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Fiber Assisted Re-Assembly Preformed Particle Gel for Conformance Control

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FIBER ASSISTED RE-ASSEMBLY PREFORMED PARTICLE GEL FOR CONFORMANCE CONTROL

by

ZHE SUN

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ABSTRACT

In Enhanced Oil Recovery technology today, gel treatments have been implemented as a cost-effective method to improve the oil sweep efficiency in reservoirs by plugging the high permeability zones. This study presents a novel gel composition to be used in conformance control in order to improve oil recovery for mature oilfields.

The product is a fiber-assist re-assembly preformed particle gel which could be generalized to the preformed particle gels (PPG). The product developed in this study could be injected into the reservoir act as a conformance control agent by plugging water thief zones and channels in the beginning process. Due to the high temperature and the high pressure under the reservoir condition, the product will re-assemble into a bulk gel and would effectively plug the fractures or channels in the reservoir to improve the oil sweep efficiency in the low permeable zones.

The study synthesized an elastomeric gel with polyacrylamide crosslinked with N,N’MBAA, Zirconium Acetate, and fibers embedded. Synthetic parameters including the type and concentration of initiator, crosslinker, fiber, and other additives were adjusted to obtain the gel with the highest strength. By employing fiber as an additive in the re-associate preformed particle gel system, the mechanic strength of the product was improved.

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1. INTRODUCTION

During the process of oil recovery, on account of the oil reservoirs subjected to a long water flooding process, excess water production had become a major issue (Bai, 2007). High levels of water production could also result in scale, corrosion, mineral dissolution, and environmental problems. Excessive water production is possibly deriving the mature wells to early abandonment and left unrecoverable hydrocarbon and leads to an increase in facility cost and lifting cost. Producing zone is frequently abandoned in order to avoid water contact, in spite of the amount of recoverable hydrocarbon still remaining in the reservoir. Therefore, it becomes one of the major problems for the oilfields to control water production. Moreover, the global oil recovery factor as low as 43% (Schulte, 2005), extending the life of mature well using enhanced oil recovery (EOR) methods is also one of the most crucial goals of the fuel industry.

Gel treatment has been widely applied in the reservoir as a cost-effective technique to improve the oil sweep efficiency in order to reduce the excess water production by plugging high permeability zones during hydrocarbon production. Gel treatment was also applied to improve the conformance and reduce water channeling in mature reservoirs. Gel treatment methods for conformance control can be ranged into two types: traditional in-situ crosslinking gels, and preformed gels. In-situ gel treatment is defined as injecting the mixture of polymers and crosslinker, also known as gelants, through the injection well into the target formation and form a bulk gel to fully or partially seal the formation at the reservoir condition (Sydansk and Moore, 1992). In spite of the improvement done by the in-situ gel, a series of lacks and problems still exist in this gel treatment method when being applied in complex reservoir conditions, including the lack of time control, uncertainty of gelation due to shear degradation, chromatographic fraction of gelation components after long-distance transportation of the liquid gel, chemical mixture contents change due to the different adsorption ability of gelants composition, and the potential formation damage caused by the in-situ gel injection in the low permeability zones.

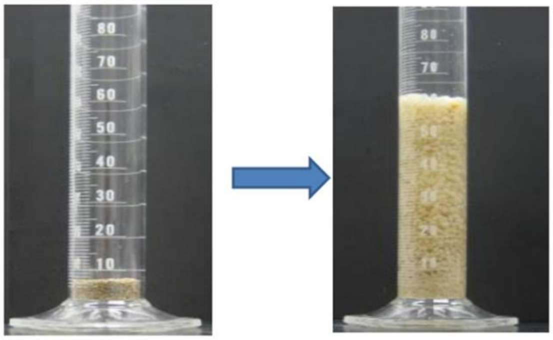


Figure 1.1 PPG before and after Swelling

To solve the problems listed above, another kind of gel treatment method is employed in EOR process, preformed gel synthesized and prepared at surface facilities before being injected into a reservoir; in this case, no gelation occurs in the reservoir, so this method could inherently overcome some distinct drawbacks occurred in the in-situ gelation systems. The flow direction of the particle gels could be controlled by the particle size, according to the requirement of the reservoir condition (Figure 1.1). After transferring into the reservoir, particle gels swell and form relatively high-intensity blocks for appropriate pores, and finally result in fluid flow to be redirected to the high remaining oil zone. Particle gels can stay in occulted pores for several months to years, depending on the reservoir situation, such as pH, temperature, formation water salinity, and the adsorption of chemicals on the reservoir rock surface.

Although preformed particle gel system can overcome some disadvantage inherent in-situ gel, current preformed particle gel cannot efficiency reduce the channeling problems of abnormal reservoir features, such as void, wormhole, open fractures, and so on. Therefore, our group develop a series of recrosslinkable preformed particle gels to solve these problems. This thesis introduces a study of a novel preformed particle gel, fiber-assist re-assembly preformed particle gel, also known as F-RPPG, which could re-assemble into an elastomeric rubber-like bulk gel after contacting with formation water in a reservoir. The product could keep stable under reservoir conditions for a specific period of time before losing properties and will serve as a plugging agent in the reservoir with abnormal channeling features. The fiber-assist re-assembly preformed particle gels employed a kind of fiber and two types of crosslinkers in order to improve the incorporation with the gel mechanical strength, swelling capacity, and the long-term thermostability to adapt the special and extreme reservoir conditions. The two types of crosslinkers will help the particle gels re-assembly into bulk gel after swelling in the reservoir.

This study involves an improvement in gel strength without sacrificing the swelling capacity under reservoir conditions for further water plugging, compared with the existing preformed gel products that do not use additives embedded. The swollen particle gel will re-assemble into bulk gel under the high temperature reservoir condition so that it could effectively plug the fractures or channel in the reservoir. After the fractures plugged, the surface crew will inject water into the well to sweep out the oil from low permeability oil-rich zones and produce oil from the well.

Moreover, fiber is widely used in the well drilling process and mud treatment as a low-cost supporting material. With the addition of fiber, the total cost of the particle gel could not be changed while the property of the plugging material is improved.

2. LITERATURE REVIEW

2.1. INTRODUCTION OF ENHANCED OIL RECOVERY

Three major recovery mechanisms, primary, secondary, and tertiary recovery are widespread applied in the oil recovery process (Figure 2.1). Primary recovery is the first step of the hydrocarbon production using natural energy to push the hydrocarbons from the reservoir and helps the transportation of the hydrocarbons towards and out of the production wells during the primary recovery process, where the technique of primary recovery includes gas cap drive, solution gas drive, water drive, gravity drainage, and combination drive using the method listed above. In most cases, only less than 15% of the original oil-in-place is obtained during the primary recovery.

Secondary recovery is the method that human intervention gets involved into the production of hydrocarbons in order to improve the recovery rate when the natural energy used in the primary recovery is diminished to low efficiencies. The most used technique during the secondary recovery are water flooding method and gas flooding method. By injecting water or gas into the reservoir through the injection well, the reservoir pressure is maintained at the level that the hydrocarbon could keep producing from the reservoir, the oil would be displaced towards production wells in this case. According to the statistics, the combination of primary and secondary recovery could help extract about 35% of the total original oil-in-place from the reservoir (Green & Willhite, 1998). After the reservoir produced a large amount of fluid that artificially injected to the reservoir , the production method is no longer economical or efficiency. Thus, further method used to help continuing produce more hydrocarbons from the reservoir is used.

Tertiary oil recovery, also known as Enhanced Oil Recovery (EOR), refers to oil production by the injection of substances like steam, chemicals, and other injection materials, that were not originally presents in the reservoir to improve the microscopic and macroscopic sweep efficiencies following either secondary recovery or directly after primary recovery (Willhite, 1998).

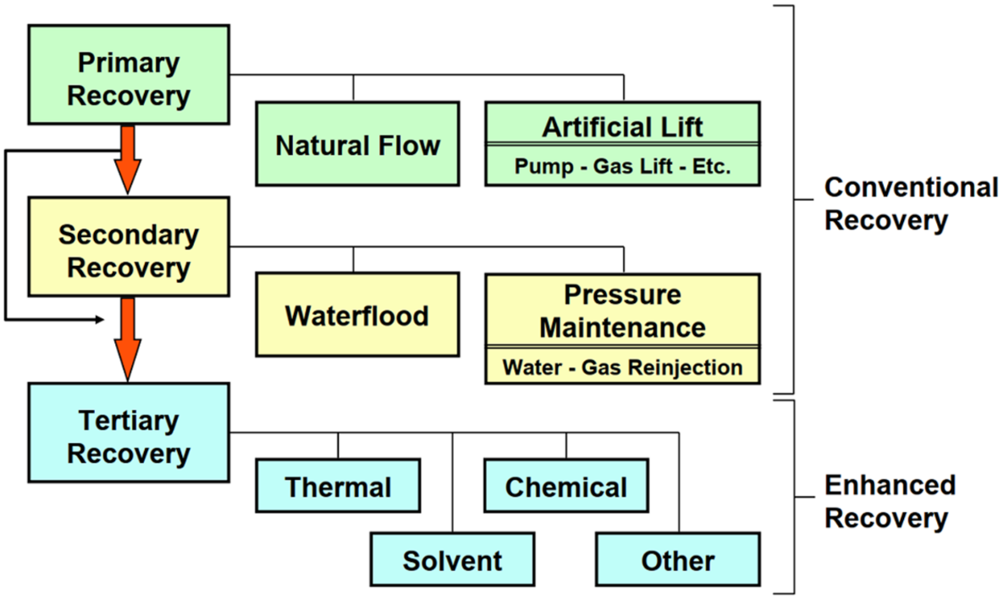


Figure 2.1 Classification of Oil Recovery Techniques (S. Thomas, 2007)

A classification of these methods is shown below in Figure 2.2. The final objectives of each enhanced oil recovery method are to overcome reservoir issues to mobilize the oil remaining in place. The five key reservoir issues are residual oil, high oil viscosity, reservoir heterogeneity, fractures, and oil wet rock. Varied EOR methods could be selected to solve the problems occur in the well based on the rock and fluid properties of the reservoir situation.

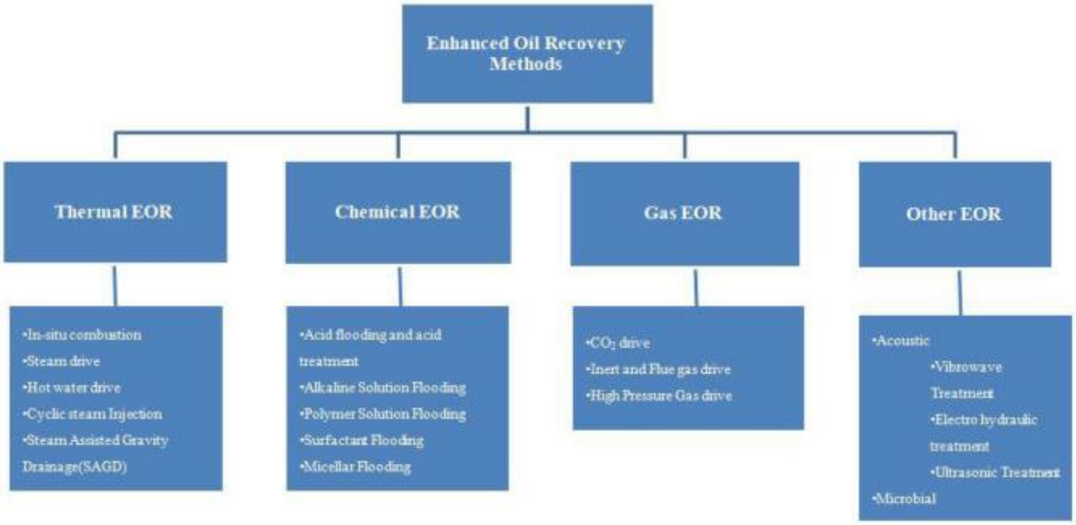


Figure 2.2 Classification of EOR Methods (K. Patel et al., 2018)

2.2. RESERVOIR CONFORMANCE PROBLEMS AND PROSPECTS

Conformance is the measure of the volumetric sweep efficiency during the flooding of displacing fluid of oil recovery process (Sydansk and Romero-Zerón, 2011). Reservoir heterogeneity and fractures are the main causes of the reservoir water control and water production issue. Water used as injection fluid breaks through and thief zones from the injection well to the production well and may cause unexpected water production increase and the oil recovery reduce. Moreover, excess water production give rise to the corrosion, scale, increased load on fluid handling facilities, environmental concerns, and finally cause the well shut down and abandoned (Liu et al., 2006; Bai et al., 2007a).

Conformance control may also refer to technologies using mechanical and chemical methods to prevent non-hydrocarbon fluid production from a reservoir. The unwanted fluid production could be attributed to the high-permeability zones, fractures, channels, and wellbore. To apply the technique, both injection well and production well could be used for water shut-off, profile control, and in-depth fluid diversion.

2.2.1. Water Shut-off. The technology of water shut-off involves two approaches, unselective and selective treatment and was mainly applied in the reservoir during the early water cut stage. In unselective water shut-off treatment, by injecting a plugging agent, the entire zone of large amount water production is plugged or sealed, so the oil production from other zones is possible after the treatment.

The technology of water shut-off was primarily applied targeting on production wells that are conducted one or more distinct water zones or high water cut zones separated from other oil production zones, shifting the reservoir heterogeneity among isolated layers in order to reduce the water production from the reservoir. Selective water shut-off treatments focus on the reduction of the water permeability, using the plugging agent capable to decrease the permeability of water which effect is more than that on oil. The plugging agents are injected through the production wells to control water from multi-layers or unidentified layers. The plugging agents preferentially congeal and harden when contact with water, so the water zone of the reservoir would be sealed in this case.

2.2.2. Profile Control. Profile control technology improves the injection profile of the injection well and then increase the reservoir oil sweep efficiency. The technology was mainly applied in the middle water cut stage of the reservoir. Profile control includes the gel treatments to the injection wells, improves the sweep efficiency in reservoirs and reduces excess water production by plugging the water thief zones. Major plugging agent used in this technology are silicate gels, acrylamide-based gels, and other polymer generated gels. Profile control is a method that has been proved to be cost-effective.

2.2.3. In-depth Fluid Diversion. In-depth fluid diversion is primarily applied in mature oilfields with low oil remaining, near well bore, dominant interlayer heterogeneity, and wells under plural treatments. To improve the oil recovery, mass volume plugging agents are injected deep into the reservoir between the wells. The followed water would easily bypass the plugged channels and pass through the previous high-permeability water paths if inadequate amount of plugging agent were injected near wellbore. Therefore, large volume of plugging agent and deep penetration are significant to this treatment method to result in a satisfactory situation. Typical chemicals used in this process includes weak gel, preformed particle gel, colloid dispersion gel, clay gels, and industry waste (Coste et al. 2000).

