KING FAHD UNIVERSITY OF PETROLEUM AND MINERALS
DHAHRAN 31261, SAUDI ARABIA

DEANSHIP OF GRADUATE STUDIES

This thesis is written by

GHAITHAN AHMAD AL-MUNTASHERI

Under the direction of his Thesis Advisor and approved by his Thesis Committee, has been presented to and accepted by the Dean of Graduate Studies, in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE IN CHEMICAL ENGINEERING

Thesis Committee

Dr. Ibnelwaleed A. Hussein (Advisor)

Dr. Hisham A. Nasr-El-Din (Co-Advisor)

Prof. Mohamed B. Amin (Member)

Dr. Usamah A. Al-Mubaiyedh (Member)

Dr. Basel F. Abu Sharkh (Member)

Prof. Mohamed B. Amin
(Department Chairman)

Dr. Mohammed A. Al-Ohali
(Dean of Graduate Studies)

Date

DEDICATION

Dedicated To My Parents

Acknowledgments

In the name of ALLAH, the Most Beneficent, the Most Merciful.

Thanks are first due to Allah almighty for his great gift of knowledge and for making this degree possible. I would like to acknowledge King Fahd University of Petroleum & Minerals for providing me support for this research work. I am also grateful to Saudi Aramco for providing materials and facilities.

With deep gratefulness, I would like to express my heartfelt thanks to my advisor Dr. Ibnelwaleed A. Hussein for his inspirational guidance, help and unique supervision of the thesis work.

I am thankful to my co-advisor Dr. Hisham A. Nasr-El-Din of the R&DC at Saudi Aramco, for his directions and important comments on my thesis work. Most of the work done in this thesis was performed in his laboratory. Working with him was indeed a wonderful and learning experience, which I thoroughly enjoyed.

I am thankful to my thesis committee members for their comments and support. Namely, Dr. Mohamed B. Amin, Dr. Usamah A. Al-Mubaiyedh and Dr. Basel F. Abu Sharkh. I am very thankful to Dr. P.L.J Zitha of Delft University of Technology for his important comments on the early drafts of my thesis. The time he put for my thesis is very much appreciated. I am thankful to Mr. Ali-Amri Mr. M. Bhuyian and Mr. Mehdi, and for their services during experiment. Thanks are also due to Support Services Division of Saudi Aramco for their help analyzing water samples.

Finally, I offer my sincere thanks to my father and mother for their support and prayers. My wife was a strong support for this success. Her understanding and patience are appreciated.

Table of Contents

Background on Water Shut-Off

List of Figures

List of Tables

THESIS ABSTRACT

Name: GHAITHAN AHMAD AL-MUNTASHERI
Title: Rheology of Gelling Polymers Used in Reservoir Water Shut-Off Treatments
Degree: Master of Science
Major Field: Chemical Engineering
Date of Degree: December, 2004

In this study, partially hydrolyzed polyacrylamide was cross-linked with polyethylene imine. This system is currently used reservoir water shut-off treatments. At the reservoir conditions, the polymer and the cross-linker react to form a three dimensional structure that will block the flow of water through the porous rock. The rheology and rheokinetics of the organically cross-linked polymeric gels was studied. High temperature gelation kinetics of organically cross-linked gel was rheologically studied. Gelation time was lowered with increasing temperature. Field water was used in preparing the gel samples and was found to increase gel times significantly. Moreover, the addition of salts lowered the activation energy of the gelation reaction ($E_a = 25{,}102\exp[-4*10^{-6}TDS]$).Activation energy of PAtBA/PEI gelling system was obtained as 28 kcal/mol in deionized water. Divalent cations have more effect on gelation time than monovalent cations. Increasing polymer and cross-linker concentrations lowered the gelation time. Pre-shearing of solutions has resulted in shorter gelation times. In order to simulate field operations, the effect of iron on gelation kinetics was studied. High iron concentrations resulted in very weak gel structures. The effect of various parameters on the final gel viscoelastic properties was investigated. Initial pH showed a strong influence on the viscosity build up of the gel. High polymer and cross-linker concentrations resulted in a high elastic nature of the gel network. However, the physical strength of the gels containing the highest cross-linker concentrations was low. The elastic modulus showed substantial increase when the gel was heated at temperatures higher than 100^{o}C suggesting the presence of a different mechanism of gel formation at temperatures above 100^{o}C. The gelation mechanism is influenced by shear and temperature.

Master of Science Degree
King Fahd University of Petroleum & Minerals
Dhahran, Saudi Arabia

December, 2004

الملخص

الإســــم: غيثان أحمد عبدالله المنتشري
عنوان البحث: ريولوجيا البولمرات المستخدمة في حجزالمياه من مكامن النفط
الدرجــــة: ماجستير في العلوم الهندسية
القســــم: الهندسة الكيميائية
تاريخ الدرجة: ديسمبر 2004م

في هذا البحث تمت دراسة ريولوجيا البولمرات المستخدمة في حجز المياه من مكامن النفط. وقد وجد أن زيادة تركيز البولمريزيد من سرعة التفاعل الذي ينتج المادة الهلامية عالية اللزوجة.وقد لوحظ أن وقت التفاعل ينقص بزيادة درجة الحرارة.وقد وجد أن آلية إنتاج المادة الهلامية تعتمد على درجة الحرارة ومن نتائج هذا البحث أن الأملاح تؤخر التفاعل.سجل معامل المرونة في هذا البحث قيماً تزيد بكثيرعن ما سبق نشره في أبحاث سابقة,كذلك فإن زيادة الأملاح أدت إلى إنخفاض قيم معامل المرونة,وقد لوحظ ترسب بعض الأملاح عند إستخدام ماء البحر في تحضير العينات قام هذا البحث بدراسة تأثير الشوائب الناتجة عن صدأ الحاويات الفولاذية وقد تبين أن زيادة تركيز الحديد قد تؤدي إلى إنعدام تكون المادة الهلامية..

