowers the fluid's capacity to carry proppant or causes damage to the proppant pack, respectively. Therefore for conventional hydraulic fracturing, a system that will delay/control the breaker release while leaving minimal to no insoluble remnants, is required.

For unconventional fracturing, waterfrac treatments are common. However, their low proppant carrying capabilities result in narrow fracture widths and high pumping rates. Therefore, to increase proppant suspendability while maintaining low pumping requirements, a polymer system that will increase fracture fluid viscosity while maintaining low tubular drag, as well as ensure hydrocarbon conductivity through the proppant pack and formation, is required.

2.2 Proposed Thesis

The aim of this research is to develop a novel self-breaking, temporary polymer gel system (PVA-SA with Cr^{3+}), with negligible degradation residue, as an alternative to current hydraulic fracturing fluids. Poly(vinyl alcohol) (PVA) is mainly used for various pharmaceutical and biomedical applications due to its desirable characteristics. These characteristics include its

high degree of swelling in water, its elastic nature, high durability, chemical stability, non-toxicity, and modification feasibility via its hydroxyl groups. Altering its hydroxyl units to carboxyl units is required to ensure crosslinking occurs, making it gel-like and insoluble. Succinic anhydride proves to be a great additive to introduce carboxyl groups, enabling three-dimensional networks to be formed for temporary gel use. (Zain, Suhaimi, & Idris, 2011)

The proposed PVA-SA [poly(vinyl alcohol)-succinic acid] is a carboxylated polymer and will be synthesized by the reaction of PVA with succinic anhydride in DMF. The carboxyl groups on PVA-SA can crosslink with multivalent metal ions to result in a 3-D gel. The resultant gel is temporarily stable and will self-break, in the absence of any internal breakers, triggered by the temperature because the carboxyl groups attached to PVA can be removed through the hydrolysis of ester bonds. This new gel system will have the following characteristics:

- Gelation at typical oilfield water pH

PVA-SA with Cr^{3+} will form a strong gel at the pH of normal oilfield brine (pH 7-8).

- Appropriate degradation activation

Gel will be stable and gel breakdown does not occur prior to the termination of a fracture job, which last approximately 2 days, because no internal breakers will be added.

- Self-breaking without any internal breakers

Gel can self-break down to a low, water-like viscosity fluid, triggered by ester bond hydrolysis, therefore, a breaker system isn't necessary, nor is there any concern about residual gel in the formation.

The key objectives of this research are:

1. To synthesize PVA-SA by the reaction of PVA with SA in DMF, and then slightly crosslink PVA-SA with DCC/DMAP in order to increase its molecular weight.

2. To provide evidence that PVA-SA gel with Cr^{3+} , can be developed, similar to guar gel.
3. To comprehensively quantify viscosity dependence of PVA-SA and its various polymer systems' rheology; rheological properties will be demonstrated as functions of temperature, polymer concentration, and crosslinker concentration.
4. To analyze PVA-SA and its various polymer systems' behavior by fitting it to a power law model.
5. To further demonstrate optimal operating/practical conditions of the system at various desired reservoir conditions. This will be achieved by varying polymer and crosslinker concentration at various temperatures and evaluating viscosities decrease over time.
6. To study self-breaking of the PVA-SA gel with Cr^{3+} at different temperatures.

Although the scope of this thesis is limited to a proof of concept view of the application of PVA-SA as a hydraulic fracturing fluid, consideration may also be given to the ultimate end goal of developing a system that is cost-effective, efficient, and easy to deploy in the field.

CHAPTER III

PROPOSED PROCEDURE

In this study, the initial formulation of PVA-SA stock is proposed by Dr. Huili Guan, who is well versed in PVA-SA preparations. Minor changes are made to the initial formula to best accommodate this study. In detail, PVA-SA is synthesized by the reaction of PVA with SA in DMF at 60°C, shown in Figure 1. The resultant PVA-SA is slightly crosslinked with DCC in the presence of DMAP as a catalyst in DMF in order to increase its molecular weight, shown in Figure 2. Chromium crosslinker will then be introduced in the form of a chromium complex, chromium (III) chloride hexahydrate, at varying concentrations, to provide the desired 3-D network, as shown in Figure 3. The gel will then be characterized by the following tests:

- 1) Viscosity measurements of varying PVA-SA gel concentrations at different incubation temperatures.
- 2) G' and G'' calculations of varying PVA-SA gel concentrations at different incubation temperatures via rheological measurements.
- 3) Gel degradation (bottle test method and viscosity profile over time) of varying PVA-SA gel concentrations at different incubation temperatures. Gel self-breaking mechanism is shown in Figure 3.

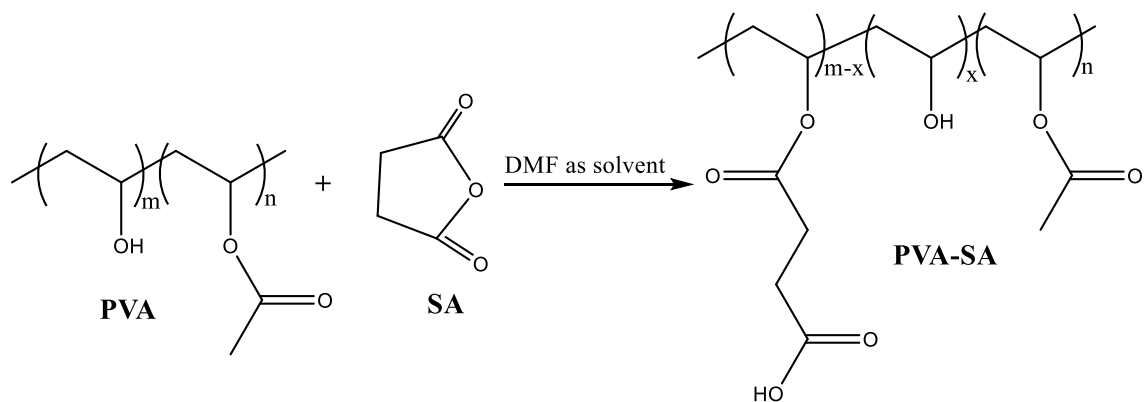


Figure 1. Synthesis of PVA-SA

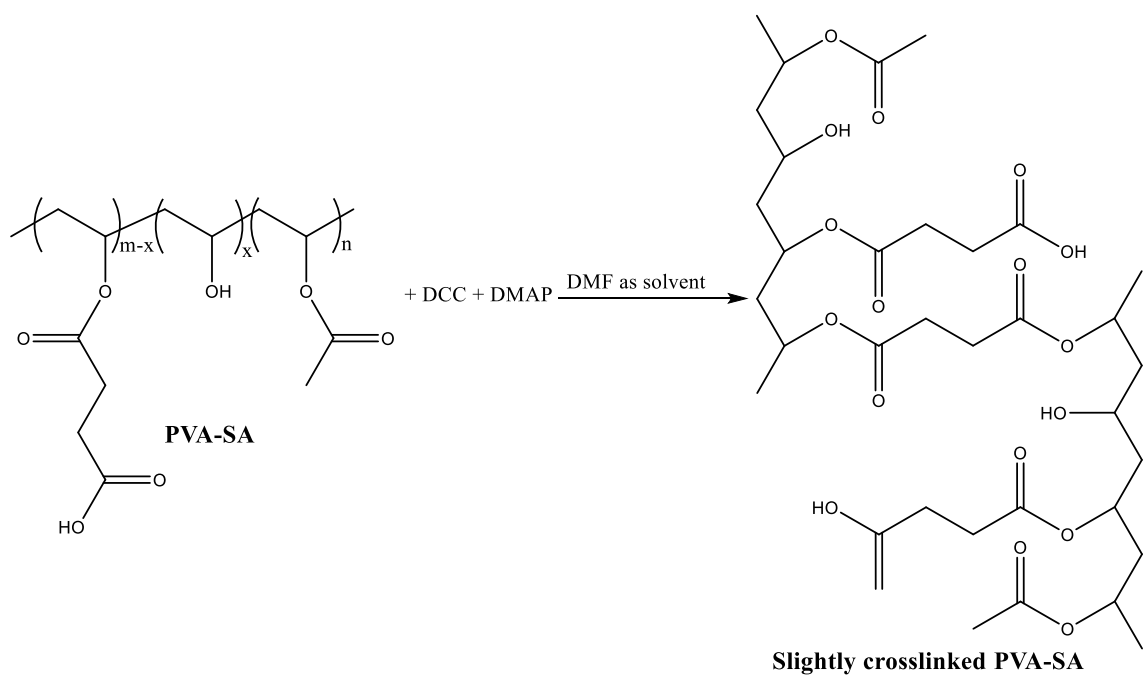


Figure 2. Synthesis of Slightly Crosslinked PVA-SA with DCC

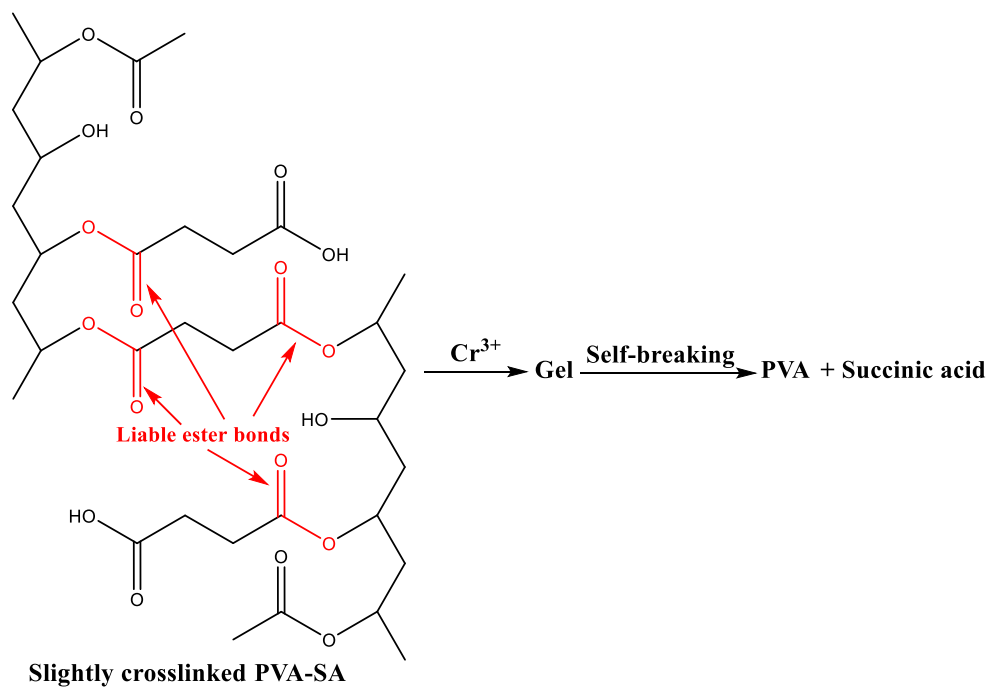


Figure 3. Gelation and Gel Self-Breaking

CHAPTER IV

SYNTHESIS

4.1 Objective

The objective of this section is to detail the preparation of a novel hydraulic fracturing linear polymer gel capable of crosslinking, and capable of increasing the viscosity of a hydraulic fracturing fluid. This will ensure proppant suspendibility while maintaining low pumping horsepower requirements and low drag effects, as the hydraulic fluid is pumped towards the target zone in both conventional and unconventional reservoirs. This section describes the synthesis of poly(vinyl alcohol)-succinic acid, poly(vinyl alcohol)-succinic acid crosslinked with DCC, and poly(vinyl alcohol)-succinic acid crosslinked with DCC and Cr^{3+} crosslinker also referred to as poly(vinyl alcohol)-succinic acid gel. For simplicity, from henceforth PVA-SA crosslinked with DCC will be referred to as PVA-SA-X, and PVA-SA-X crosslinked with Cr^{3+} will be referred to as PVA-SA-X gel.


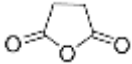

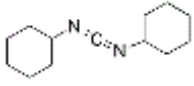
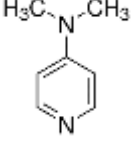
4.2 Material and Methods

Several attempts were made at establishing an ideal recipe for PVA-SA-X and PVA-SA-X gel. The procedures detailed below proved to be the most successful of all attempts made. All components of the synthesis can be seen in Table 1. Poly(vinyl alcohol)-succinic acid synthesis components can be found in Table 2; PVA-SA-X synthesis components can be found in Table 3. PVA-SA-X gel synthesis components can be found in Table 4.

The Brookfield DV2T Viscometer and M5600 HPHT Rheometer were used to measure the viscosity of varying concentrations of PVA-SA, PVA-SA-X, and PVA-SA-X gel at different

polymer concentrations (1.0%, 1.6%, and 2.5%), and at three different temperatures (25°C, 65°C, and 80°C).

Table 1. List of Reagents

Reagents	Function	Structure	Supplier
Mowiol/Poly(vinyl alcohol) (PVA)	Polymer		Sigma-Aldrich
Succinic Anhydride, 99%	Polymer Modifier		Alfa Aesar
N,N-Dimethylformamide (DMF)	Solvent		Sigma-Aldrich
DI Water	Solvent	H ₂ O	-
Chromium III Chloride Hexahydrate	Crosslinker	Cl ₃ Cr*6H ₂ O	Sigma-Aldrich
N,N'-dicyclohexylcarbodiimide (DCC)	Mild Crosslinker		Sigma-Aldrich
4-(Dimethyl amino)pyridine (DMAP)	Catalyst		Sigma-Aldrich
Sodium Hydroxide	pH balance	NaOH	Sigma-Aldrich

4.3 Experimental Equipment

Viscosity measurements were made with both a Brookfield DV2T Viscometer, and M5600 HPHT Rheometer manufactured by Grace Instrument. It should be noted that viscosity measurements above 1000 cP indicates a gel that cannot be accurately measured by the

viscometer, due to the bob's inability to properly grip the gel. Therefore, viscosity values above or equal to 1000 cP have been constrained to a 1000 cP limit in the plots generated from the viscometer presented in the thesis. The viscometer can be seen in Figure 4 and the rheometer can be seen in Figure 5.