2.3. GENERAL PROPERTIES OF RE-ASSEMBLY PREFORMED PARTICLE GEL

Gel treatments have been widely implemented as a cost-effective method to reduce the reservoir heterogeneity. Gels play a role in the reservoir as a plugging agent to seal the high permeability zones in order to lower the water production rate and reduce the production operation cost. Thus, it can reduce the volume of water produced with the oil (Liang and Seright, 2000).

Different types of gel treatments have been utilized in an attempt to solve conformance control problems which include 1) In-situ gel technology and 2) Preformed Gel Technology (Figure 2.3).

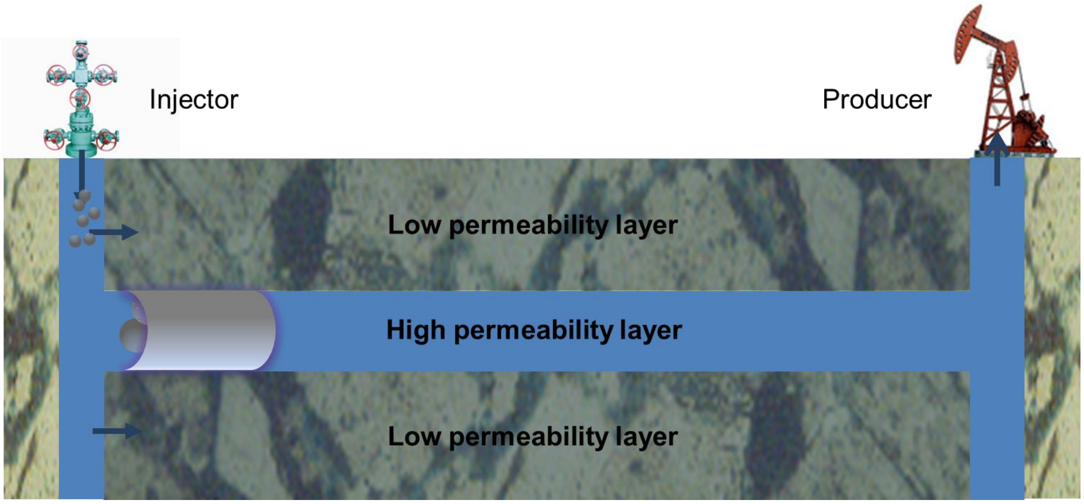


Figure 2.3 Gel Treatment Mechanism (J. Pu, 2018)

2.3.1. In-situ Gel Technology.

In-situ gels have been widely applied in oilfield for conformance control and have been developed for decades. In-situ gel literally means the gel is formed in the reservoir, by injecting gelants, the mixture of polymers and crosslinkers through the injection well into the target formation and complete the gelation in the reservoir condition which can fully or partially seal the formation at the reservoir temperature (Sydansk and Moore, 1992). Issues exists with the successfully application of in-situ gels due to the difficulty on transporting the mixture to target location and on controlling the reaction of the chemicals in a heterogeneous reservoir (Seright, 2007).

The gelants system could be used specifically designed for varied reservoir situations. Different types of polymers in this technology have been tested and applied on the oil fields, including hydrolyzed polyacrylamide (HPAM), polyethyleneimine (PEI), and polyvinyl alcohol (PVA). Most common crosslinkers used in in-situ gel system are metallic and organic crosslinkers.

2.3.1.1. Metallic crosslinked system. The most commonly used metallic crosslinkers includes aluminum, chromium, boron, titanium, ferric, and zirconium based crosslinkers. Aluminum sulfate ($Al_2(SO_4)_3$) was used in the crosslinking HPAM in early 1970s (Scoggins and Miller 1979; Lake 1989) and was uncontrollable at the in-depth formation.

Thus, the gelants system can only be applied as a permeability controller at the near-wellbore formation. Chromium/HPAM system was tested and observed to be to form a 3-dimensions bulk gel under the effect of the Cr(III) crosslink reaction (Rouston, 1972). The xanthan/Chromium based system was reported by Abdo et al. (1984) where Guar/Chromium system and CMC/Chromium based gelants systems was also been reported in the further development of in-situ gel technology. The HAPM/Chromium based gelants system achieved great success in the oilfields in 1994 (Southwell and Posey), while the Chromium Acetate crosslinker based gel showed a precursor to block the high permeability channels within a reservoir (Sydansk 1984, Sydanksk 1988, Sydansk and Smith 1988). PAM/Zirconium gelants system was also reported to be used in water shut-off and is controllable by Chauveteau (1999). Moffit (1996) reported that PAM/Zr(III) is a lower toxicity polymer crosslinking system than those commonly used chromium-gelling systems, inflicting lower damage to both the formation and be relatively safer to the oilfield workers and environments.

2.3.1.2. Organic crosslinked system. Not only metallic crosslinkers used in the polymer gel system, but organic crosslinkers have also been applied in the gelation of in-situ gels in which the crosslinkers forms covalent bonds with the polymer functional groups, which makes stronger composition than metallic crosslinkers do under most conditions (Raje et al. 1999).

The organic systems are generally stronger than metallic gel systems in many ways besides the gel mechanic strength, including the ability to stand harsh environments of high temperatures, high salinity, and high pH conditions. Chang (1985) synthesized a PAM gel based on the crosslinking reaction between phenolic compounds and formaldehyde. Seright and Martin (1991) designed an organically crosslinked sulfomethylated resorcinol gel system which produced a permeability reduction of 99% in the application and tolerates high salinity environments. Organic crosslinkers systems showed a larger reaction temperature range that could be formed under 149°C (Moradi-Araghi et al. 1989).

2.3.1.3. Limitation of in-situ gel system. The limitation of the in-situ gel system was mentioned above. The formation in the reservoir is complex where the profound differences between high and low permeability zones exist in the matrix, some of the gelants may flow into the low permeability zones, the oil-rich region and damage the area or block the oil production (Liang et al,. 1990; Seright, 1990).

When the gelants passes through the formation with large fractures, the gelants may possibly lost during the transportation. The gelants may also diluted or dispersion by contacting the formation water, which would possibly cause the composition lose function, either be not effective or impossible to crosslink (Young et al., 1988). Dilution could be caused by chromatographic separation, adsorption, or the formation water mixed with the gelants, resulting in the decrease in the concentration. Dispersion refers to mixing caused by the variations in the velocity within each flow channel and from on channel to another

(Arya et al, 1988). The reaction rate and condition are uncontrollable in the reservoir, thus the selection of the crosslinkers is under restrictions due to the extreme reaction conditions.

2.3.2. Preformed Particle Gels. In recent years, the study of the other gel treatment approach to improve sweep efficiency has been developed and gained considerable interest among the gel based EOR process, the preformed gel treatment. Seright (1997, 2000) studied the behavior of preformed bulk gel through fractures, the research showed the preformed gel presents better placement than in-situ gel and could possibly reduce the gel damage on the unswept low-permeability oil zones.

Chauveteau et al. (2000,2001, 2003) synthesized a group of preformed microgel particles that could recrosslink under the shear. This kind of gel has only one component during injection and the gel property is less sensitive to physical-chemical conditions in the reservoir such as pH, salinity, multivalent ions, hydrogen sulfide, and temperature (Bai et al., 2007a, 2007b, Bai 2012). The main difference between preformed particle gel technology and in-situ gel technology is that the gel was synthesized and processed at surface facilities, and no gelation occurs under reservoir condition.

Preformed particle gel, also known as PPG, consists of dried, crosslinked, polyacrylamide particles (Bai et al., 2013). Once the particle gel contact with water, the xerogel could absorb moisture and swell from a few to 200 times its original volume. Thus, PPG is a kind of super-absorbent polymer in which the particles are elastic and deformable. The swollen particles were injected into reservoirs to control the fluid flow fully or partially in fractures or fracture-like channels.

Since 1997, a series of PPGs have been researched and developed for conformance control, including polymer-clay composite gels, soft-deformable-rubber-like particles, swelling retarding PPG, low surface tension PPGs, and strength-adjustable PPG. PPGs are in the category of the super-absorbent polymers (SAP) which are 3D hydrophilic crosslinked polymers. PPGs are prepared with a solution polymerization method followed by grind and sieve to the desired particle size. To prepare a group of PPGs, the bulk gel was synthesized with monomer, initiator, crosslinker, and additives under room temperature in surface facilities. The major monomer being selected for PPG synthesis is acrylamide, due to the low cost and the relatively stable chemical characteristic; thus, the major ingredient of most PPGs is polyacrylamide. The bulk gel was later cut into pieces and then oven- or air-dried to form xerogel. Dried particles are grounded and sieved according to the desired size according to the condition of the reservoir. The dried particle gels are strength- and size-controlled, resistant to reservoir minerals and formation water salinity. Comparing with traditional in-situ gel treatment technology, the development of PPGs comes with a number of advantages, where the surface condition synthesis may overcome some distinct drawbacks inherent in in-situ gelation systems; also, PPG is a kind of strength- and size-controlled, environmentally friendly, thermostable, non-sensitive to reservoir minerals or formation water salinity; PPG could resist up to 120 °C, up to 300000 mg/L salinity; PPG suspension can be prepared with produced water to save fresh water; PPG injection operation processes and surface facilities are simple, reducing the operation and labor cost; PPG is a cost-effective method to correct permeability heterogeneity for reservoirs with fractures and channels.

2.3.2.1. PPG transport through porous media and openings. In an attempt to study the transportation mechanism of PPGs, Coste et al. (2000) developed a glass micromodel as shown in Figure 2.4, three main mechanisms was elucidated on particles through a large pore throat, including the particle deformation, particle shrinking by the expulsion of water, and particle breakage (Figure 2.5) (Coste et al. 2000).

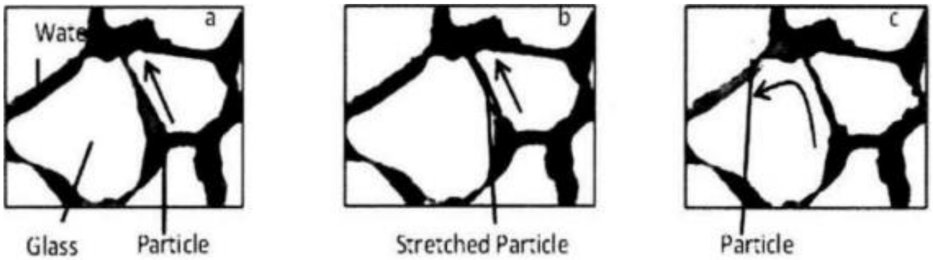


Figure 2.4 A Deformable Particle Passing through a Pore Throat (Coste et al. 2000). a) Particle moving to the throat entrance. b) Stretched particle filling the throat. c) A particle passing through the throat and mobbing to another throat.

Bai described six patterns of PPG propagation through pore throats: direct passing, adsorption and retention, deformation and passing, snap-off and passing, shrinking, and passing, and trapping (Bai et al. 2004; Bai et al. 2007).

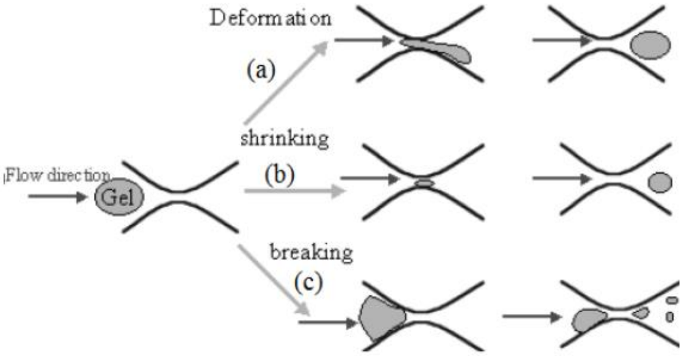


Figure 2.5 Different Mechanisms of how Particle Gels Pass through a Pore Throat (Coste et al. 2000). a) Deformation and passing, b) Shrinking and passing, c) breaking and passing

The application of PPGs on the fields could verify that particle gels can plug highly permeable channels mobbing to continuous long-tie water or polymer flooding (Liu et al. 2006). However, as long as PPGs are relatively large particles with good swelling kinetics, the application is limited to the reservoir with fractures or fracture like channels.

2.3.2.2. Recent development of PPG. Preformed particle gel treatment for conformance control was initiated in 1996 by RIPED, PetroChina (Bai et al. 2013). The first successful large volume of PPG treatment applied in the oil field was in 1999, at Zhongyuan oilfield presented by Sinopec. The well chosen for the PPG treatment was under severe reservoir conditions, with a high temperature and high salinity. Nowadays, more than 10,000 wells have been treated with PPG or the combination treatment with PPG and other kinds of polymers. Reservoir temperature from 20 to 120 Celsius and brine salinity from 2900 to 300,000 mg/L, in both sandstone reservoirs and carbonate reservoirs, were selected for PPG treatment. A series of typical applications in which PPGs successfully in mature reservoirs are described below:

1. Application in high-salinity, high-temperature reservoirs, Zhongyuan oilfield, Sinopec, 1999
2. Application in low-temperature, low-salinity sandstone reservoirs with Thick Layers, Daqing oilfield, PetroChina, 2000
3. Application in a reservoir with severe sand production, Shengli oilfield, Sinopec, 1999
4. Application in polymer flooding areas, Daqing oilfield, PetroChina, 2003
5. Remediate Super Permeable channels and large fractures using PPG combined with weak gel, Dagang oilfield, Shengli oilfield, and Zhongyuan oilfield, Sinopec, 2003

6. Remediate unwanted communication in a CO_2 flooding reservoir, Kelly-Synder field, 2008
7. Plug void conduit in Anton Irish field, 2006

From more than 10,000 wells treated with PPGs or combination of PPGs and in-situ gels, several common grounds between the applied oilfields could be found that mostly the treated oilfields are without natural or international hydraulic fractures, the reservoir are with naturally fractured, able to be treated with CO_2 or polymer flooding, with reservoir temperature from 30 to 120 Celsius, formation water salinity between 2,900 to 300,000 mg/L. Thus, from the similarities between the wells, the criteria for well selection could be concluded with the reservoir temperature below 120 Celsius, reservoir with high-permeable channels or fractures, high injectivity and low pressure index, high water cut and high liquid rate of connected producers, well grouped with low oil recovery preferential. Figure 2.6indicates a simple development process of PPG.