Chapter 1

1.1 Introduction

In the petroleum industry, production of gas and/or oil is number one priority. However, petroleum reservoirs do not deliver pure hydrocarbons. Water is associated with gas and oil production. For example, in the U.S. more than 8 barrels of water are produced for every barrel of oil. These volumes of waste water need to be disposed and that costs \$40 billion annually worldwide. Therefore, every effort should be made to reduce water production in oil/gas wells. From environmental point of view, if waste water produced from petroleum reservoirs is considered as a hazardous waste, then it is going to contribute to 98% of wastes in the U.S.A (Seright, 2001).

Water production problems in the oil field were addressed during the last 40 years (Thomas et al., 1996). Excessive water production is a real problem that leads to the processing of large volumes of water in the downstream facilities (Chauveteau et al., 1997). Water shut-off treatments are applied in either type of wells, oil or gas. When super-K zones (thin zones with high permeabilities) are present, water shut-off is needed to keep good reservoir sweep efficiency (Alqam et al. 2001; Seright, 1988). Also, for producing oil wells, as the water cut (vol% of water in produced oil) increases, those wells become more difficult to flow. When high (> 90 vol%) water cuts levels are reached, the heavier water present in the wellbore causes a high hydrostatic pressure lowering well deliverability of hydrocarbons (Farooqui et al., 1998). This is due to the fact that the water has a higher density than oil and therefore, the hydrostatic pressure, ρgh, (ρ= water density, g = gravitational constant & h= height of water column) in the wellbore will be more than the reservoir pressure leading to zero net production.

On the gas production side, unwanted water production becomes a motivating environment for scale formation, a promoter for corrosion. Another feature of water flood problems in the gas reservoirs is the flow channeling of water through natural fractures, which has been realized as a serious problem (Okasha et al., 2001). Hence, efforts are made to minimize water volumes produced through water shut-off operations.

Oilfield operators use variety of ways to account for the excessive water production. Both mechanical and chemical methods can be used to control water production. Mechanical devices are suitable for isolating water when there is no cross flow within the wellbore. The chemical methods make use of gelling polymers in order to perform the necessary permeability modifications of the reservoir (Nagra et al., 1986; Aslam et al., 1984). Gels are used in one of the most common ways of chemical methods, which is selective plugging and cementing (Avery et al., 1985). They are suitable for isolation of reservoirs, high permeability zones, and fractures.

In reservoir stimulation, gels are widely utilized. These high viscosity fluids are able to form three-dimensional polymeric structures. Gels consist of a polymer and a cross-linker. The reaction between the polymer and the cross-linker generates the high viscosity needed in many applications (Jerroen et al., 2001). Applying these gels results in either reductions in the water production or totally block water producing zones downhole (underground) (Hoek et al., 2001).

Polymer systems such as polyacrylamides and polysaccharides have been studied as water shut-off polymers since 1950s (Prud'homme et al., 1983). Stability of chromium/polyacrylamide cross-linked gels is low at high temperatures. Therefore, at high temperature reservoirs, more stable systems are needed. Organically cross-linked polymers are known to have good stability at elevated temperature ranges (Okasha et al., 2001).

One of the objectives of this research was to study the kinetics of gelation using rheology. Viscosity build up during gelation was followed with steady shear viscometry. From different measurements of gelation time at different temperatures, activation energy values were extracted. Also, the effect of salinity of mixing water on gelation kinetics was investigated. Field and sea mixing water samples were used in preparing some of the gel samples. The effect of polymer and cross-linker concentrations was studied. Moreover, pH effects were investigated. The effects of these parameters on the final gel properties were also studied.

NOTE: This thesis is written in paper format. Hence, the reader can skip the following two chapters and go directly to the results and discussion part given in Chapter 4. The first paper is entitled “A Rheokinetic Study of an Organically Cross-linked Gel Used in Water Shut-off Treatments”. The second paper is entitled as “Viscoelastic Properties of an Organically Cross-linked Water Shut-Off Gel”.

Chapter 2

Background on Water Shut-Off

2.1 Water Production Mechanisms

In petroleum fields, it is necessary to thoroughly understand the mechanism of water presence downhole in the petroleum producing reservoir. In other words, the communication type between the oil and/or gas reservoirs with the water producing zone is essential. When applying a gel treatment to a certain field, minimizing water production is the target. Designers of water shut-off treatments must ensure that the gel solution is going to block water not the hydrocarbons zones interfering with water layers in a way or another. Many forms of water presence in petroleum producing wells are identified. These forms include water coning which is shown in Figure 2.1.

This phenomenon occurs when the well is produced at a high rate. That will pull the oil hard enough to take water from the bottom layer forming the cone shape shown in the above figure. Another type of water presence is shown in 2.1.

This is commonly called water production through natural fractures. This takes place when there are natural fractures connecting the water producing zone to the oil zone. Well casing (piece of pipe between the ground and the producing pipe in a petroleum well) leaks and bad cements can also enhance water production. Figure 2.3 shows a diagram of this type of water presence where a water producing zone starts to produce water into the production pipe (well tubing) due to the leak in casing.