Figure 4. Brookfield DV2T Viscometer

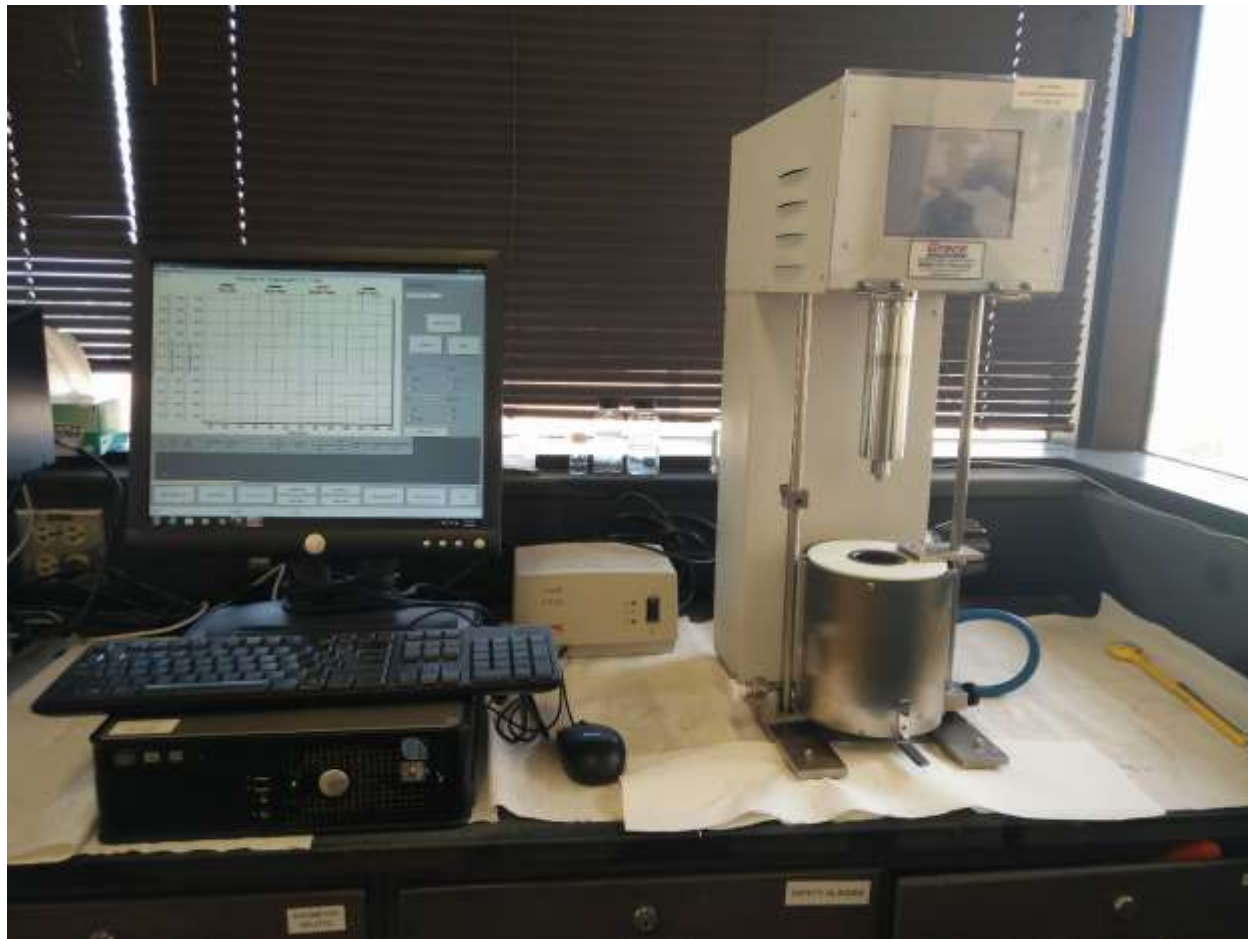


Figure 5. M5600 HPHT Rheometer manufactured by Grace Instrument

4.4 Synthesis of PVA-SA

The objective of this synthesis is to create the necessary functional group required for crosslinking on the PVA polymer, by converting the hydroxyl group on PVA to a carboxyl group with SA. This is important because this will enable the polymer to crosslink with multivalent metal ions, contributing to an increased hydraulic fracturing fluid viscosity. This will aid in

suspending the proppant that will be transported to keep fractures widths open for adequate hydrocarbon conductivity.

Table 2. Synthesis Reagents for PVA-SA

Reagents	Details	Amount, g	wt. %
Mowiol/Poly(vinyl alcohol) (PVA)	MW ~130,000 86.7-88.7 mol% hydrolysis	4.05	6.87
Succinic Anhydride (SA)		0.91	1.54
N,N-Dimethylformamide (DMF)		54.02	91.59

The following is the procedure for preparing 8.41% Poly(vinyl alcohol)-Succinic Acid. The overall procedure is represented schematically in Figure 6, below:

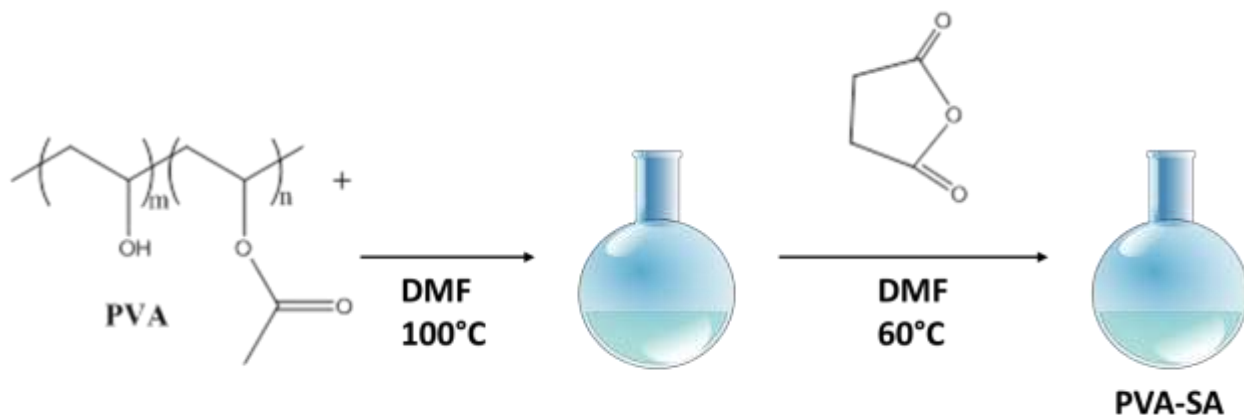


Figure 6. Schematic Representation of Preparation of PVA-SA

Add PVA and DMF to round bottom flask. Attach water condenser to round bottom flask with joint plastic clamp clip and place the round bottom flask–water condenser system in an oil bath while stirring at 150 rpm. Heat the oil bath to 100°C and stir for 24 hours. Reduce oil bath temperature to 60°C and once the solution is cooled to ~70°C, carefully add succinic anhydride to the solution. Place the round bottom flask-water condenser system in oil bath while stirring at 150 rpm, for 24 hours. All solids should be dissolved in the flask within this time. Turn off hot plate and let the solution cool.

4.5 Synthesis of PVA-SA-X

The objective of this synthesis is to increase the molecular weight of the PVA-SA polymer, using DCC, with DMAP as the catalyst, to enable intermolecular reactions between carboxyl groups on the polymer. This synthesis is important because to achieve a desired viscosity, a lower concentration of PVA-SA when slightly crosslinked with DCC is required instead of a higher concentration of PVA-SA without DCC. Consequently, this system ensures minimal polymer residue post-fracturing, and can prove to be cost-effective when scaled up.

First, a stock solution of DCC, DMAP, and DMF is prepared. The objective of this mixture is to create a bulk solution (56.91g) from which desired amounts can be taken out for the synthesis of PVA-SA-X. Measure 600mg DCC and 60mg DMAP into appropriately sized beaker. Add 56.25g DMF with stir bar, cover beaker and stir semi-vigorously for 15 minutes to ensure complete dissolution.

Table 3. Synthesis Recipe for 3.0% PVA-SA-X

Reagents	Amount, g	wt. %
8.41% PVA-SA	25.000	35.714
DMF	11.875	16.964
DCC/DMAP/DMF Stock Solution	13.125	18.750
DI Water	20.000	28.572

The following is the procedure for preparing a 70g stock solution of 3.0% Poly(vinyl alcohol) slightly crosslinked with a mixture of 2.8g DCC/g polymer solution, DMF, and DMAP.

1. Prepare ~4.21% PVA-SA with DCC, DMF, and DMAP at 2.8mg DCC/g polymer solution.

This creates a slight crosslink of the PVA-SA polymer with DCC.

- a. Measure 8.41% PVA-SA solution.
- b. Calculate DCC amount needed in solution

$$m_{\text{DCC, g}} = \frac{2.8 \text{ mg DCC}}{1000 \text{ mg}} * m_{\text{tot, 4.21\% PVA-SA}} \text{ g}$$

- c. Calculate amount required from 56.25g DCC/DMAP/DMF stock solution

$$m_{\text{DCC.DMAP.DMF stock, g}} = (m_{\text{DCC, g}}) * \frac{1000 \text{ mg}}{\text{g}} * \frac{56.25 \text{ g DCC, DMAP, DMF stock}}{600 \text{ mg DCC}}$$

- d. Dilute PVA-SA solution in DMF

$$m_{\text{DMF, g}} = m_{\text{8.41\% PVA-SA, g}} - m_{\text{DCC.DMAP.DMF stock, g}}$$

- e. Place appropriate stir bar and stir at 400 rpm.
- f. While stirring, add calculated required amount of DCC/DMAP/DMF solution to diluted 8.41% PVA-SA solution in appropriate beaker.

- g. Stir solution for 5 hours.
2. After 5 hours, measure viscosity of a small sample via a viscometer to ensure viscosity is between 200-400 cP at a shear rate of 2.25 s^{-1} . If viscosity isn't within this range, check viscosity approximately every 5 minutes until desired viscosity is reached.
3. Quench/significantly slow reaction down by adding DI water.
4. Very gently mix solution until it is a homogenous solution. Bubbles and exothermic heating are expected.
5. Ensure thorough quench by allowing solution and produced precipitate to settle for at least 12 hours in low temperature.
6. Gently centrifuge solution and decant liquid solution into a beaker, making sure to leave any precipitate behind.

4.6 Synthesis of PVA-SA-X Gel

The objective of this section is to detail the preparation of PVA-SA-X gel capable of increasing the viscosity of a hydraulic fracturing fluid and controlling the final gel viscosity necessary for conventional hydraulic fracturing treatments. This is important because it ensures proppant carrying capability, while maintaining low drag effects as the hydraulic fluid is pumped towards the target zone in conventional reservoirs. This section describes the synthesis of poly(vinyl alcohol)-succinic acid crosslinked with DCC and Cr^{3+} crosslinker.

Table 4. Synthesis Equations & Recipe for PVA-SA-X Gel

Equation 1.

$$m_{4000\text{ppm Cr}^{3+},\text{g}} = 100\text{ppm} * \frac{(m_{3.0\% \text{PVA-SA sxlndk}, \text{g}} + m_{\text{DI}, \text{g}} + m_{4000\text{ppm Cr}^{3+}, \text{g}} + m_{1\% \text{NaOH}, \text{g}})}{4000 \text{ ppm}}$$

Equation 2.

$$70\text{g} = m_{3.0\% \text{PVA-SA sxlndk}, \text{g}} + m_{\text{DI}, \text{g}} + m_{4000\text{ppm Cr}^{3+}, \text{g}} + m_{1\% \text{NaOH}, \text{g}}$$

Equation 3.

$$\text{PVA-SA wt.}\% = 0.03 * \frac{m_{3.0\% \text{PVA-SA sxlndk}, \text{g}}}{m_{3.0\% \text{PVA-SA sxlndk}, \text{g}} + m_{\text{DI}, \text{g}} + m_{4000\text{ppm Cr}^{3+}, \text{g}} + m_{1\% \text{NaOH}, \text{g}}}$$

Equation 4.

$$m_{1\% \text{NaOH}, \text{g}} = 0.1 * m_{3.0\% \text{PVA-SA sxlndk}, \text{g}}$$

Reagents	Sample PVA-SA-X Gel Concentrations, g		
	1.8 wt.%	2.0 wt.%	2.5 wt.%
3.0% PVA-SA with DCC	42.00	46.67	58.33
DI Water	22.05	16.92	4.08
1% NaOH	4.20	4.67	5.83
4000 ppm Cr ³⁺ stock soln	1.75	1.75	1.75

The following is the procedure for preparing 70g PVA-SA-X gel, consisting of 100ppm Cr³⁺, at any desired concentration:

Measure PVA-SA with DCC into an appropriately sized vial with stir bar. Add DI water and NaOH into the vial and gently stir after each reagent has been added. Chromium [III] from the chromium [III] stock solution is then added, and the mixture stirred for ~2 mins.

4.7 Results and Discussion

4.7.1 Viscosity Measurements of PVA-SA, PVA-SA-X, and PVA-SA-X Gel

The results plotted below in Figure 7 show the effects of crosslinking PVA-SA with DCC. Using the rheometer, the room temperature viscosities of three different polymer concentrations of PVA-SA with a measured pH of 7-8 were analyzed at a shear rate of 50s^{-1} : 1.0%, 1.6%, and 2.5%. These three concentrations showed three different polymer strengths, with increasing polymer concentration resulting in increasing strength and viscosity. These results are compared to PVA-SA-X at the same concentrations, and at three different temperatures: 25°C , 65°C , and 80°C . At 25°C , 1.0% PVA-SA and PVA-SA-X measured at ~11 cP and ~37 cP, respectively. 1.6% PVA-SA and PVA-SA-X measured at ~12 cP and ~103 cP, respectively. 2.5% PVA-SA and PVA-SA-X measured at ~15 cP and ~262 cP, respectively. It is evident that at 25°C , increasing PVA-SA concentration has a very minimal effect on overall viscosity change, while increasing PVA-SA-X concentration has a significant effect on overall viscosity change. Even at higher temperatures of 65°C and 80°C , PVA-SA-X proved to have greater viscosity than PVA-SA at room temperature. Based on these results, we can justifiably say that slightly crosslinking PVA-SA with DCC increases the overall viscosity of PVA-SA, which invariably indicates an increase in the polymer's average molecular weight.

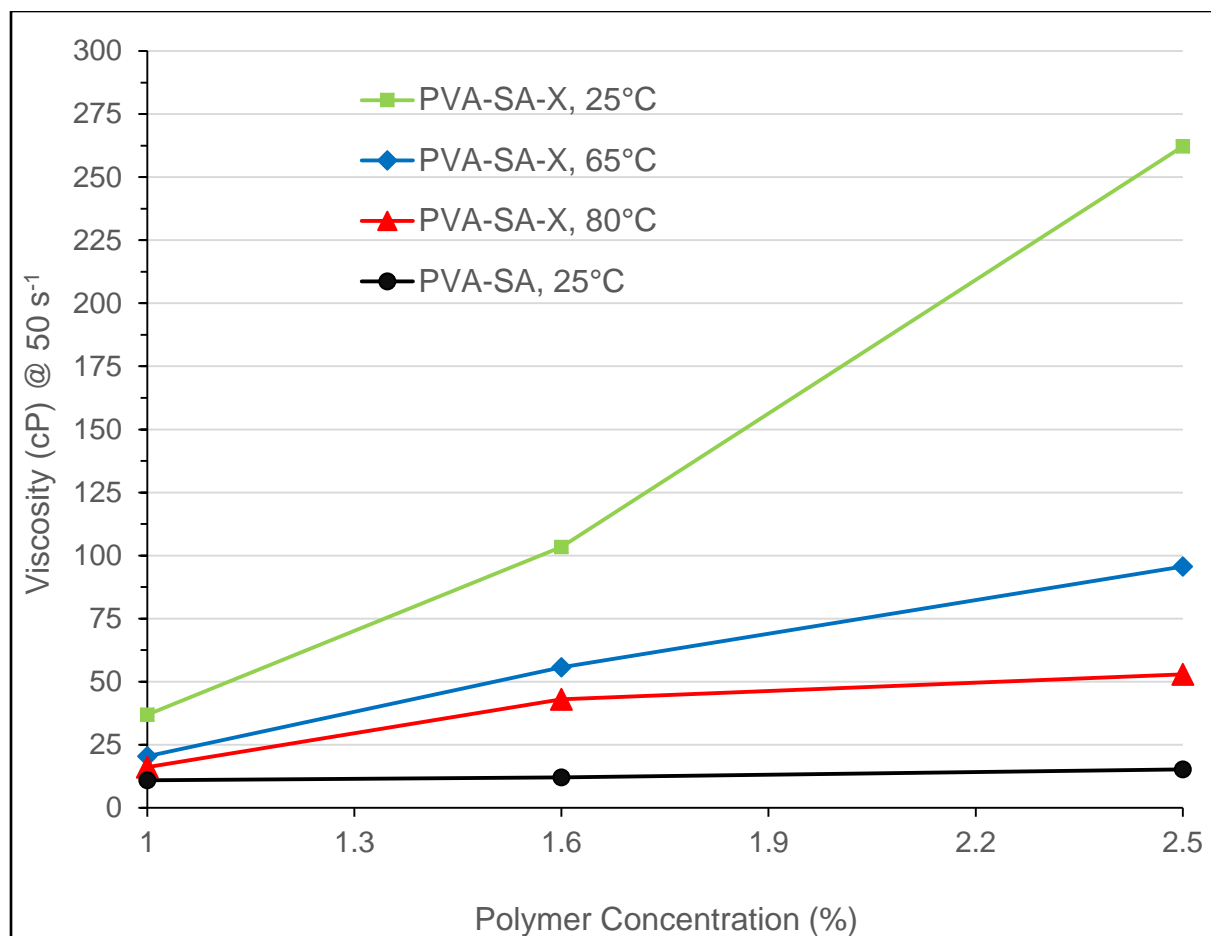


Figure 7. Effect of Crosslinking PVA-SA with DCC at different temperatures

Figure 8 depicts a plot of PVA-SA, PVA-SA-X, and PVA-SA-X gel prepared and measured at 25°C, at pH values within the 7-8 range. Measurements were made with the viscometer at a shear rate of 2.25s^{-1} . Viscosity measurements above 1000 cP indicates a gel that cannot be accurately measured by the viscometer, due to the bob's inability to properly grip the gel. Therefore, viscosity values above or equal to 1000 cP have been constrained to a 1000 cP limit in the plots presented in Figure 8. PVA-SA solutions proved to be the lowest overall viscosity when measured at a shear rate of 2.25s^{-1} . PVA-SA-X showed an increase in viscosity overall when compared to all PVA-SA concentrations, but showed to be greater in viscosity than

PVA-SA-X gel, up until approximately 1.2% polymer concentration, before showing a lower viscosity than PVA-SA-X gel. This is due to syneresis. Due to the insufficient amount of polymers at lower polymer concentrations, adding 100ppm Cr^{3+} crosslinker causes over-crosslinking to occur, separating out liquid from the gel and exhibiting an overall lower concentration. By increasing the polymer concentration, the crosslinking mechanism in PVA-SA-X gel switches from a predominantly intramolecular crosslinking reaction, to an intermolecular crosslinking reaction.

