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CHARACTERIZATION OF FREE-RADICAL SOLUTION POLYMERIZATIONS OF ACRYLAMIDE INITIATED BY PERSULFATE INITIATOR SYSTEMS

by

YASHU CHEN

A THESIS

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Approved by

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Dr. Lizhu Wang

ABSTRACT

In order to reduce the water production and improve the oil recovery of mature reservoir, various conformance control technologies have been extensively developed. Preformed particle gel (PPG), a cost-effective plugging agent, has been successfully applied to block the high permeability zone and thus to displace the water to up-swept zone.

A common PPG based on polyacrylamide hydrogel have been wildly used. Identifying the parameters that affect gelation performance and understand how these parameters affect the performance is very useful to predict and manipulate the gelation time and to control the performance of gels.

The objective of this research is to optimize the concentration of three persulfate initiator systems and to study the effect of some factors (water content, initiator concentration, temperature and pH value) on the gel performance (gelation time, gel strength, swelling ratio and exothermicity). The four types of initiators test during this research are ammonium persulfate (APS), ammonium persulfate (APS)/potassium persulfate(KPS), ammonium persulfate (APS) / sodium thiosulfate (STS) and ammonium persulfate (APS) / sodium metabisulfite (SMS) initiator system.

Experimental results showed that different initiator system will be selected according to the different synthetic conditions. All the factors which tested in this research can sensitively affect the gelation time. The gel strength is scarcely influenced by initiator concentration and temperature and greatly affected by water content and pH value.

ACKNOWLEDGMENTS

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I would like to show my inmost gratitude to my parents. Thank you for their spiritual and economic support.

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1. INTRODUCTION

Excessive water production is a serious environmental and economically inefficient problem which faced by the mature oilfield and cared by oil companies. The injected water especially during secondary recovery process usually tends to pass through high permeability zone (channels and fractures) leading to low displacement efficiency and low recovery of the reservoir.

Reservoir heterogeneity is one of the principle reasons that has resulted excessive water production and low sweep efficiency of water flooding. The complex geological conditions of natural fracture or channel produced during water flooding which is the main reason that cause reservoir heterogeneity. Many technologies have been widely used to reduce the water production and improve the oil recovery such as polymer flooding, alkaline flooding, gel treatment, surfactant flooding, and alkali-surfactant-polymer flooding.

Gel treatment, one of a cost-efficiency conformance control method, has been developed to solve the reservoir heterogeneity problem. In term of gel treatment, superabsorbent polymer hydrogels will be injected into the target area of the reservoir to block the high-permeability zones and divert the water to un-swept zone where is remaining oil distribution. Phillips invented the first in-situ gel system for conformance control in the 1970s. Traditionally, in-situ gels that is injected into reservoir before gelling and gelation in target zone have been used for conformance control. However, the traditional in-situ gels suffer from disadvantages of insufficient control of gel time and gelation process.

As time goes on and the application evolves, a new type of gel treatments preformed particle gel has been wildly applied in mature oil fields. Several authors have recommended preformed particle gels due to the easy-controlled gelation process and better placement of preformed particle gels.

The synthesis of preformed particle gels is composed of monomer, crosslinkers, initiator, and some additives. Acrylamide usually used as the major component for preformed particle gels. Crosslinkers have been classified into two main types: metallic crosslinker and covalent crosslinker. Four types of initiator systems have been used for polymerization of acrylamide.

In order to predict gelation time, to manipulate gelation time, and to control the properties of gels, identifying the experimental parameters that affect gelation rates and understand how these parameters affect the rate is very important.

In this research, the polymerization of acrylamide with three initiator systems based on peroxydisulfate salt have been synthesized. The three types of initiators are ammonium persulfate (APS) / potassium persulfate (KPS) initiator system, ammonium persulfate (APS) / sodium thiosulfate (STS) initiator system and ammonium persulfate (APS) / sodium metabisulfite (SMS) initiator system. The effect of four experimental parameters (water content, initiator concentration, temperature and pH value) on gelation time and gel strength for three gel systems have been evaluated. Compare with the result of gelation and gel strength for all systems, the system of acrylamide with APS/STS initiator has been selected to evaluate the swelling ratio, SEM, reaction heat.

2. BACKGROUND AND LITERATURE REVIEW

2.1. ENHANCED OIL RECOVERY

Enhanced oil recovery (EOR) technologies employ methods that can help produce oil and reduce the oil saturation below the residual oil saturation (Lake & Venuto, 1990). After primary and secondary recovery, two-thirds of the oil in place cannot be produced (Brown, 2010). By using EOR methods, 30-60% or more of the reservoir's original oil can be produced (Hemsath, 1991). The EOR methods can be divided into three primary techniques: thermal recovery, miscible flooding, and chemical injection (Donaldson, Chilingarian, & Yen, 1989).

2.1.1. Thermal EOR Methods. Thermal methods are normally applied for heavy oil and tar sands to reduce the viscosity and hence the mobility ratio of a reservoir by applying heat to the reservoir and vaporizing the oil (Thomas, 2008). The methods include cyclic steam injection, steam flooding, and combustion (Ali, 2003). These methods have been successfully used in the United States, Canada, Indonesia and other countries since the 1950s (Lake & Venuto, 1990).

2.1.2. Miscible EOR Methods. The certain gases used in miscible EOR methods include carbon dioxide, natural gas, or nitrogen (Holm & O'Brien, 1986). The methods help to reduce the interfacial tension between water and oil by injecting gases in the reservoir (Shah et al., 2010). Miscible flooding has been researched to enhance oil recovery since the 1960s. Miscible flooding is presently the most commonly used method for light oil (Holm, 1982). The various miscible flooding methods include miscible slug process, high-pressure gas injection enriched gas drive, and so on (Thomas, 2008).

2.1.3. Chemical EOR Methods. Chemical EOR methods inject specialized chemicals into the reservoir to aid mobility and reduce interfacial tension or conformance control (Kong & Ohadi, 2010). The major chemical EOR methods include polymer flooding, alkaline flooding, gel treatment, surfactant flooding, and alkali-surfactant-polymer flooding (Sheng, 2014). Polymer flooding is the most common method in chemical EOR (Taber, Martin, & Seright, 1997). The main beneficial property of polymer solutions used in oil displacement reservoirs is to increase the viscosity (Wever, Picchioni, & Broekhuis, 2011).

2.2. CONFORMANCE CONTROL

Conformance control refers to the technology that mobilizes un-swept oil by increasing its drive capability that can help to improve the production profile (Yu et al., 2015). Conformance control is an effective solution to be developed in the oil fields to solve excess water production problem and reservoir heterogeneity problem (Bailey et al., 2000). In the oil industry, water flooding is one of the most popular methods to increase pressure and stimulate the production of a reservoir (Fakhru’l-Razi et al., 2009). Due to water flooding in the reservoir, many oil fields were faced with an excess water production problem. Excess water products include injected water, formation water, and condensate (Dawson & Van Le, 1995). Water poses a threat to the environment, and waste oil disposal is an extra task for oil companies. In 2001, the annual cost of disposing produced water was estimated to be approximately 40 billion dollars worldwide (Seright, Lane, & Sydansk, 2001).The cost of produced water handling and treatment in the United States alone was estimated to be approximately 18 billion dollars in 2015 (Kneese, Ayres, & d'Arge, 2015). For each barrel of oil, about three barrels of water are produced (Seright et al., 2001).

Reservoir heterogeneity refers to vertical and lateral variations in porosity and permeability (Warren & Price, 1961). The volume of hydrocarbon displaced divided by the volume of hydrocarbon in place (Welge, 1952). The macroscopic (volumetric) displacement efficiency results from a combination of areal sweep efficiency and vertical sweep efficiency (Figure 2.1) that is a measure of the three-dimensional effect of reservoir heterogeneities (Wardlaw, 1996). Reservoir heterogeneity has resulted in undesirable water channel that leads to a high water cut and low recovery of a reservoir (A Zaitoun, Kohler, Bossie-Codreanu, & Denys, 1999). To encounter reservoir heterogeneity, gel treatment has been reported by several researchers as a successful technique to solve the excessive water production problem and reservoir heterogeneity problem.

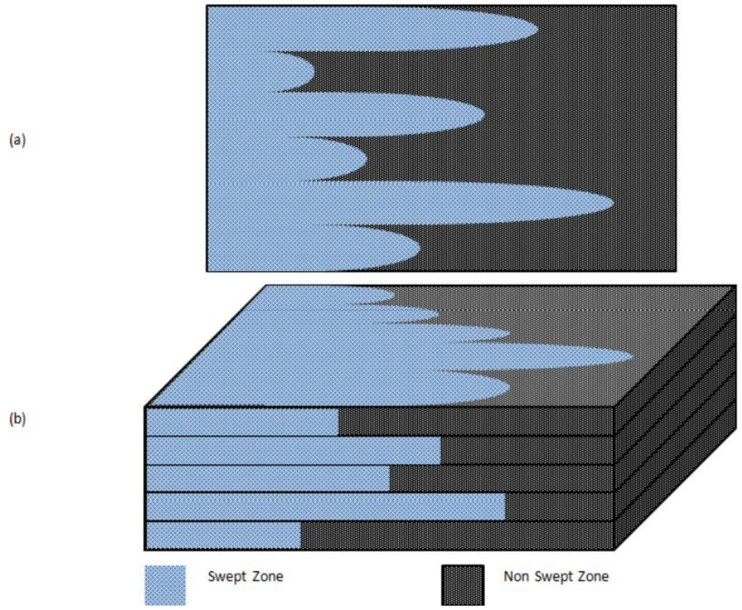


Figure 2.1. Schematic showing the sweep efficiency (a)areal sweep efficiency; (b)vertical sweep efficiency

2.3. GEL TREATMENT FOR CONFORMANCE CONTROL

Gel treatment acting as a plugging agent that can block high permeability zone to reduce the flow capacity of channels and divert the water to un-swept zone (Bai, Zhou, Liu, & Tongwa, 2013). The main mechanism of gel treatment is injecting gels into the target formation of the reservoir and placing gels in high-permeability zones and reduce permeability disproportionally (Stavland & Nilsson, 2001). In the 1970s, Phillips invented the first polymer hydrogel for conformance control (Bawa, Pillay, Choonara, & Du Toit, 2009). Since the 1990s, gel treatment has been successfully used to solve reservoir heterogeneity problem in more than 20 counties (Seright & Liang, 1994).

2.3.1. Superabsorbent Polymer Hydrogel. Superabsorbent polymer (APS) hydrogels refer to the hydrophilic three-dimensional networks materials that can absorb huge amounts of aqueous solutions and retain the volume as much as 1000 times of their own weight (Figure 2.2) (ZOHOURIAN & Kabiri, 2008). The APS hydrogels are composed of a water-soluble polymer, crosslinkers, and some additives.

Due to the properties of high absorbency and expected strength, APS hydrogels have been wildly used to gel treatment for conformance control (Ramazani-Harandi, Zohuriaan-Mehr et al. 2006). Two types of APS hydrogels that have been used for conformance control are in-situ gels and preformed particle gels (Durán-Valencia, Bai et al. 2014).

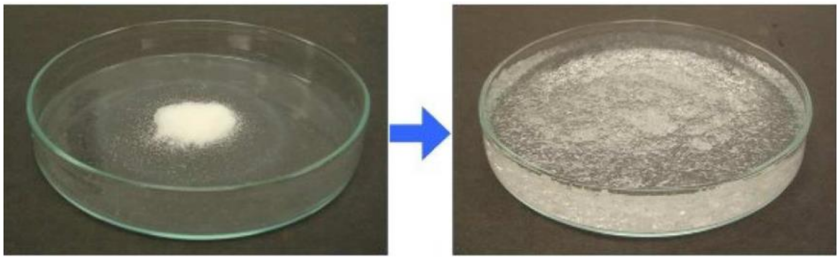


Figure 2.2. Dry SAP hydrogels powder and after swollen (Kabir, 2001)

2.3.2. In-situ Gel Systems for Conformance Control. In-situ gel systems refer that a bulk gel with a three-dimensional network structure formed under reservoir conditions as the gelant is injected in the target area in order to divert the flow of injected water or gas to un-swept zones (Jia, Pu, Zhao, & Liao, 2011). The first in-situ gel was developed in the early 1970s using a combination of partially hydrolyzed polyacrylamides and multivalent cations, including calcium, magnesium, and aluminum cations (Needham, Threlkeld, & Gall, 1974). The most common polymer used in gel system is polyacrylamide (PAM) which has an added advantage of being cost-efficient. Two main types of in-situ gel systems have been developed depending on the type of the crosslinkers (Yang, Adrus, Tomicki, & Ulbricht, 2011). Gels crosslinked with trivalent metal ions developed by Marathon Oil Company (Sydansk, 1988) and Gels crosslinked with an organic agent (Norman & Desai, 2006).

2.3.2.1 Metallic crosslinking polymer gel systems. The main mechanism of metallic crosslinking gel systems is the metallic crosslinkers form the ionic bonds between the negative sites and the multivalent cations of the polymer (Moradi-Araghi, 2000). Some kinds of multivalent cations can be used as a crosslinker for anionic polyacrylamides, such as chromic ion ($\mathbf{Cr^{3+}}$), aluminum ion ($\mathbf{Al^{3+}}$), or zirconium ion ($\mathbf{Zr^{3+}}$), which can be packaged with inorganic ions in a solution or soluble chemical complexes in which the trivalent ion is associated with small inorganic or organic groups called ligands (Figure 2.3) (Kabir, 2001).