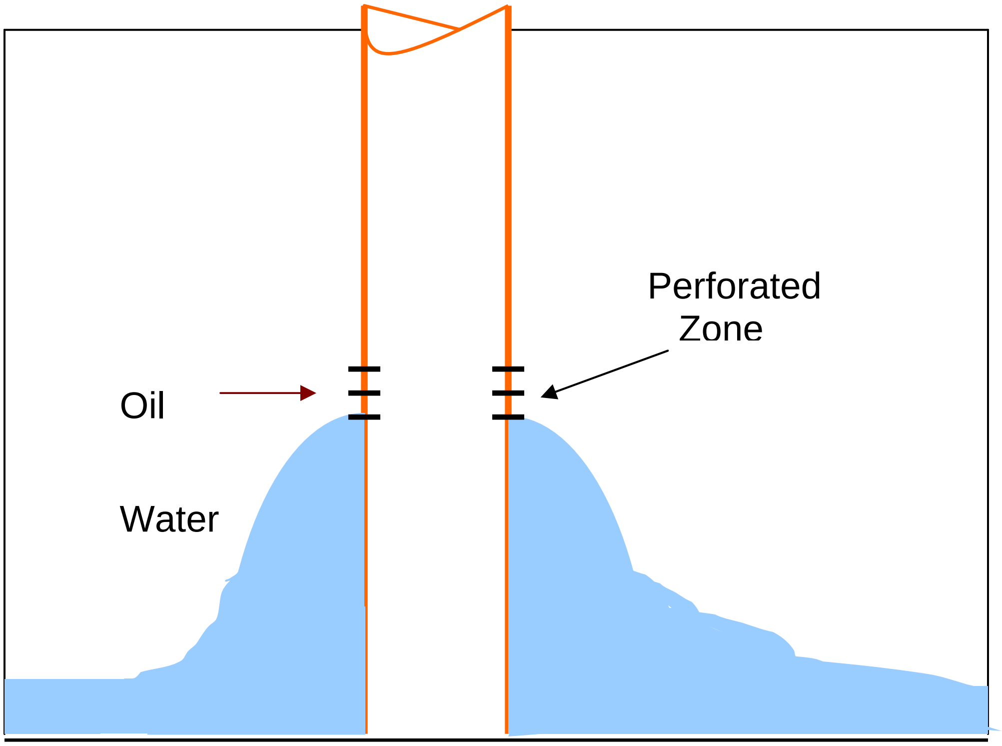


Figure 2.1.1: Water Coning

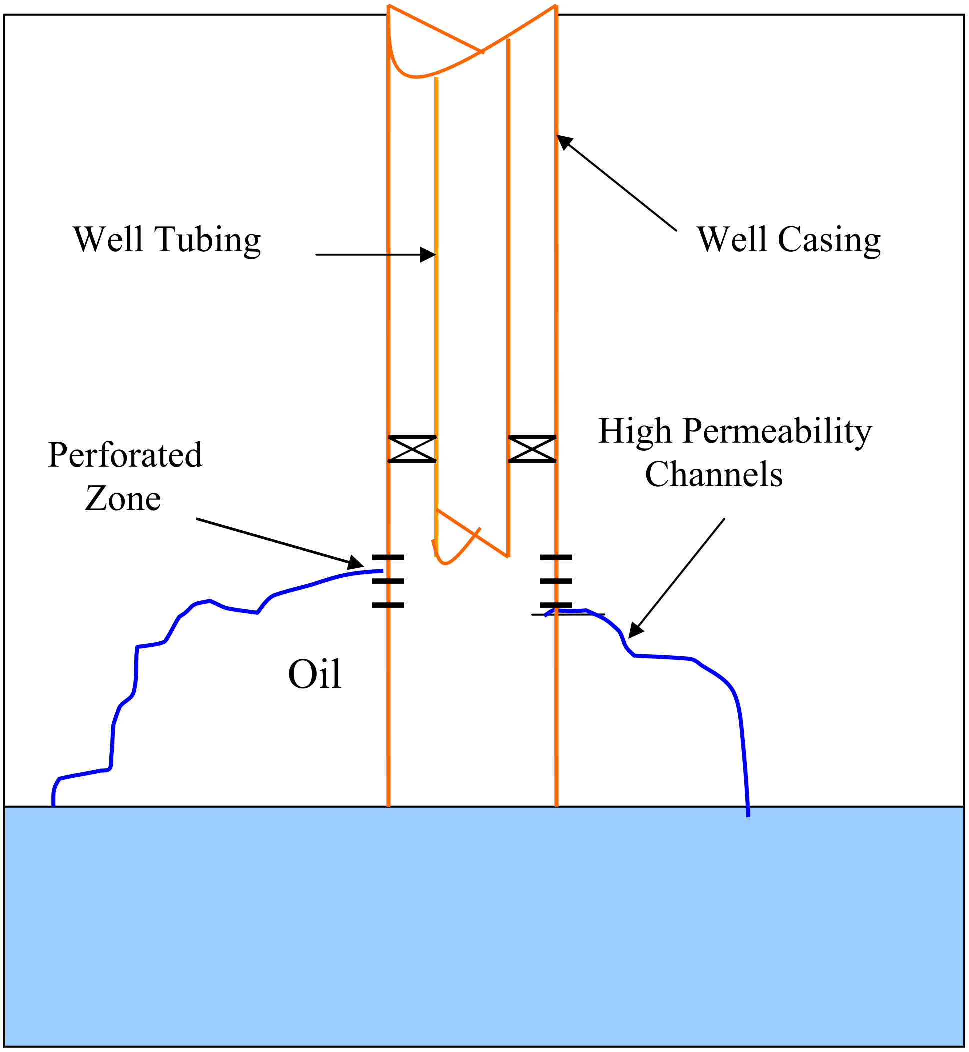


Figure 2.1.2: Water Production through Natural Fractures

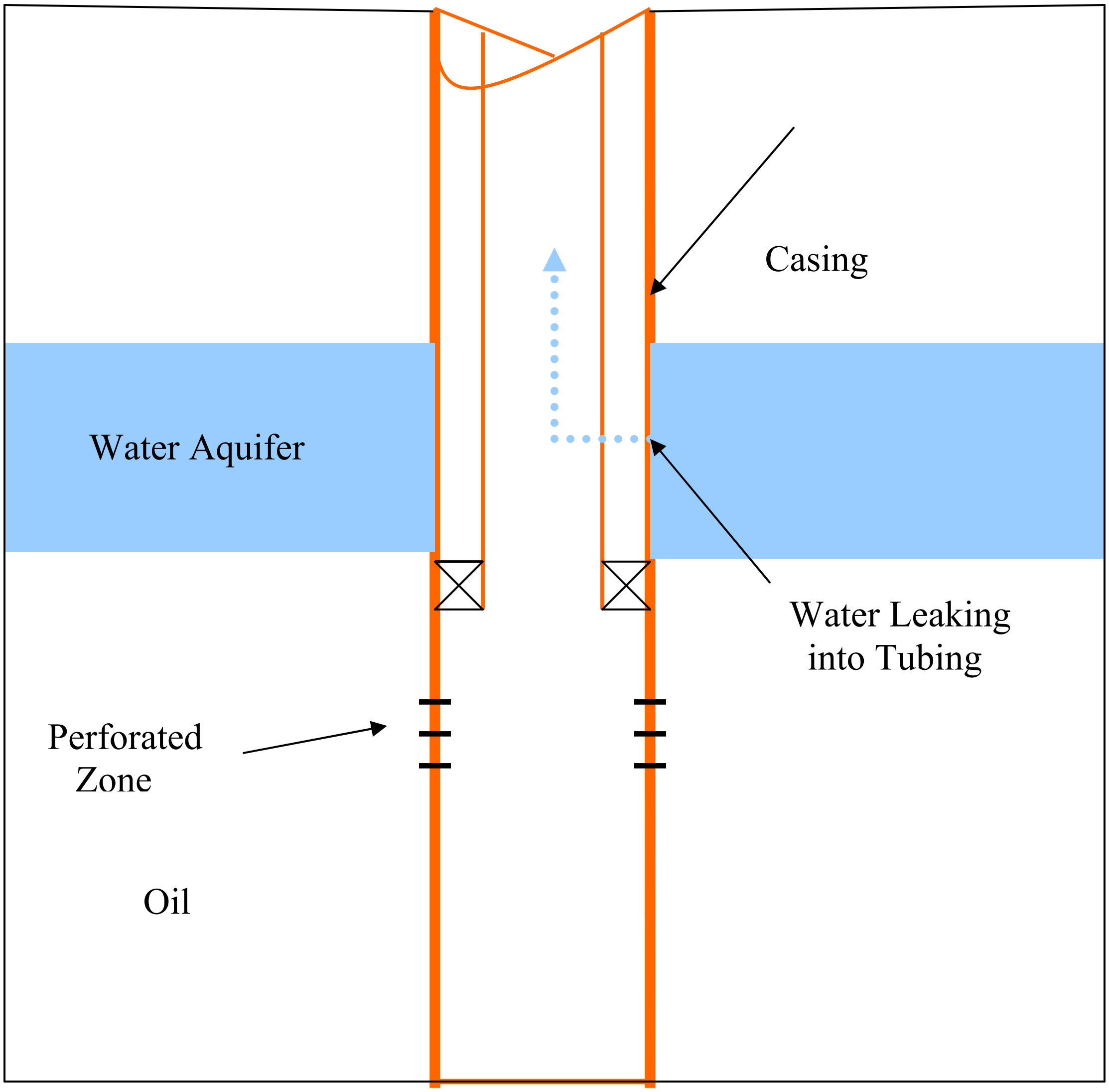


Figure 2.1.3: Casing Leak

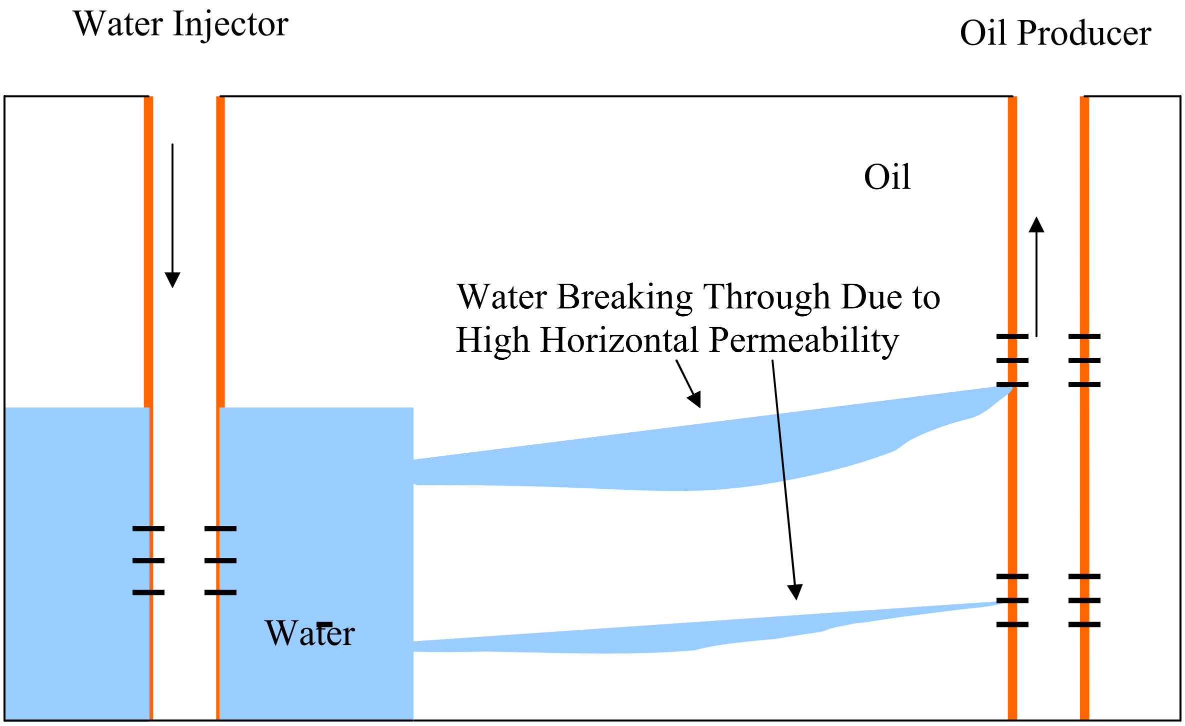


Figure 2.1.4: High Permeability Layer Breakthrough

High permeability layer breakthrough could be one source of water as shown in Figure 2.4. Water is injected into the oil reservoir for pressure maintenance. Unfortunately, this water might go through a high permeability layer of the oil producing zone and arrives at the perforations of the oil producing well nearby.

2.2 Available Solutions for Excessive Water Production

As stated earlier, mechanical methods are applicable in shutting-off water. Plastic plugs and cement can be used to selectively block water producing zones. Chemical methods make use of gels. The advantages polymeric gels have over other competitive techniques (like cement squeezes and plastic plugs) include lower costs, the ease of application, compatibility with formation fluids and the control over the gelation time (Hutchins et al., 1996). These systems consist of polymers that undergo phase transition from liquid to solid at a critical point known as the gelation point (Winter et al., 1986). The most common types of polymers used in polymeric gels are polyacrylamides and polysaccharides. Polyacrylamides are cost effective and therefore more utilized than polysaccharides. Cross-linkers are generally classified as inorganic or organic.