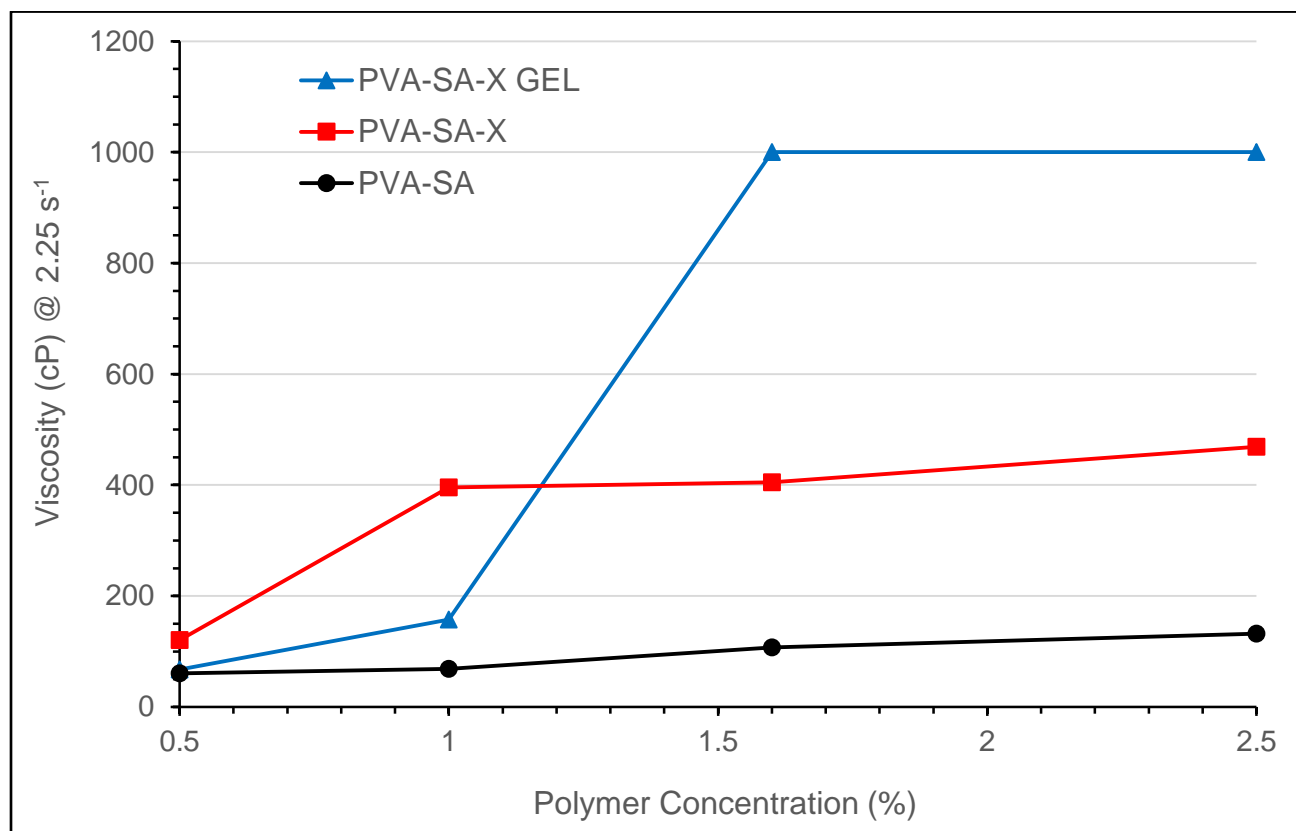


Figure 8. Viscosity versus polymer concentration for different polymer systems at 25°C – PVA-SA, PVA-SA-X, PVA-SA-X gel

4.8 Synthesis Conclusions

The objective of this synthesis section is to prove that DCC is capable of increasing the molecular weight of PVA-SA, and thus show that the same fluid viscosity can be achieved with a lower PVA-SA polymer amount when slightly crosslinked with DCC, than without DCC. Resultantly, PVA-SA-X gives a greater viscosity at 25°C, 65°C, and 80°C, than just PVA-SA at 25°C. Although the increase in viscosity is not significant for conventional fracturing treatment (which requires a fluid viscosity of at least 1000 cP), the viscosity increase enabled by DCC is suitable as a linear polymer gel that acts as a hydraulic fracturing viscosifier, enabling proppant suspendability and transport, while acting as a drag reducing agent for reducing friction pressure losses along the tubulars. Further, this polymer system is capable of creating the fracture networks necessary to increase hydrocarbon conductivity in unconventional reservoirs, and effectively reduce the amount of polymer left in the formation post-fracturing.

Furthermore, the viscosity of PVA-SA-X can further increase via intermolecular crosslinking with Cr^{3+} crosslinker. This creates a high viscosity fluid that will improve the proppant carrying capacity necessary for conventional fracturing treatments.

CHAPTER V

RHEOLOGICAL STUDIES

5.1 Objective

The objective of this section is to characterize the various polymer systems that include PVA-SA-X, and PVA-SA-X gel. This is important because by determining the rheological behavior(s) of this novel polymer fluid, we can better understand its functionality at various reservoir conditions and optimize its use. Further analysis will also help determine fluids appropriate for proppant suspendability and transport.

5.2 Material and Methods

The compositions of the gelling solutions involved are: DI water, 10% NaOH (for maintaining solutions to pH 7-8), 100ppm chromium (III), and PVA-SA-X. All gels are incubated at room temperature. All component concentrations are determined according to the equations shown in Table 4.

5.3 Experimental Equipment

Rheological measurements were made with a M5600 HPHT Rheometer manufactured by Grace Instrument, while viscosity measurements were made with both the rheometer and viscometer. The rheometer can be seen in Figure 5 and the viscometer can be seen in Figure 4.

5.4 Results and Discussion

5.4.1 PVA-SA-X

Rheological test results below show that PVA-SA solutions crosslinked with DCC at room temperature and then measured at 25°C, 65°C, and 80°C, show an exponentially declining

viscosity curve under increasing shear rates in Figure 9. On a log-log plot, shear stress versus shear rate for the varying concentrations of PVA-SA-X at the three temperatures, is linearized and fitted using a power-law model as shown in Figure 10. The flow behavior indices (n') and flow consistency indices (K') for 1.0%, 1.6%, and 2.5% polymer concentration with DCC are recorded in Table 5. With n' less than 1 for all concentrations at all temperatures, coupled with a declining viscosity trend with increasing shear rate, this data further supports that PVA-SA-X is a shear thinning fracturing fluid. Additionally, at each temperature, K' increases with increasing polymer concentration, pointing to the greater crosslinking network between DCC and PVA-SA as additional polymer becomes present in the solution.

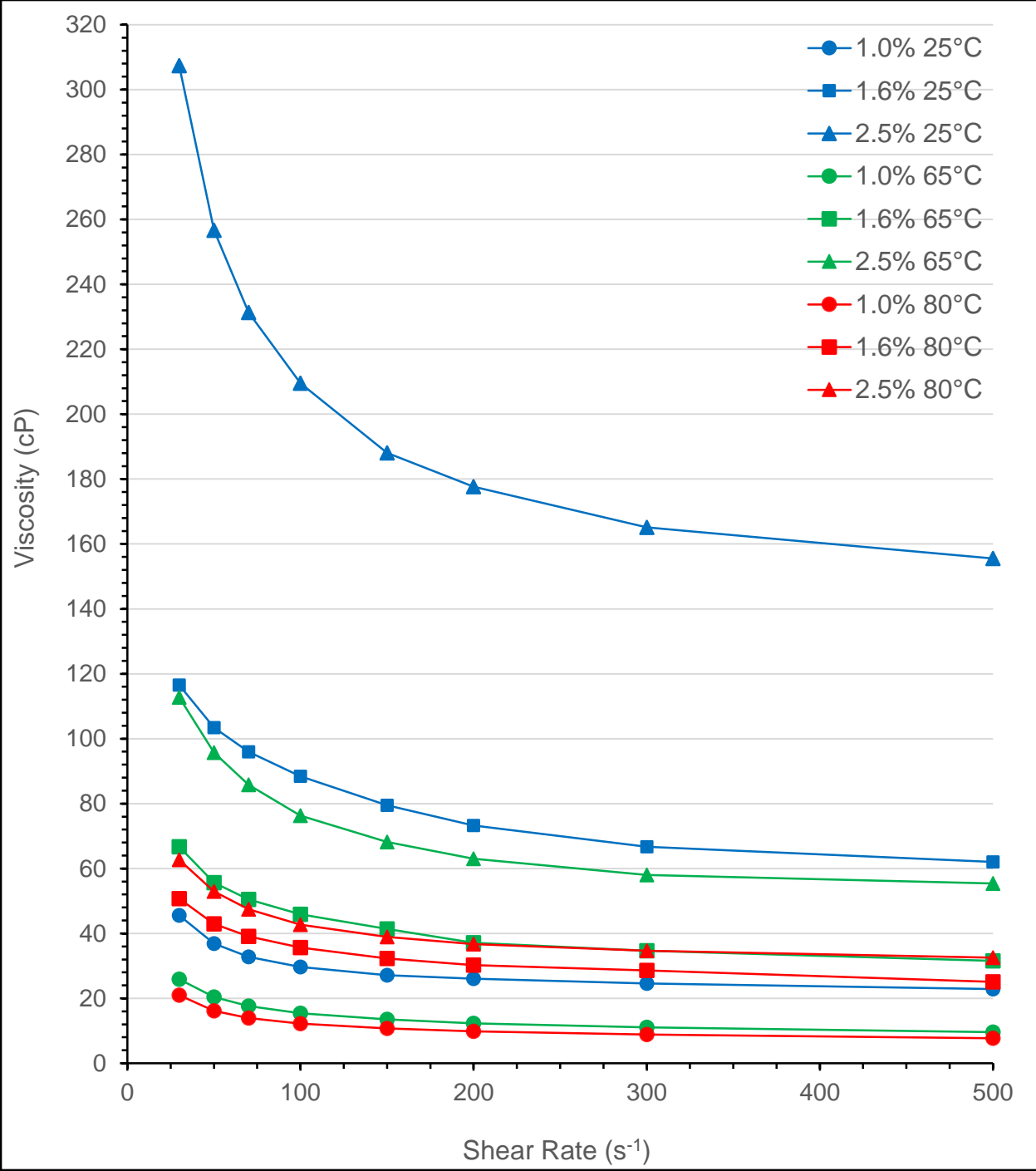


Figure 9. Viscosity versus shear rate of varying concentrations of PVA-SA-X at different temperatures.

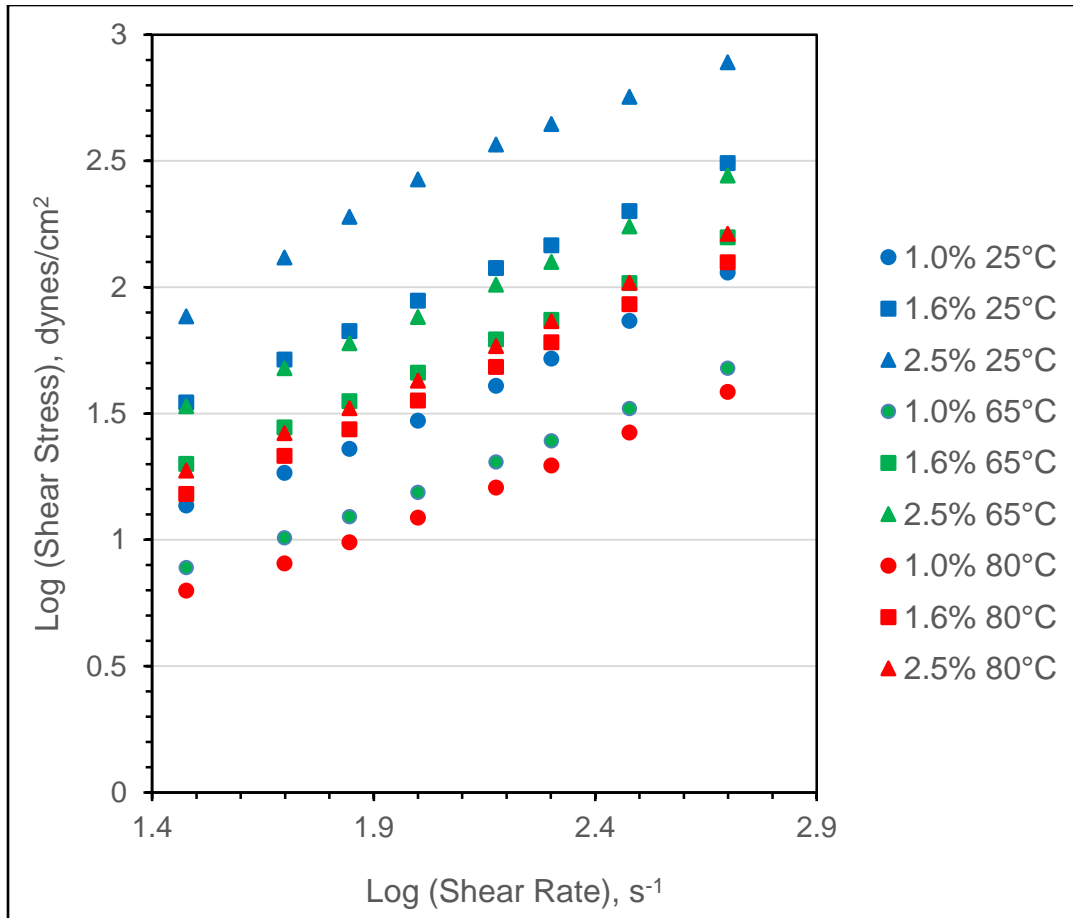


Figure 10. Log shear rate versus log shear stress for varying concentrations of PVA-SA-X at different temperatures using the power law model.