The first crosslinker used in metallic crosslinked PAM gel systems is aluminum sulfate ($Al_2(SO_4)_3$) (Sandiford, 1977). The gelant solution mixes on the surface, while the aluminum sulfate is pH dependent. Because the pH rises rapidly in the reservoir, the gel forms immediately in the reservoir, the system works in a very limited environment, and the reaction suffers from a lack of control and delay (Chen, 2016). Another drawback of this system is that other multivalent ions can lead to the precipitation of Al^{+3} and polymers (Fakhru'l-Razi et al., 2009).

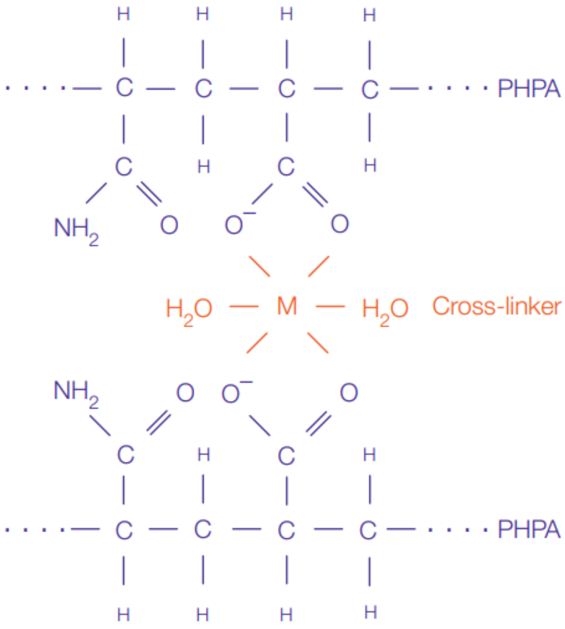


Figure 2.3. Chemical linking of PAM with trivalent metal ions indicated generically as M (Borling, Chan, Hughes, & Sydansk, 1994)

Due to the drawbacks of Al^{3+}, a Cr^{6+}/PAM gel system was employed in the 1980s (Southard, Green, & Willhite, 1984). The results of the experiment show that the Cr^{6+}/PAM gel system is better than the Al^{3+}/PAM gel system because it has two steps reactions. First, the Cr^{6+} is reduced to Cr^{3+}, and then the Cr^{3+} is crosslinked with PAM. The first step gives some time delay of the reaction, but the gelation time achieved was not long enough in high temperatures, and the system also has some weaknesses (Kabir, 2001). The system is sensitive to hydrogen sulfide (H_2S), and Cr^{6+} was identified as toxic and even a carcinogenic substance (Padhi, 2012).

In order to solve these problems, Marathon Petroleum Technology Center developed a controllable chromium system in the 1980s (Sydansk 1988). In this system, the Cr^{3+} was packaged as a metal-carboxylate complex, chromium acetate. The Cr^{3+} is attracted to both the acetate ligand and the carboxylate groups with complex reaction on the PAM (Figure 2.4) (Moradi-Araghi, 2000). This system can achieve a long gelation time up to 124℃ and is easy to control. It also claimed that insensitive between pH 2 to 12.5, and ions in formation fluids, H_2S and CO_2 (Chen, 2016).

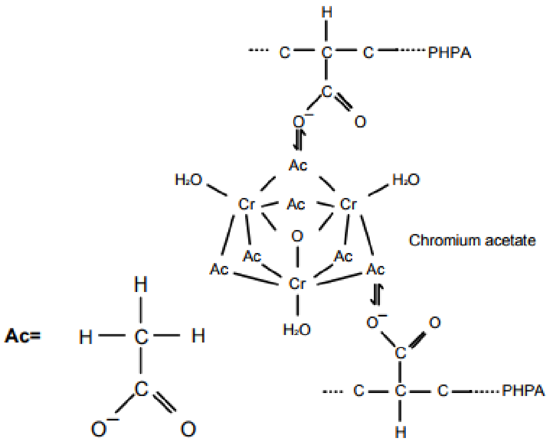


Figure 2.4. Chemical structure of chromium acetate linked PAM (Moradi-Araghi, 2000)

The main factors affecting the gelation process are the charge density of the polymer and the source of the trivalent or tetravalent cation. Other factors include, but are not limited to, the polymer/ crosslinker concentration, temperature, and pH (Fink, 2003).

Since the metal ion crosslinked gels are caused by ionic bonding between a negatively charged carboxylic acid group and a multivalent cation, their ionic bond cleavage occurs at temperatures above 75°C, and therefore ionic gels are thermally unstable. Organically crosslinked PAM gel systems are stable over a wider temperature range (Al-Muntasheri, Nasr-El-Din, Peters, & Zitha, 2005) and have been successfully used in controlling water production in a wide variety of geological situations.

2.3.2.2 Covalent crosslinking polymer gel systems. Covalent crosslinking polymer gel systems are based on covalent bonds, which are more stable than ionic bonds. Typically, a covalent bond involves the amide groups in the polymer backbone (Al-Muntasheri et al., 2005). The covalent crosslinkers that have been used include, but are not limited to, phenols or their precursors, such as phenylacetate, in combination with formaldehyde or its precursors, glutaraldehyde, polyvinyl alcohol, and polyethylenimine (PEI) (Hardy, Botermans, Hamouda, Valdal, & Warren, 1999; Kabir, 2001). An organically crosslinked PAM gel system that is based on PAM/tert-butyl acrylate (PAtBA) copolymer crosslinked with PEI was first applied in a high temperature reservoir, which can reach higher than 200°C (Zohuriaan-Mehr, Omidian, Doroudiani, & Kabiri, 2010). Hardy et al. (1999) described a mechanism of PAM by PEI that involves the formation of covalent bonds between the carbonyl carbon at the ester group and imine nitrogen. Reddy et al. proposed a second mechanism of PAM and PEI in which the PEI nitrogen forms covalent bonds with the carbonyl carbon at the amide group of PAtBA through a transamination reaction (Reddy, Arias, Nicolas, & Couvreur, 2012)

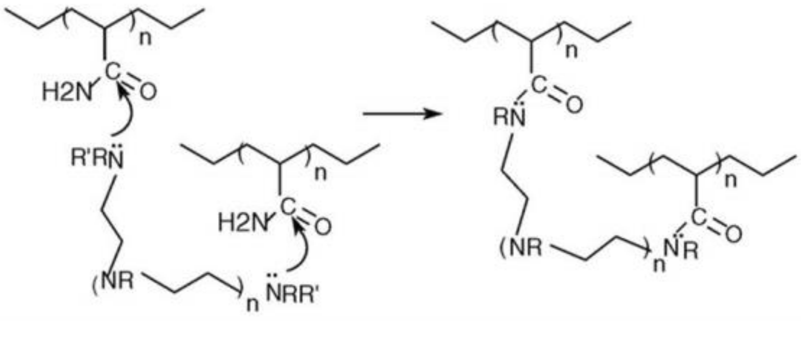


Figure 2.5. Gelation mechanism between PAM and PEI (Reddy et al., 2012)

Traditional in situ gels have been widely used for conformance control. However, both in-situ gel systems suffer from disadvantages of insufficient control of gel time, the uncertainty of gelation caused by shear degradation, chromatographic separation of changes in gel composition, and dilution of formation water (Bai, Huang, Liu, Seright, & Wang, 2008).

2.3.3. Preformed Gel Systems for Conformance Control. Due to the disadvantage of in situ gels, a new gel processing technique has been developed that forms a gel at the surface conditions and injects the preformed gel into the target formation of the reservoir (Bai et al., 2008; Bai, Li, Liu, Wang, & Liu, 2004; Bai, Liu, Coste, & Li, 2007). Because gelation does not occur in the reservoir, the gelation process is easier to control. Several types of preformed gel systems have been distinguished due to the particle sizes and swelling times used for conformance control, including preformed particle gels (PPGs) (Bai et al., 2004; Coste et al., 2000), preformed bulk gels (Seright, Prodanovic, & Lindquist, 2004), microgels (Chauveteau et al., 2001; Feng et al., 2003), pH-sensitive crosslinked polymers (Al-Anazi & Sharma, 2002; Benson, Nghiem, Bryant, & Huh, 2007), and swelling micron-sized polymers (Eoff, Dalrymple, Reddy, Morgan, & Frampton, 2003). Three types of preformed gel systems have been developed based on the particle size: submicro-sized particle gels, micrometer-sized preformed particle gels, and millimeter-sized preformed particle gels.

2.3.3.1 Submicro-sized particle gels. The particle size of submicro-sized particle gels is less than 1μm. A submicro-sized particle gel system named Bright Water has been developed by Chevron, BP, and Tiorco (Elue, 2015). Bright Water's deep consistency control approach is a new technology for polymer flooding and is used in several regions

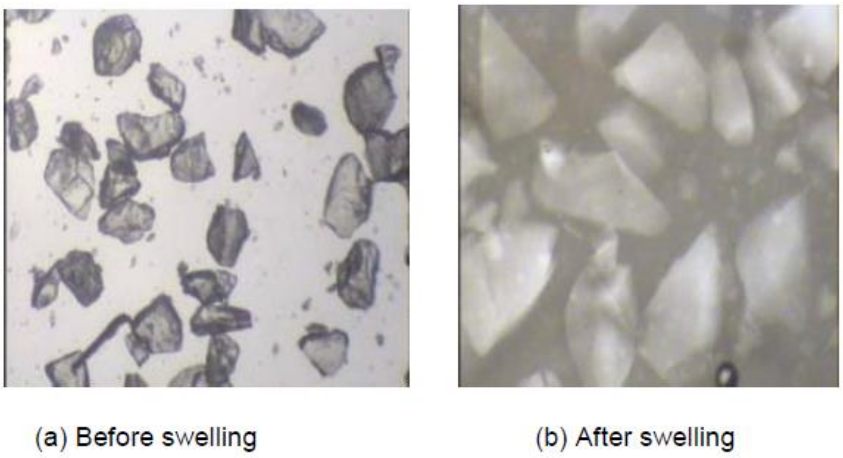
(Pritchett et al., 2003). The principle of the Bright Water system consists of injecting a suspension of crosslinked polymer particles. The mechanism of Bright Water provides low-viscosity properties for injection fluids and can be used in deep formations (Al-Adasani & Bai, 2010). The first pilot test of the treatment was pumped in the Minas field in November 2001, and a number of treatments were performed in the North Sea (Pritchett et al., 2003), Argentina (Fethi et al., 2010), Alaska (Ohms et al., 2010), and Tunisia (Ghaddab et al., 2010). The Bright Water system has been wildly used in more than 60 injection wells. However, because of the poor thermal stability and limited application range, Bright Water is not widely used in fields (Bai, Zhou, & Yin, 2015).

2.3.3.2 Micrometer-sized preformed particle gels. The particle size of the micrometer-sized preformed particle gel is between 1 to 10 μm. The advantage of microgels is that the gels can be easily injected into porous media without any plugging (Feng et al., 2003). A new size-controlled microgel has been developed by IFP to reduce water permeability by forming thick absorbent layers. Chauveteau et al. (2001) focused on synthesis microgels under a constant shear rate during the injection process in porous media. The terpolymer of acrylamide used for the system contains 2% acrylates, 2% sulfonated groups, and a solution at 7.2% by weight zirconium oxide stabilized by a lactate complexing agent used as a crosslinker (Chauveteau et al., 2001). The properties of the microgels at different shear rates, temperatures, and pH levels of both polymers and crosslinkers and concluded the particle size decreases as the shear rate increases. Typical microgels are about 1-3 microns in size with a typical gel concentration of 3000 ppm. Microgels can be infused into porous media with a permeability of up to six nuclei without any evidence of continuous blockages (Alain Zaitoun et al., 2007). The system has been used for more than 10 injection wells.

2.3.3.3 Millimeter sized preformed particle gels. The particle size of millimeter sized preformed particle gels is between 10 μm to mms. Millimeter sized PPGs are mainly used for reservoirs with fractures or channels that have a high permeability. Li et al. (1999) proposed a new system of millimeter sized preformed particle gels used for conformance control in China in 1996, and Bai and Coste (2004) analyzed the properties of Millimeter sized PPGs.

The preparation of millimeter sized PPGs has several steps, and acrylamide is usually used as a monomer. The first step is preparing a water solution of acrylamide, a crosslinker, and an initiator according to a certain ratio, crushing the gel into particles after the solution formed a bulk gel, and then drying particles at a high temperature. The dried particles can swell 10 to 200 times the original volume (Figure 2.6). The advantages of millimeter sized PPGS are the swelling ratio and strength are easily controlled and the insensitivity of salinity or reservoir minerals. The temperature resistance of millimeter sized PPGs is up to 120℃ (Bai et al., 2013). The first successful large volume of millimeter sized PPG treatment was in the Zhongyuan Oilfield in China in 1999 (Bai et al., 2004) and the millimeter sized PPGs have been applied to more than 5000 wells for conformance control (Bai et al., 2015).

As mentioned above, performed gel systems can be successfully used for conformance control with small fractures or channels with a high permeability. Nonetheless, they also have some limitations. Preformed particle gels cannot be injected into normal porous media or applied with very severe open channels or super high permeability open fractures (Bai et al., 2008).


(a) Before swelling

(b) After swelling

Figure 2.6. Morphology of PPG particles before/after swelling

2.4. POLYMERIZATION

The polymerization process of the PPGs is an important part of gel treatment system. Polymerization is the process of linking the repeating units (monomer) together to form polymer chains (Hawker, Frechet, Grubbs, & Dao, 1995). After polymerization of many repeating units, the physical properties relative to the large molecular weight have been changed including toughness, viscoelasticity, and the tendency to form glass and semi-crystalline structures rather than crystals (Van Krevelen & Te Nijenhuis, 2009). In the 1920s, a German organic chemist Hermann Staudinger proposed that natural compounds such as rubber and cellulose consist of macromolecules, which he characterized as polymers, containing 10000 or more atoms (Cowie & Arrighi, 2007). Staudinger also elucidated the molecular structures of pyrethrin I and II at the same time (Casida, 1980). Nowadays, polymers are widely used advanced materials, which are found almost in every material used in human daily life such as polyethylene, polypropylene, nylon etc.