From the post application of PPGs, the limitation of PPGs could also be found during the experiment and the industry application. PPGs cannot be injected into normal porous media without fractures or channels. Furthermore, PPGs cannot be applied in the reservoir with open fractures or super-high-permeable channels since the swollen polymers would be flushed through the fractures to the production well.

2.3.2.3. RPPG. During the application of PPG in the oilfield, PPG technology had represented the limitation of the properties due to the characteristics of the product. The rheology ability and the stability after swollen depend on the swelling equilibrium of the particle gel, which would be influenced by the salinity, pH, temperature, and other

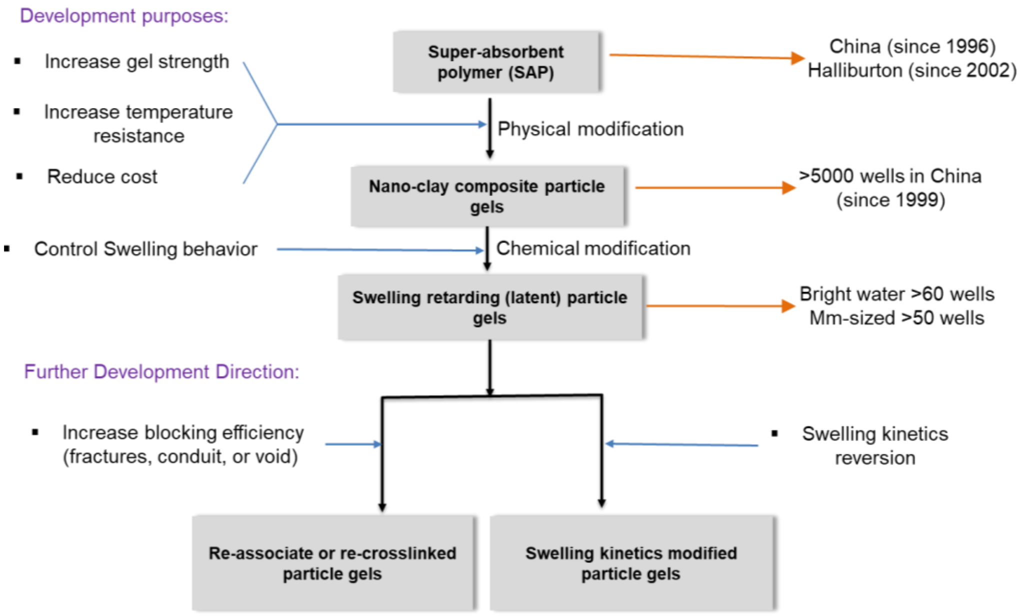


Figure 2.6 Development of Preformed Particle Gel (J.Pu, 2018)

factors under the reservoir condition, so the strength and the size of the gel is hard to control. Moreover, the volume of the swollen gel is limited by the size of the PPG, so that the PPG would have difficulty blocking the opening channels as long as the stacking of PPG is uncontrollable in the reservoir (Figure 2.7).

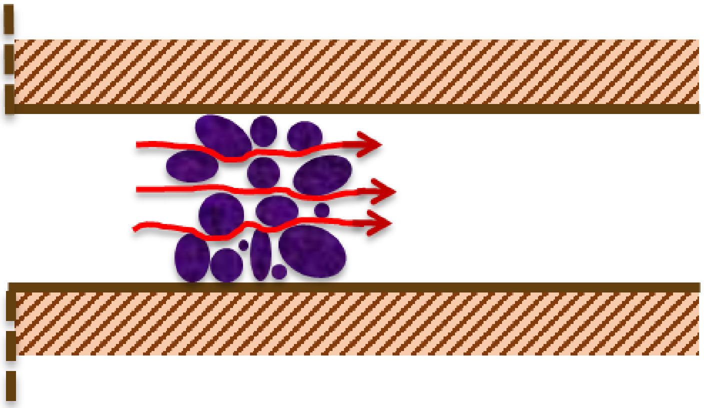
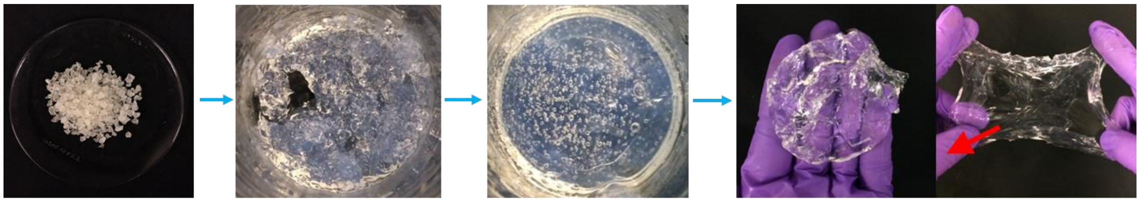


Figure 2.7 Failure of PPG on Blocking off the Big Pore Throat (J. Pu, 2018)

Therefore, a new kind of gel that the final size could be controlled and improved in order to block opening channels is developed. Re-assembly Preformed Particle Gel (RPPG), using a secondary crosslinker during the synthesis which would help the particle gel re-crosslink to form a rubbery bulk gel after the particles are fully swollen(Figure 2.8). This technology can sigificantly improve the sealing capacity of the gel treatment and thus RPPG can be potentially applied in the oil fields with abnormal heterogeneity problems.


RPPG particles (1-4 μm)

equilibrium swelled RPPG

re-assembling

re-assembled bulk gel

Figure 2.8 Re-Assembly of RPPG (J.Pu, 2019)

2.3.2.4. Fiber-assist preformed particle gel. Under the effect of the crosslinker in the RPPG, the particle gels are re-assembled to a rubbery bulk gel so it could be applied in the reservoirs with large opening. However, the mechanic strength of the previous product is not high enough in some situations. To improve the gel strength, the method of synthesizing the RPPG could be improved.

Many studies have tested embedded the gel with clays, chemicals, and other additives to improve the re-assembly gel with mechanical strength, thermostability, and other properties specifically designed for varied reservoir conditions (Xing et al., 2002; Sada et al., 2004; Li et al., 2017). While fibers are a proven cost-effective material that has

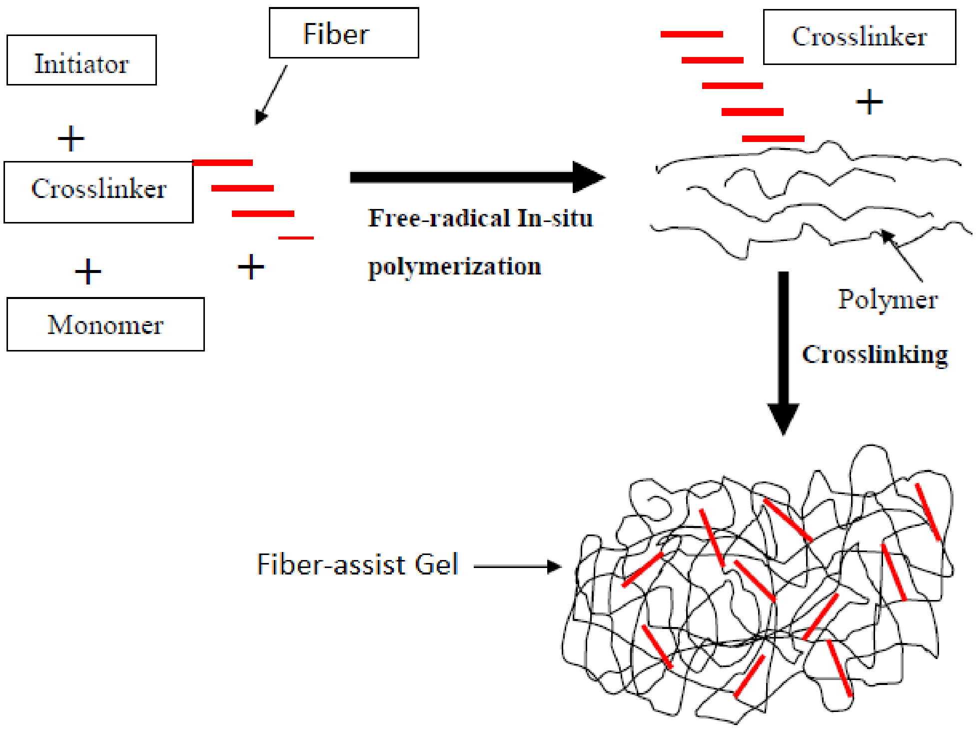


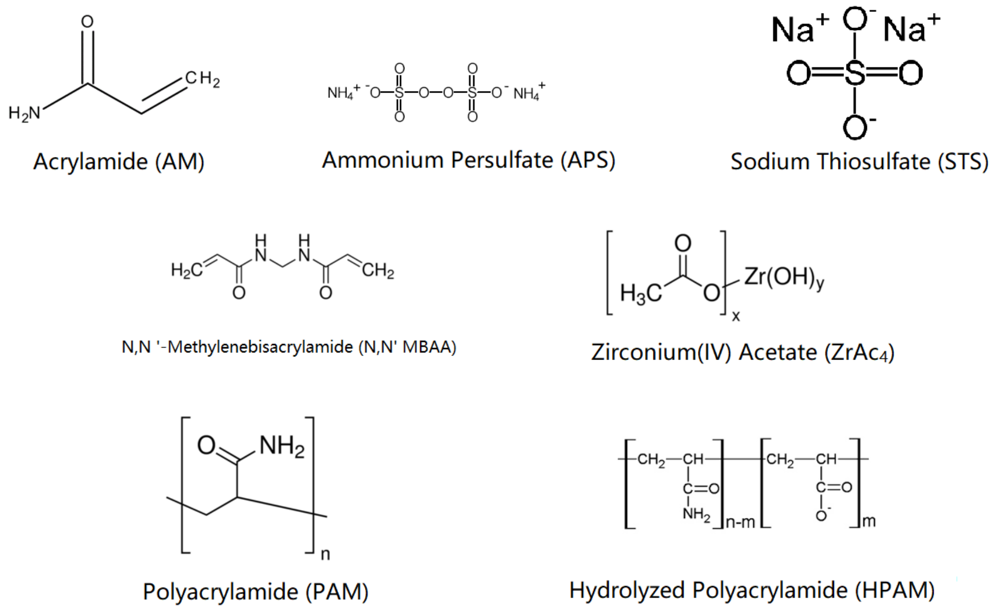
Figure 2.9 Free Radical Polymerization of Fiber-Assist Gels

been widely applied in petrochemical industry, with good thermostability, strength, tenacity. Also, the density is controlled to be relatively lower. Chen (2019) synthesized polyacrylamide-based hydrogel for profile modification using polyvinyl alcohol(Chen et al, 2019) and proved that the fiber could improve the bulk gel stability and accelerate the gelation. Fiber-assisted gels are synthesized by the addition of fibers to the gel formulation under radical conditions, involving monomers, crosslinker, initiator, additives, and fibers (Figure 2.9).

3. EXPERIMENTAL STUDIES

3.1. MATERIAL SYNTHESIS

The materials used in the study includes one type of monomer, an initiator, a co-initiator, 2 types of crosslinkers, thickener, and fibers. The monomer used in this study was acrylamide (AM). Acrylamide (98%) was purchased from Alfa Aesar Company (Ward Hill, MA). Figure 3.1 shows the chemical structure of the monomers.



Acrylamide (AM)

Ammonium Persulfate (APS)

Sodium Thiosulfate (STS)

N,N '-Methylenebisacrylamide (N,N' MBAA)

Zirconium(IV) Acetate (ZrAc4)

Polyacrylamide (PAM)

Hydrolyzed Polyacrylamide (HPAM)

Figure 3.1 Molecular Structures of Compounds used in the Study

The initiator used in the study is Ammonium persulfate (APS), and the co-initiator is Sodium Thiosulfate (STS), obtained from Fisher Scientific. The crosslinkers tested in this study is 16wt. % Zirconium Acetate ($ZrAc_4$) and N, N'-Methylenebisacrylamide (MBAA), purchased from Sigma Aldrich. Reverse Osmosis (RO) water was used for the synthesis experiments. 2wt. % potassium chloride (KCl) and formation water was prepared for the swelling and re-assembly experimental evaluation. KCl was purchased from Fisher Scientific Inc. and used as received.

Four types of thickener were tested in the study includes polyacrylamide (PAM), hydrolyzed polyacrylamide (HPAM), methyl cellulose (MC), and Alginic acid.

Fiber used in the study was polypropylene, provided by Forta Corporation. Three different sizes of the fiber were tested, including the length of 0.5 in (13mm), 0.125 in 3.2mm), and 1 mm.

3.2. SYNTHESIS AND PERPARATION OF FIBER-ASSISTED RPPG

The fiber-assisted re-assembly PPG was synthesized under a free-radical polymerization. Two methods were tested in the study. The first method used $ZrAc_4$ as the only crosslinker, making the acrylamide monomer solution physically being crosslinked and resulting in a thick and viscous polymer; the other method used both N,N' MBAA and $ZrAc_4$ as crosslinkers in that the gel would recrosslink to a strong bulk gel after the particle gel absorb water and swell. The synthesis mechanism was shown in Figure 3.2 below.

The fiber used in the study were microfibers with the concentration from 0.03 to 0.012 wt%. Basically, the monomer concentration was in the range of 19-24 wt% with the 16% $ZrAc_4$ and the N,N'MBAA concentration in the range of 15-16wt% and 5-8 ppm, respectively. The concentration of the initiator, Ammonium Persulfate, was in the range of 182-516 ppm, where the co-initiator, sodium thiosulfate, had a concentration in the range of 182-484 ppm. Both initiators were employed to polymerize the monomer solution of acrylamide. A flowchart showing the synthesis process of the fiber assisted RPPG was shown by Figure 3.3.