Table 5. Power law parameters for varying concentrations of PVA-SA-X at different temperatures.

Polymer Concentration	Temp	n'	K' (lbf s ^{n'} / ft ²)
2.5%	25°C	0.82	6.30
	65°C	0.74	3.04
	80°C	0.77	1.51
1.6%	25°C	0.77	2.95
	65°C	0.73	1.84
	80°C	0.76	1.29
1.0%	25°C	0.76	1.07
	65°C	0.65	0.92
	80°C	0.65	0.73

5.4.2 PVA-SA-X Gel

Figure 11 shows the effect of concentrations of PVA-SA-X with 100ppm Cr^{3+} on viscosity at 25°C. The apparent viscosity was measured with the viscometer for each concentration at a shear rate of 2.25s^{-1} . Viscosity measurements above 1000 cP indicates a gel that cannot be accurately measured by the viscometer due to the bob's inability to properly grip the gel. Therefore, viscosity values above or equal to 1000 cP have been constrained to a 1000 cP limit in Figure 11. It is apparent that at low polymer concentrations, the apparent viscosity is low, and no significant changes in viscosity is observed from 0.4-1.0% PVA-SA-X concentrations. The apparent viscosity then increases rapidly when the critical overlap concentration of 1.1% is reached, and then a gel is formed at the critical entanglement concentration of 1.4%, showing viscosity values greater than 1000 cP. With increasing polymer gel concentration, viscosity gradually increases until it reaches a critical overlap concentration at approximately 1.1% polymer concentration, after which the slope abruptly increases. Viscosity continues to increase exponentially until the threshold gelation viscosity of 1000 cP is reached at approximately 1.4% polymer concentration. At this point, the apparent viscosity of the gelling solution is out of range of the viscometer, and a gel is visibly formed. At gel concentrations greater than or equal to 1.4%, it is safe to assume that the consequent solutions are gel like and further viscosity measurements by the viscometer insufficiently describe the gel's characteristics, since the viscometer's top plate no longer properly grips the gel. Thus additional gel properties were studied for varying polymer concentrations of PVA-SA-X at 25°C using the rheometer.

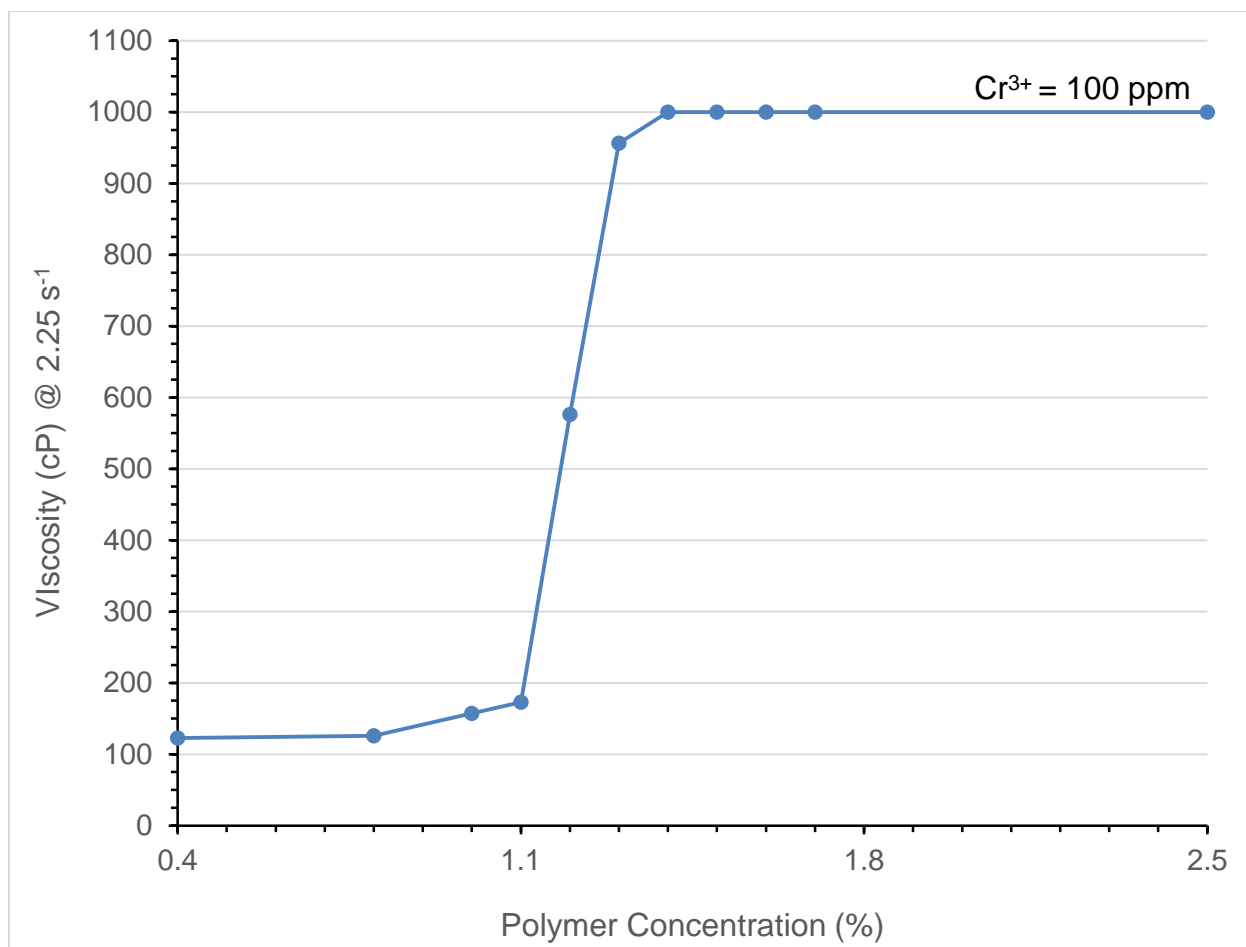


Figure 11. Viscosity versus polymer concentration for PVA-SA-X gel at 25°C.

5.4.3 Characterization of PVA-SA-X Gel

The composition of the gelling solutions involved are: 100ppm chromium (III), and PVA-SA-X. All component concentrations are determined according to the equations shown in Table 4.

Dynamic measurements were performed after the gel had developed to its full strength. By applying an oscillatory shear stress to the gel confined in a shear geometry and measuring the displacement, the complex shear modulus, G^* , can be determined. Within the linear viscoelastic

regime, both oscillatory stress, σ , and oscillatory strain, γ , are harmonic. These can be described by the following equations:

$$\gamma = \gamma_0 \cos \omega t$$

$$\sigma = \sigma_0 \cos(\omega t + \delta)$$

Where ω is the excitation frequency in rad/s, and δ is the phase angle by which the oscillatory strain lags behind the oscillatory stress. G^* can then be defined by

$$G^* = \frac{\sigma_0 e^{i(\omega t + \delta)}}{\gamma_0 e^{i\omega t}} = G' + iG''$$

Where i^2 is -1, G' is the storage modulus, and G'' is the loss modulus. The storage modulus G' is associated with the storage of energy during the applied stress, and is an indicator of the building of a network structure in a crosslinking reaction, while G'' is associated with the loss of energy as heat (Klaveness, Ruoff, & Kolnes, Kinetics of the Crosslinking of Poly (acrylamide) with Cr (III) Rheological Measurements of the Gelation, 1995).

The rheometer is used to measure the viscoelasticity of varying concentrations of PVA-SA-X gel, while the Syndansk gel code, Table 6, is used to qualitatively describe its strength. Oscillatory frequency sweep tests were performed to determine the rheological behavior of the gelling system, varying with an applied frequency range of 0.01-5.00 Hz, as illustrated in Figure

12. A deformation amplitude of 10% was selected to ensure that the oscillatory deformation is within the linear regime. The rheometer also measured viscosity values of different gel concentrations at varying temperatures at increasing and decreasing shear rates. Gel strength is expressed as an alphabetic code of A through I, which is shown in Table 6. For no detectable gel that has the same viscosity as the initial solution, it is coded as “A”. Likewise, code “I” indicates that there is no deformation on the gel surface upon inversion.

Table 6. Syndansk Gel Code / Gel Strength Code (Reprinted from Jia, Pu, Zhao, & Liao, 2011).

Gel Strength Code	Gel Description
A	No detectable gel formed: The gel appears to have the same viscosity as the original polymer solution.
B	Highly flowing gel: The gel appears to be only slightly more viscous than the initial polymer solution.
C	Flowing gel: Most of the gel flows to the bottle cap by gravity upon inversion.
D	Moderately flowing gel: Only a small portion (5-10%) of the gel does not readily flow to the bottle cap by gravity upon inversion (usually characterized as a tonguing gel).
E	Barely flowing gel: The gel can barely flow to the bottle cap and/or a significant portion (>15%) of the gel does not flow by gravity upon inversion.
F	Highly deformable non flowing gel: The gel does not flow to the bottle cap by gravity upon inversion.
G	Moderately deformable non flowing gel: The gel deforms about half way down the bottle by gravity upon inversion.
H	Slightly deformable non flowing gel: only the gel surface slightly deforms by gravity upon inversion.
I	Rigid gel: There is no gel surface deformation by gravity upon inversion.

According to Figure 12, G'' is initially larger than G' at the low PVA-SA-X gel concentration of 1.0%, with G' valued at 0 dyne/cm². This is expected since the sample is still in the liquid state where viscous properties dominate, and most of the energy is lost as viscous heat. With the viscous modulus dominating the elastic modulus at this concentration, the gel solution is mainly fluid-like and is characterized as 'A' according to the Syndansk gel code, since no detectable gel is formed and the solution is water-like. As polymer gel concentration increases from 1.2% - 2.0%, the gelant begins to gel and a crosslinked network is formed, decreasing the difference between G' and G'' ; the plots show both parameters almost overlapping each other. With the viscous modulus similar to the elastic modulus at these concentrations, the gel solution is both fluid-like and gel-like and characteristically progresses from a highly flowing gel, 'code B', at 1.2%, to a flowing gel, 'code C', at 1.4%, to a moderately flowing gel, 'D', at both 1.6% and 2.0%, according to the Syndansk gel code. At polymer concentrations of 2.5% (and above), the difference between G' and G'' increases, with G' larger than G'' . With the elastic modulus dominating the viscous modulus at this concentration, the gel solution is mainly solid-like and is characterized as a highly deformable gel, 'F', according to the Syndansk gel code, and is like a rubbery material. The consistent increase in G' and G'' with increasing PVA-SA-X gel concentration, suggests the viscoelastic nature of this hydrogel under the applied physical conditions.

—■— G'' =Viscous Modulus (dyne/cm²) —●— G' =Elastic Modulus (dyne/cm²)

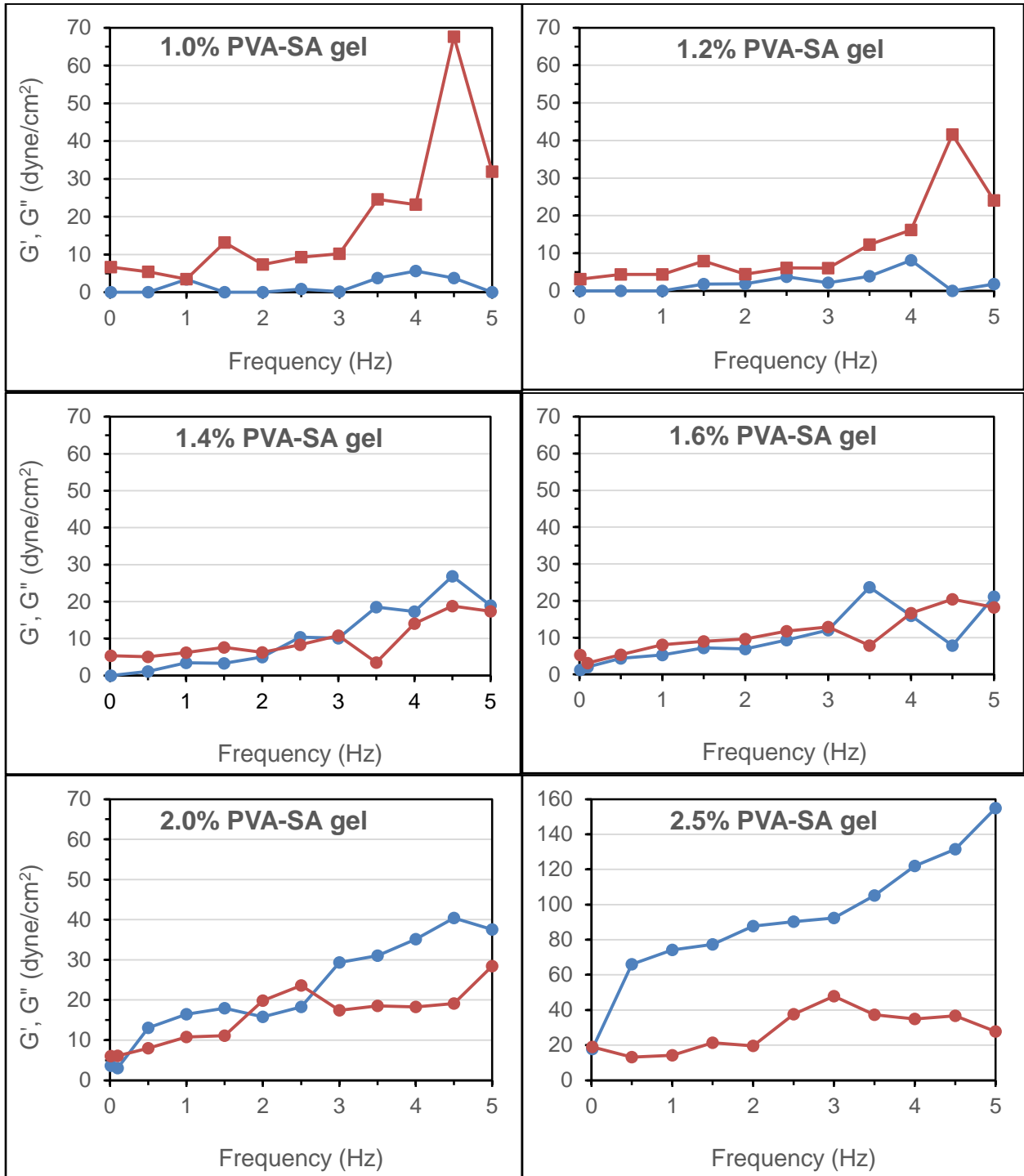
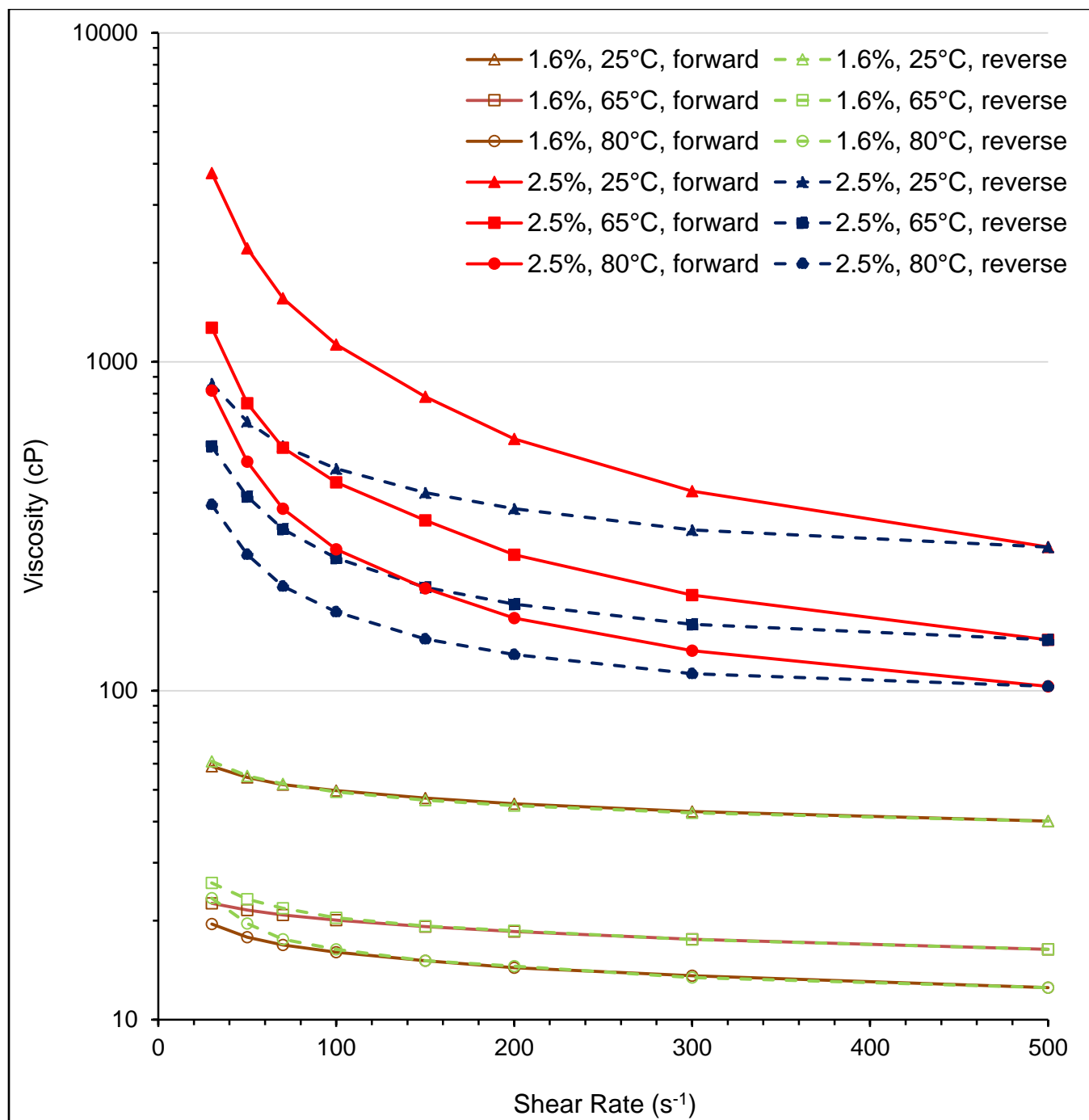