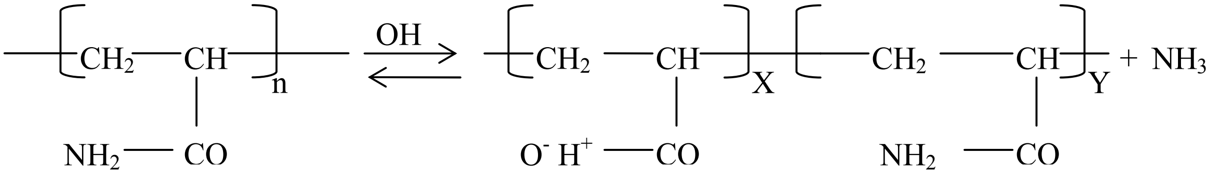
2.2.1 Inorganically Cross-linked Gels

Metallic cross-linkers are the most widely used type of inorganic cross-linking materials applied in water shut-off treatments (Hutchins et al., 1996). Chromium is the most widely used metallic cross-linker. The cross-linking metal ion Cr^{+3} can be placed in solution in the form of chromium acetate (Fulleylove et al., 1996), chromium nitrate (Kolnes et al., 1997) or chromium malonate (Lockhart et al., 1991). In order to control the gelation reaction, the chromium ion is introduced into solution as Cr^{+6}, which is further, reduced to

Cr^{+3}, which is the cross-linking metal ion. This can result in a good control over the gelation time when deep-water producing zones are treated.

Other types of polymer- Cr^{+3} cross-linking systems are available. These types include Cr^{+3} carboxylate/polyacrylamide system (Wibowo et al., 1999 & Sydansk and Southwell, 1998) and Cr^{+3} /Xanthan systems (Jousset et al., 1990). Biopolymers like xanthan gum type do have good stability upon mixing with high total dissolved salts brines. They are expensive and difficult to prepare for field applications (Wellington, 1983). Other metallic cross-linkers used include aluminum added to polyacrylamides in the form of aluminum citrate. In high TDS water (> 30,000 ppm), the gel strength of this system was found to decrease substantially with time (Stavland et al., 1996). Titanium and zirconium that have lower toxicity than Cr metal ions are also frequently used in near well-bore applications (Moffit et al., 1996).

In order to control the gelation time of Cr^{+3} /polyacrylamide gelling systems, reducing agents like sodium thiosulfate ($Na_2S_2O_3$) are added to reduce the Cr^{+6} (inert to polymer cross-linking) ion to the Cr^{+3} state. Then, the cross-linking reaction takes place slowly, which enables field designers to place the gelling solution deeper into water producing zones of the reservoir (Batycky et al., 1982 & Olsen, 1986). Another controllable factor is the degree of hydrolysis of the polymer. In order to define the degree of hydrolysis, α, let us take the following example (Nasr-El-Din et al., 1991):



$$-\left[CH_2-\underset{\underset{NH_2-CO}{|}}{CH}\right]_n- \overset{OH}{\underset{\longleftarrow}{\longrightarrow}} -\left[CH_2-\underset{\underset{O^-H^+-CO}{|}}{CH}\right]_X\left[CH_2-\underset{\underset{NH_2-CO}{|}}{CH}\right]_Y + NH_3$$

where X and Y are the numbers of carbocxylate and amide groups. Therefore,

$$\alpha = \frac{X}{Y + X} \quad ; \qquad 0 \le \alpha \le 1 \qquad (2.2.1)$$

When a low degree of hydrolysis polymer is used, the cross-linking reaction can be delayed. However, as the temperature increases, more carboxylate groups become available for over cross-linking with the divalent cations resulting in polymer precipitation. The temperature limit varies with the divalent cations concentration. Moradi-Araghi et al., 1987 reported that polyacrylamides will precipitate at temperatures more than 75^{o}C at hardness levels of 2,000 ppm, which is typical of oilfield brines. In the presence of a metallic cross-linker, that will result in gel syneresis. Syneresis is defined as the expulsion of water out of the gel structure due to the shrinkage in gel volume as a result of over cross-linking. The second reason why inorganically cross-linked polymeric gels are not suitable for high temperature applications is the nature of the bonds formed between the PHPA and the metallic cross-linker. These bonds are ionic resulting from the interaction between the carboxylate groups produced in the reaction above and the metallic cation such as Cr(3). Unfortunately, these bonds are unstable at high temperatures (Moradi-Araghi, 2000). Hence, the need aroused for using a more stable class of gels.

In order to overcome the thermal stability problem of the polymer, new monomers are introduced into the polymer chain. These new groups will limit the thermal hydrolysis of the acrylamide group. A copolymer of 9wt% acrylamide and sodium-2-acrylamido-2-methlpropane sulfonate is reported to be stable at temperatures as high as 250^{o}F in seawater (Moradi-Araghi et al., 1987). Lowering the polymer molecular weight is also reported to enhance thermal stability of water shut-off polymers (Chang et al., 1983).

2.2.2 Organically Cross-linked Gels

Due to the previously mentioned disadvantages of inorganic cross-linkers, other organic alternatives were developed. Phenol and formaldehyde can be used as cross-linkers for polyacrylamide gelling polymer systems. Due to the high level of toxicity of these two organic cross-linkers, other alternatives were developed like hexamethylenetetramine, HMTA, (Moradi-Araghi, 1994). Other types of organic cross-linkers were applied in the water shut-off treatments such as salicylamide and resorcinol (Moradi-Araghi et al., 1991 and Sydansk et al., 1998). During the 1980s, melamine formaldehyde, polyvinyl alcohol/glutaraldehyde and lignosulphonate/Cr^{+6} systems were introduced (Frampton, 1994).

This type of gels (organically cross-linked) can penetrate deeply into the treated zones providing more efficient water shut-off operations. Also, it has a better stability over the metal ion cross-linked type. This is due to the covalent bond formed between the cross-linker and the polymer rather than the ionic bond type formed in metal-polymer cross-linking reactions (Stahl et al., 1998).