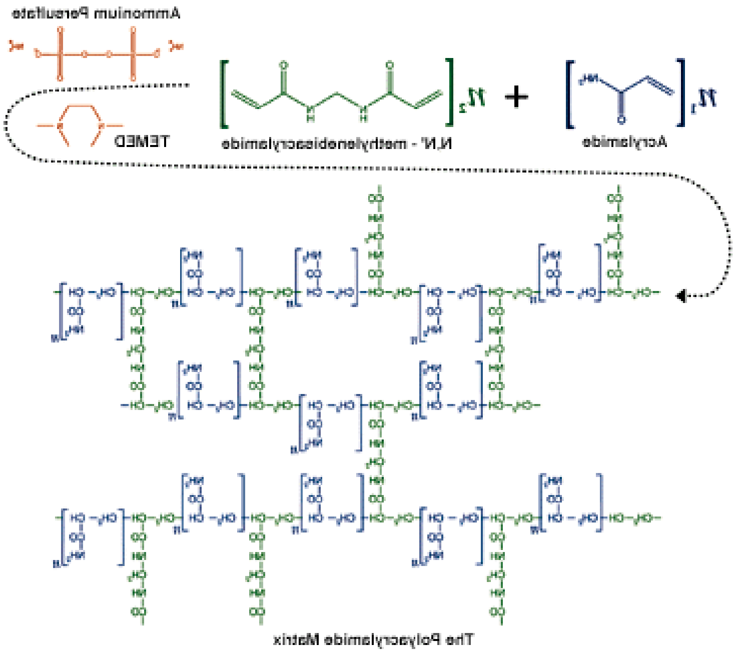


Figure 3.2 Sample Synthesis of Polyacrylamide

To demonstrate the synthesis process of the F-RPPG, the following steps are provided. First, dissolve 0.1g thickener in 100g of RO water in a 250 mL beaker, stirring under room temperature until the solute was fully dissolved in the solution. At the same time, dissolve 30g acrylamide monomer into 50 mL RO water with stirring under room temperature and deoxygenate operation. Then, 25 mL of $ZrAc_4$ and 8 ppm of the N,N' MBAA (if needed) were added into the monomer solution. After a 20 min deoxygenation with nitrogen gas, 258 ppm of APS was added into the solution, add 0.1g polypropylene fiber into the solution after being mixed. Then, add 50 mL of the prepared thickening agent into the solution and evenly stir the solution until mixed thoroughly. To ensure the polymerization could be performed completely, after adding 258 ppm of the co-initiator, STS, place the sealed container into the 35°C-water bath for 8 hours. Meanwhile, the full gelation occurred through the polymerization and crosslinking as shown in Figure 3.4 that finally formed a strong and elastic bulk gel. The gel was cut into small pieces and then dehydrate with air drying or oven heat, and later grinded into 20-40 mesh size for further evaluation and characterization. When evaluating the gel, the particle gel would be placed into brine, with either 2% KCl, formation water provided by the site, or RO water. The solution was kept in enclosed containers for re-assembly under 80, 65, 40°C, or room temperature (Figure 3.3).

3.3. EVALUATION METHODOLOGIES

After the F-RPPG was synthesized and prepared, several properties of the gel need to be evaluated at elevated temperature to test if the product could satisfy the industrial requirement.

3.3.1. Swelling Kinetics of Fiber-Assisted PPG before Re-Assembly.

The evaluation first measures the maximum swelling capacity of the F-RPPG since this measurement is essential for the determination of the capacity and the ability to plug at the high permeability zones in the fractures in reservoirs.

In addition, evaluation of the RPPG swelling kinetics under simulating temperature gives a consultant of the mixing and pumping process from the surface to the desired formation. This test helps to select the suitable field and injection technique depending on the formation temperature.

The evaluation of swelling kinetics requires a 2.1g of dried and ground particle gel with 2% KCl brine, and formation water provided from the field, respectively. Meanwhile, the temperature of the swelling test was controlled to be 80, 60, 45℃, and room temperature to summarize the temperature effects on the swelling capacity. To calculate the swelling ratio of the particle gel, following equation was used:

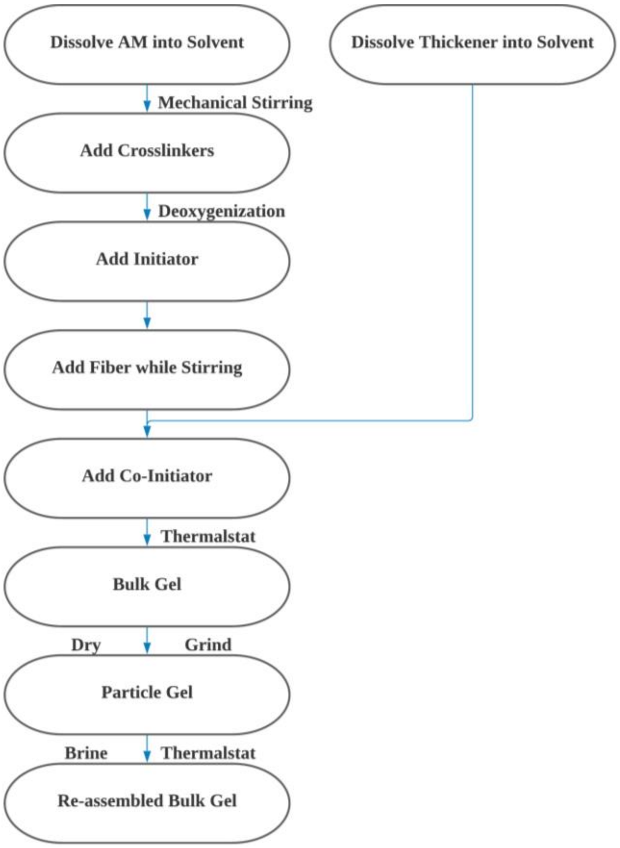


Figure 3.3 Fiber-Assisted Re-Assemble Preformed Particle Gel Synthesis and Fabrication

$$\text{Swelling Ratio} = Vs / Vi$$

where, Vs is the volume of the gel that fully swollen, and Vi is the volume of the dry particle gel.

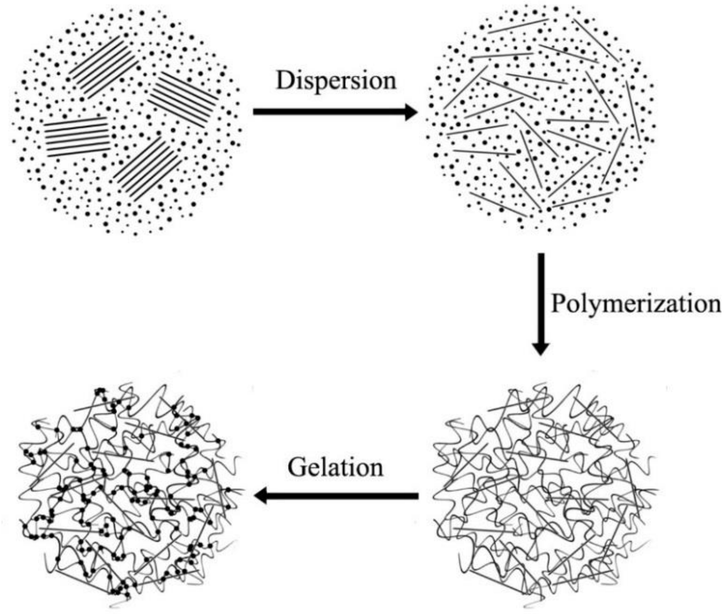


Figure 3.4 Dispersion, Polymerization, and Gelation of Fiber Assisted RPPG

3.3.2. Evaluation of Fiber-Assisted PPG after Re-Assembly. Both the strength and the thermostability of the RPPG are critical evaluation criterions. Both properties are evaluated to determine the performance of the gel. The strength of the gel would determine the capability to plug at the high permeability zones and the effect of the formation sealing. The thermostability determines the time of the re-assembled gel which could be functional under the formation situation as a plugging material.

3.3.2.1. Rheology test. The rheological properties of the gel were measured using a Haake Rheometer MARS from the Thermo Scientific Corporation, shown in Figure 3.5. The P35 Ti with a gap of 1 mm sensor was chosen for the evaluation. The re-assembled gel sample was cut into a thin piece with approximately 20 mm radius and 2.5 mm height. The measurements were settled as an oscillation model where the frequency of the experiments was first performed in the range of 1-10 Hz in order to establish the extent of the linear viscoelastic region. According to the data, all subsequent oscillation time-based experiments were performed at a fixed frequency of 1 Hz and controlled stress of 1,0 Pa to obtain the values of G’ and G’’ as a function of time, where G’ is the elasticity of the gel an the G’’ is the viscosity of the gel. The elastic and viscous moduli over strain were tested with a fixed frequency at 1Hz and the strain varied from 0.1% to 1000%. All runs were repeated for at least 3 times to reduce the measurement error.

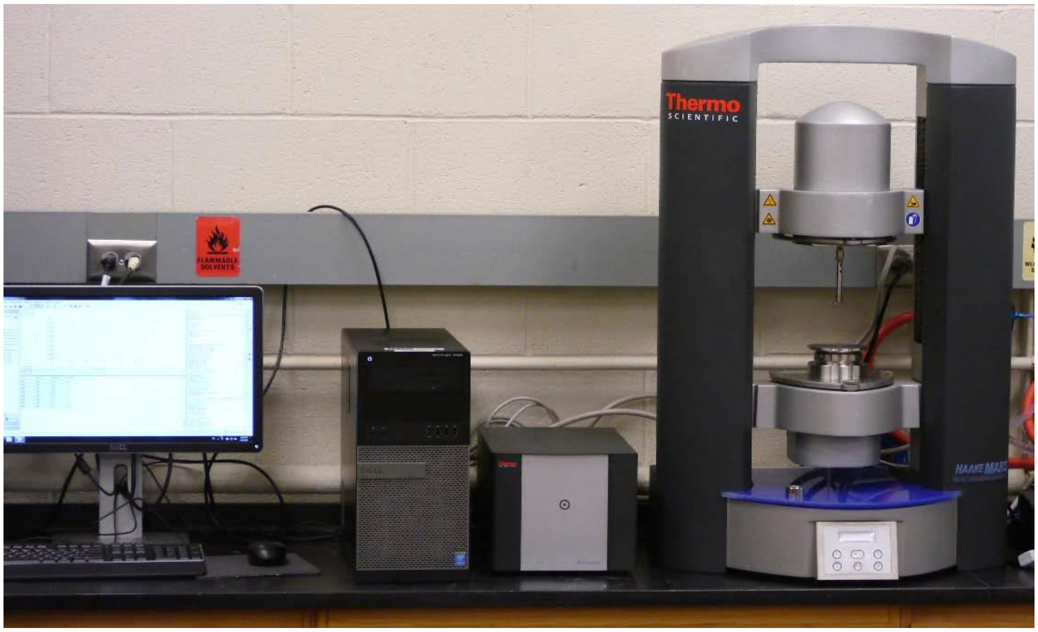


Figure 3.5 Haake Rheometer for the Measurement of Gel Rheology Evaluation

3.3.2.2. Thermostability test. A significant criterion to judge if that the material could be successfully applied in the reservoir is the amount of time that the gels could be effectively functional under the reservoir conditions (Nagra et al.,1986). The duration of the thermal degradation indicates the time of the fiber-assist re-assembly preformed particle gel could keep function as a plugging material after a time period of degradation in the simulated temperature. After which it will degrade into viscous polymer solution which will then move deeper into the reservoir and augment polymer flooding.

To evaluate the thermostability of the material, a series of methods were used in the lab where the reservoir conditions were taken into consideration as a difficulty for the simulation. The method which most commonly used is the high-temperature and high-pressure ampoules ((Wellington, 1983; Ryles, 1988; Sydansk, 1990; Seright and Henrici, 1990; Eriksen et al., 1997; Wu et al., 2009; Bai et al., 2013; Dupuis et al., 2013). There are also other methods that could involve the evaluation of the gel thermostability, for instance, sandpack (Mercado et al., 2009), TGA analysis, and FTIR analysis (Foschiera et al, 2001).

Thermostability tests were performed in a simple method after consulting the studies listed above. The re-assembled gels were aged in a flask fitted with screw caps. Each flask was partially filled with re-assembled fiber-assist RPPG and 2% KCl brine solution, then the remaining of the space was filled with air, without de-oxygen. The evaporative losses due to leakage were found to be negligible in this method. Same with the swelling capacity test, 2.1 g of dried particle gel was placed in 35 mL of brine to recover to same sizes. To simulate the reservoir condition, the flasks were placed in different ovens with set temperature of 80, 60, and 45°C. After a specific period of time aging, the gel mechanical properties changes were observed.

4. THE CHEMICAL COMPOSITION AND SYNTHESIS CONDITIONS EFFECT ON FIBER-ASSISTED PPG PROPERTIES BEFORE RE-ASSEMBLY

Fiber-assisted re-assembly preformed particle gels were synthesized through a multi-component reaction, with monomer, initiator, crosslinkers, thickening agent, and fibers being combined in a sequential method in a single reaction container. The reaction was followed by a stepwise process which leads a conversion of monomer to polymer, and subsequently crosslink the polymer to attain bulk gels. The fibers played a role as a filled material which was employed to re-enforce the properties of the gel in strength.

The conversion of monomer to polymer takes place through free-radical reaction, where the heat induces free radical. With the temperature rises, the free radicals would dissociate and released by initiator. The free radicals attract neutral molecules which results in a polymerization to form a polymer chain with a series of linked monomers. When pairs of radicals combine, the chain reactions would terminate since the reaction was carried by the free radicals. After this process, two methods are employed in this study.

The first method uses a specific chemical crosslinker to make the formed polymer chains crosslink by the formation of junction points between two or more polymer chains at different points along polymer chain length, leading to a 3-dimensional gel structure in microscale. The crosslinked polymer becomes a bulk gel in appearance. The second method uses physical crosslinker, combines the polymer chains together to form a thick polymer solution, without crosslinking the polymer chains to form a 3-dimensional structure since it does not form a covalent bond between the polymer chain. The second method would only be considered when the amount of the crosslinker is too sensitive to control during the synthesis.

The polymerization and crosslinking processes are affected by several factors, and consequently the properties of the synthesized gel are also affected by these factors. The alleged factors include temperature, concentration of the ingredients, covers monomers, initiators, crosslinkers, and the amount of the additives. These factors have been examined in the study in order to obtain the gel with be best effect on physical, chemical properties , and economical values.

Figure 4.1 shows the failures in the experiments which provided considerable inspiration for improving thinking and future works. Failure A was a sample that was synthesis in the early work to determine the best reaction condition and the total volume of the solution. Excessive amount of the solution leads to too much reaction energy, where the reaction occurred in a 45℃ oven so the combination of two factors caused the sample bumping and exploded. Failure B was the sample using fiber with half-inch length, where the fiber twisted together and filed to disperse evenly in the solution. This problem was resolved by using fine fiber with 1/8 inches long. Failure C is the first sample using fine fiber. The fiber in the solution separated into two layers, where the top layer float to the top under the effect of the buoyancy of the solution, so it still cause a problem that the fiber could not spread evenly throughout the solution. Types of thickening agents was employed in the following experiments to avoid the float of the fiber by thickening the solution. Failure E is a sample using an inadequacy thickener for the system, the thickener reacted with the $ZeAc_4$ crosslinker and caused the precipitate occurred during the synthesis. Failure D is the sample synthesized in the experiment testing the concentration of N,N’MBAA used in the system and will be explained in detail in section 4.3.1. The sample failed to recrosslink after fully swollen due to the concentration sensitivity of N,N'MBAA.