Figure 12. Frequency sweep test for varying PVA-SA-X gel concentrations at 25°C and 10% amplitude.

Figure 13 highlights the effects of shear rate on 1.6% and 2.5% PVA-SA-X gel concentrations (lower gel concentrations are not included as they classified as code C and below, and did not form a visibly strong enough gel), at 25°C, 65°C, and 80°C. All concentrations show a decrease in viscosity with increasing shear rate (forward and reverse) for all temperatures, indicating that PVA-SA-X gel is a shear thinning fluid. The fact that viscosity reaches low values at high shear rates indicates that fluid flow encounters less resistance at higher shear rates. This can be attributed to the fact that as shear rate is increased, the polymer chain disentangles and stretches, flowing in the direction of the applied force, resulting in a reduced polymer gel viscosity. Figure 13 also shows the viscosities achieved by increasing and decreasing shear rates. The rheometer was programmed to continuously measure viscosity from shear rates 30 s^{-1} to 500 s^{-1} for increasing shear measurements, and immediately followed by a continuous shear from 500 s^{-1} to 30 s^{-1} , for decreasing shear measurements. This data shows that both shearing methods provided closely related viscosity values for 1.6% PVA-SA-X gel, indicating that hysteresis is negligible for polymer gel concentrations that exhibit fluid-like characteristics. However, hysteresis is evident for 2.5% PVA-SA-X gel, indicating incomplete re-crosslinking post-shear between the crosslinker and polymer for polymer gel concentrations that exhibit solid-like characteristics. The higher the gel concentration, the more shear dependent the solution viscosity is.

At all PVA-SA-X gel concentrations, gel viscosity decreases with increasing temperature. With higher temperatures, intermolecular crosslinking becomes weaker, and thus the gel is broken, lowering overall gel viscosity.



**Figure 13. Semi-log plot of the effects of shear rate, reversibility and temperature on PVA-SA-X gel at 25°C, 65°C, 80°C in the range 30-500 s^{-1} ;
Solid lines = increasing shear; Dotted lines = decreasing shear.**

PVA-SA-X gel solutions at 25°C, 65°C, and 80°C show an exponentially declining curve under increasing shear rates. On a log-log plot, Figure 14, the shear stress vs shear rate curve is linearized and fitted using a power-law model. The flow behavior indices (n') and flow consistency indices (K') for 1.6% and 2.5% PVA-SA-X gel are recorded in Table 7. With $n' < 1$ for all temperatures, in addition to the declining viscosity trend with shear rate, this data further supports that this polymer gel solution is a shear thinning fracturing fluid. This data reveals that for weak gels, n' generally tend toward unity and K' decreases with increasing temperature.

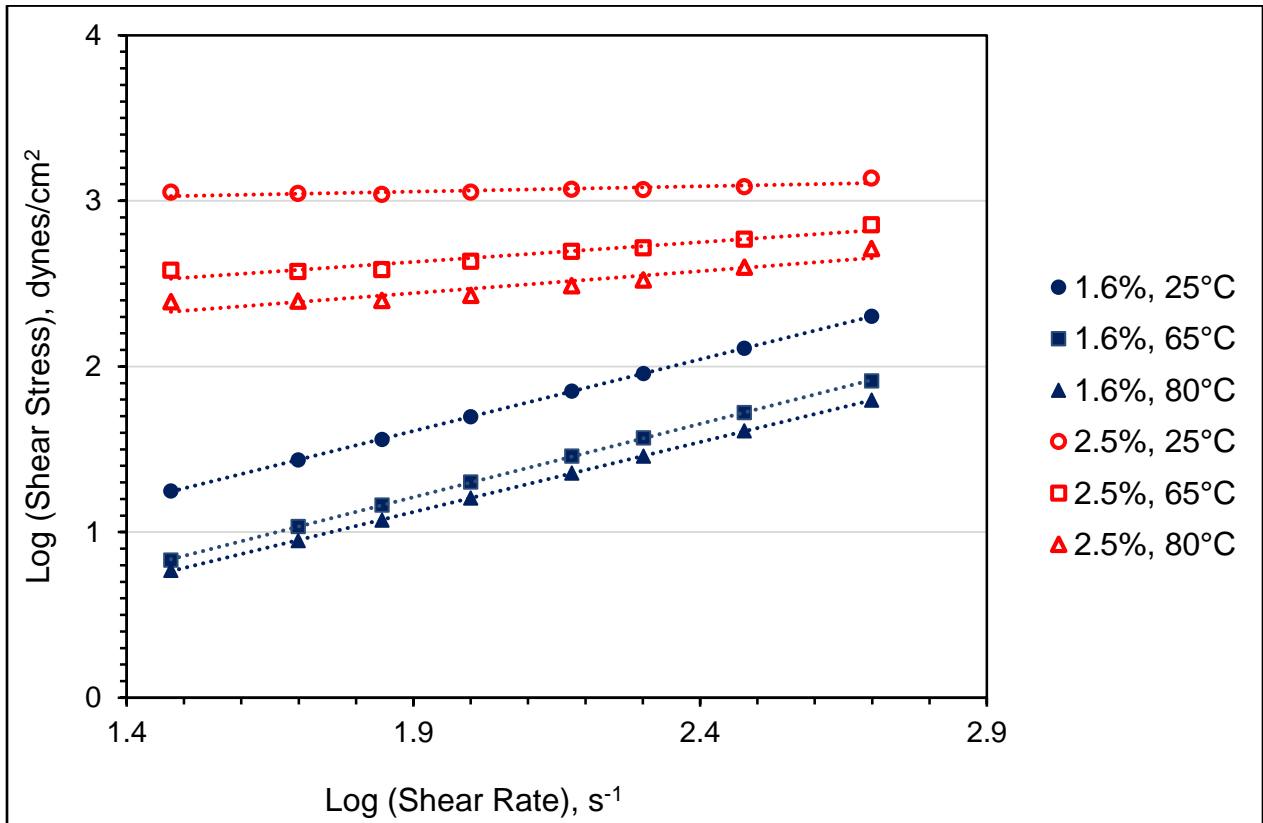


Figure 14. Log shear rate versus log shear stress for 1.6% and 2.5% PVA-SA-X gel at 25°C, 65°C, and 80°C using the power law model.

Table 7. Power law parameters for 1.6% and 2.5% PVA-SA-X gel at 25°C, 65°C, and 80°C.

PVA-SA-X Gel Concentration	Temp	n'	K' (lbf s^{n'}/ ft²)
1.6%	25°C	0.87	1.06
	65°C	0.89	0.39
	80°C	0.84	0.38
2.5%	25°C	0.06	943.99
	65°C	0.24	171.34
	80°C	0.27	98.76

5.5 Rheological Studies Conclusions

The objective of these rheological studies is to show that PVA-SA-X, and PVA-SA-X gel has the capacity to suspend and carry proppant in an unconventional and conventional hydraulic fracturing treatment, respectively. Based on the data presented previously we can conclude the following:

1. Crosslinking PVA-SA with DCC is a non-Newtonian fluid capable of improving proppant carrying capabilities while maintaining low pumping requirements, even at high temperatures up to 80°C.
2. The viscosity of PVA-SA-X can further increase via intermolecular crosslinking with Cr³⁺ crosslinker. This creates a non-Newtonian fluid capable of improving proppant carrying capabilities while maintaining low pumping requirements.
3. With this polymer gel system, 1.4% is defined as the gelation critical concentration at a viscometer shear rate of 2.25 s⁻¹.
4. PVA-SA-X gel viscoelastic properties can be modified to suit desired proppant suspendability and achieve eventual gel strength, by changing its concentration.

5. G' , G'' data qualitatively proves that the more gel-like the solution is, the greater its ability to suspend proppant and minimize proppant settling velocity.
6. PVA-SA-X gel is a shear thinning fluid with hysteresis evident at higher polymer gel concentrations.
7. PVA-SA-X gel is temperature sensitive with increasing temperature resulting in decreasing viscosity.
8. The greater crosslinking network of PVA-SA-X provides the elevated viscosity suitable for unconventional fracturing, without the additional need of a metal crosslinker like Cr^{3+} , which could potentially damage the well.
9. PVA-SA-X gel's ability to exhibit solid-like characteristics with viscosity values greater than 1000 cP make it a suitable polymer for fracturing conventional reservoirs.

CHAPTER VI

DEGRADATION STUDIES

6.1 Objective

The objective of this section is to prove that PVA-SA-X and PVA-SA-X gel have the ability to self-break/degrade without any internal breakers at elevated temperatures. This is important because it ensures that there will be little to no gel residue post fracturing, minimizing formation damage in both unconventional and conventional fracturing treatments.

6.2 Material and Methods

Samples of PVA-SA-X and PVA-SA-X gel were prepared and incubated for ~48 hours at room temperature, incubated in Thermo Scientific ovens at three different temperatures (65°C, 80°C, and 95°C), and loaded periodically into the viscometer to measure the viscosity at room temperature for safety measure. Two analytical methods were utilized to measure gel breaking: bottle testing method and monitoring viscosity over time.

6.3 Experimental Equipment

Viscosity measurements were made with the Brookfield DV2T Viscometer. The instrument can be seen in Figure 4.

6.4 Results and Discussion

6.4.1 Bottle Testing Method

The bottle testing method is a quick and inexpensive method that provides a semi-quantitative method of gelation rate and gel strength. Gel strength during degradation is expressed as an alphabetic code of A through I, which is shown in Table 8. For no detectable gel

that has the same viscosity as the initial solution, it is coded as “A”. Likewise, code “I” indicates that there is no deformation on the gel surface upon inversion.

Table 8. Syndansk Gel Code / Gel Strength Code (Reprinted from Jia, Pu, Zhao, & Liao, 2011).

Gel Strength Code	Gel Description
A	No detectable gel formed: The gel appears to have the same viscosity as the original polymer solution.
B	Highly flowing gel: The gel appears to be only slightly more viscous than the initial polymer solution.
C	Flowing gel: Most of the gel flows to the bottle cap by gravity upon inversion.
D	Moderately flowing gel: Only a small portion (5-10%) of the gel does not readily flow to the bottle cap by gravity upon inversion (usually characterized as a tonguing gel).
E	Barely flowing gel: The gel can barely flow to the bottle cap and/or a significant portion (>15%) of the gel does not flow by gravity upon inversion.
F	Highly deformable non flowing gel: The gel does not flow to the bottle cap by gravity upon inversion.
G	Moderately deformable non flowing gel: The gel deforms about half way down the bottle by gravity upon inversion.
H	Slightly deformable non flowing gel: only the gel surface slightly deforms by gravity upon inversion.
I	Rigid gel: There is no gel surface deformation by gravity upon inversion.

The effect of polymer concentration on gelation strength and gel degradation is shown in Table 9. The samples were prepared with different PVA-SA-X and PVA-SA-X gel concentrations, tested at 65°C, 80°C, and 95°C temperatures, and at a pH of 7-8. From the results, it is observed that the gel strength decreased with time, and the rate of degradation for both polymer systems at all temperatures is highest within the first few hours of incubation. It is also observed that the gel concentration affects the degradation time. Based on the results, one can infer that it takes longer for gel degradation to occur at higher polymer and polymer gel concentrations. This is due to the greater DCC-carboxylate and chromium-carboxylate group networks that are present in higher polymer and polymer gel concentrations, respectively, which require more time to dissociate, resulting in the decrease of viscosity and gel strength.

From this data, one can estimate the flow-ability of the various PVA-SA polymer system during post-fracture process. With a typical flowback duration of approximately 2 days¹, Table 9 shows that at ~2.1 days (highlighted), all polymer systems will exhibit a solution that has no detectable gel, ensuring negligible residue in the formation, except for 2.5% PVA-SA-X gel at 80°C which exhibits a highly flowing gel, 1.6% PVA-SA-X gel at 65°C which exhibits a highly flowing gel, and 2.5% PVA-SA-X gel at 65°C which exhibits a moderately flowing gel.

¹ Dunn, Sharon. "Fracking 101: Here's the inside Mud on How the Process Works." *Post Independent Citizen Telegram*, The Tribune, 20 Mar. 2016, www.postindependent.com/news/local/fracking-101-heres-the-inside-mud-on-how-the-process-works/.