2.4.1. Polymerization Techniques. The principal free radical polymerization techniques are bulk, solution, suspension, and emulsion.

2.4.1.1 Bulk (Mass) polymerization. Bulk (mass) polymerization refers to add a soluble radical initiator to monomer. Bulk polymerization method is the simplest technique requiring only monomer and monomer-soluble initiators that initiated by heating or exposing to radiation (Saunders, 2012). The advantages of bulk polymerization are easy to produce high polymer yield per reaction volume and easy polymer recovery. The disadvantage of the technique is difficult to remove unreacted monomer and heat control (Carraher Jr, 2012). Due to the negative features of bulk polymerization, the process can be carried out in a solvent, which is known as solution polymerization.

2.4.1.2 Solution polymerization. In solution polymerization, all the monomers are dissolved in an aqueous solution and polymerized in the presence of a water-soluble initiator or redox initiator pair at a certain temperature(Carraher Jr, 2012). The advantage of solution polymerization is that the reaction process easy to control and the heat that released by the reaction can absorb by the solvent. In order to produce high purity polymer, solvent recovery and removal is necessary for solution polymerization. However, solution polymerization is difficult to produce high molecular weight polymer like bulk polymerization.

2.4.1.3 Suspension polymerization. Suspension polymerization refers to the process in which liquid monomers are polymerized in liquid droplets suspended in a liquid phase to form spheres of polymer (Timm & Leng, 1986). The particles size is range from

10 to 1000nm. In suspension polymerization, the solvent recovery and treatment problems are minimal due to the liquid is water-based (Carraher Jr, 2012).

2.4.1.4 Emulsion polymerization. For an emulsion polymerization system, it contains a water-soluble initiator, chain transfer agent, and a surfactant (Pham et al., 2003). Droplets of monomer are emulsified in a continuous phase of water. Emulsion polymerization is differing from suspension polymerization in the mechanism and the particle size produced by emulsion polymerization is range from 0.05 to 5nm which is less than suspension polymerization (Carraher Jr, 2012). Emulsion polymerization can produce high molecular weight polymer with narrow molecular weight distribution and the heat is easy to remove from the reaction. The disadvantage of emulsion polymerization is that the resulting resin is often contaminated with emulsifiers, almost inevitably leading to poor transparency and other undesirable properties (Kamigaito, Ando, & Sawamoto, 2001).

2.4.2. Types of Polymerization. Two general types of polymerization reactions usually are distinguished: step-reaction (polycondensation) and chain-reaction (addition) polymerization, as shown in, as shown in Figure 2.7.

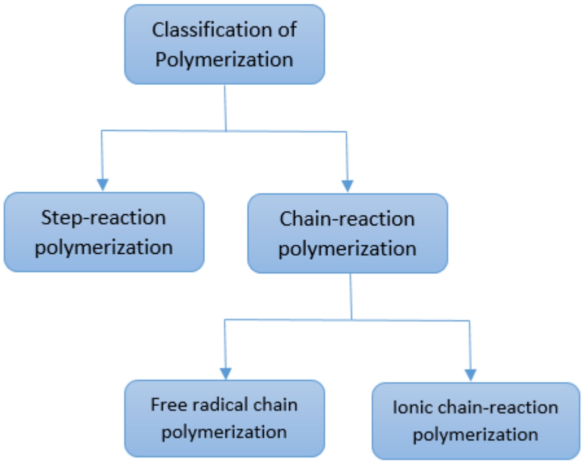


Figure 2.7.Classification of polymerization

2.4.2.1 Step-reaction (condensation) polymerization. Step-reaction polymerization is a polymerization technique that involves the self-addition of several bifunctional monomers to each other are takes place accompanying the elimination of simple molecules (H_2O, HCl, etc.) (Jenkins, Kratochvil, Stepto, & Suter, 1996). Nylon is a common condensation polymer. An example reaction of nylon (Figure 2.8) is by reacting dicarboxylic acid with one amine and one carboxylic acid group on the same molecule. Then two molecules of water are eliminated and the nylon is formed (Haken, 1986).

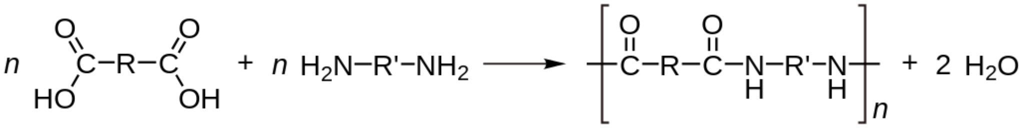


Figure 2.8.The general reaction of nylon

2.4.2.2 Chain-reaction (addition) polymerization. Chain-reaction polymerization is another common type of polymerization in which is unsaturated monomer molecules are added to the active site of a growing polymer chain one at a time (Young, Downer, & Eardly, 1991). Two forms of chain-growth polymerization usually are distinguished: free radical chain and ionic chain reaction. Among them, ionic addiction polymerization is of limited use due to stringent reaction conditions. Polyacrylamide is a common addition polymerization (Figure 2.9).

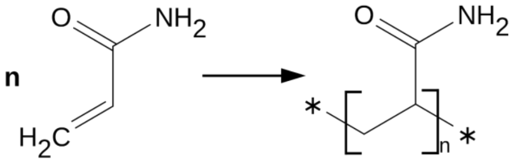


Figure 2.9. Reaction of polymerization of acrylamide to polyacrylamide

Due to cost effectiveness and the ease of application in the reservoir, polyacrylamide polymer gel systems have been used successfully in many oil fields (Abidin, Puspasari, & Nugroho, 2012). Polyacrylamide hydrogel is one of the most common plugging agents applied in conformance controls, and it is preferred because of its low cost, non-toxic and biological inertness, long chain length, and adjustable properties (Chen, 2016). Polyacrylamide hydrogel formed by monomer crosslinking polymerization is one of the most common particle gels. In this monomer crosslinking polymerization process, Acrylamide reacts with an initiator, crosslinker and other additives to form three-dimensional networks (Mohan, Murthy, & Raju, 2005). An example of a network that utilizes polymerization of acrylamide crosslinking with N,N'-Methylenebisacrylamide (MBAA) initiated by ammonium persulfate as shown in Figure 2.10. Polymerization kinetics can be manipulated by changing reaction conditions such as temperature, water content, or initiator concentration (Watkins & McCarthy, 1995).

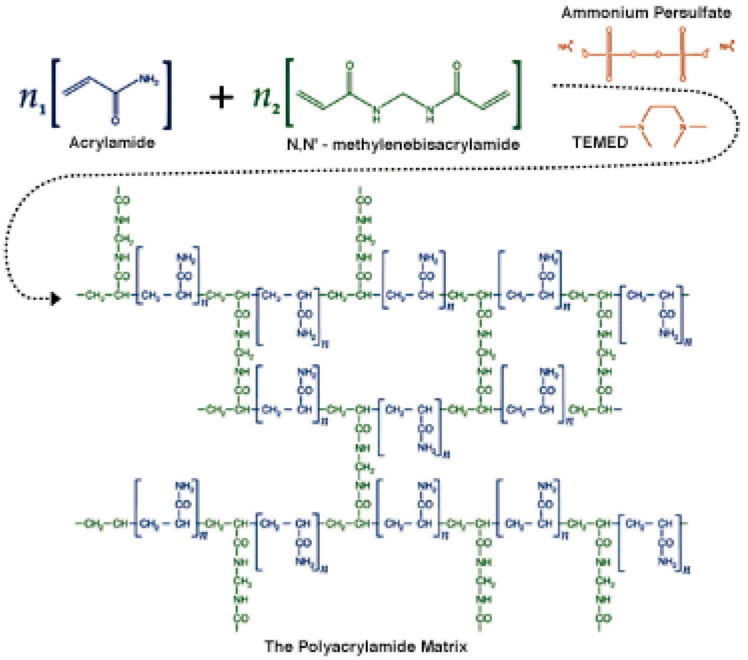


Figure 2.10. The polymerization of a polyacrylamide matrix with acrylamide crosslinking

2.4.3. Mechanism for Free Radical Chain Polymerization. Like other chain reactions, radical polymerization is a rapid reaction process that includes the characteristic steps of initiation, propagation, and termination (Cowie & Arrighi, 2007). Free-radical initiators are generated by the cleavage of covalent bonds and many radiation-related processes (Gorbunov & Sharma, 2015).

Free radicals are formed in the initiation reactions. The initiation step is considered to involve two reactions. The first step is that the initiator (I) produces free radicals with rate constant (kd)

$$I \xrightarrow{k_d} 2R^* . \tag{1}$$

The second initiation step is the production of the first monomer radical by a combination of R* with monomer (M) with rate constant (ki)

$$R^* + M \xrightarrow{k_i} RM^* . \tag{2}$$

As propagation continues and each monomer unit is added, the propagation process ensues with the rate constant (kp)

$$\mathrm{RM}^* + nM \xrightarrow{kp} RM_nM^* . \tag{3}$$

The last process is the termination of the radical centers that occurs by two mechanisms: disproportionation and addition (coupling) of two growing polymers with the rate constant (kt)

$$M_nM^* + M_mM^* \xrightarrow{kt} M_{n+1} + M_{m+1} \tag{4}$$

$$M_nM^* + M_mM^* \xrightarrow{kt} M_{n+m+2} . \tag{5}$$

The first kinetic equation states that the rate of initiation (Ri) is the same as the rate of initiator decomposition (Rd) from Equation (1) and (2), where f is the efficiency of the initiator

$$R_i = R_d = \mathrm{d}[M^*]/dt = 2k_d f[I] \quad (6)$$

The second kinetic equation is the rate of propagation Rp, which can be described as

$$R_\mathrm{p} = k_p[M][M^*] \quad (7)$$

The last kinetic equation is the rate of termination, which can be described as

$$R_\mathrm{t} = -d[M^*]/dt = 2k_t[M^*]^2 \quad (8)$$

Under the steady-state approximation, the concentration of the active growing chains remains constant, so the rate of initiation is equal to the rate of termination (Bremer & Dennis, 1996). The rate of chain propagation can be used as the overall rate of polymerization, which further describes using a function of the initiator concentrations

$$R_\mathrm{p} = k_p\left(\frac{fk_d}{k_t}\right)^{1/2}[I]^{1/2}[M] \quad (9)$$

2.4.4. Factors Effecting Polymerization Rate. Several factors can affect polymerization rate have been explored. In order to predict polymerization rate, to manipulate gelation time, and to control the properties of gels, identifying the experimental parameters that affect polymerization rates and understand how these parameters affect the rate is necessary. The results of previously publication have provided some parameters which can affect the polymerization rate and how these parameters affect the rate. Especially the factors effect on the polymerization rate of acrylamide.

2.4.4.1 Effect of organic solvents. The addition of solvent and retardants decrease the rate of polymerization (LeBaron, Wang, & Pinnavaia, 1999). The affecting might be caused by three follows possible (Sarac, 1999): First, the presence of these solvents may consume a certain amount of catalyst leading to a decrease of polymerization rate and limit the conversion of polymerization. Moreover, due to the addition of organic solvent to the aqueous medium, the shielded area of the hydration layer reduced, resulting in the possibility of termination increase and the free radical end of the growing chain. In addition to these, a decrease of the propagation rate was observed due to the transfer of macromolecular chains, resulting in the decrease of polymerization rate.

Through experiment and observation, the result shown adding 5% aliphatic alcohol and dimethylformamide to mandelic acid/permanganate redox system in acrylamide polymerization decrease the polymerization rate. Some of the retardation effect from largest to lowest have been reported as ethanol, methanol, dimethylformamide and isopropyl alcohol (Bajpai et al. 1990). The effect of solvent and retardants also reported of polymerization of N, N'-methylenebisacrylamide with peroxidiphosphate-Ag redox system (Gupta, 1994); acrylonitrile polymerization by thioacetamide/permanganate redox system (Samal, Nayak, Suryanarayan, Panda, & Das, 1981), and methylmethacrylate polymerization by Ce(IV)/alcohol redox system (Fernandez, Kurz, & Luca, 1989).

2.4.4.2 Effect of oxygen. In most situation, oxygen plays as initiator will enhance the polymerization rate due to the decomposition of peroxides at high temperature condition (Matyjaszewski & Xia, 2001). And it also can react with monomers to produce peroxides which may subsequently decompose to produce peroxide radicals as shown as follow reaction

$$R^{*} + O_2 \rightarrow R - O - O^{*} . \tag{10}$$

Narain et al. provide the oxygen effect for the polymerization of acrylamide by peroxydisulfate ascorbic acid redox system in 1981. In this system, Oxygen acts as a catalyst that reacts with ascorbic acid was observed that can reduce the polymerization time (Narain, Jagadale, & Ghatge, 1981). However, oxygen also can depress the polymerization rate as an inhibitor when the peroxide radicals are less reactive than their predecessors (Sarac, 1999). Oxygen has a strong resistance to the polymerization of free radical polymerization, mainly due to the oxygen can easily lead to the decomposition of free radicals combined with the leading termination of the polymerization reaction (Beyler & Hirschler, 2002). If the reaction before the oxygen is not fully discharged, the polymerization will not be fully carried out, or even cause the phenomenon of non-convergence of the material.