Figure 4.1 Failures in the Experiment

4.1. EFFECT OF FIBER OF GEL PROPERTIES

The fiber tested in this study is polypropylene provided by Forta Corporation. The swelling capacity of the fiber effects on the swelling ratio of the fiber-assist RPPG could be affected by both the size and the concentration of the fiber used during the synthesis of the polymer gel.

4.1.1. Effect of Fiber Size. In the beginning, the Super-Sweep Fiber provided by Forta Corporation was tested in the study, which was found not a satisfactory choice for industry since the fiber cannot disperse evenly in the solution with stir bar but requires manual separation before adding into the reaction container. Otherwise the fiber in the solution would twist and stacked at the middle of the polymer, so it cannot achieve the purpose of the research. In order to resolve the distribution issue of the fiber, a shorter fiber, Super-Sweep Fine Fiber was tested. This kind of fiber was in a 1/8-inch size. Benefited by the smaller size, the fiber could distribute evenly in the solution under the effect of the stirring process.

However, after the stirring process and the reaction vessel is placed in the water bath for the polymerization, the fine fiber could not well suspend in the solution but float to the top. Although the floating issue occurs during the synthesis, the fine fiber is still the superior choice comparing with the long fiber. Thus, to solve the buoyancy problem, extra volume of $ZrAc_4$ solution and chosen type of thickener were added into the solution as an ingredient of the gel. Also, a co-initiator was employed to accelerate the gelation process to ensure that the polymerization occurs before the fiber float.

Since the recipes of the gel using 1/8-inch fiber and half-inch fiber are different, the variate control method cannot be effectively used in this case. Therefore, the half-inch fiber was eliminated, and the study would only consider 1/8-inch fine fiber as the additive of the fiber-assisted preformed particle gel.

4.1.2. Effect of Fiber Concentration. The swelling test was done with using 2% KCl brine as the solvent to compare the swelling capacity with gels without adding fibers. Furthermore, the evaluation was done at different conditions: room temperature oscillation, 40℃, and 65℃ so as to mimic the different reservoir temperatures and pumping condition.

Table 4.1 Formulas of Fiber-Assist RPPGs with Different Fiber Concentration

No.	AM (g)	DIW (mL)	$ZrAc_4$ (mL)	0.1% HPM 905 (mL)	APS (ppm)	STS (ppm)	MBAA	Fiber (ppm)
PL-03	40	50	25	50	258	258	8 ppm	0
FB-64	40	50	25	50	258	258	8 ppm	3
FB-65	40	50	25	50	258	258	8 ppm	6
FB-66	40	50	25	50	258	258	8 ppm	30
FB-67	40	50	25	50	258	258	8 ppm	60
FB-68	40	50	25	50	258	258	8 ppm	90
FB-69	40	50	25	50	258	258	8 ppm	120

Table 4.1 shows the formula of F-RPPG with different fiber concentration, which clearly reflects in Figure 4.2 Effect of Fiber Concentration on Gel Swelling Equilibrium using 2% KCl, the gels with fibers have higher swelling ratio than the gels without fibers embedded. An increase trend occurs with increase of fiber concentration between 0% to 0.003%, where a decrease trend occurs with increase of fiber concentration between 0.003% to 0.012%.

Figure 4.3 Effect of Fiber Concentration on Gel Swelling Kinetics using 2% KCl represents the swelling kinetic test which measures the amount of time that the dry gels take until fully swollen under room temperature. This test mimics the gel mixed with brine and pumped into the reservoir condition through the injection well. From the Figure it could be found that the gels with fibers have higher swelling rate than gels without fibers embedded in a specific fiber concentration. An increase trend occurs with increase of fiber concentration between 0% to 0.006% and is over the swelling rate of the gel without embedded with fiber, where a decrease trend occurs with increase of fiber concentration between 0.006% to 0.012% and the swelling rate is below the gel without fiber.

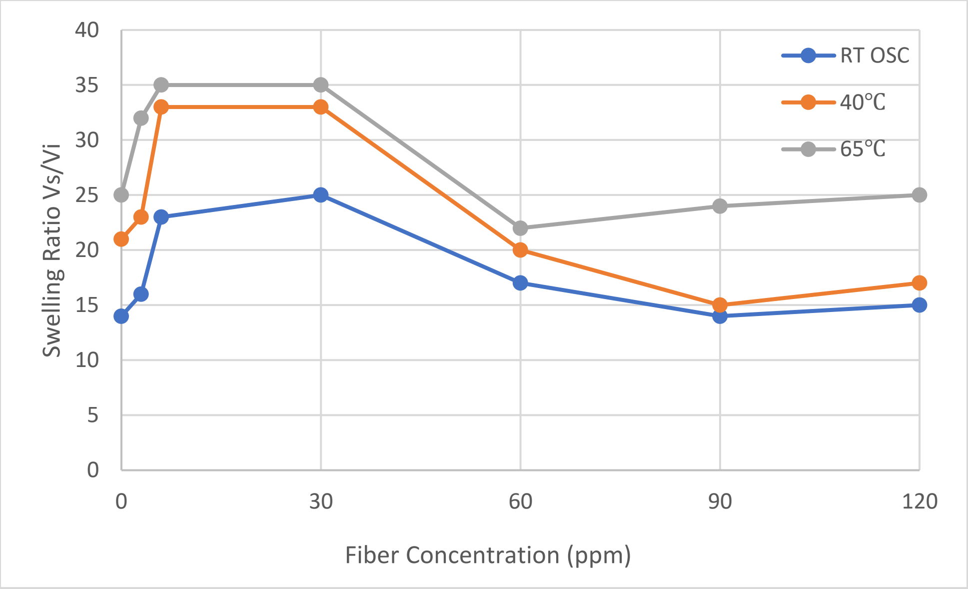


Figure 4.2 Effect of Fiber Concentration on Gel Swelling Equilibrium using 2% KCl

4.2. EFFECT OF INITIATOR ON GEL PROPERTIES

In this study, ammonium persulfate (APS) was used as the initiator, where sodium thiosulfate (STS) was used as co-initiator to increase the reaction rate to ensure that the polymerization occurs before the floating of the fine fiber.

4.2.1. Effect of APS Concentration. To evaluate the effect of the initiator on RPPG properties, the experiments were performed to control the temperature, monomer, and crosslinker concentration to be maintained constant while the initiator concentrations were varied. The temperature was kept by a 35℃-water bath during the reaction, where the monomer, acrylamide amount was kept at 40g, the concentration of the MBAA was controlled as 8 ppm, $ZrAc_4$ was 25mL, respectively. The concentration of the initiator was controlled from 182 to 516 ppm, shown in Table 4.2.

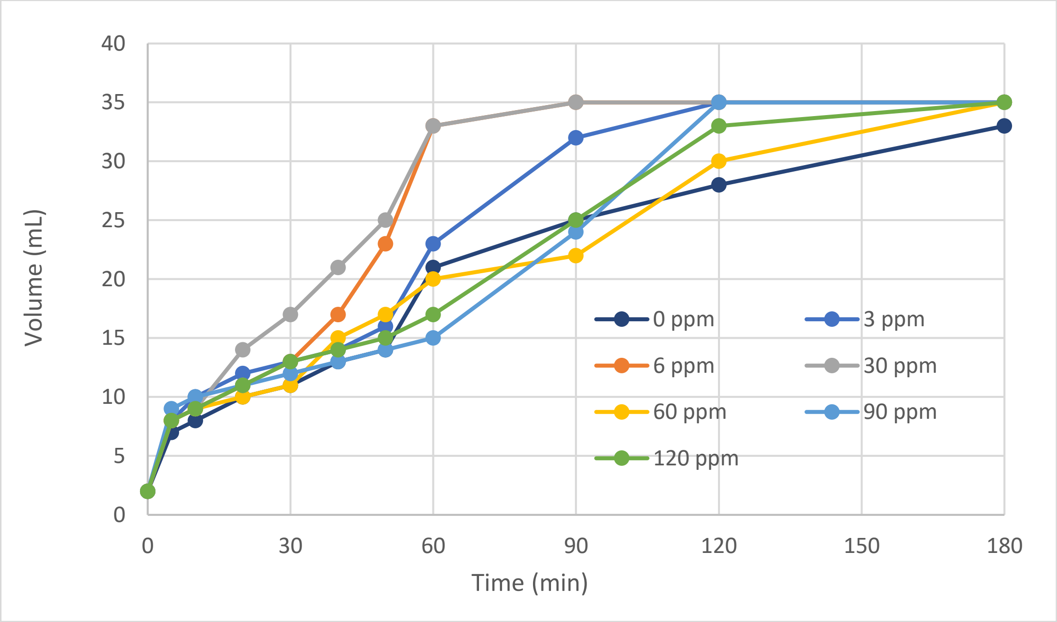


Figure 4.3 Effect of Fiber Concentration on Gel Swelling Kinetics using 2% KCl

As it could be found in Figure 4.4, the swelling ratio of the gel synthesized with varied concentration of initiator. With an increase of initiator concentration, a trend of decrease on the volume swelling ratio was represented. As the initiator concentration increased, the crosslinking density of the polymer was increased, which resulted in the swelling ability of the 3-dimensional network of the polymer gel was reduced. When the initiator concentration increased, the concentration of the radicals in the polymer solution would rise. The chain termination and transfer occurred simply before adequate chain propagation. As a consequence, the polymer chain length was shortened, which would cause a lower water absorbency.

Table 4.2 Formulas of Fiber-Assist RPPGs with Different Initiator Concentration

No.	AM (g)	DIW (g)	$ZrAc_4$ (mL)	APS (ppm)	STS (ppm)	MBAA (ppm)
FB-19 A	40	100	25	182	0	8.0
FB-20 A	40	100	25	212	0	8.0
FB-20 B	40	100	25	242	0	8.0
FB-20 C	40	100	25	258	0	8.0
FB-20 D	40	100	25	273	0	8.0
FB-22	40	100	25	303	0	8.0
FB-23	40	100	25	484	0	8.0
FB-24	40	100	25	516	0	8.0

In Figure 4.5, the swelling rate of each sample is shown, where the sample with 242 ppm and 258 ppm initiator concentration shows the highest swelling rate while the sample with 273 ppm initiator concentration cannot fully swell to 35mL in the evaluation.

4.2.2. Effect of Co-Initiator. To control the gelation time, STS (sodium thiosulfate) was employed as a redox co-initiator to ensure the gelation occur before the fine fiber float. The concentration of the co-initiator is controlled to be same with the concentration of the initiator to keep the reaction rate.

To evaluate the effect of the co-initiator with the initiator in the system on gelation kinetics, the experiment was performed to control the temperature, monomer, and crosslinker concentration to be maintained constant while the initiator and co-initiator concentrations were varied. The temperature of the reaction was kept by a 35℃-water bath during the gelation process, where the monomer, acrylamide amount was kept at 40g, the concentration of the MBAA was 8 ppm, and the 16% wt. $ZrAc_4$ was 25mL. The

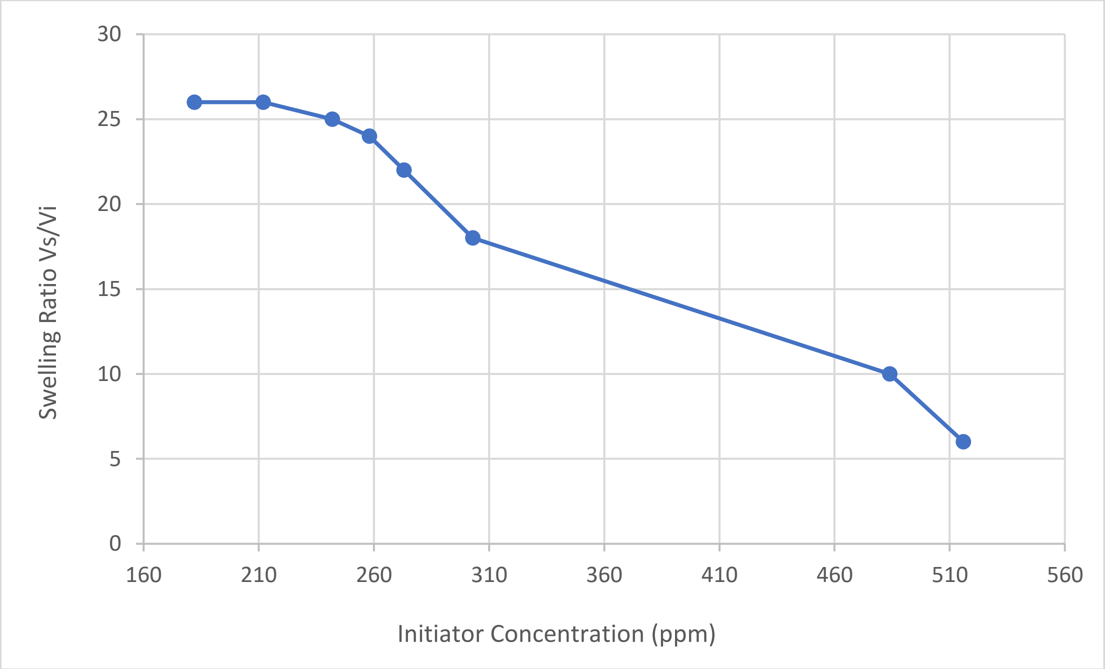


Figure 4.4 Effect of Initiator Concentration on Gel Swelling Equilibrium using 2% KCl

concentration of the initiator and co—initiator was controlled from 182 ppm to 484 ppm, shown in Table 4.3 below.

As shown in Figure 4.6, a decrease trend of gelation time occurs with the increase of both initiator concentration. Under the combined effect of the thickener and the redox co-initiator, the fiber was well distributed in the solution until gelation occurs.

Figure 4.7 represents the effect of the joint of the co-initiator on the swelling ratio of the fiber-assist RPPG. Due to the complexity of the redox co-initiator, an increase trend occurs with the increase on the concentration of the initiator in the relatively lower amount. However, the trend shows decrease on the swelling ratio while the initiator concentration keeps increasing and emerged that the swelling ratio reaches a peak when the concentrations of two initiators are between 242 ppm and 273 ppm.