Organic cross-linked gels are formed via covalent bonds between the polymer functional group and the cross-linker. Hence, these gels can be stable at high temperatures. One example of the organic cross-linking of polyacrylamide is the formaldehyde-phenol system.

2.3 Rheology of Reservoir Fluids

Fluids (gases or liquids) exhibit resistance to flow. When a fluid is subjected to a shear stress, it undergoes a continuous deformation. On the other hand, solids undergo deformations and may or may not return to their original shape depending on the level of deformation. In this section, some rheological concepts of fluids will be presented. Fluids like water that obey Newton's law fall into the Newtonian fluids class. The governing equation of Newton's law is

$$\tau = -\mu \dot{\gamma} \tag{2.3.1}$$

where τ is the shear stress, $\dot{\gamma}$ is the shear rate exerted on the fluid and μ is the dynamic or shear viscosity. Fluids not obeying the above relationship are classified as either time-independent or time-dependent non-Newtonian fluids.

2.3.1 Time-Independent Non-Newtonian fluids

This type of fluids is characterized by the fact that the viscosity is a function of shear rate (or the shear stress). However, the viscosity is not a function of the shear history of the fluid. These fluids are also called Non-Newtonian viscous fluids. Figure 2.5 shows a typical diagram of different types of time-independent fluids. Examples of these fluids follow:

2.3.1a Pseudoplastic (Shear Thinning) Fluids

One of the most encountered types of the time-independent non-Newtonian fluids is the pseudoplastic fluids class. For a typical pseudoplastic fluid, a plot of τ vs. $\dot{\gamma}$ is characterized by linearity at very low and very high shear rates. The slope at the very low shear rate range gives the viscosity at zero shear rate, η_0. On the other extreme of the curve, the slope at the very high shear rate portion gives the viscosity at infinite shear rates, η_∞.

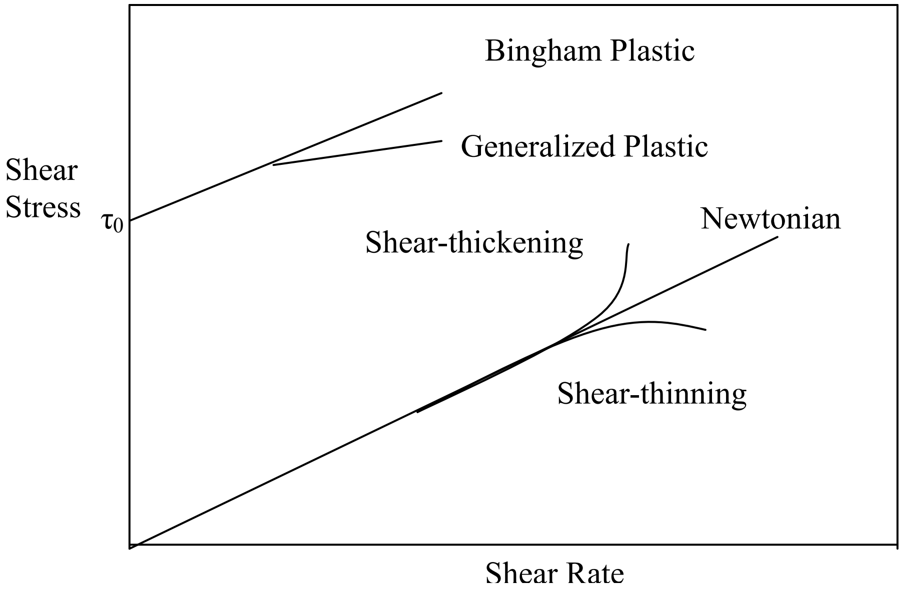


Figure 2.3.1: Shear diagram of various types of fluids

In the intermediate range of the shear rate, the viscosity is a variable and it decreases with shear rate. In this region of the τ vs. $\dot{\gamma}$ curve, the Ostwald -de Waele equation is usually used to represent the relationship between shear rate and shear stress. This equation is widely known as the power-law model. The governing equation for the apparent viscosity and shear rate relationship in the intermediate region is

$$\eta = k \, | \dot{\gamma} |^{n-1} \tag{2.3.2}$$

where n and k are the model parameters. When n = 1 a Newtonian fluid model (Newton's Law) is obtained with $k = \mu$. For pseudoplastic fluids, the model parameter n is always less than unity. In the region of the τ vs. $\dot{\gamma}$ plot where the power-law is applicable, a log-log plot of τ vs. $\dot{\gamma}$ gives a straight line with a slope of (n-1). As stated earlier, the power-law model doesn't describe the τ - $\dot{\gamma}$ relationship at regions where shear rates are either too high or too low. Some other proposed models are used to correlate the τ - $\dot{\gamma}$ relationship. At low $\dot{\gamma}$, the Ellis model is used while at high $\dot{\gamma}$ the Sisko model is used to predict such a relationship. The mathematical representation of the Ellis model is

$$\dot{\gamma} = -\tau \left[\frac{1}{\eta_0} + k_1 |\tau|^{(\alpha - 1)} \right] \tag{2.3.3}$$

and the Sisko model is

$$\tau = -\dot{\gamma} \left(\eta_\infty + k_2 \, | \dot{\gamma} |^{(\Delta - 1)} \right) \tag{2.3.4}$$

Where k_1, k_2, α and Δ are adjustable parameters. Both of the Sisko and the Ellis models contain Newton's law and the power-law as limiting cases.

To fit the whole range of the τ vs. $\dot{\gamma}$ plot, the four-parameter Carreau model may be used:

$$\frac{[\eta - \eta_\infty]}{[\eta_0 - \eta_\infty]} = [1 + (\lambda\dot{\gamma})^2]^{(n-1)/2} \qquad (2.3.5)$$

(Bird et al., 2002) where η_o is the zero shear viscosity, η_∞ is the viscosity at the high shear rate, λ is the relaxation time and n is a dimensionless index. Pseudoplastic fluids can also exhibit viscoelastic properties.