2.4.4.3 Effect of ionic detergent. The addition of anionic detergents increases the rate of polymerization (Hepburn, 1992). Termination can occur in both the aqueous and precipitated phases. However, termination always occurs mainly in the large bases (Shoesmith, Taylor, Bailey, & Owen, 1980). This is considered that the negative charge may exert repulsion force between the growing polymer chains and reduce the possibility of bimolecular termination (Rozenberg & Tenne, 2008). On the other hand, the addition of the cationic detergent increases the positive charge on the micelles formed. And as the positive charge increase, the possibility of termination increases and the termination rate increase. Therefore, the rate of polymerization increases when the anionic detergent exists and decrease when the cationic detergent exists. The examples of the effect for polymerization rate have been reported of acrylamide in glyceric acid/permanganate redox system (Gupta, Verma, & Behari, 1986) and vinyl acetate and methyl acrylate in potassium persulfate redox system (Morris, Hall, & James, 1966; Napper & Parts, 1962).

2.4.4.4 Effect of alkali metal salts. The addition of alkali metal salts caused a depressing of the polymerization rate (Varshney, Hautekeer, Fayt, Jérôme, & Teyssié, 1990). Two possible explanations can explain the effect of alkali metal salts (Sarac, 1999): The first possible reason is that the alkali metal salts will formation complexation with the metal ionic of the initiator, resulting in the decrease of the polymerization rate. The conclusion was made from the polymerization of acrylonitrile by thioacetamide/permanganate redox system with the addition of sodium ions (Eromosele, 1994) and the polymerization of acrylamide by thiomalic acid/persulfate redox system with the addition of iron ion (Fe^{2+}), manganese ion (Mn^{2+})and cupric ion (Cu^{2+}). One of the exceptions of alkali metal salts is manganese salts. The result shows the addition of Mn^{2+}increase the polymerization rate due to the manganese ionic can react as initiator (H. P. Misra, 1979).

The other possible factor in reducing the rate of polymerization is that the effect of the ionic radius (M. Z. Hussain, Bhatnagar, & Lee, 1977). As the ionic radius increases, the action of the alkali metal chloride increases to inhibit the rate of polymerization and maximum conversion. The polymerization rate and the conversion also decreased as the ammonium chloride exit in the system. The retardation effect of some alkali metal chloride from largest to lowest has been reported as Lithium chloride, sodium chloride, potassium chloride, rubidium chloride and ammonium chloride (MacLeod & Snell, 1948).

2.4.5. Initiator Systems. Free radical initiation is any process that can create essential free radicals (Slater, 1988). Based on various initiating systems and polymerization methods, a series of commercial PAMs have been developed.

2.4.5.1 Azo compounds. Azo compounds refer to a free radical initiator whose molecular structure contains a double-bond between nitrogen and nitrogen (N=N) (Manzi-Nshuti, Chen, Su, & Wilkie, 2009). The general formula of azo compound is R-N=N-R, wherein the R-N bond is a weak bond that is easily broken to form a free radical. The decomposition temperature is related to the alkyl structure (Sheppard & MacLeay, 1978). The use of triphenyl aobenzene by Schulz (1939) drew first attention to azo compounds as polymerization initiators. The AIBN achieves the initiation by decomposition and eliminating a molecule of nitrogen gas to form two 2-cyanoprop-2-yl radicals (Figure 2.11) (Moad, Rizzardo, & Thang, 2005).

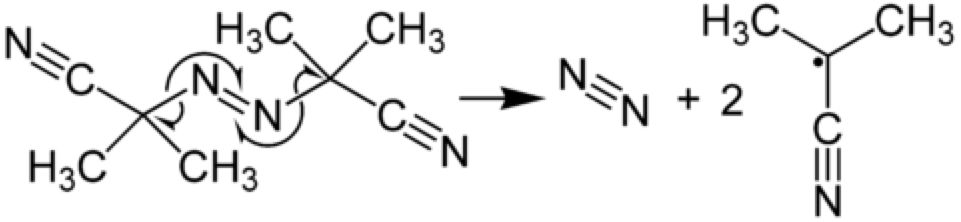


Figure 2.11. Formation of radicals from AIBN

Almost all azo-initiator systems decompose for the first reaction, which means the reaction only forms one free radical, with no side effects (Braunecker & Matyjaszewski, 2007). It is widely used in industrial production and scientific research. Azo compounds are stable and easy to store and transport. There are many different types of azo initiators available for different polymerization temperatures.

Thiele and Heuser (1896) discovered in 1896 the first and most commonly used aliphatic azo initiator AIBN. AIBN is a common initiator with the formula $(CH_3)_2C(CN)]_2N_2$, for acrylamide polymerization (Bartoň, 1991; Liu, Chen, Yu, Wu, & Gao, 2011; Qi, Jones, & Schork, 2007).

2.4.5.2 Redox initiator systems. Redox initiator systems form free radicals by a redox reaction between an oxidizing agent and a reducing agent (Sarac, 1999). Redox initiator systems of initiation reaction can extend to many combinations of non-peroxide oxidizing agents with organic reducing compounds. In the last 30 to 40 years of the 20th century, scientists from Germany, the United States, Britain and other countries have found that the redox initiators can not only shorten the induction period, but also increase the polymerization rate (De & White, 2001). In September 1945, the Faraday Society organized an "Oxidative General Discussion" on electron transfer reaction. At this meeting, Bacon (1948) reported on a wide range of studies on redox-initiator polymerization conducted at the Imperial Chemical Industry Laboratory since October 1940 (Bacon, 1955). The redox system has a lower chain-initiated activation energy of about 40-60 kJ/mol compared to a single hydrolysable single initiator, thereby reducing the polymerization temperature at or below room temperature (G. Misra & Bhattacharya, 1982; Moad & Solomon, 2006; Sarac, 1999).

Winnacker and Patat have found that in alkaline media and in the presence of oxygen, the rate of polymerization can be significantly increased by the addition of reducing agents, such as sulfites or thiosulfates (Kern, Antoshkiw, & Maiese, 1948). Metal chelates have been used as initiators for polymerizations. The polymerization rates of some metal chelate from rapid to slow have been reported as Mn(III), Ce(IV), Co(III), Fe(III), Al(III), Cr(III) and V(III) (Sarac, 1999). The ratio of the Mn (III)/Co (III) chelates and the polymerization rates are consistent with the mechanism of free radical polymerization. Radicals are initiated to originate from the ligand, so this process can be used to introduce these groups into the terminal position of the polymer chain. And a variety of organic compounds can increase the rate of metal chelate initiation (Kastning, Naarmann, Reis, & Berding, 1965).

Redox initiator systems have been extensively used as initiators for acrylamide polymerization. Two main types of redox initiator systems commonly used for acrylamide polymerization are the ceric ion redox system and the manganese ion redox system.

Ceric ion used for acrylamide polymerization can be combined with many organic compounds such as alcohols (H. Hussain & Mohamud, 2006; Narita, Okimoto, & Machida, 1970; Rout, Rout, Singh, & Santappa, 1977), acids (Hsu, Kuo, & Chen, 1993; G. Misra & Khatib, 1983), thiols (Hepburn, 1992), and amines ((H. Hussain & Mohamud, 2006) to form redox initiator systems. Most mechanisms of the redox initiator systems are depicted in Equation 11, where R is the chelating agent.

$$\begin{aligned} & Ce(IV) + R \overset{k}{\rightleftarrows} (Ce(IV) - R) \\ & (Ce(IV) - R) \xrightarrow{k_d} R^{*} + Ce(III) + H^{+} \end{aligned} \qquad (11)$$

The manganese ion initiator systems consisting of a transition metal (such as chromium, manganese, cobalt, nickel, molybdenum, tungsten) and an organic halide, in particular carbon tetrachloride, initiates polymerization of methyl methacrylate at 80-100°C (Husain, Misra, & Gupta, 1976; K. Misra & Seshadri, 1968; K. C. Misra & Fleet, 1974; Shukla & Misra, 1973). The mechanism consists of the following: the transition metal by a single electron transfers itself to form a higher oxidation state and carbon tetrachloride decomposition of an anion and chemokine ligand 3 (· CCl3) free radicals. The initiation reaction of manganese ion can be expressed as:

$$\begin{aligned} &Mn(IV)+R \rightarrow (Mn(IV)-R) \\ &(Mn(IV)-R) \xrightarrow{k_d} R^{*}+Mn(III)+CO \end{aligned} \quad . \qquad (12)$$

In addition, sodium chlorate-sodium sulfite (NaClO3-Na2SO3), potassium permanganate (KMnO4)-oxalic acid, thiols and potassium bromate (KBrO3) also can form redox initiator systems.

2.4.5.3 Peroxide initiator. Peroxide initiators are a class of compounds that contain the peroxide group (-O-O-) (Sanchez & Myers, 2000). In the initiation process, the bond of peroxide group cleavage splits into two oxygen-centered radicals after heating. Peroxide initiator points inorganic peroxide and organic peroxide into two categories: inorganic peroxide initiators that are soluble in water, which are used as an aqueous solution polymerization, and emulsion polymerization initiator(Araújo, Sayer, Giudici, & Poco, 2002). Fritz Klatte developed the first peroxide initiator for vinyl polymerization in 1912 (Kaufman, 1969). In the 1940s, peroxide initiator systems were generally accepted as a method for initiation of polymerization (Bevington & Toole, 1958; Nozaki, 1946; Price & Krebs, 1943). Kern summarized these results in 1974 and formulated the main steps of the initiation process of peroxide initiator systems.

Acrylamide polymerization can initiate with peroxydisulfate salts, such as ammonium persulfate (APS) (Bartoň, 1991; Lozinsky, Ivanov, Kalinina, Timofeeva, & Khokhlov, 2001; Ray & Mandal, 1997; Suen, Jen, & Lockwood, 1958), potassium persulfate (KPS) (Lin, 2001; G. Misra & Dubey, 1979; Seabrook & Gilbert, 2007; Singh, Tiwari, Pandey, & Singh, 2006; Stahl & Schulz, 2012; Zhou, Yao, & Kurth, 1996), potassium persulphate, etc. In the solution, peroxydisulfate dissociates to give sulfate radicals, as shown in the following reaction:

$$[O_3SO - OSO_3]^{2-} \overset{\Delta}{\rightleftarrows} 2SO_4{*}^{-} \, . \qquad (13)$$

3. EXPERIMENT

3.1. MATERIALS

The monomer acrylamide (AM) (98.5%) was purchased from Alfa Aesar Company. The crosslinker N, N' – methylene bisacrylamide (MBAA) (99%) was purchased from Sigma-Aldrich. Different initiators ammonium persulfate ($(NH_4)_2S_2O_8$, Certified ACS), potassium persulfate ($K_2S_2O_8$, Certified ACS), sodium thiosulfate ($Na_2S_2O_3$, Certified ACS) and sodium metabisulfite ($Na_2S_2O_5$, Ceritified ACS) was purchased from Fisher Chemical. Oxygen-free nitrogen was used for purging the polymerization solution. Distilled (DI) water was used for all experiments.

3.2. PREPARATION AND SYNTHESIS

The gels were synthesized by free radical crosslinking polymerization. First, Acrylamide and 10% MBAA solution were dissolved in distilled water. Then the mixture was stirred at room temperature and purged with nitrogen gas for 15 minutes. At the same time, 1g initiator was dissolved in 10 g distilled water a small flask. After deoxygenation, different concentration of initiator solution was dissolved in the reaction mixture. The mixed solution was stirred for 10 minutes and kept at different temperature.

The pH effect of the gelation time also adjusted by addition of 2% hydrochloric acid (HCl) and 2% sodium hydroxide (NaOH) solution. After the initiator dissolved in the mixture, 200ul 2% HCl/NaOH and 60ul HCl/NaOH were added to samples which should be discussed Ph effect of polymerization. Then the mixed solution was stirred for 5 minutes and recorded the pH value of samples and kept in the 45°C oven.

After the strong bulk gel formed, the bulk gel was snipped into small pieces and then dried in the 65°C oven until the total weight has no change. In order to get the target size particle (5-10 mesh), the dried particles were crushed by blender machine and screened by the shaker. The schematic of the gel synthesis process as shown in Figure 3.1. The amounts of reagents for synthesis are summarized in Tables. The first initiator used for polymerization of acrylamide is ammonium persulfate (APS) in different water content (A1-1 to A1-5), initiator concentration (A2-1 to A2-4), temperature (A3-1 to A3-4) and pH value (A4-1 to A4-5) as shown in Table 3.1

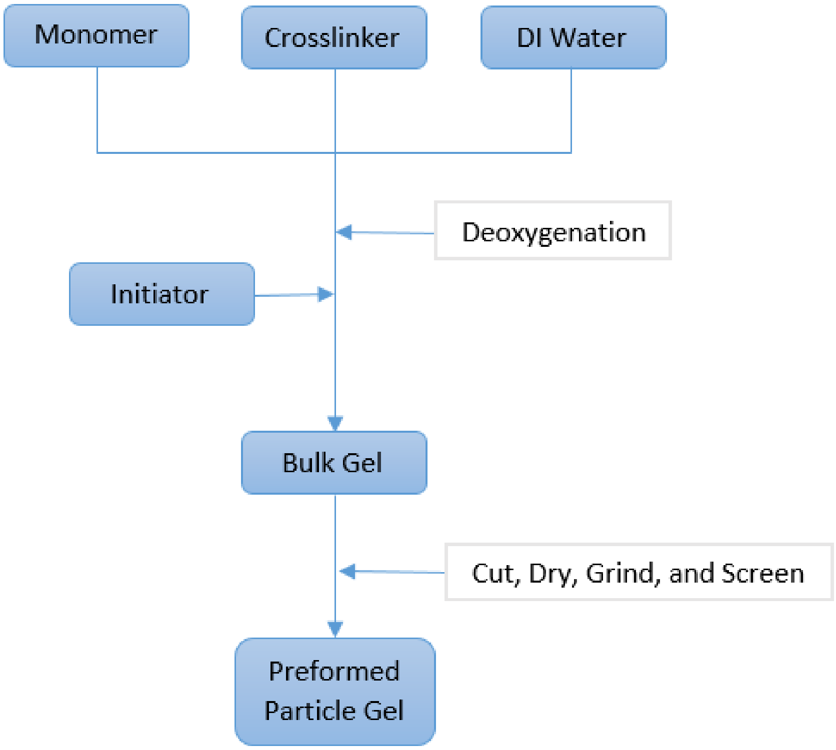


Figure 3.1. Schematic of gel synthesis

Table 3.1. Formulations for polymerization of AM initiated by APS

Sample	AM /g	DIW /g	MBAA /g	APS /g	T/C	pH
A1-1	20	20	0.004	0.015	45	7
A1-2	20	40	0.004	0.015	45	7
A1-3	20	60	0.004	0.015	45	7
A1-4	20	80	0.004	0.015	45	7
A1-5	20	100	0.004	0.015	45	7
A2-1	20	80	0.004	0.02	45	7
A2-2	20	80	0.004	0.015	45	7
A2-3	20	80	0.004	0.0125	45	7
A2-4	20	80	0.004	0.01	45	7
A3-1	20	80	0.004	0.015	23	7
A3-2	20	80	0.004	0.015	45	7
A3-3	20	80	0.004	0.015	65	7
A3-4	20	80	0.004	0.015	80	7
A4-1	20	80	0.004	0.015	45	3.7
A4-2	20	80	0.004	0.015	45	6.1
A4-3	20	80	0.004	0.015	45	7
A4-4	20	80	0.004	0.015	45	10.2
A4-5	20	80	0.004	0.015	45	11

The first initiator system used for polymerization of acrylamide is ammonium persulfate (APS) and potassium persulfate (KPS) in different water content (K1-1 to K1-5), initiator concentration (K2-1 to K2-4), temperature (K3-1 to K3-3) and pH (K4-1 to K4-5) (Table 3.2).