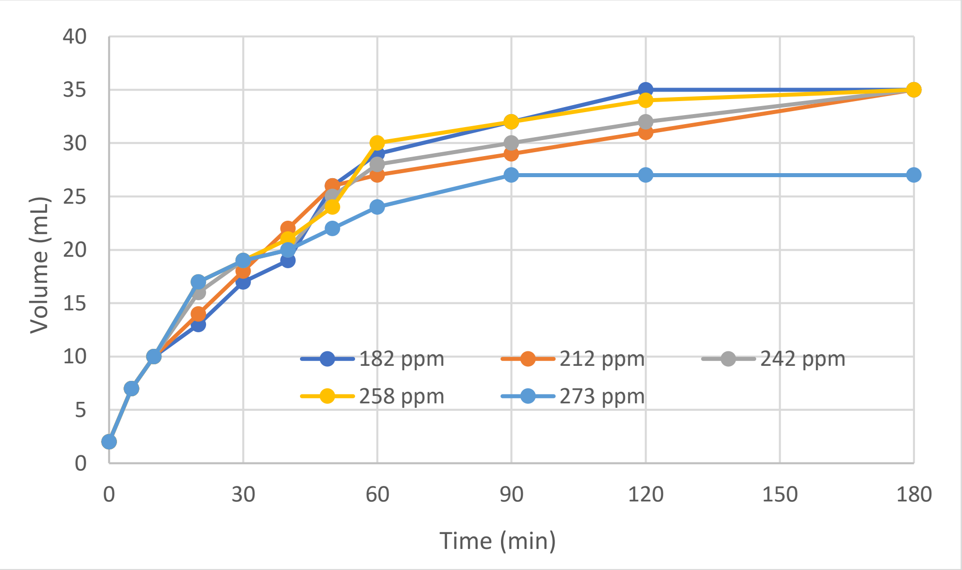


Figure 4.5 Effect of Initiator Concentration on Gel Swelling Kinetics using 2% KCl

Table 4.3 Formulas of Fiber-Assist RPPGs with Different Initiator and Co-initiator Concentration

No.	AM (g)	DIW (g)	$ZrAc_4$ (mL)	APS (ppm)	STS (ppm)	MBAA (ppm)
FB-19 B	40	100	25	182	182	8.0
FB-21 A	40	100	25	242	242	8.0
FB-21 B	40	100	25	258	258	8.0
FB-21 C	40	100	25	273	273	8.0
FB-22B	40	100	25	303	303	8.0
FB-23B	40	100	25	484	484	8.0

Figure 4.8 shows the swelling rate of the fiber-assist RPPG with varied concentration of initiators. It could be found that the initiator with concentration between 242 ppm and 273 ppm provides the gel the highest swelling rate.

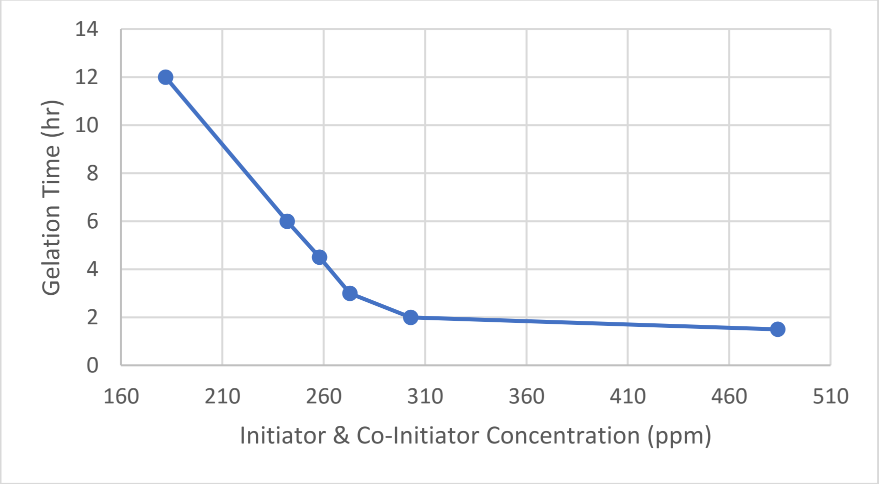


Figure 4.6 Effect of Initiator and Co-Initiator Concentration on F-RPPGs Gelation Time

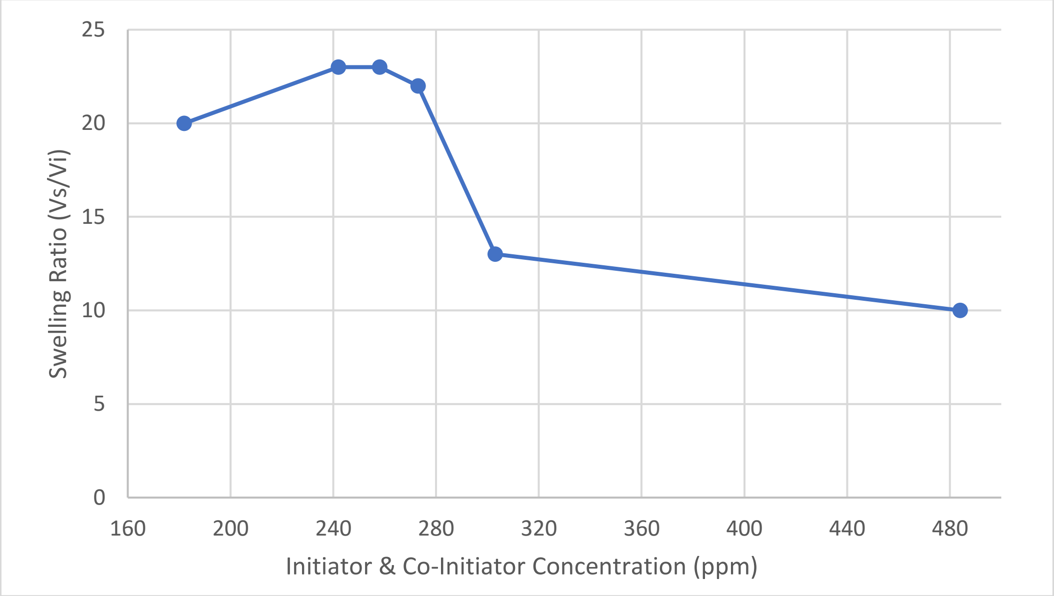


Figure 4.7 Effect of Initiator and Co-Initiator Concentration on F-RPPGs Swelling Equilibrium using 2% KCl

Additionally, similar with the result of Figure 4.5, the samples with the highest concentration of initiators did not fully swell, and the swelling rate was lower than the samples with lower initiator concentration.

4.3. EFFECT OF CROSSLINKER ON GEL PROPERTIES

N,N'MBAA and $ZrAc_4$ were employed as crosslinkers in this study for synthesizing the fiber-assist re-assemble preformed particle gels. On the one hand, N,N' MBAA was treated as a chemical crosslinker to make the formed polymer chains crosslink by the formation of junction points between two or more polymer chains at different points along polymer chain length, leading to a 3-dimensional gel structure in microscale, so the crosslinked polymer becomes a bulk gel in appearance. On the other hand, $ZrAc_4$ played a role in the physical crosslinker, which combines the polymer chains together to form a thick polymer solution, without crosslinking the polymer chains to form a 3-dimensional structure.

4.3.1. Effect of MBAA Concentration. During the research, the effect of the N,N’ MBAA on the gel properties, all other reactants were held constant and the only varied factor was the concentration of MBAA. The temperature was controlled by a 35℃-water bath during the gelation process, where the monomer acrylamide amount was kept at 40g; the concentration of the initiator and the co-initiator are both 258 ppm, and the 16% wt. $ZrAc_4$ was 25mL. The concentration of the initiator and co-initiator was controlled from 182 ppm to 484 ppm, shown in Table 4.4 below.

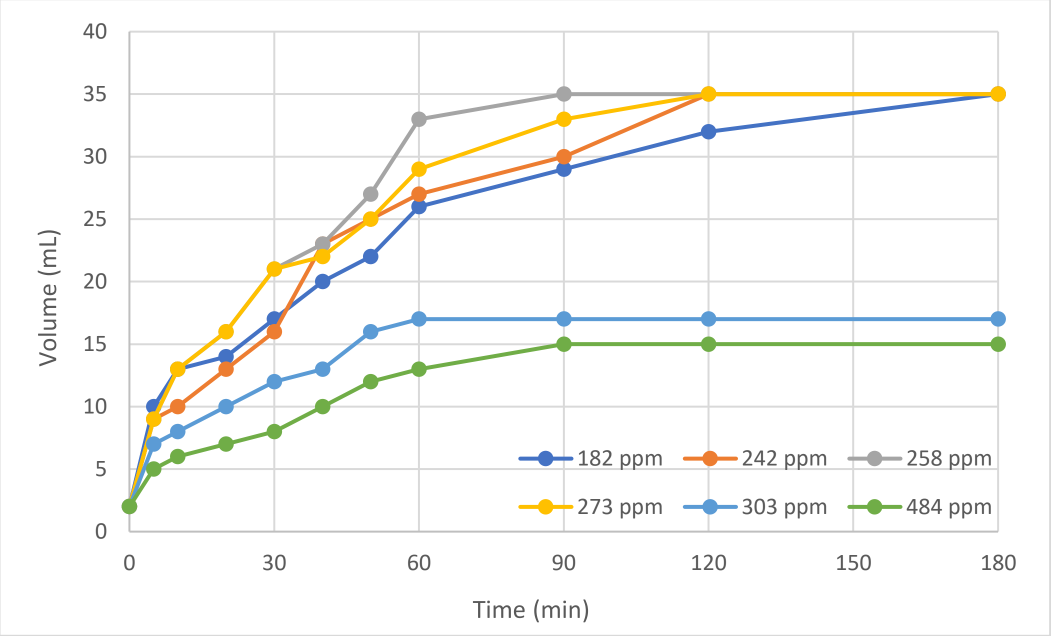


Figure 4.8 Effect of Initiator and Co-Initiator Concentration on Gel Swelling Kinetics using 2% KCl

Table 4.4 Formulas of F-RPPGs with Different N,N'MBAA Concentration

No.	AM (g)	DIW (g)	$ZrAc_4$ (mL)	APS (ppm)	STS (ppm)	MBAA (ppm)
FB-28	40	100	25	258	258	9.0
FB-29	40	100	25	258	258	8.0
FB-30	40	100	25	258	258	7.0
FB-31	40	100	25	258	258	6.0
FB-32	40	100	25	258	258	5.0
FB-33	40	100	25	258	258	4.0

N,N' MBAA is a kind of concentration-sensitive crosslinker when using in the polymer synthesis. When the concentration was over a specific amount, the gel would not re-crosslink after fully swollen or the swelling process would be interrupted. Inversely, when the concentration is below the specific value, the crosslinker would not be functional during the recrosslinking process, making the polymer either cannot recrosslink to form the bulk gel or weaken the strength of the recrosslinked gel.

Figure 4.9 shows the volume swelling ratio of the samples with varied concentration of N,N' MBAA. As shown in the plot, the sample FB-28 and FB-33 with 9 ppm and 4 ppm MBAA shows a bad swelling capacity since the swelling ratio experienced a big drop comparing with other samples.

Also, the sample did not recrosslink due to the concentration sensitivity of the crosslinker, shown in Figure 4.11. It could be found from Figure 4.10 that the swelling times taken by each sample are almost same, but the range of the MBAA amount was limited from 5 to 8 ppm during the experiment.

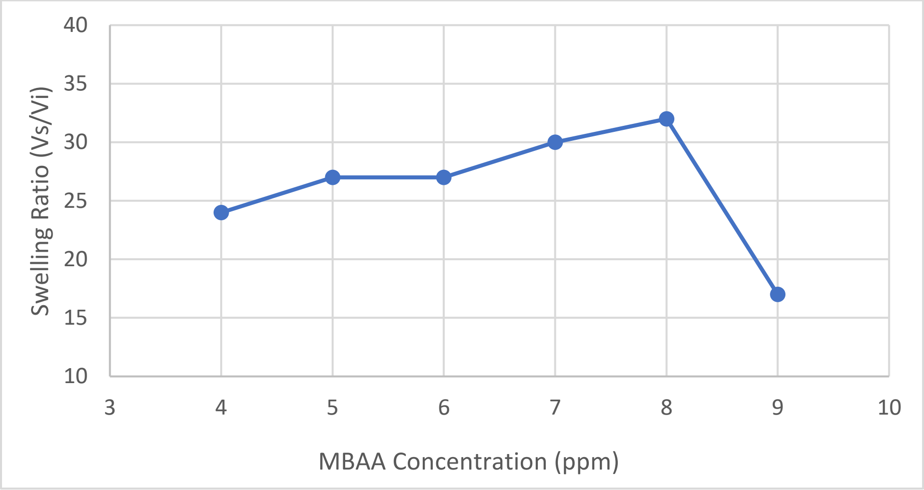


Figure 4.9 Effect of MBAA Conc. on Gel Swelling Equilibrium using 2% KCl

4.3.2. Effect of Zirconium Acetate Concentration. This study was first used to determine the concentration of the MBAA since it plays a significant role in the synthesis. ZeAc4 was used as a secondary crosslinker for several purposes. $ZrAc_4$ could act as a physical crosslinker during the recrosslink process in the reservoir when the MBAA is not functional in some situation, forming the swollen particle gel into a thick polymer to achieve similar results. Parallelly, During the gelation process, over amount of $ZrAc_4$ also plays a role as a thickener to prevent the untimely float of the fine fiber.