2.3.1b Dilatant (Shear Thickening) Fluids

This type of fluids is less encountered than the shear thinning (pseudoplastic) fluids. Dilatancy behavior is characterized by an increase in the viscosity with increasing shear rate due to the build up of networking structures. The power-law model with n values greater than unity is used to fit curves of τ vs. $\dot{\gamma}$ for these fluids. Examples of these fluids include concentrated suspensions (Gleasure, 1990).

2.3.1c Fluids with a Yield Stress (Bingham and Generalized Plastic Fluids)

The previously mentioned time-independent non-Newtonian fluids (dilatant and pseudoplastic) do not require finite shear stress to make them flow. On the other hand, a fluid with a yield stress is characterized by the fact that a finite shear stress is required to start its flow. A Bingham fluid is a fluid obeying the following relationship:

$$\tau_y = \tau_0 - \eta_B \dot{\gamma} \qquad (2.3.6)$$

where η_B is a constant, which is not a real viscosity and τ_y is the yield stress. η_B is a viscosity defined after the gamma-axis is shifted to τ_0 (Figure 2.5). As it is seen from the above equation, the Bingham model assumes that a material behaves as an elastic solid up to some stress level, which is the yield stress level, τ_y , and then behaves as a Newtonian fluid above the yield stress point (Cloud et al., 1980). Many fluids possess a yield stress; the plastic viscosity η_B is a function of shear rate. Such fluids are known as generalized plastic. One example of the generalized plastic fluids is drilling mud (Pal et al., 1992).

2.3.2 Time-Dependent Non-Newtonian Fluids

The viscosity of this type of fluids is a function of both shear rate and shear history. Examples of these fluids follow:

2.3.2a Thixotropic Fluids

Thixotropic fluids are known to have a decrease in their viscosities with time at a constant shear rate and a fixed temperature.

2.3.2b Rheopectic Fluids

These fluids are characterized by an increase in their viscosities with time at constant temperatures and shear rates. Examples of these fluids are bentonite clay suspensions.

2.3.2c Viscoelastic Fluids

These fluids exhibit both viscous and elastic properties. Gels are a very good example of these fluids. As we stated earlier, η is used to characterize flow of non-Newtonian fluids. However, the viscosity alone is not enough to characterize the type of stresses acting on the flow of viscoelastic fluids. Additional parameters are needed.

Newtonian fluids have normal stresses, (τ_{33}, τ_{22} & τ_{11}) of zero. On the other hand, for viscoelastic fluids, the normal stress differences are non-zero.

$$\tau_{11} - \tau_{22} = -\psi_1 \dot{\gamma}^2 \qquad (2.3.7)$$

$$\tau_{22} - \tau_{33} = -\psi_2 \dot{\gamma}^2 \qquad (2.3.8)$$

where ψ_1 and ψ_2 are the primary and secondary (first and second) normal stress coefficients. All of the three variables shown above (τ_{11} , τ_{22} , τ_{33}) are functions of shear rate $\dot{\gamma}$.

Subscripts 1, 2 and 3 refer to the force direction, momentum diffusion and neutral axis, respectively. For a Newtonian fluid, the left hand side of the above two equations is reduced to zero and the governing equation will be Newton's law.

Both ψ_1 and ψ_2 are functions of $\dot{\gamma}$ or τ and usually ψ_2 is 10-15 % of ψ_1 (Bird et al. 2002). ψ_1 is usually a positive value while ψ_2 is negative (Pal et al., 1992).

In the oil industry, steady shear viscosity is usually measured in couette geometry (two concentric cylinders). However, steady shear measurements are not good for the analysis of rheological behavior of viscoelastic fluids. The steady shear data produced from such methods is impossible to reproduce. This irreproducibility is due to a couple of reasons (Clark, 1979). The first is the Weissenberg effect, which is known as die-swell effect. This phenomenon is simply a fluid climbing up a rotating shaft (climbing out of the containing cup). This is due to the presence of stresses generated in the fluid that are normal to the direction of shear. In other words, the presence of tension forces in the tangential direction pulls the fluid towards the rotating rod overcoming the centrifugal force (Bird et al., 2002). This can be represented mathematically by the positive values of $(\tau_{11} - \tau_{22})$. The other reason why simple steady shear measurements are not reproducible, if used to predict the rheological behavior of viscoelastic fluids, is the resistance of the fluid to flow created by the semi-structured nature of a cross-linked fluid. In addition, steady shearing can destroy the network nature of the gel.

Researchers since late seventies and till now (Clark, 1979 & Liu et al. 2000) have been using dynamic mechanical analysis (DMA) techniques for rheological studies of viscoelastic fluids. DMA preserves the molecular structure and the morphology of the polymer gel especially at low frequencies.

2.4 Dynamic Mechanical Analysis

Viscoelastic fluids as appears from the name exhibit properties that are between those of viscous liquids and those of elastic solids. Usually, the elastic nature dominates over short time periods while the viscous nature dominates over longer time scales (Liu et al., 2000).

In dynamic mechanical analysis (DMA) techniques, a sinusoidal shear strain (or shear stress) is applied and the resulting stress (or strain) is measured. The use of these oscillatory rheological measurements was reported in the literature to monitor the gelation without affecting the 3-dimensional gel structure and to minimize effects on cross-linking rates (Prud'homme et al., 1983).

In controlled strain rheometers, the governing equation of applied strain, γ, is

$$\gamma = \gamma_0 \sin(\omega t) \tag{2.4.1}$$

where γ_0 is the shear strain amplitude applied while ω is the frequency of the strain wave. The measured stress wave τ is described by:

$$\tau = \tau_o \sin(\omega t + \delta) \tag{2.4.2}$$

where the phase angle δ is zero for elastic solid and 90^o for a Newtonian fluid. Hence, whenever the tested material is viscoelastic, the phase angle will lie between zero and 90^o. In the case of a controlled stress rheometer, stress is applied and strain is then measured. The expressions for the applied stress and the measured strain are similar to Equations 2.4.1 and 2.4.2, respectively. For the sake of analysis, the stress wave is usually separated into two waves with the same frequency. One of those two waves is the elastic component, τ', which is in phase with the strain wave. The second wave is the viscous component wave, τ'', which is 90^o out-of-phase.