Table 3.2. Formulations for polymerization of AM initiated from APS and KPS

Sample	AM /g	DIW /g	MBAA /g	APS /g	KPS /g	T/C	pH
K1-0	20	20	0.004	0.015	0.015	RT	7
K1-1	20	20	0.004	0.015	0.015	45	7
K1-2	20	40	0.004	0.015	0.015	45	7
K1-3	20	60	0.004	0.015	0.015	45	7
K1-4	20	80	0.004	0.015	0.015	45	7
K1-5	20	100	0.004	0.015	0.015	45	7
K2-1	20	20	0.004	0.02	0.02	45	7
K2-2	20	20	0.004	0.015	0.015	45	7
K2-3	20	20	0.004	0.0125	0.0125	45	7
K2-4	20	20	0.004	0.01	0.01	45	7
K2-5	20	20	0.004	0.0075	0.0075	45	7
K2-6	20	20	0.004	0.005	0.005	45	7
K3-1	20	80	0.004	0.015	0.015	45	7
K3-2	20	80	0.004	0.015	0.015	65	7
K3-3	20	80	0.004	0.015	0.015	80	7
K4-1	20	80	0.004	0.015	0.015	45	3.7
K4-2	20	80	0.004	0.015	0.015	45	5.8
K4-3	20	80	0.004	0.015	0.015	45	7
K4-4	20	80	0.004	0.015	0.015	45	8.8
K4-5	20	80	0.004	0.015	0.015	45	11.3

The second initiator system used for polymerization of acrylamide is ammonium persulfate (APS) and sodium thiosulfate (STS) in different water content (T1-1 to T1-5), initiator concentration (T2-1 to T2-4), temperature (T3-1 to T3-3) and pH (T4-1 to T4-5) (Table 3.3).

Table 3.3. Formulations for polymerization of AM initiated from APS and STS

Sample	AM /g	DIW /g	MBAA /g	APS /g	STS /g	T/C	pH
T1-1	20	20	0.004	0.015	0.015	45	7
T1-2	20	40	0.004	0.015	0.015	45	7
T1-3	20	60	0.004	0.015	0.015	45	7
T1-4	20	80	0.004	0.015	0.015	45	7
T1-5	20	100	0.004	0.015	0.015	45	7
T2-1	20	80	0.004	0.02	0.02	45	7
T2-2	20	80	0.004	0.015	0.015	45	7
T2-3	20	80	0.004	0.0125	0.0125	45	7
T2-4	20	80	0.004	0.01	0.01	45	7
T3-1	20	80	0.004	0.015	0.015	45	7
T3-2	20	80	0.004	0.015	0.015	65	7
T3-3	20	80	0.004	0.015	0.015	80	7
T4-1	20	80	0.004	0.015	0.015	45	3.7
T4-2	20	80	0.004	0.015	0.015	45	6.1
T4-3	20	80	0.004	0.015	0.015	45	7
T4-4	20	80	0.004	0.015	0.015	45	10.2
T4-5	20	80	0.004	0.015	0.015	45	11

The third initiator system used for polymerization of acrylamide is ammonium persulfate (APS) and sodium metabisulfite (SMS) in different water content (M1-1 to M1-5), initiator concentration (M2-1 to M2-3), temperature (M3-1 to M3-3) and pH (M4-1 to M4-5) (Table 3.4).

Table 3.4. Formulations for polymerization of AM initiated from APS and SMS

Sample	AM /g	DIW /g	MBAA /g	APS /g	SMS /g	T/C	pH
M1-1	20	20	0.004	0.015	0.015	45	7
M1-2	20	40	0.004	0.015	0.015	45	7
M1-3	20	60	0.004	0.015	0.015	45	7

Table 3.5. Formulations for polymerization of AM initiated from APS and SMS(Cont.)

M1-4	20	80	0.004	0.015	0.015	45	7
M1-5	20	100	0.004	0.015	0.015	45	7
M2-1	20	80	0.004	0.02	0.02	45	7
M2-2	20	80	0.004	0.015	0.015	45	7
M2-3	20	80	0.004	0.0125	0.0125	45	7
M2-4	20	80	0.004	0.01	0.01	45	7
M3-1	20	80	0.004	0.015	0.015	45	7
M3-2	20	80	0.004	0.015	0.015	65	7
M3-3	20	80	0.004	0.015	0.015	80	7
M4-1	20	80	0.004	0.015	0.015	45	3.7
M4-2	20	80	0.004	0.015	0.015	45	6.2
M4-3	20	80	0.004	0.015	0.015	45	7
M4-4	20	80	0.004	0.015	0.015	45	10
M4-5	20	80	0.004	0.015	0.015	45	11.2

3.3. EVALUATION METHODOLOGIES

3.3.1. Gelation Time Test. The gelation time was defined as the time interval between the addition of initiator into the mixture and the formation of the bulk gel. To determine the gelation time, a cost-effective method named bottle-test gel strength code has been used by varying the gel parameters.

3.3.2. Gel Rheology Test. The gel strength of various gel parameters was measured using the HAAKE MARS Rheometers from Thermo Scientific (Figure 3.2 (a)). First, the samples were prepared by cutting as the same round thin sheet within 1.5 mm radius and 0.2 mm thick (Figure 3.2 (b)). For measure the gel strength of the samples, a parallel plate geometry PP35 Ti (Figure 3.2 (c)) with a gap of 1 mm was used for all experiment. All subsequent oscillation time-dependent experiments were performed at a fixed frequency at 1 Hz and controlled stress at 1.0 Pa to obtain the values of storage modulus (G’) and loss modulus(G’’) as a function of time.

3.3.3. Exothermic Profile. Exothermic refers to a transformation in which a system releases energy (heat) to the surroundings. The samples were keep in room temperature. A thermometer has been inserted into the center of gelant (Figure 3.3) and observe the temperature change during the gelation process.

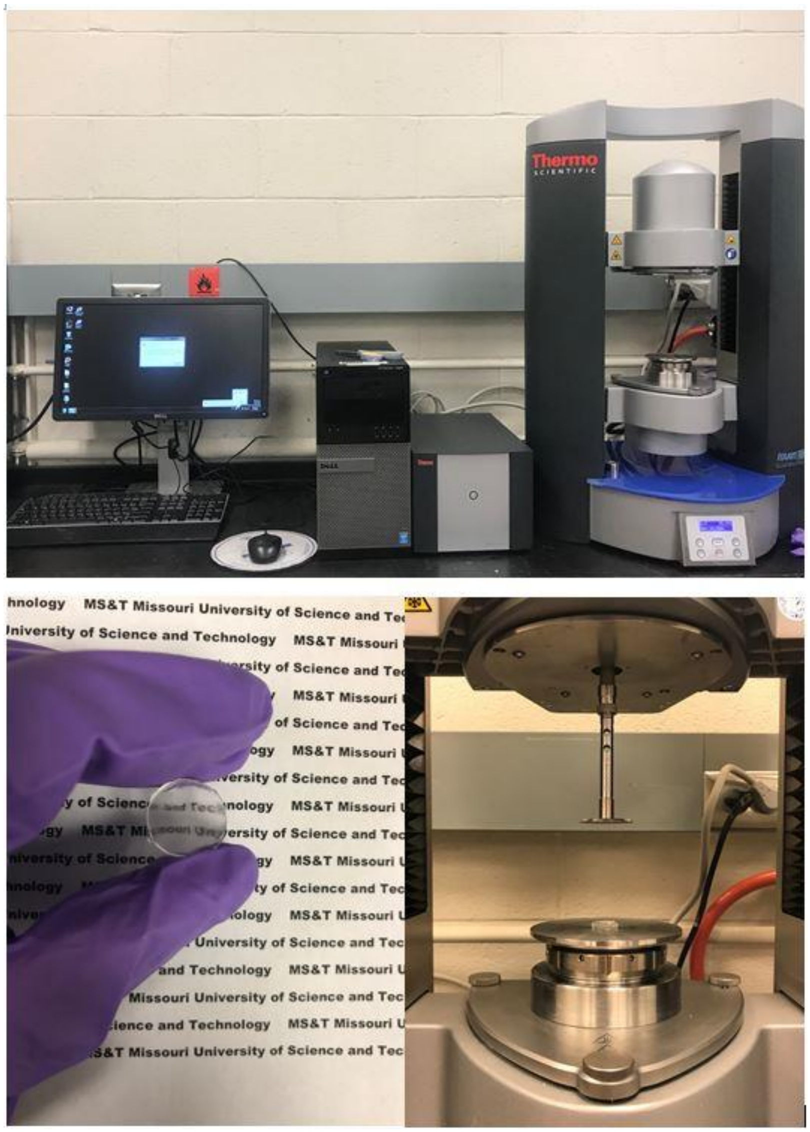


Figure 3.2. Gel rheology test (a) HAAKE MARS with RheoScope module; (b) samples size; (c) gel rheology test process

Figure 3.3. Sample for exothermic profile test

3.3.4. Swelling Test. To test the absorbency of the gels, the dried particle gels were placed in aqueous solution and the particles will absorb a portion of the aqueous solution and subsequently swell. In this experiment, the swelling ratio was measured by volume change. The swelling ratio (SR) of the gels is calculated by the following equation:

$$SR = \frac{V_t}{V_i} . \tag{14}$$

where Vi is the initial volume of the dried particle gels before swelling and Vt is the volume of the swelled particle gels at time t.

During the test, 1g dried particles ware immersed in 1wt% sodium chloride solution for enough hours at room temperature and recorded the volume every 5 minutes for the first 30 minutes and then once an hour until the volume of the swollen particles has no change. Finally, the swelling ratio equation was used to calculate the swelling ratio and draw the swelling ratio curve with time.

3.3.5. Morphology Determination. The morphology of RPPG samples was evaluated using a scanning electron microscope (SEM) (Hitachi S4700, Tokyo, Japan, with EDS function for elemental analysis) operated at an accelerating voltage of 5 kV in a high vacuum mode. Dry RPPG was directly observed by microscopy to calculate the initial M-SAP diameter time. The microsphere samples initially swolled equilibrium to show their final cross-linked network structure and freeze-dried in a Christ ALPHA 2-4LD device (SciQuip, Newtown, UK) for 24 hours. Lyophilized microsphere samples were placed in liquid nitrogen for a sufficient time, cut off with a razor blade to expose the internal structure and adhered to the sample holder. All samples were sputter coated with gold for 120s prior to observation.

4. RESULTS AND DISCUSSION

4.1. GELATION TIME TEST

In this section, the gelation time of acrylamide initiated by three types initiator systems have been recorded. All the four types initiator systems are based on peroxydisulfate salts: ammonium persulfate (APS), ammonium persulfate (APS) - potassium persulfate (KPS) initiator system, ammonium persulfate (APS) - sodium thiosulfate (STS) initiator system and ammonium persulfate (APS) - sodium metabisulfite (SMS) initiator system.

Among these initiator system, the initiation type of APS and APS-KPS belongs to thermal decomposition. The initiator is heated until a bond is homolytically cleaved, producing two radicals. Both reaction scheme of APS and APS-KPS as shown in Equation (13). On the other hand, APS-STS and APS-SMS initiator system to give radical by redox reactions. The reaction of APS-STS leading to formation of free radicals is expressed by following equation:

$$S_2O_8^{2-} + S_2O_3^{2-} \rightarrow SO_4^{2-} + SO_4^{*-} + S_2O_3^{*-}.$$

The SMS seems to help establish a continuous process for free radical creation, so the APS-SMS redox system is believed to be responsible for starting the formation of free radicals according to the following complex reaction:

$$S_2O_5^{2-} + H_2O \rightarrow 2HSO_3^{-}$$
$$S_2O_8^{2-} + HSO_3^{-} \rightarrow SO_4^{2-} + SO_4^{*-} + HSO_3^{*}$$

As for the combination of the initiator concentration of the samples and the reaction schemes, the first series of samples based on APS initiator were be regarded as basic model to compare with others.