Thus, in the following experiment, the $ZrAc_4$ is already known as over amount, and the study is to confirm the range of the $ZrAc_4$ that would not bring a negative effect to the RPPG. In the experiment, the reaction temperature is controlled with a 35℃-water bath where the amount of monomer, initiators, and MBAA are all constant in order to maintain the effect on the gel. The monomer is fixed at 40g, where the concentration of the initiator and the redox co-initiator are both 258 ppm, the concentration of the MBAA was fixed at

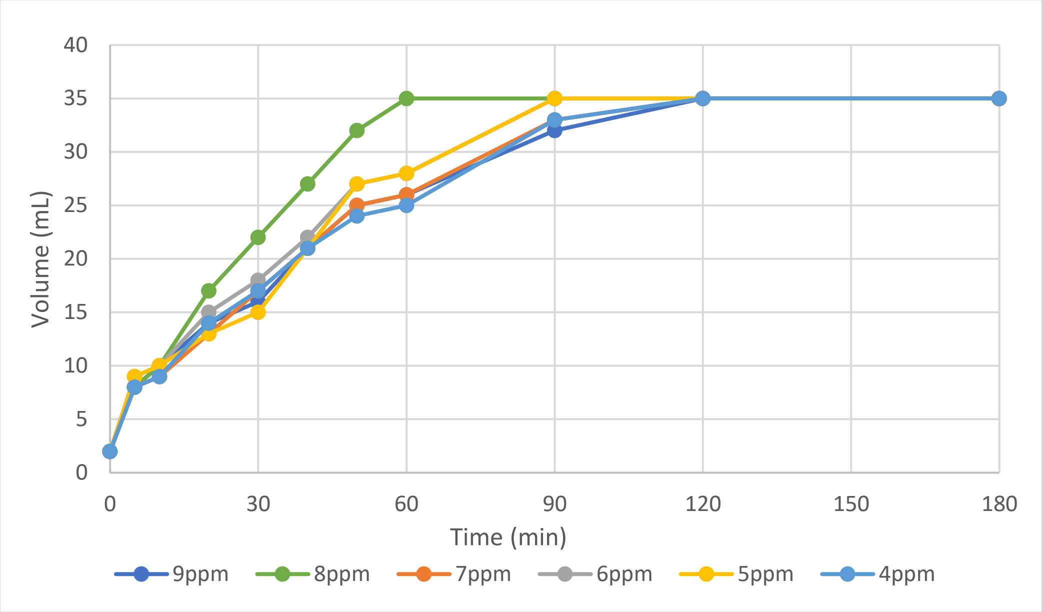


Figure 4.10 Effect of MBAA Concentration on Gel Swelling Kinetics using 2% KCl

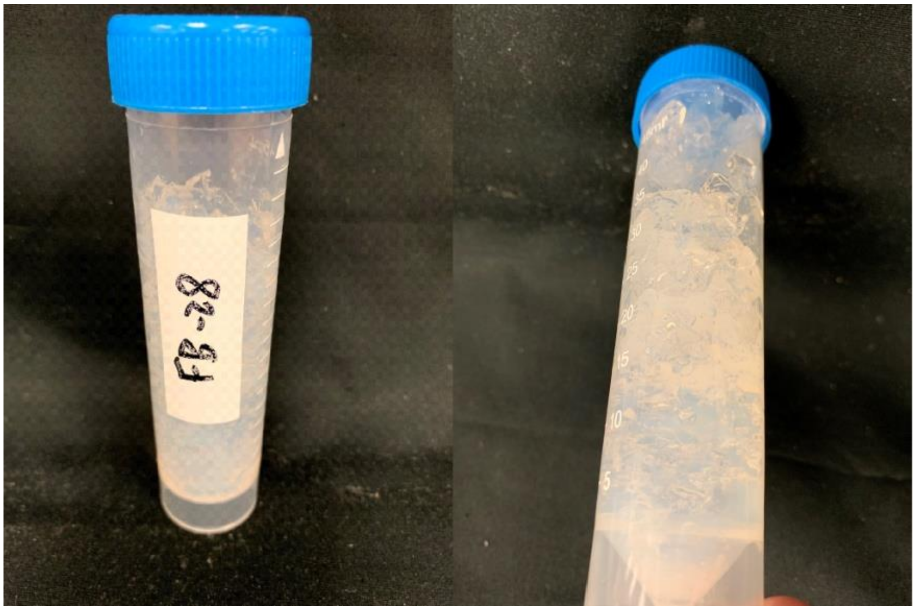


Figure 4.11 Sample cannot Re-Crosslink after Swollen

8 ppm. The $ZrAc_4$ was initially 16 wt.% and was diluted to different concentration and used as the only varied factor in the experiment during the synthesis, shown in Table 4.5.

Table 4.5 Formulas of Fiber-Assist RPPGs with Different $ZrAc_4$ Concentration

No.	AM (g)	DIW (g)	Concentrated $ZrAc_4$ (mL)	$ZrAc_4$ (%)	APS (ppm)	STS (ppm)	MBAA (ppm)
FB-34	40	100	25	1.55%	258	258	8.0
FB-35	40	100	25	2.00%	258	258	8.0
FB-36	40	100	25	2.42%	258	258	8.0
FB-37	40	100	25	2.82%	258	258	8.0
FB-38	40	100	25	3.56%	258	258	8.0
FB-39	40	100	25	4.21%	258	258	8.0

Figure 4.12 represented the effect of the $ZrAc_4$ concentration on the swelling ratio of the RPPG. From the plot it could be found that there was no significant change between different concentration of the $ZrAc_4$ during the synthesis since the amount of the crosslinker is already over the amount required in the reaction.

Figure 4.13 is the plot showing the effect of the $ZrAc_4$ concentration on the swelling time during the swelling test. The trends again showed similar in the plot while the fluctuation found was the sample with 2.42% concentration $ZrAc_4$ which did not fully swell in the first 3 hours.

Therefore, the varied concentration of the $ZrAc_4$ did not show obvious change since the amount used in the experiment was already over the dosage demand for the reaction.

The result shows that extra amount of $ZrAc_4$ did not make apparently negative effect on the gel.

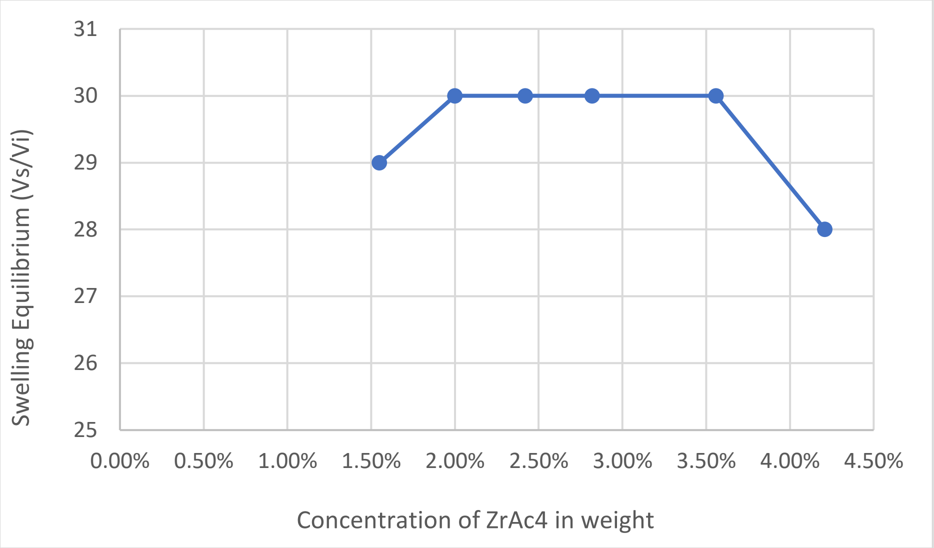


Figure 4.12 Effect of $ZrAc_4$ Conc. on Gel Swelling Equilibrium using 2% KCl

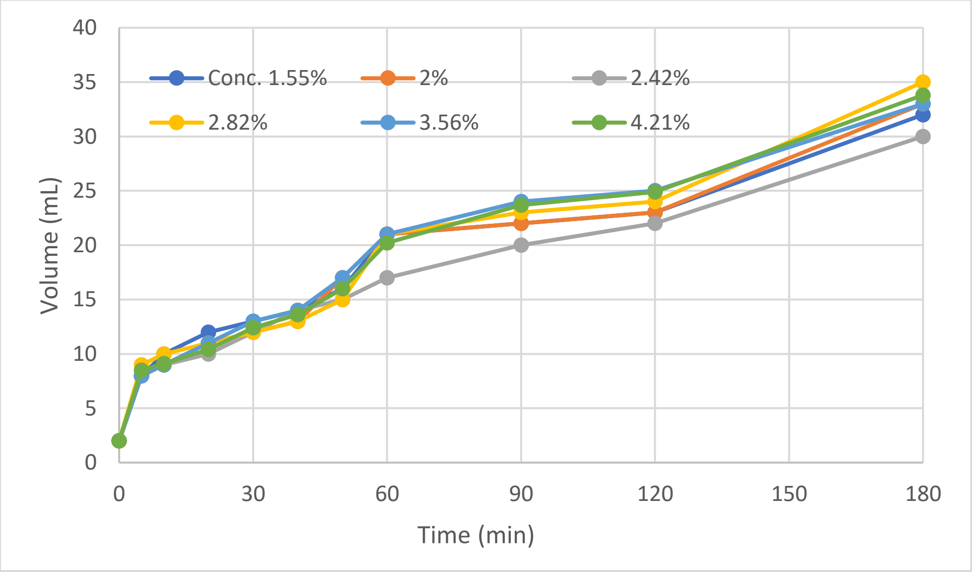


Figure 4.13 Effect of $ZrAc_4$ Conc. on Gel Swelling Kinetics using 2% KCl

5. THE CHEMICAL COMPOSITION AND SYNTHESIS CONDITIONS EFFECT ON FIBER-ASSISTED RPPG PROPERTIES AFTER RE-ASSEMBLY

5.1. EFFECT OF FIBER ON GEL PROPERTIES

The rheology evaluation data of the fiber-assisted re-assemble preformed particle gels and gels without fiber embedded were compared and studied (Table 4.1). Figure 5.1 represents the re-assembled gels strength synthesized with varied fiber concentrations. The mechanical strength of the gel could be estimated by the properties including the elasticity (G') and the viscosity (G"). The experiment employed polypropylene fine 1/8-inch fiber as the additive, with concentration range from 0.0003% to 0.012% and was compared against the gel without embedded with fiber.

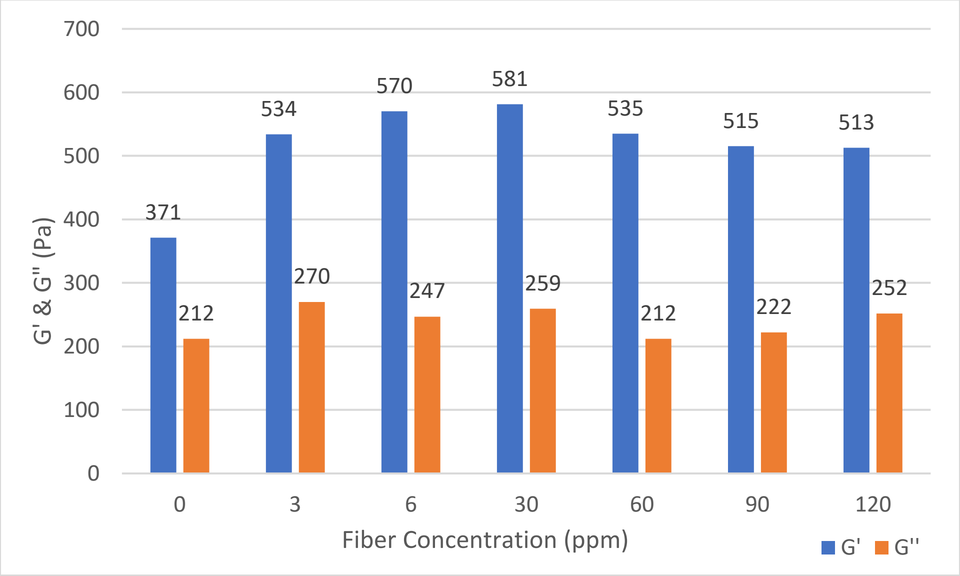


Figure 5.1 Effect of Fiber Concentration on Gel Strength using 2% KCl after Re-Assembly

From Figure 5.1, it can be found obviously that the fiber does make an improvement on the mechanical strength between the gels with fiber and those without additives. Comparing with the plain gel with a G’ of 371 Pa, the G’ of gels embedded with fiber could achieve 500 Pa or even higher. The trend of the G’ shows an increase on the elasticity while the concentration of the fiber is increasing, and the gel strength reaches a peak when the fiber concentration is at 0.003%. After reaching the peak, the increase concentration of the gel causes a decrease trend on the plot. This phenomenon occurs since the extra amount of the fiber interferes the recrosslink of the gel, which may derive to a failure on the function of N,N’MBAA.

Clearly, the fiber makes an improvement on the elasticity of the gel, but the amount of the fiber is sensitive since the shortage or extra amount of the fiber can result in a decrease on the strength property.

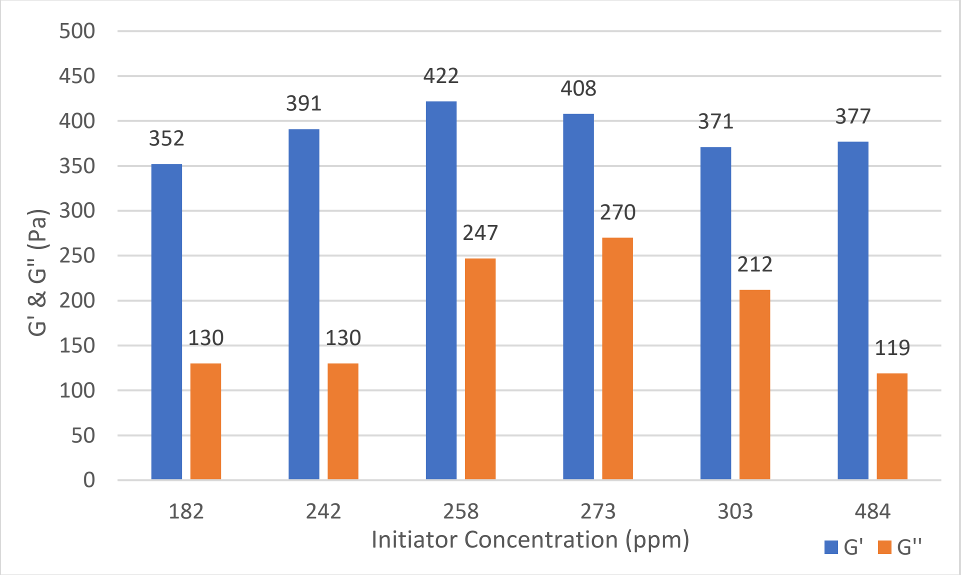


Figure 5.2 Effect of Initiator Concentration on Gel Strength using 2% KCl after Re-Assembly

5.2. EFFECT OF INITIATOR ON GEL PROPERTIES

Figure 5.2 shows the effect of the varied initiator and redox co-initiator concentration on the gel strength. In the plot, the initiator concentration at the peak of gel elasticity reaches 258 ppm, where a decrease trend appears when the concentration of the initiators excesses the peak. With the increase of the initiator concentration, the crosslinking density was increased during the synthesis.

However, extra initiators participation could possibly cause the amount of polymer chain in the reaction increase, so it reduces the chain length of the polymers since the total molecules of the monomers are fixed, and would result in the drop of the total polymer strength. The experiment demonstrated that the concentration of initiator and co-initiator at 258 ppm performed better in the certain situation.