Table 9. Degradation Performance of PVA-SA-X and PVA-SA-X gel

TIME		PVA-SA-X		PVA-SA-X GEL								
		65°C, 80°C, 95°C		95°C			80°C			65°C		
~Days	~Hours	1.0%	1.6%	1.0%	1.6%	2.5%	1.0%	1.6%	2.5%	1.0%	1.6%	2.5%
0	0	A	B	A	D	E	A	D	E	A	D	E
0.01	0.3	A	A	A	C	D	A	C	D	A	C	E
0.02	0.6	A	A	A	B	D	A	C	D	A	C	E
0.05	1.1	A	A	A	A	D	A	C	D	A	C	E
0.5	12	A	A	A	A	C	A	C	C	A	C	D
0.7	17	A	A	A	A	B	A	C	C	A	C	D
1.0	25	A	A	A	A	A	A	C	C	A	C	D
1.7	40	A	A	A	A	A	A	B	C	A	C	D
1.9	46	A	A	A	A	A	A	A	B	A	C	D
2.1	51	A	A	A	A	A	A	A	B	A	B	D
7.0	168	A	A	A	A	A	A	A	A	A	A	C
8.0	192	A	A	A	A	A	A	A	A	A	A	B
11.0	264	A	A	A	A	A	A	A	A	A	A	A

6.4.2 Monitoring Viscosity Over Time

Polymer and polymer gel degradation were quantitatively examined by measuring the apparent viscosities using the Brookfield DV2T Viscometer, placing the solution in 6mL glass vials at different temperatures. The apparent viscosities of varying concentrations of PVA-SA,

PVA-SA-X, and PVA-SA-X gel, were measured at 25°C after incubation at different temperatures, 65°C, 80°C, and 95°C. For accurate measurements with the viscometer, varying shear rates are used to make viscosity measurements over time: for viscosities greater than 200 cP, a shear rate of 2.25s⁻¹ is used; for viscosities less than 200 cP and greater than 20 cP, a shear rate of 9.00s⁻¹ is used; for viscosities less than 20 cP, a shear rate of 22.50s⁻¹ is used. The results are plotted in the graphs to follow.

According to the plots (Figure 15, Figure 16, Figure 17, Figure 18, Figure 19, Figure 20, Figure 21, and Figure 22), all viscosity profiles start off with a high slope, indicating a high rate of gel breakdown, before decreasing in slope and leveling off; this further substantiates results from the bottle testing experiment above depicting that the highest rate of degradation is within the first time period of breakdown.

6.4.2.1 PVA-SA Degradation

As a control, a viscosity profile of varying concentrations of PVA-SA is plotted below to gauge the anticipated final viscosity of PVA-SA-X and PVA-SA-X gel at various temperatures. By determining the final stable viscosity of PVA-SA, we are able to determine if either crosslinked polymer is capable of breaking down to its constituents after a period of time at the various temperatures.

As Figure 15 shows, the starting viscosities for 0.5%, 1.0%, 1.6%, and 2.5% PVA-SA are ~11.5 cP, ~11.8 cP, ~17.7 cP, and ~20.1 cP, respectively. After a week of incubation at different temperatures, final viscosity values range from approximately 11 cP-19 cP at 65°C, 5 cP-11 cP at 80°C, and 4.7 cP-10.2 cP at 95°C.

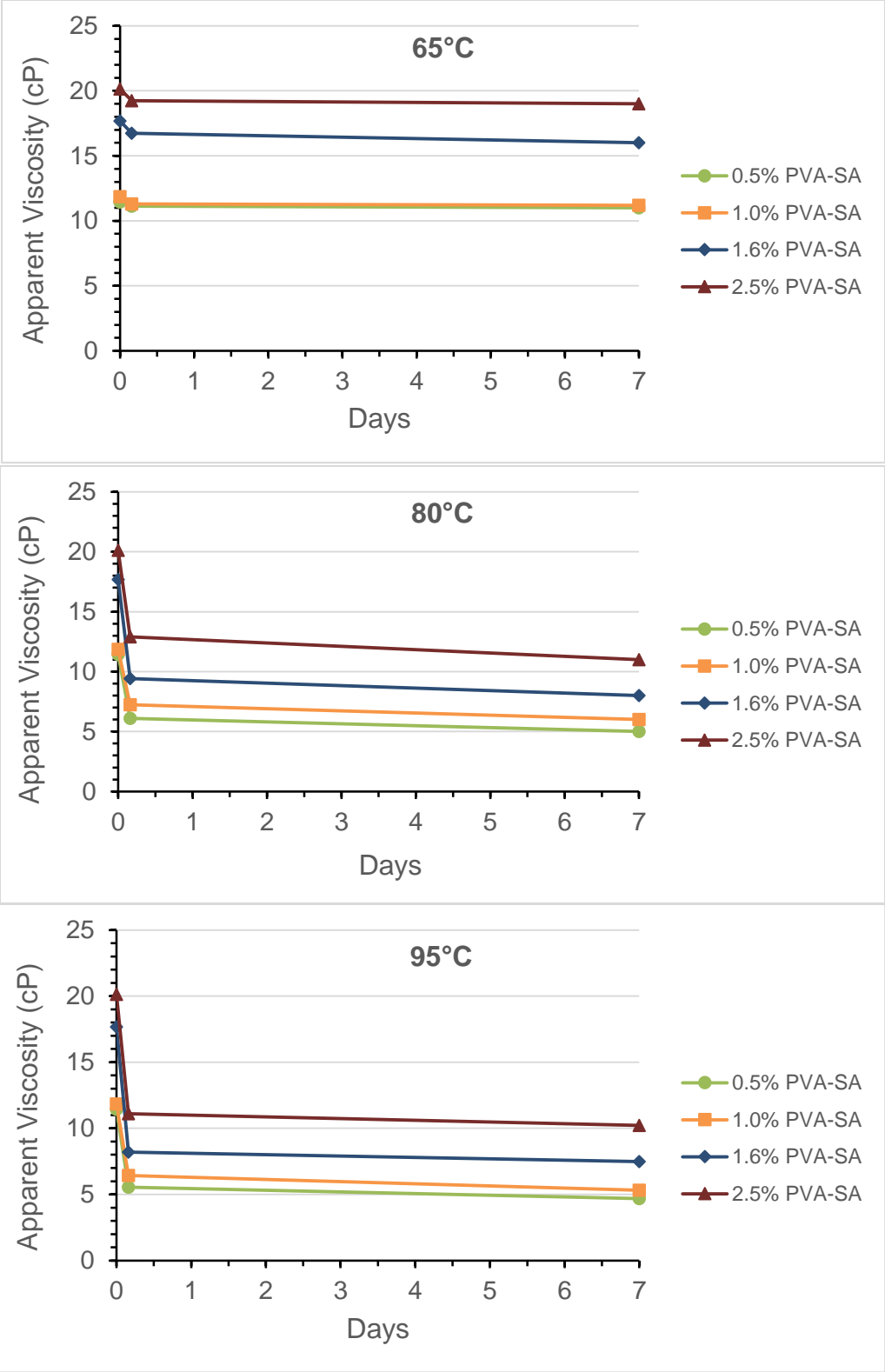


Figure 15. Degradation of PVA-SA – 65°C, 80°C, and 95°C.

Figure 16 shows the effect of temperature on apparent viscosity for PVA-SA. It can be seen that the fluid degrades minimally over time, and that for elevated temperatures, the effects are more noticeable.

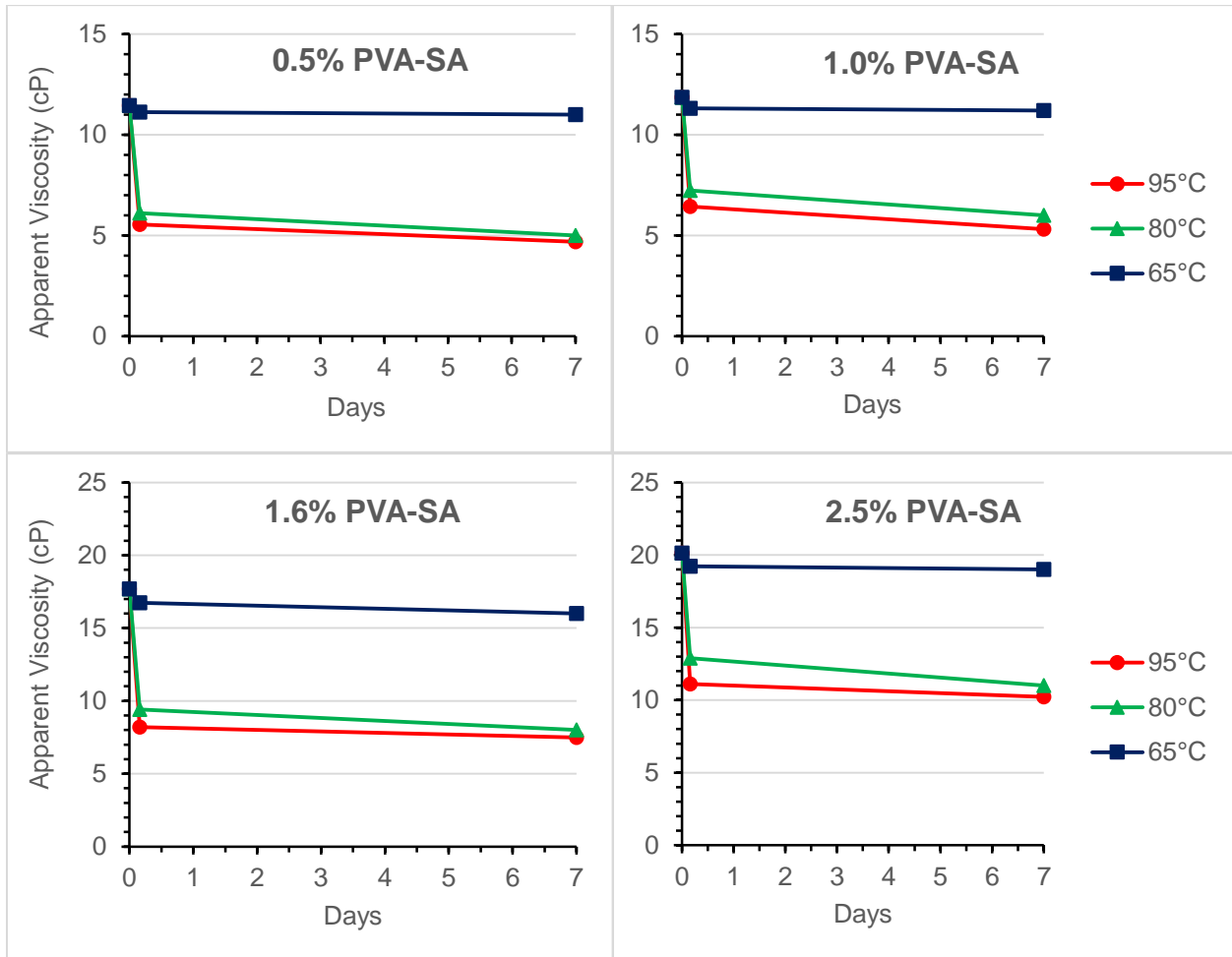


Figure 16. Degradation of 0.5%, 1.0%, 1.6%, and 2.5% PVA-SA at 65°C, 80°C, and 95°C.

6.4.2.2 PVA-SA-X Degradation

Figure 17 shows the viscosity profile of 0.5%, 1.0%, and 1.6% PVA-SA-X at 65°C, 80°C, and 95°C, over time. As expected, 1.6% PVA-SA-X concentration at 65°C took the

longest time to break. At 80°C and 95°C, it took all concentrations a maximum of 4 days to break down to a final viscosity ranging from ~9 cP to ~69 cP. At 65°C, 1.6% PVA-SA-X gel took ~7 days to break from ~500cP to 42cP, 1.0% PVA-SA-X gel took ~6 days to break from ~395 cP to 42 cP, while 0.5% PVA-SA-X gel took ~2.3 days to break from ~120 cP to 42 cP. Furthermore, it is evident that at greater molecular polymer weights, longer times are required to achieve a low final breakdown viscosity, especially at lower temperatures.

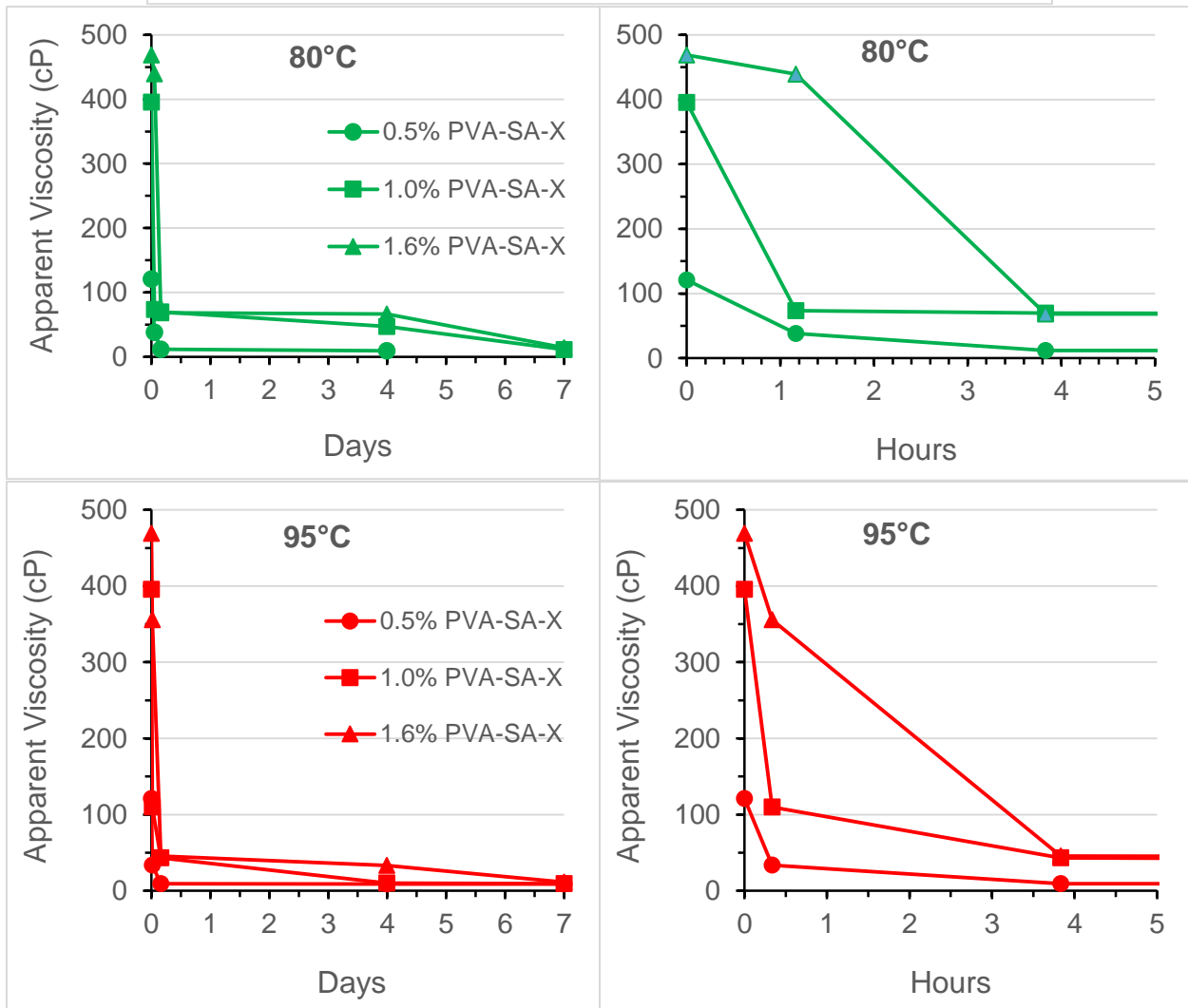
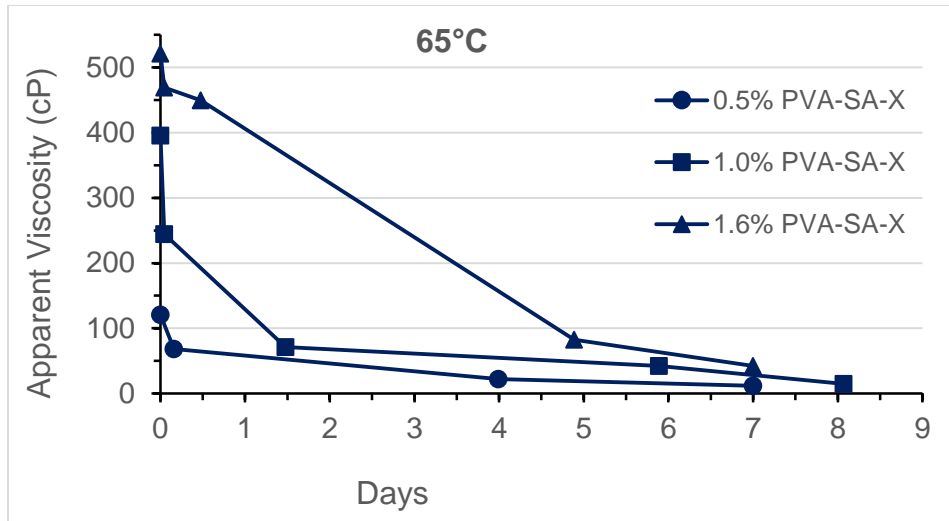


Figure 17. Degradation of PVA-SA-X - 65°C, 80°C, and 95°C.