4.1.1. Effect of Water Content. The water content effect on gelation time with three types of initiator system is illustrated in Figure 4.1. 20g acrylamide initiated by 0.015g initiator crosslinking with 0.004g N, N’- methylene bisacrylamide (MBAA) has been employed for the test. The gelation temperature is 45℃. Five levels of water content (20g, 40g, 60g, 80g and 100g) have been tested and the result shows that the gelation time increase as the water content increase. The higher level of the water content is, the faster the speed rate of gelation time grows.

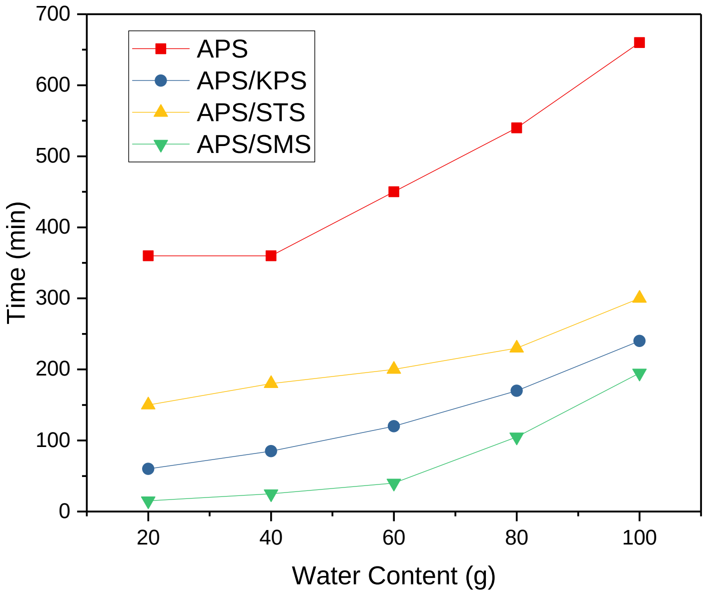


Figure 4.1. Gelation times vs. water content of the three types of systems (20g acrylamide, 0.004g MBAA and 0.015g of both initiators as synthesized at 45℃).

In order to explain the trend of curves in Figure 4.1, some equations should be used. Based on Equation (9), the polymerization rate of acrylamide can be expressed as:

$$R_p = -\frac{d[M]}{dt} = k_p\left(\frac{fk_d}{k_t}\right)^{1/2}[I_1]^{1/2}[I_2]^{1/2}[M] \tag{9}$$

where t, I1, I2 respectively denotes the gelation time, the concentration of APS and the concentration of activator (KPS or STS or SMS).

The I1 equal to I2 for all samples and the concentration of initiator is defined as the mass of the initiator (mi) divided by the volume of the mixture. To explain the relationship of gelation time and water content, integrating Equation (14) yields Equation (15):

$$t = \frac{\ln \frac{[M_o]}{[M]}}{k_p (\frac{fk_d}{k_t})^{1/2} [\frac{m_I}{V_m + V_I + V_c + V_w}]} \tag{15}$$

where [M0] is the concentration of acrylamide at the beginning of reaction (t=0). Vm, Vi, Vc, Vw denotes the volume of monomer, initiator, crosslinker and distilled water.

Equation (15) shows that the gelation time increase as the volume of distilled water increase when the other parameters have no change.

Comparing gelation time of the gels prepared with APS, APS/KPS, APS/STS and APS/SMS initiator systems, the gelation time of polyacrylamide initiated by APS/SMS is the fastest on a variety of water content and the samples initiated by APS shows the slowest gelation rate. The initiator concentration of APS/KPS gel is two times of APS gel and both of the two systems are same initiation mechanism, so the gelation time of APS/KPS gel is much more quickly than APS gel. However, the mechanism of APS system is heat activated, the temperature is not enough to support the decomposition rate, so the gelation rate of the APS/STS gel and APS/SMS gel are faster than APS gel. The gelation time of APS/KPS gel is shouter than APS/STS is because the initiator concentration is higher.

4.1.2. Effect of Initiator Concentration. In order to investigate the influence of the initiator systems concentration to gelation time, a series of experiments were performed using gels prepared from acrylamide, crosslinker MBAA, and initiator system of APS/KPS or APS/STS or APS/SMS at 45℃. 20% acrylamide monomer concentration and 0.004g (400 ppm) MBAA was fixed in this test. The concentration of initiators of APS/KPS varied from 0.005g (50 ppm) to 0.02g (200 ppm). The concentration of the APS/STS and APS/SMS initiators changed from 0.1g (100ppm) to 0.02 (200 ppm). Figure 4.2 shows the results of the gelation time changes with initiator concentration of three types of initiator systems. As displayed in the figure, the increase in initiator concentration led to a decrease in the gelation time due to the increased amount of initiators decomposition into free radicals.

The effect also can be explained by the kinetics theory of polymerization. According to Equation (14), the relation between gelation time and initiator concentration could be expressed as:

$$t = \frac{\ln \frac{[M_o]}{[M]}}{k_p \left(\frac{f k_d}{k_t}\right)^{1/2} [I_1]^{1/2} [I_2]^{1/2}} \quad . \qquad (15)$$

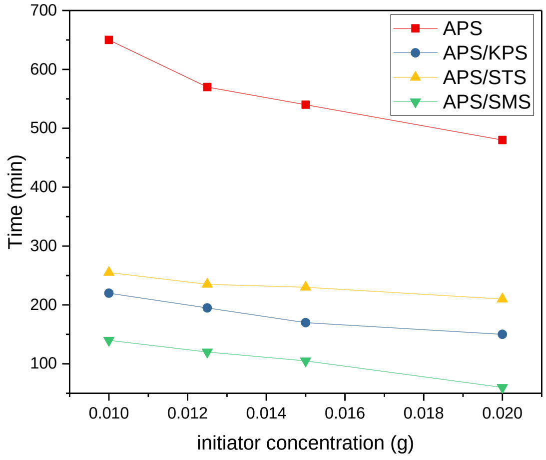


Figure 4.2. Gelation times vs. initiator concentration of the three types of initiator systems (20% acrylamide, 400 ppm MBAA as synthesized at 45℃).

The initiator concentration is the only variable, the other parameters are kept constant. Based on the equation, the fitting curves which fit the data from the experiment results as shown in Figure 4.3. The fitting curves are looks well consonant with the observation data.

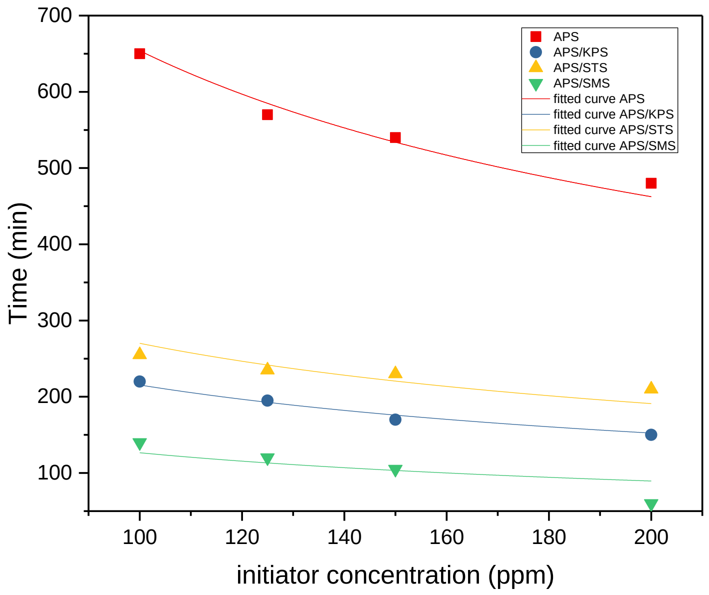


Figure 4.3. Fitting curves of the initiator concentration effect on gelation time

4.1.3. Effect of Temperature. As illustrated in Figure 4.4, the synthesis temperature makes a significant impact on gelation time of all three initiator systems. The gels were synthesized with the same monomer concentration (20% acrylamide), crosslinker concentration (400 ppm MBAA) and same initiator concentration (150 ppm APS, APS/KPS, APS/STS and APS/SMS) under various temperature (23°C, 45°C, 65°C and 80°C). The results of the experiment under 23°C showed the gel based on APS, APS/KPS, and APS/STS initiator system cannot gelation due to the APS and APS/KPS release free radical by heat activated, so the decomposition of persulfate is limited at low temperature. However, because the decomposition mechanism of APS/STS and APS/SMS system are different than the free radical of the two systems are produced by redox reaction, the decomposition of these two system can occur in low temperature. The reason why APS/STS sample cannot gelation at room temperature is that the initiator concentration is too low to release enough free radicals. Figure 4.4 represents that the gelation time decrease with the temperature due to the increased dissociation rate of the initiators into free radicals. The Arrhenius Equation (Equation 16) gives the quantitative basis of the relationship between the temperature and the reaction rate. Ea is the activation energy, k is the reaction rate constant, and R is the gas constant. Since at temperature (T) the molecules have energies according to a Boltzmann distribution, one can expect the proportion of collisions with energy greater than Ea to vary with the rate constant. So the tendency of curves can be explained by the Arrhenius equation.

$$k = Ae^{-\frac{E_a}{RT}} \qquad (16)$$

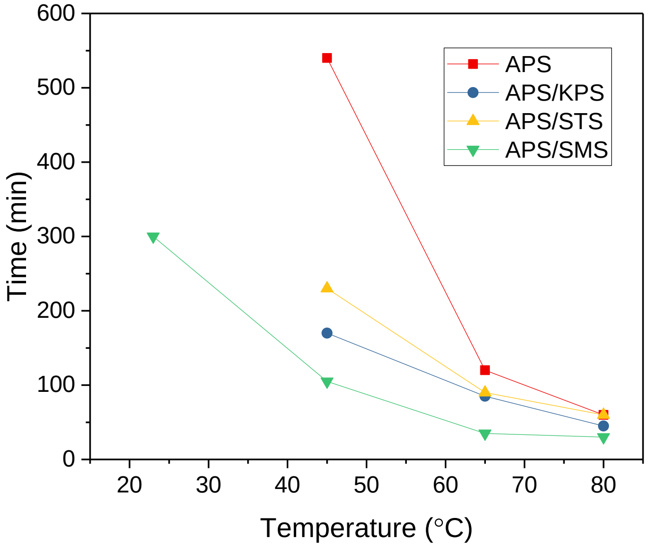


Figure 4.4. Gelation times at various synthesis temperatures of the three types of systems (The gels were synthesized with 20% acrylamide, 400ppm crosslinker MBAA and 150 ppm initiator).

4.1.4. Effect of pH Value. To study the effect of pH value on gelation time, five pH values have been implemented to synthesize gel with 20% acrylamide concentration, 400 ppm crosslinker MBAA, and 150 ppm initiator concentration of four initiator systems (APS, APS/KPS, APS/STS and APS/SMS) under 45℃ synthesis temperature. Figure 4.5 shows the results that the gelation time generally increased as the pH value increased from 3.7 to 11.3. When the samples of APS/STS and APS/SMS initiator system assumed the acidic condition (3.7 and 6), the samples appear no gel surface deformation upon inversion in 30 minutes, but the samples deformation as a thick polymer when the glass rod has touched the surface. This is caused by STS and SMS are stable only in neutral or alkaline solutions, but not in acidic solutions, due to reaction with hydrochloric:

$$\mathrm{Na2S2O3} + 2\ \mathrm{HCl} \rightarrow 2\ \mathrm{NaCl} + \mathrm{S} + \mathrm{SO2} + \mathrm{H2O} \tag{17}$$

$$\mathrm{Na2S2O5} + 2\ \mathrm{HCl} \rightarrow 2\ \mathrm{NaCl} + \mathrm{H2O} + 2\ \mathrm{SO2}. \tag{18}$$

4.2. GEL STRENGTH TEST

The gel strength (G’) of acrylamide initiated by three types initiator systems was evaluated by HAAKE MARS Rheometers. All the samples based on the same initiator systems as the gelation time test (APS/KPS, APS/STS and APS/SMS). The effect of water content, temperature and pH value on gel strength will be recorded and discussed in this section.

4.2.1. Effect of Water Content. In order to test the effect of water content on gel strength, the monomer acrylamide, crosslinker MBAA, and initiator concentration were maintained at 20g, 0.004g and 0.015g respectively. The synthesis temperature was maintained in 45℃. Five levels of water content (20g, 40g, 60g, 80g and 100g DIW) have been measured in this section. As displayed in Figure 4.6, the strength of the gel weaker as the higher distilled water content. When the water content was 20g, many air bubbles formed during the gelation process. After fully swollen in 1% NaCl solution, the gel strength of samples increase only slightly from 120 PA to 170 PA as shown in **Figure 4.7**.

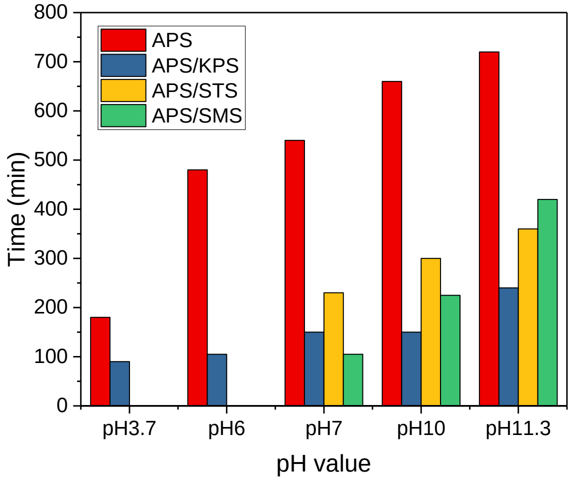


Figure 4.5. Gelation times at various pH values of the three types of systems (The gels were synthesized with 20% acrylamide, 400ppm crosslinker MBAA and 150 ppm initiator at 40°C).