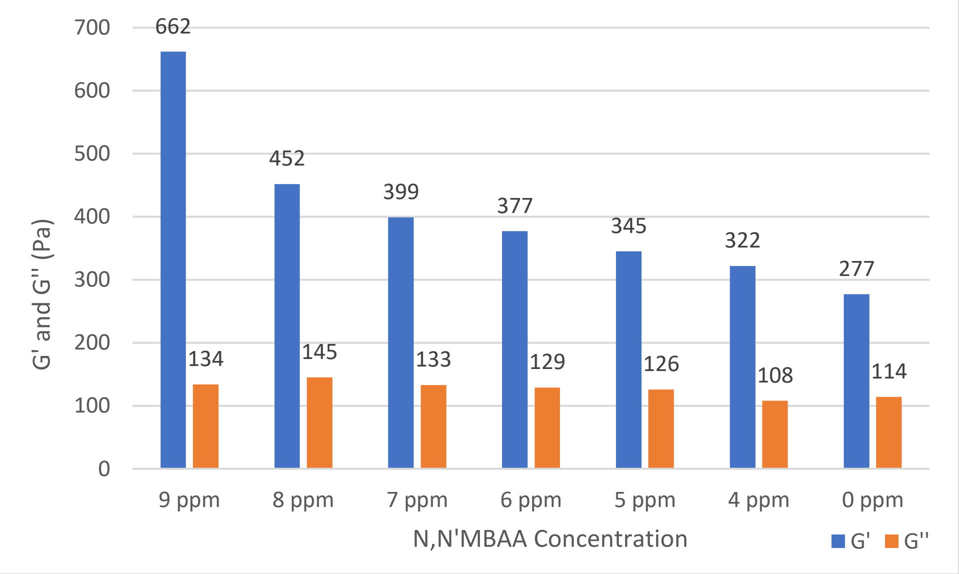


Figure 5.3 Effect of MBAA Concentration on Gel Strength using 2% KCl after Re-Assembly

5.3. EFFECT OF CROSSLINKER ON GEL PROPERTIES

5.3.1. Effect of MBAA. Figure 5.3 represents the effect of changing N,N'MBAA concentration on the gel strength property. Comparing with other samples, the sample with 9 ppm MBAA used in the gel synthesis shows outstanding intensity of elasticity. However, the 9-ppm sample did not recrosslink after fully swollen, which could not be treated as an available sample since the performance of this gel is not reliable. In the rest samples of the experiments, the reliable samples used the concentration range from 5 to 8 ppm, where the 8-ppm sample performed to be the best in the samples that had successfully recrosslinked.

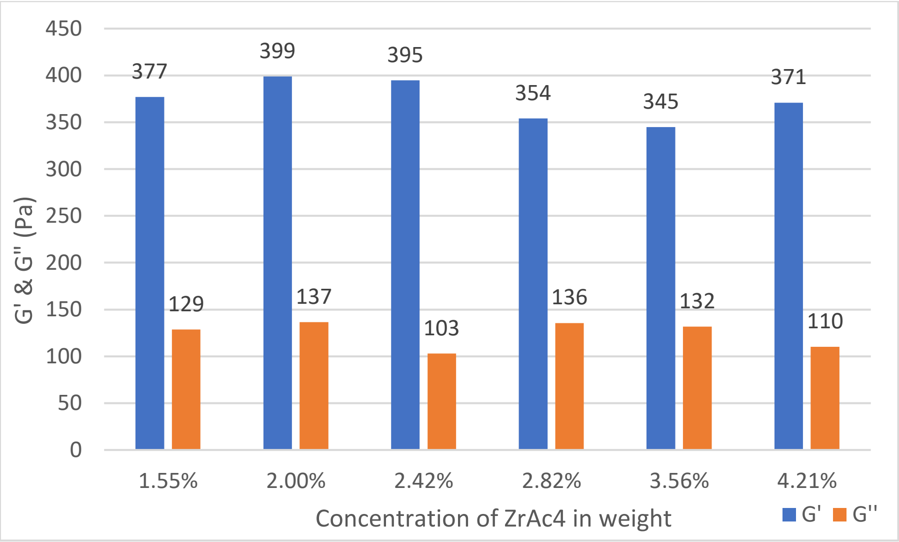


Figure 5.4 Effect of $ZrAc_4$ Concentration on Gel Strength using 2% KCl after Re-Assembly

5.3.2. Effect of Zirconium Acetate Concentration. As mentioned above, $ZrAc_4$ in this study was employed for both a physical crosslinker and a thickener. Hence, excess $ZrAc_4$ was used in the synthesis, so the varied amount of $ZrAc_4$ would not make a significant change on the swelling capacity or the rheological property. As expected, Figure

5.4 shows that the effect of the varied concentration of $ZrAc_4$ have slight effect on the elasticity property of the gel.

5.4. THERMOSTABILITY EVALUATION

The evaluation testing the thermostability of the re-assembly fiber-assist preformed particle gel have been done in this section. The re-assembled bulk gel had been placed in a sealed flask and left in a 65°C oven to imitate the reservoir condition. A comparison was made between the gel using 2.1g dry gel, 35 mL of the 2% KCl brine, for the controlled trial. Figure 5.5 reflects the effect of the time aging on the gel in a certain temperature.

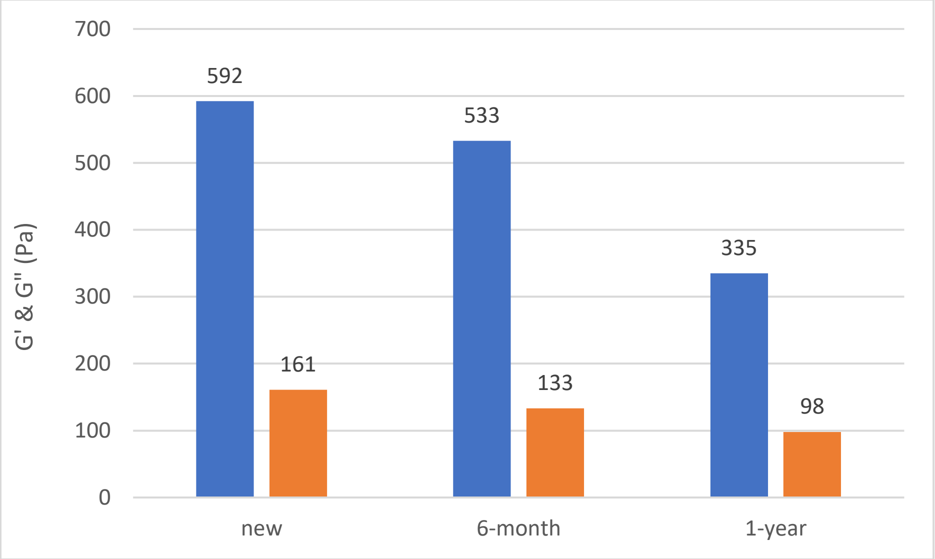


Figure 5.5 Effect of Time Ageing in 65°C on Gel Strength using 2% KCl

It could be found that the gel strength had slightly dropped in the first 6 month and experienced a significant drop after one-year under the thermostat condition. This effect is caused by the thermal effect on the polymer chain which make the chain break and thus the degradation of the gel occurred. Figure 5.6 shows the difference between the form of the gel that right after the re-assembly and the gel under one-year aged in a 65℃ oven. The new gel shows clear and with tenacity, where the aged gel looks turbid and soft due to the degradation of the polymer.

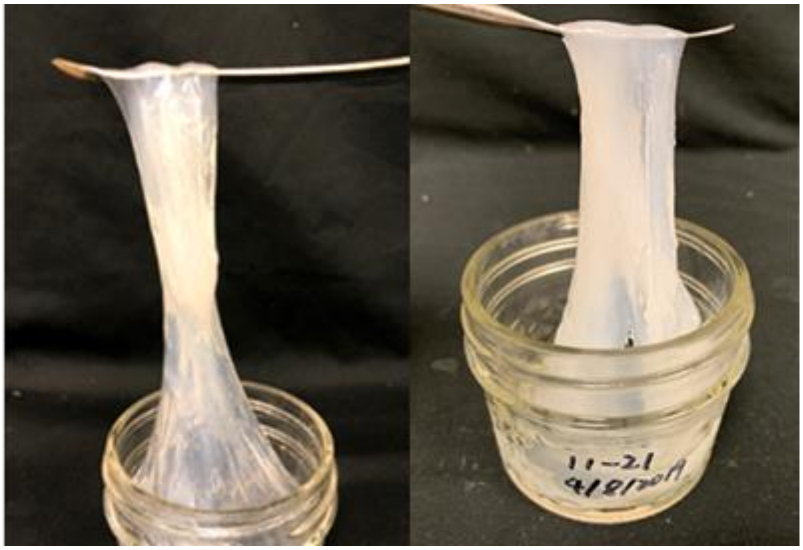


Figure 5.6 Thermal Effect on F-RPPG. 1. Newly re-assembled gel; 2. Gel after 1-year aged in a 65℃ oven

Figure 5.7 is the picture taken through scanning electron microscope, showing the micro-structure of the F-RPPG. The gel samples were cooled and dried in order to avoid the disturb of moisture during the photographing. The left picture is the micro-structure of a newly re-assembled bulk gel while the right is the bulk gel aged for one year in a 65℃ oven. The pore structure in the right picture shows the polymer attached to the surface of the frozen water molecules, where the pore structure formed after the water was sucked out by the instrument. Thus, the pore structure of the gel in the right picture could reflect the drop on the gel strength under the thermostat aging effect.

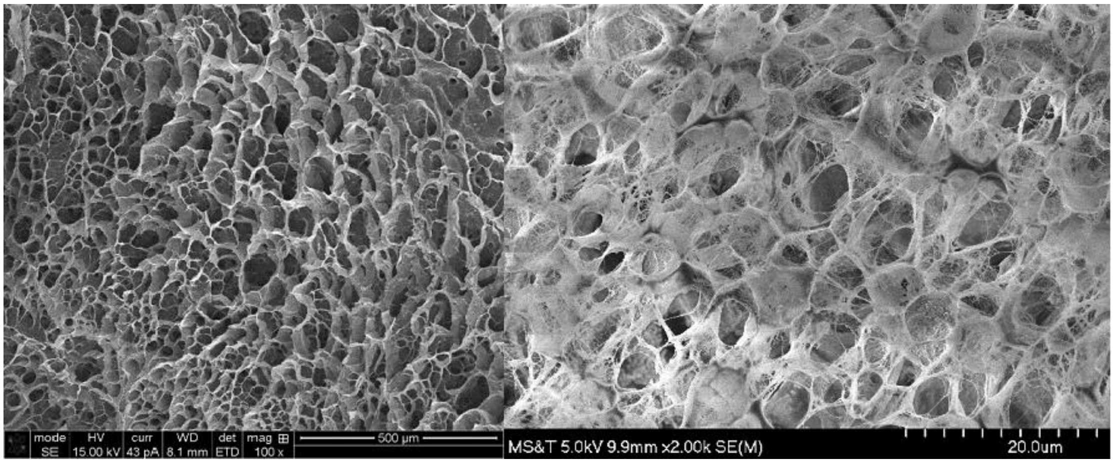


Figure 5.7 SEM Micrograph of Fiber-Assist RPPG. a) Left represents the structure of the newly re-assembled gel. b) Right shows the structure of the gel after one-year aging under 65°C condition.

6. CONCLUSIONS

A novel fiber-assist re-assemble preformed particle gel has been synthesized which is able to potentially apply in the mature oil fields. The product developed in this study could be injected into the reservoir and act as a conformance control agent by plugging water thief zones and channels. Due to the high temperature under the reservoir condition, the product will re-assemble into bulk gel and would effectively plug the fractures or channels in the reservoir to improve the oil sweep efficiency in the low permeable zones.

Polypropylene fiber in the size of 1/8 inch long was employed in the synthesis of the product and evaluated for the purpose. Swelling ratio of the preformed particle gels was improved by adding the fiber additives, meanwhile, swelling time was reduced. The mechanical strength of the recrosslinked gel had been significantly enhanced by the participation of fiber. The 0.003% concentration fiber-assist re-assembled preformed particle gel using 2% KCl solution achieved the highest gel strength at 581 Pa, where the plain gel without fiber participation was 371 Pa in elasticity.

For each crosslinker, $ZrAc_4$ and N,N’MBAA, had different performance in the study. In the one hand, N,N’MBAA increased the gel strength by increasing the concentration in a certain range. Once the concentration of N,N’MBAA excesses the upper range of 8 ppm, the gel will not recrosslink after swelling. As for the other crosslinker, $ZrAc_4$ played a role in both a crosslinker and a thickener in the synthesis, and therefore, the concentration of $ZrAc_4$ was for beyond the amount that is required for the reaction. Whereas $ZrAc_4$ concentration showed slight (marginal) impact on G' and G". With the increasing concentration of the initiator and redox co-initiator, the gelation rate and the crosslinking density were increased until initiator concentration reached 258 ppm , then the gel strength occurs a slightly drop as the initiator concentration keep increasing due to the reduction of the polymer chain length.

According to the study, the most economic fiber-assist re-assemble preformed particle gel with the large swelling ratio of 35 times the dry gel volume, and the highest gel strength of 581 Pa was formed by 24% acrylamide, 8 ppm N,N’MBAA, 2.4% $ZrAc_4$, 0.003% fiber, 258 ppm ammonium persulfate and 258 ppm sodium thiosulfate.

7. SUGGESTED FUTURE WORK

In the current product, gaps and limitations still exist in facilitating the deployment of particle gel conformance control technology. In order to enhance the properties of the fiber-assist re-assemble preformed particle gel, further theoretical and experimental research is required.

Core flooding test could be employed to the study for the evaluation of the plugging efficiency of the F-RPPG. The pH sensitivity test could help mimic the gel performance in different reservoir conditions, where the performance with application of super critical CO2 could also be tested.

In the current study, the limitation of the fiber concentration was less than 0.1% of the total weight since the excessive fiber concentration used during synthesis would possibly impede the recrosslink process. In this case, a physical mixing method, synthesis and prepare particle gel without participation of fibers then mix with fiber during the swelling process could be attempted to test if more fiber applied in the bulk gel could make further improvement on the total swelling ratio and the strength. The maximum concentration of fiber that the pump applied in the oil field is 4%, which is far beyond the concentration tested in this study.

Also, due to the relatively high soften temperature and harsh degradation conditions of fibers, the afterwards treatment of fiber remaining in the reservoir and the environmental impact by the fiber in the formation should be considered if the product would be widely applied.

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