Figure 18 shows the effect of temperature on apparent viscosity for PVA-SA-X. It can be seen that the fluid degrades over time, and that for elevated temperatures, the effects are more pronounced.

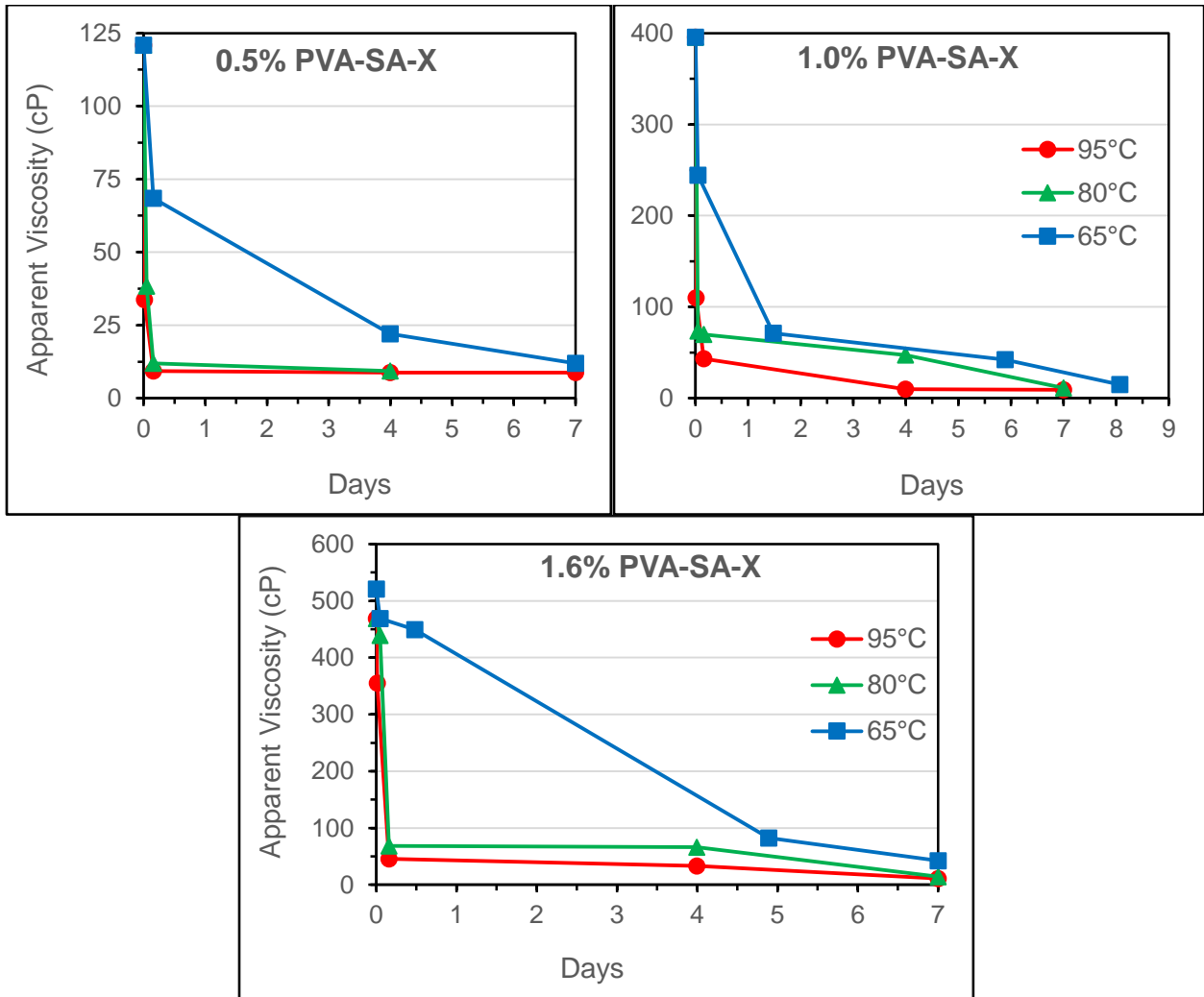


Figure 18. Degradation of 0.5%, 1.0%, and 1.6% PVA-SA-X at 65°C, 80°C, and 95°C.

6.4.2.3 PVA-SA-X Gel Degradation

Adding chromium crosslinker to PVA-SA-X strengthens the polymer's resistance to temperature, and increases its breaking time. Figure 19 shows the viscosity profile of 1.0%, 1.6%, and 2.5% PVA-SA-X gel at 95°C, 80°C, and 65°C, over time. As expected, 2.5% PVA-SA-X gel concentration at all temperatures took the longest time to break to the approximate viscosity range of 20-40 cP; it took ~3.9 days to break from >1000 cP to ~30 cP and ~32 cP at 95°C and 80°C, respectively, and it took ~11 days to break to ~39cP at 65°C. 1.6% PVA-SA-X gel concentration took ~1 day, ~3.7 days, and >6.8 days to break from >1000 cP to ~26 cP at 95°C, 80°C, and 65°C, respectively. Meanwhile, it took 1.0% PVA-SA-X gel concentration less than 24 hours to break down to approximately half its initial viscosity, from ~20 cP to ~10 cP, for all temperatures.

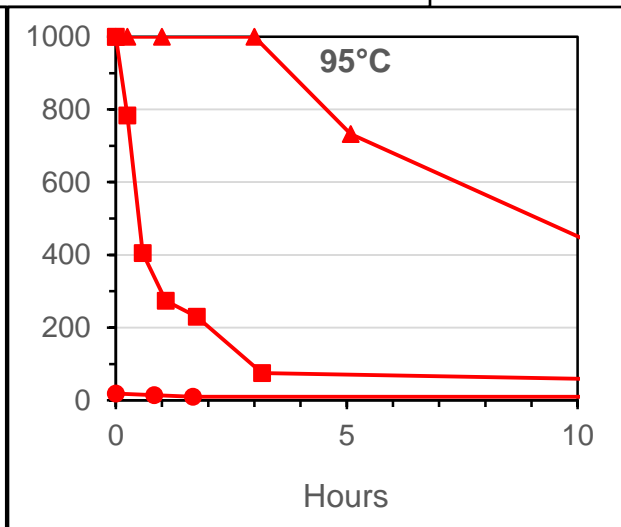
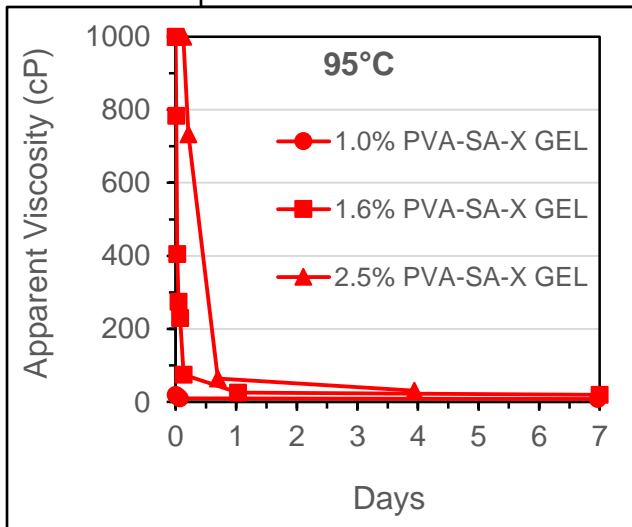
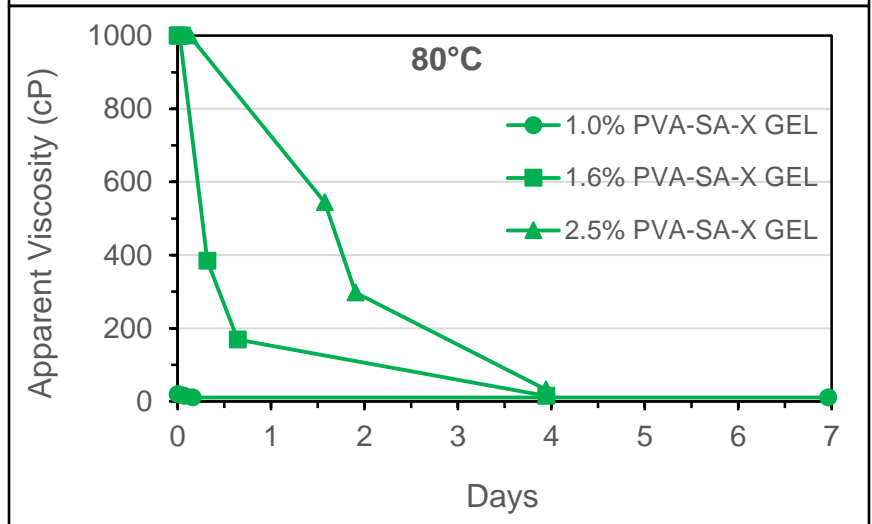
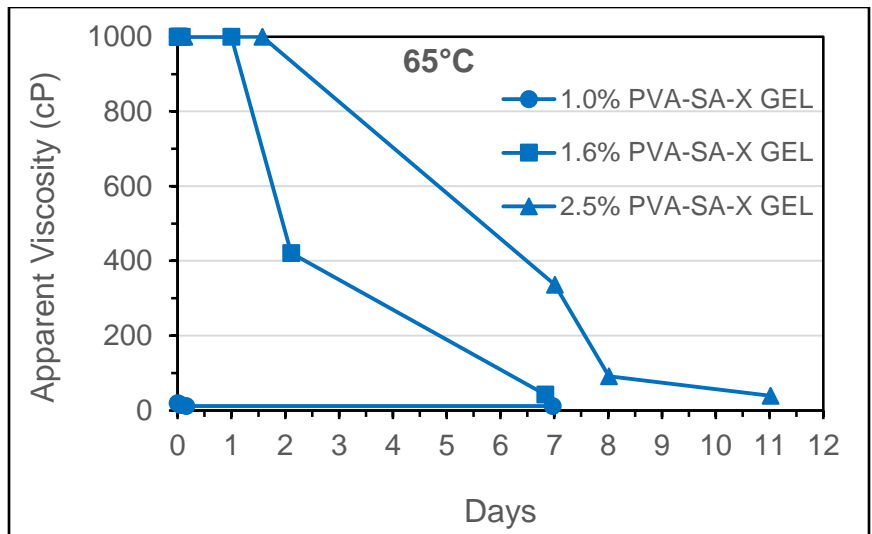


Figure 19. Degradation of PVA-SA-X Gel – 65°C, 80°C, and 95°C.

Figure 20 shows the effect of temperature on apparent viscosity for PVA-SA-X gel. It can be seen that the fluid degrades over time, and that for elevated temperatures, the effects increases drastically.

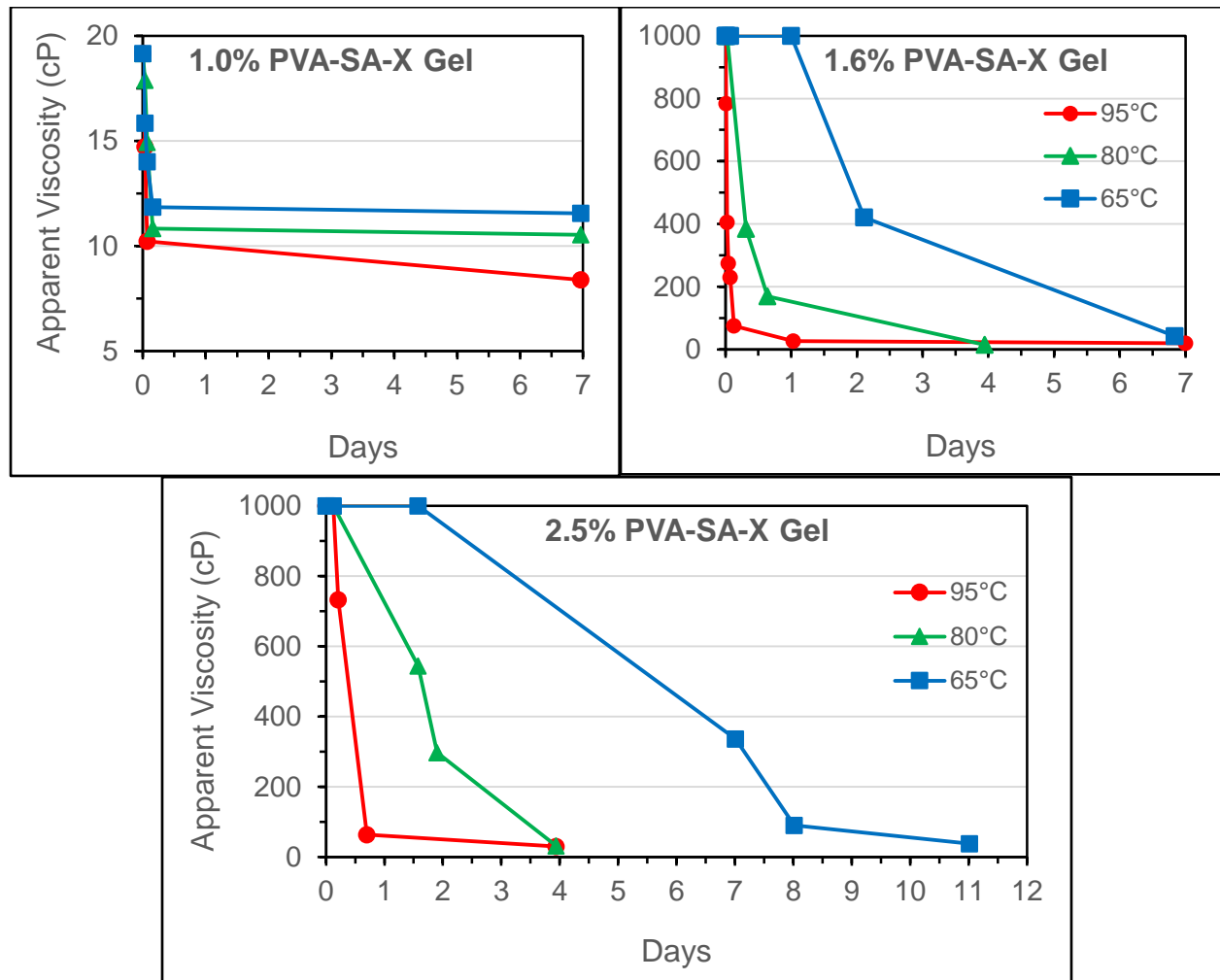


Figure 20. Degradation of 1.0%, 1.6%, and 2.5% PVA-SA-X Gel at 65°C, 80°C, and 95°C.