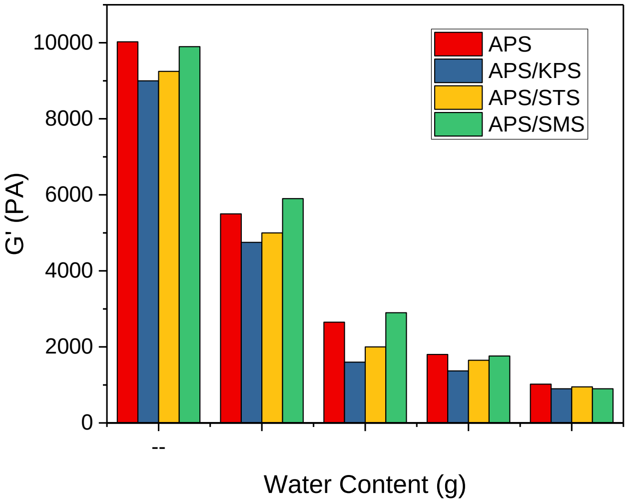


Figure 4.6. Gel strength vs. water content of the three types of systems (20g acrylamide, 0.004g MBAA and 0.015g of both initiators as synthesized at 45℃).

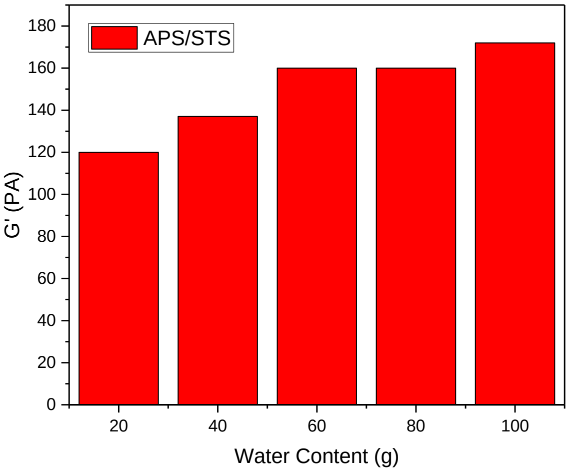


Figure 4.7. Gel strength vs. water content of the APS/STS sample after fully swollen

4.2.2. Effect of Initiator Concentration. Through varying synthesis temperature (45°C, 65°C and 80°C), the temperature influence has been studied using the same recipe which has 20g acrylamide, 80g distilled water, 400 ppm MBAA and 150 ppm initiators. Figure 4.8 represents the relationship between gel strength and temperature. The result shows the strength of gel strengthened as the temperature goes up.

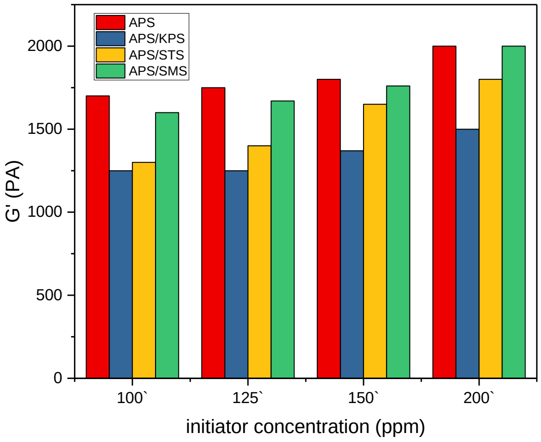


Figure 4.8. Gel strength at various initiator concentration of the three types of systems (synthesized with 20% acrylamide, 400ppm crosslinker MBAA and 150 ppm initiator).

Figure 4.9 shows the gel strength with varying initiator concentration after fully swollen. With the higher initiator concentration, the gel strength after fully swollen increase due to the chain length of polymer decrease, the density of network increase.

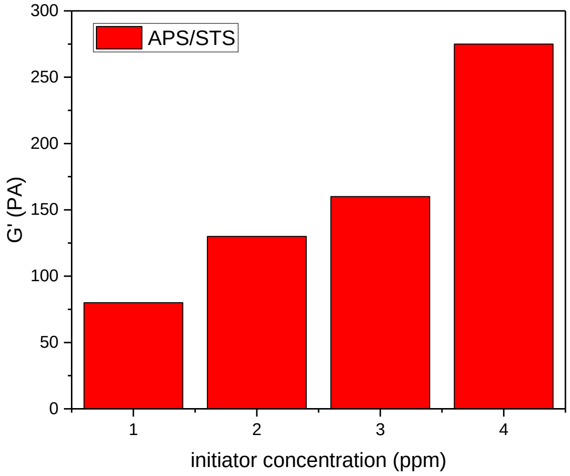


Figure 4.9. Gel strength vs. initiator concentration after fully swollen

4.2.3. Effect of Temperature. Through varying synthesis temperature (45°C, 65°C and 80°C), the temperature influence has been studied using the same recipe which has 20g acrylamide, 80g distilled water, 400 ppm MBAA and 150 ppm initiators. Figure 4.8 represents the relationship between gel strength and temperature. The result shows the strength of gel strengthened as the temperature goes up. Then the samples were swollen in a 1% NaCl brine solution for 24 hours to test gel strengths after fully swollen. The result as shown in Figure 4.11 that the higher temperature results in the lower gel strength. The tendency can be explained by the Arrhenius equation. With the increase of temperature, the rate of initiator decomposition increase, resulting in longer chain length.

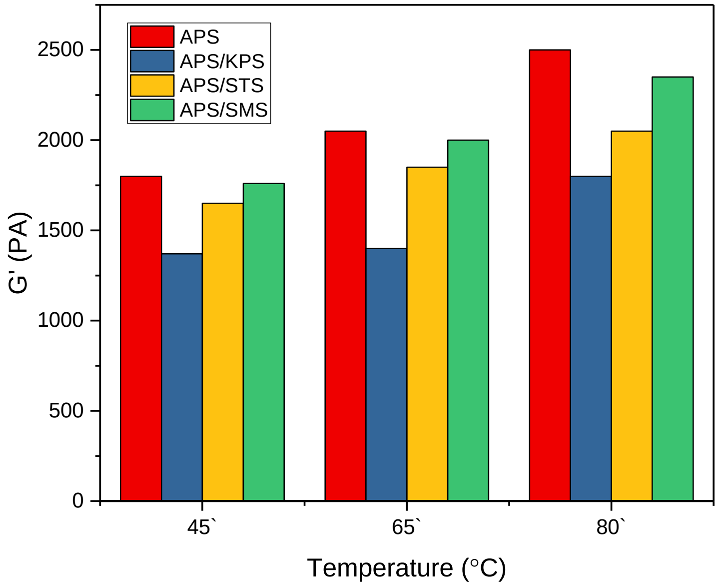


Figure 4.10. Gel strength at various pH values of the three types of systems (The gels were synthesized with 20% acrylamide, 400ppm crosslinker MBAA and 150 ppm initiator at 45℃).

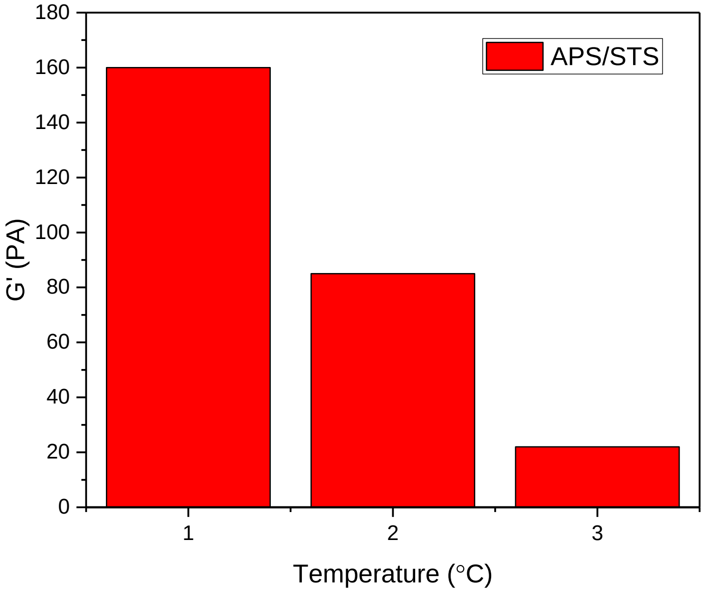


Figure 4.11. Gel strength vs. temperature of the APS/STS sample after fully swollen

4.2.4. Effect of pH Value. Figure 4.10 shows the strength of the gel that synthesized by 20g acrylamide, 80g distilled water, 400 ppm MBAA and four types of initiators (150 ppm APS, APS/KPS, APS/STS and APS/SMS) under 45°C temperatures with varying pH value. The result clearly displayed that the gel has higher strength under acidic and alkaline condition and weaker in the neutral condition. As mentioned in section 4.1.4, the samples of acrylamide initiated by APS/SMS system cannot gelation during acidic condition, the gel strength cannot be measured. The tendency of gel strength after fully swollen in 1% NaCl brine solution with varying pH value is same as the result before swelling as shown in Figure 4.13 due to the entanglement increase as the pH value increase (electrical property).

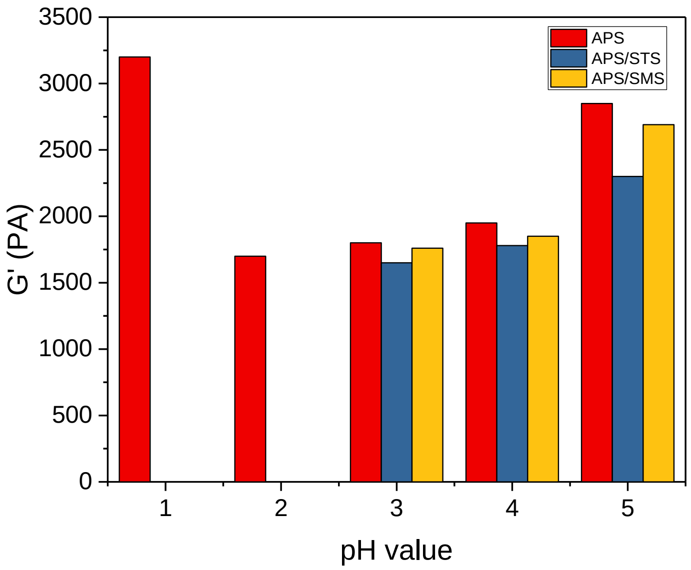


Figure 4.12. Gel strength at various pH values of the three types of systems (The gels were synthesized with 20% acrylamide, 400ppm crosslinker MBAA and 150 ppm initiator at 45℃).

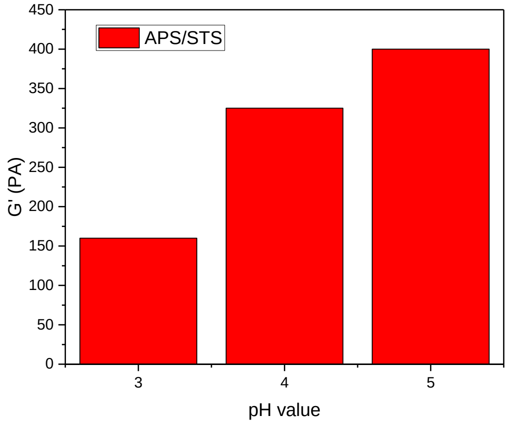


Figure 4.13. Gel strength vs. pH value of the APS/STS sample after fully swollen

4.3. EXOTHERMIC PROFILE

Figure 4.14 showed initiator concentration effect on gelant polymerization temperature (environment temperature= 23℃). Different concentration of APS/STS from 400 ppm to 1200 ppm have been used for this test. Temperature peaks increased by adding more initiators and maximum temperature was achieved at 86℃ with 1200ppm APS/STS. The termination time were around 10 hours. Based on the observed result, when the initiator concentration achieves 1000 ppm, the sample can form high polymerization degree (>95%) gel.

4.4. SCARE-UP TEST

During the scale-up production, it was found that gelant with different scales showed varying initiating behaviors. One consideration may occur to explain this phenomenon is the purity of the monomer. Some additives in monomer neutralized initiator in gelant and changed the initiating temperature. Figure 4.15 showed the gelation percentages with varying total solution amount and initiator concentration. As displayed in the figure, the gelation percentage increase as the total solution amount or initiator concentration increase. The reason is that more amount of initiators decomposition into free radicals when the initiator concentration increase.

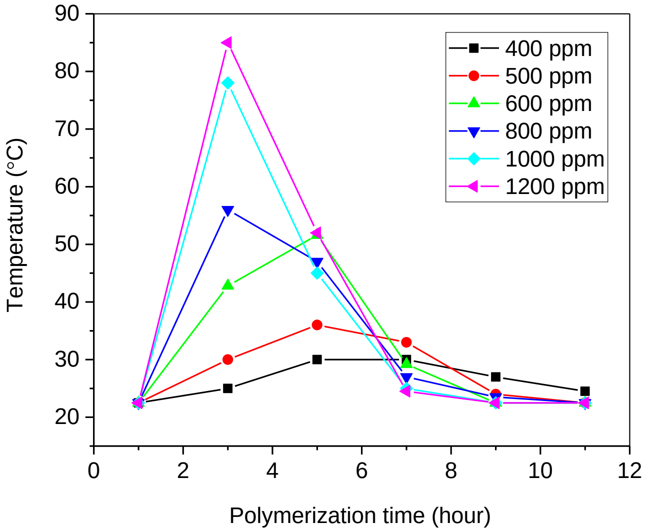


Figure 4.14. Changes in the temperature with react time under varying APS concentrations (Initiator=APS/STS, Wtotal=500g).

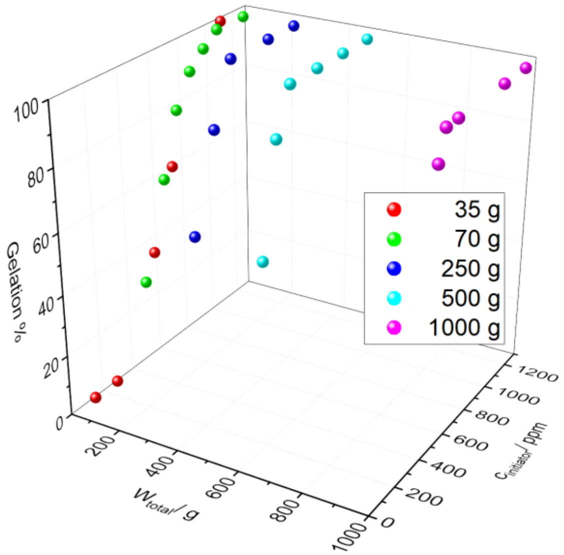


Figure 4.15. Gelation percentages with varying total solution amount and initiator concentrations.

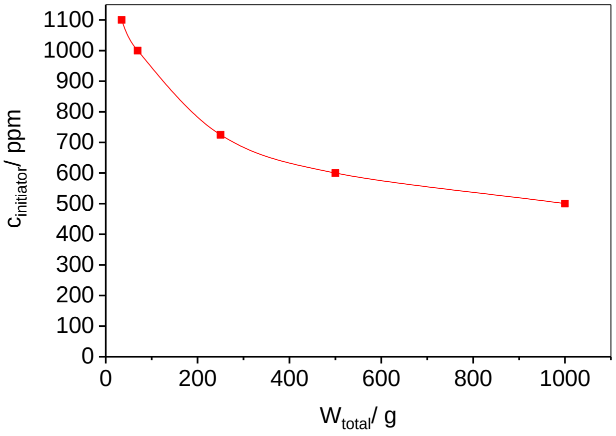


Figure 4.16. Gelation percentages with varying total solution amount.

4.5. SWELLING KINETICS

The samples shown in Figure 4.17 was prepared under 45℃ with AM as the monomer (20%), crosslinker MBAA of 400 ppm, and initiator APS/STA concentration ranged from 600 ppm to 1200 ppm. For this particle gel, the individual dry particle gels used here were sieved through 0.6 to 0.84 mm. The result suggested that the swelling ratio is more than 42 times in 1% NaCl brine and the swelling ratio decreased with increasing initiator concentration. The swelling capacity is determined by the pore size and amount of pores. With an increase in initiator concentration, more amount of free radicals were produced in the gelation reaction, resulting in shorter chain length and smaller pore size in the gel network.

The Samples were prepared under 45℃ with 20g AM, 0.04 g MBAA. When the water content increase from 20g to 100g, as shown in Figure 4.18, the swelling ratio of APS/STS sample took the longer time to completely swelling and the swelling ratio decrease from 55 to 40 times. When the initiator concentration increased in the mixture, the swelling capacity of the particle gels reduced due to the same reason as explained of the Figure 4.17. The swelling ratio changed from 41 to 43 times in the Figure 4.19, the swelling ratio not change much due to the variation range of initiator concentration small.

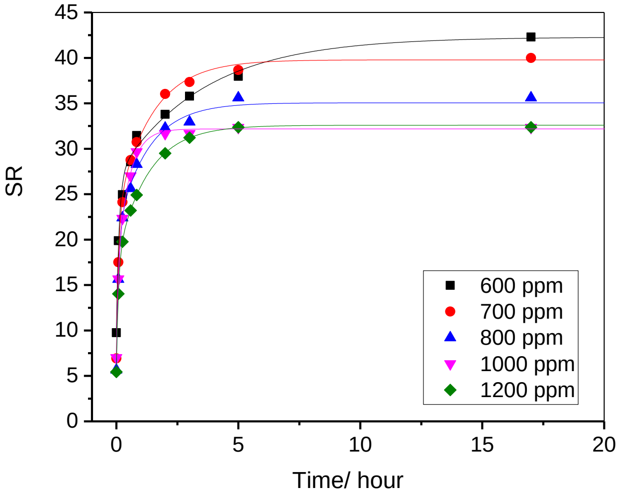


Figure 4.17. Swelling kinetics of samples with various initiator concentration in 1% NaCl(The gels were synthesized with 20% acrylamide, 400ppm crosslinker MBAA at room temperature).

The gels were synthesized with the same monomer concentration (20% acrylamide), crosslinker concentration (400 ppm MBAA) and same initiator concentration (150 ppm APS/STS) under various temperature (23℃, 45℃, 65℃ and 80℃). Under varying temperature from 45°C to 80°C (the APS/STS sample cannot gelation at room temperature with 150 ppm initiator concentration), as shown in Figure 4.20, The swelling ratio decrease as the temperature increase because the size of the gel and the boundary between the gel and the brine cannot be differentiated only by visual contact.

The samples shown in Figure 4.21 were employed to study pH value on the gel's swelling rate and swelling ratio (The APS/STS samples cannot gelation at acidic condition). At neutral condition, the sample swelled quickly in the first couple minutes and higher swelling ration. As the pH value increase to alkaline condition, the samples have a lower swelling ratio because the activation energy increase with the pH value increase.

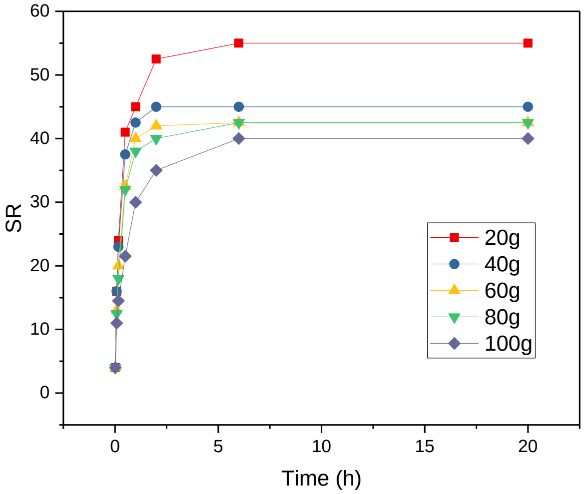


Figure 4.18. Swelling kinetics of samples with various water content in 1% NaCl brine (The gels were synthesized with 20% acrylamide, 400ppm crosslinker MBAA at 45℃).

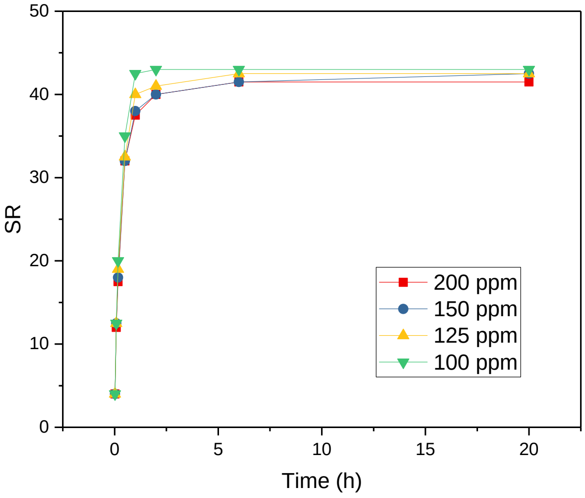


Figure 4.19. Swelling kinetics of samples with various initiator (APS/STS) concentration in 1% NaCl brine (The gels were synthesized with 20% acrylamide, 400ppm crosslinker MBAA at 45℃).

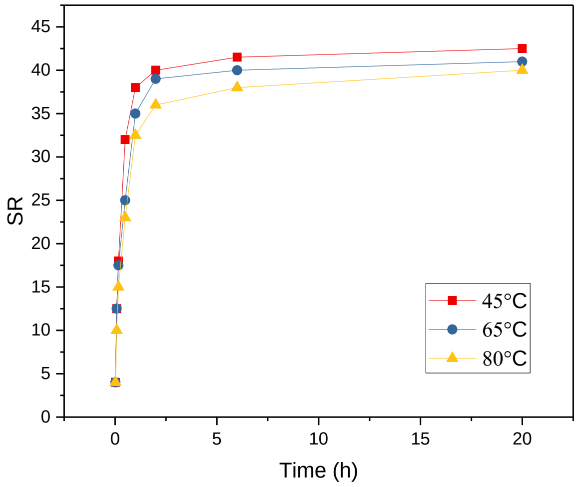


Figure 4.20. Swelling kinetics of samples with various temperature in 1% NaCl brine (The gels were synthesized with 20% acrylamide, 400ppm crosslinker MBAA at 45℃).

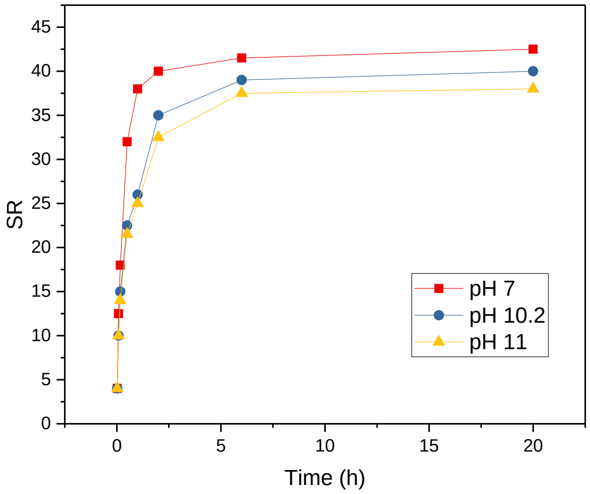


Figure 4.21. Swelling kinetics of samples with various pH value in 1% NaCl brine (The gels were synthesized with 20% acrylamide, 400ppm crosslinker MBAA at 45℃).

4.6. SEM CHARACTERIZATION

The scanning electron microscopy observation was employed to study the morphology of gels. Figure 4.22 give the SEM observations of the surface morphology characterization of a dried particle gel. The layer structure can be clearly observed in the surface of dried particle. Figure 4.23 illustrates the SEM observation of a typical swollen particle gel networks. When comparing Figure 4.22 through Figure 4.23, the particle gel structure remains very dense when dry, after contact with distilled water, the pores in the gel network open up and expand.

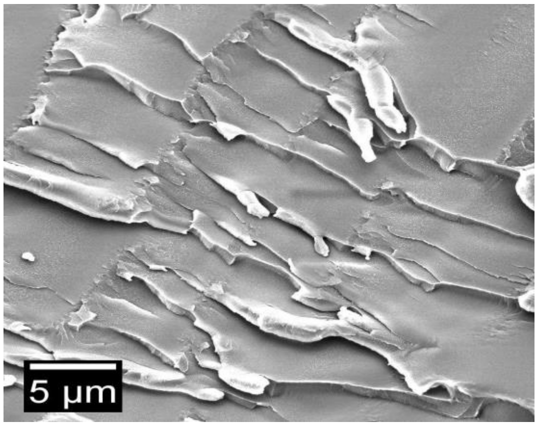


Figure 4.22. The surface morphology characterization of a dried particle gel by SEM

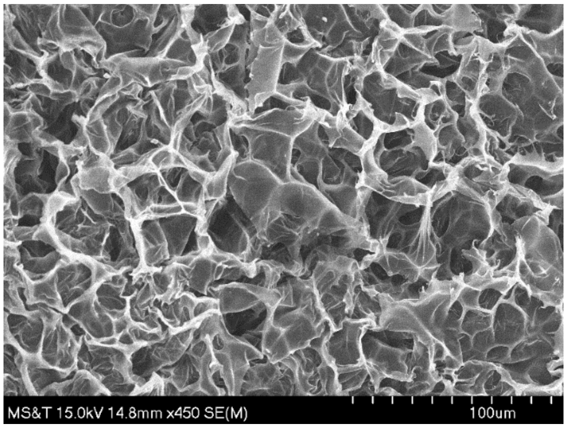


Figure 4.23. SEM observation of a swollen particle gel network

5. CONCLUSION

Four types of persulfate initiator system were examined in this study. Experimental results showed that different initiator system will be selected according to the different synthetic conditions. Persulfate redox initiator system (APS/STS or APS/SMS) is the best choice for polymerization of acrylamide for low temperature, especially APS/SMS initiator system, which caused by the shortest gelation time; Thermal decomposition initiator system (APS or APS/KPS) is the best choice for acid condition.

Initiator concentration, water content, temperature, and pH value were evaluated for gel synthesis:

Initiator concentration is essential for the optimal performance of particle gels. When the initiator concentration is too low, gelation either does not take place or it takes a very long time, while with too high of an initiator concentration, the polymer chain between the junction sites is too short (lower water absorption capacity) and the bumping may occur.

Water content has a significant impact on both gelation time and gel strength. The effect on gelation time can be explained by the polymerization rate equation and the gel strength is highly associated with the water interactions with the gel network.

Temperature has a significant influence on the gelation time and the gel strength is scarcely influenced by temperature. As the temperature increase, the gelation time decrease. The relationship between temperature and gelation time can be explained by Arrhenius equation.

During the scale-up production, it was found that gelant with different scales showed varying initiating behaviors. Since the synthesis process is exothermic reaction, as the gelent scale increase, the heat releasing increase. The higher polymerization temperature led to higher polymerization degree.

Morphology of particles before and after swelling were measured by SEM. After fully swollen, three-dimensional networks can be clearly observed by SEM.

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