6.4.2.4 Comparing PVA-SA, PVA-SA-X, and PVA-SA-X Gel Degradation

Degradation of PVA-SA polymer and its various crosslinked systems is accomplished via an ester hydrolysis mechanism. Since the polymer solution is prepared to a slightly basic pH between 7 and 8, it is very likely that gel breaking occurred via a base hydrolysis of esters. Saponification is initiated by a hydroxide nucleophile attacking the electrophilic carbon atom of the ester C-O bond, leading to an acyl-oxygen cleavage. The rate of this reaction is temperature dependent with higher temperatures resulting in higher degradation rate.

To accurately analyze the breakdown of this novel polymer system, PVA-SA, and PVA-SA-X, and PVA-SA-X gel are comparatively studied at 1.6% and 2.5% concentrations at 95°C, 80°C, and 65°C. At these concentrations, we are ensuring that the PVA-SA gel is at or above its critical gelation concentration, and thus exhibits a viscosity (>1000 cP) that can be utilized for conventional hydraulic fracturing treatments. According to Figure 21 and Figure 22, we can note that after some incubation time period at the three different temperatures, the viscosity profile of PVA-SA-X gel either approaches or closely aligns with that of PVA-SA-X, while PVA-SA-X generally approaches that of PVA-SA. The former indicates that PVA-SA-X gel is being broken down via a dissociation of the chromium [III] crosslinker and PVA-SA-X polymer, weakening the 3D structure of the gel. The latter indicates that PVA-SA-X is broken down into smaller average molecular weight polymers, however its slightly higher viscosity than PVA-SA can be attributed to the presence of DCC and DMAP in the broken down solutions.

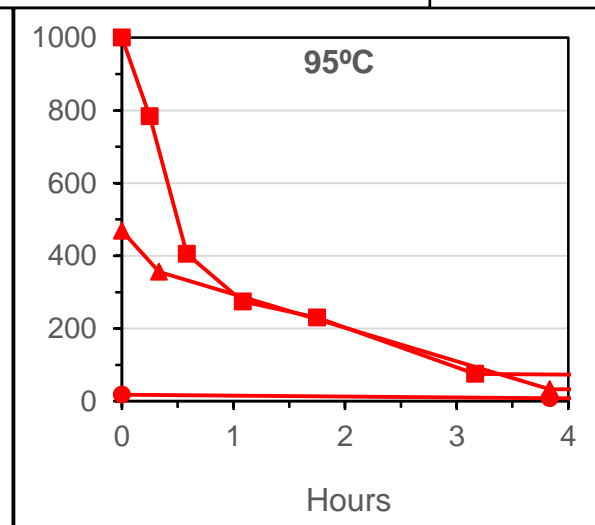
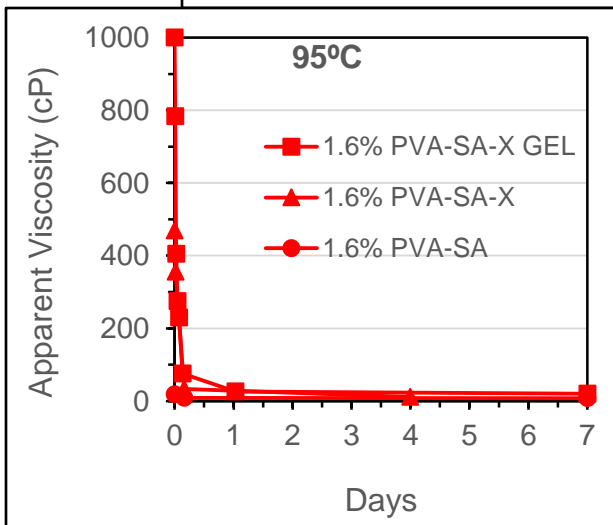
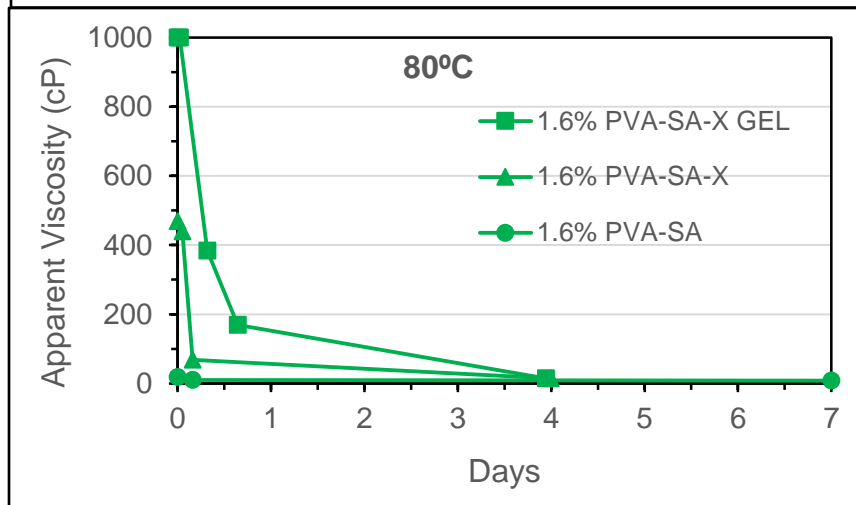
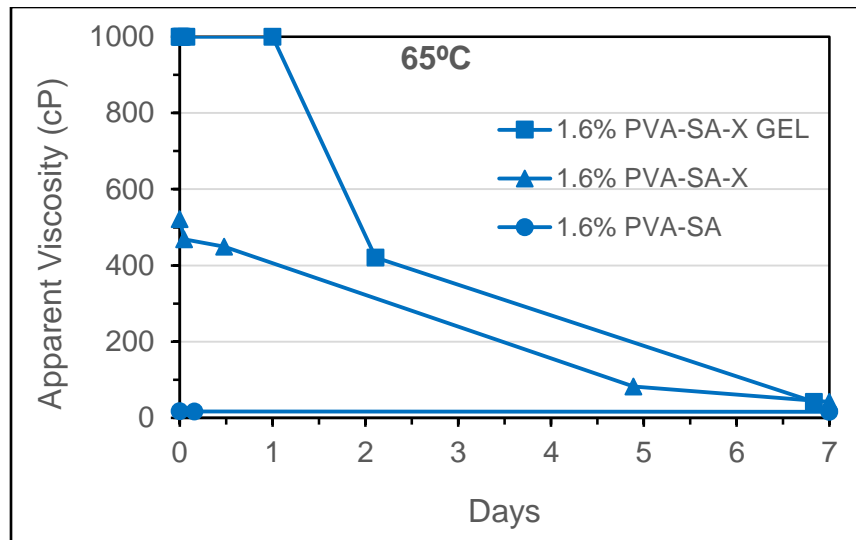


Figure 21. Degradation of 1.6% PVA-SA, PVA-SA-X, PVA-SA-X gel – 65°C, 80°C, and 95°C.

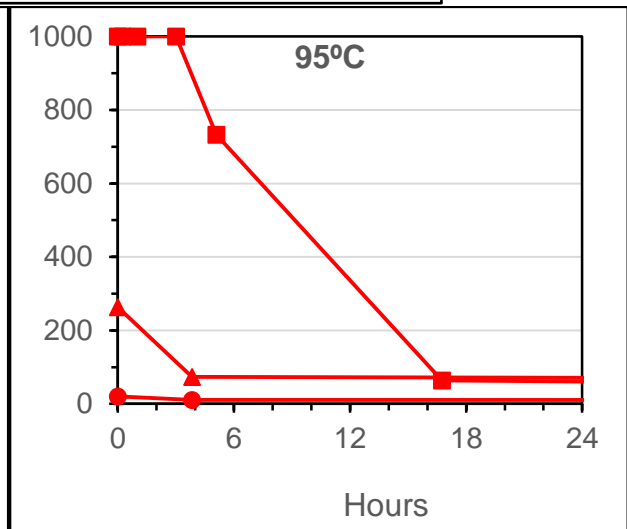
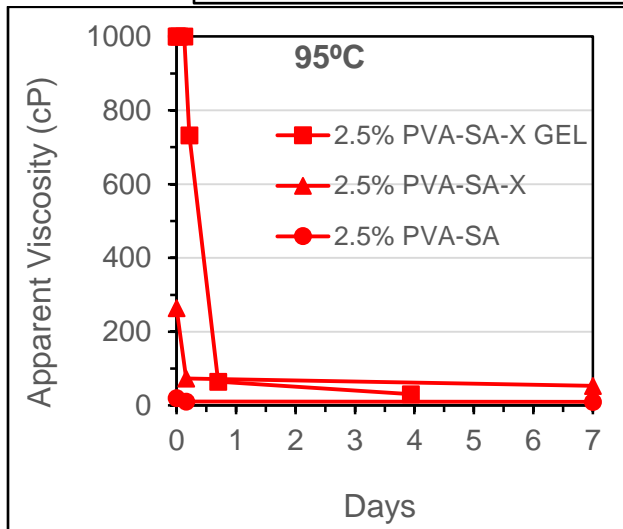
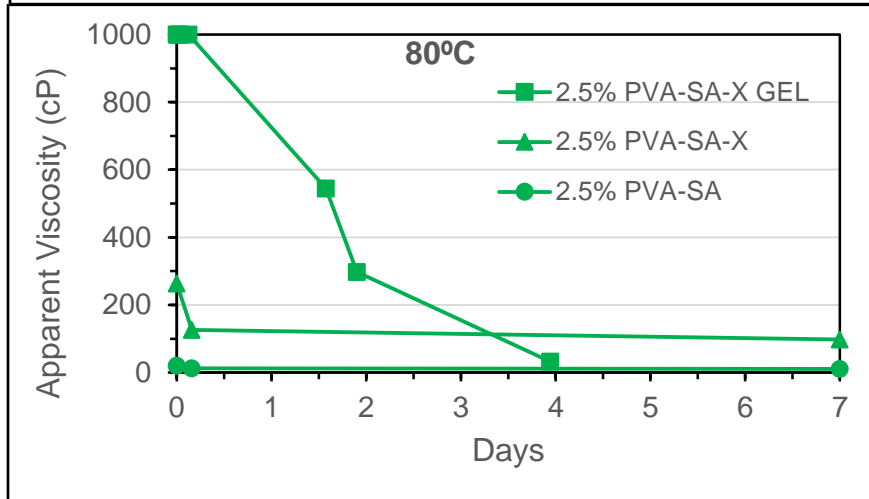
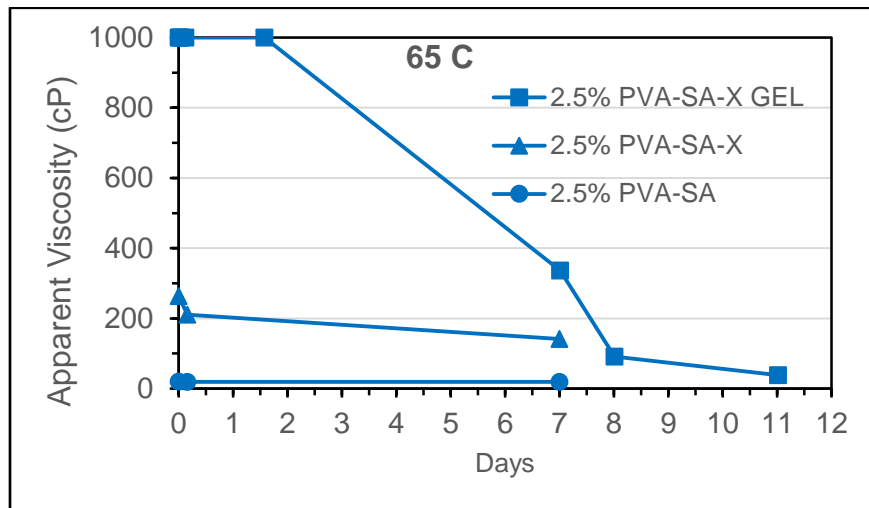


Figure 22. Degradation of 2.5% PVA-SA, PVA-SA-X, PVA-SA-X gel – 65°C, 80°C, and 95°C.

6.5 Degradation Conclusions

The objective of this degradation section is to show that PVA-SA-X and PVA-SA-X gel is capable of self-breaking under typical reservoir conditions, leaving negligible degradation residue after the fracturing treatment is administered, without the aid of internal breakers. Based on the data presented previously we can conclude the following:

1. The rate of all PVA-SA polymer systems' breaking is proportional to temperature, and inversely proportional to polymer and crosslinker concentration.
2. The rate of degradation is highest within the first 24 hours, before leveling off.
3. Complete breakdown of polymer can be achieved at higher temperature reservoirs, and the higher the incubation temperature, the shorter the breakdown time.
4. Degradation of PVA-SA-X is a result of a saponification reaction at the ester linkages, reducing average molecular weights of the polymer solution.
5. Degradation of PVA-SA-X gel is a result of a weakened 3D gel structure, as the crosslinker is dissociated from the polymer, PVA-SA-X.

This proves that without the use of internal breakers, PVA-SA-X gel is capable of degrading into a solution that will flow during post-flush, minimizing formation and proppant-pack damage.

CHAPTER VII

CONCLUSIONS

7.1 Summary of Results

The objective of this research is to synthesize and characterize a novel hydraulic fracturing fluid that can suspend proppant long enough to be properly placed within the fracture network of a hydraulic fracturing treatment, and break down after a conventional and unconventional fracturing treatment is complete, restoring proppant pack conductivity and ensuring proper hydrocarbon flow. Our system proves that it can be tailored specifically to fit the needs of the reservoir, as the process involves synthesizing a gel that can be modified. Using DCC and Cr^{3+} , we can control the final fracturing fluid viscosity and fluid break down time depending on the concentrations used. PVA-SA slightly crosslinked with DCC (also known as PVA-SA-X) is a non-Newtonian fluid capable of increasing a hydraulic fracturing fluid viscosity necessary for proppant suspendability in unconventional hydraulic fracturing treatments. Adding chromium [III] crosslinker to this polymer system further enhances the viscosity of the hydraulic fracturing fluid necessary for proppant transport and fracture creation in conventional reservoirs, via the creation of 3D polymer networks. Both PVA-SA-X and PVA-SA-X gel are capable of self-breaking, especially under elevated temperature conditions, without the aid of internal breakers, minimizing formation and proppant-pack damage during the post-flush process of a hydraulic fracturing treatment.

7.2 Primary Obstacles

By far the biggest difficulty in experimentation is attributed to maintaining consistent gel strength when making new batches of PVA-SA. In order to obtain reproducible results in the

gelation studies, a consistent way of preparing the gelling solution/linear polymer was established and carefully followed. To combat the issue of gel strength inconsistency, it is highly recommended that a fresh batch of PVA-SA-X be synthesized immediately before use or test. Also, to ensure consistent gel strength after PVA-SA polymer preservation of approximately 24 hours, it would be recommended to measure the polymer viscosity before application to confirm polymer strength stability.

7.3 Recommendations for Future Work

Based on our experiments, we have evidence of enhanced viscosity by this polymer system. To further understand the proppant carrying properties of this novel hydraulic fracturing fluid, recommended future work could include:

1. Study the capacity of PVA-SA-X or PVA-SA-X gel to carry different types of proppant during hydraulic fracturing.
2. Perform simulations of PVA-SA-X or PVA-SA-X gel application for hydraulic fracturing by investigating its performance after flowing through a porous media via a sandstone core flood experiment.

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