The elastic modulus, G′, is defined by the following equation:

$$G' = \tau'_0 / \gamma_0 \tag{2.4.3}$$

where τ'_0 is the maximum component of the elastic stress.

The loss modulus, G", is defined as follows

$$G'' = \tau''_0 / \gamma_0 \tag{2.4.4}$$

G′ and G″ are related to the phase angle through the following equation:

$$\tan(\delta) = G''/G' \tag{2.4.5}$$

The complex modulus, |G*| is defined by:

$$|G^*| = [G''^2 + G'^2]^{0.5} = \tau_0 / \gamma_0 = \eta^* \omega \tag{2.4.6}$$

where η^* is the complex viscosity which is related to the dynamic viscosity, η', and η'' by:

$$\eta^* = [\eta''^2 + \eta'^2]^{0.5} \tag{2.4.7}$$

The above relations are important in investigating the rheological behavior of gels. The above parameters change at the transition from solution to gel phase. A typical plot of G' and G" changes during this process is shown in Figure 2.4.1. Time-temperature superposition can be used in order to predict gel properties after long time periods. Experiments are done with the gel at different temperatures and then shifting it to a reference temperature. This idea is applicable for all viscoelastic properties. The following equation (Williams-Landel-Ferry (WLF)) holds for any of the viscoelastic properties. For example, for G (t):

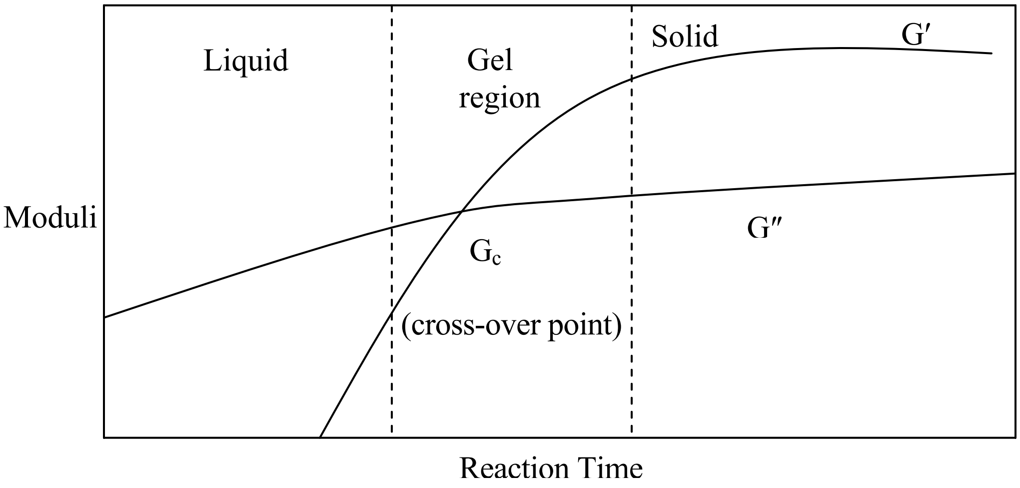


Figure 2.4.1: Representation of the dynamic mechanical behavior during a cross-linking reaction

$$\frac{\log G(t,T)\, T_r\, \rho_r}{G(t,T_r) T \rho} = \log a_T = \frac{-C_1\,(T - T_r)}{C_2} + (T - T_r) \qquad (2.4.8)$$

where subscript r refers to conditions at some arbitrary reference condition, a_T is a shift factor, C_1 and C_2 are constants.

The viscosity of synthetic polymers decreases with increasing temperature. On the other hand, the form of temperature dependence is rather complex.

At elevated temperatures, the viscosity follow a simple exponential relation called the Andrade-Eyring equation:

$$\eta = A \exp\,[E_\eta / RT] \qquad (2.4.9)$$

Where E_η is the activation energy for viscous flow, R is the universal gas constant, T is temperature and A is a constant (Macosko, 1994).

Chapter 3

Literature Review

3.1 Rheological Testing of Polymeric Gels

Many researchers have tested the rheology of cross-linking polymers. Robert et al. (1982) studied the effect of temperature on the gelation time of a polyacrylamide/Cr^{3+} with sodium bisulfide as a reducing agent. It was found that the gelation time decreases with increasing temperature. The reaction temperature was correlated with the gelation time through an Arrhenius-type equation. Whitney et al. (1996) studied the gel strength for a polyacrylamide/Cr^{+3}. The gel was placed in 1 ft tubes and a differential pressure was applied across the tube to initiate flow. Liu et al. (2000) studied some rheological aspects of a Cr^{+3} acetate/ HPAM system. It was shown that the elastic modulus, G', increased with gel aging. Also, the loss modulus, G", increased with the increase of polymer concentration. Values of G' were fairly constant for frequencies in the range 1 to 100 s^{-1}, while G" increased as frequency increased which is a characteristic of rubber. Another feature of rubber like materials is that the G' values are not affected by changes in temperature.

Omari (1994) studied gelation kinetics of a scleroglucan cross-linked with zirconium. It was proposed that G′ is proportional to the density of the formed cross-links, v, as indicated by the following model:

$$G' - G'_0 = qvkT \tag{3.1.1}$$

where G'_0 is the elastic modulus of the fresh polymer solution, k is Boltzman constant, T is temperature and q is a constant ranging from 0.4 to 1 depending on the system under study. In order to investigate the effect of pH on the reaction kinetics, HCl and NaOH were used to adjust the pH of solutions studied. G′ increased gradually upon the addition of the cross-linker until it reached a constant level indicating that the gel formation reaction is over. Addition of cross-linker to the solution increased, G′ until it reached a maximum where increasing the cross-linker lead to a decrease in G′. Higher concentrations of cross-linker prevented gel formation. Therefore, there are concentration limits that cross-linker should not exceed in order for the gel to form known as critical cross-linker concentration which was found to be 30 ppm for the Scleroglucan-Zr system.

Vogelsberger et al. (2000) used rheology to determine the kinetic parameters of the solution-gel transformation of a tetraethoxysilane-water-ethanol (TEOS) system. After solution preparation, it was placed in the rheometer right away for viscosity measurement as a function of time before the gel started to form where the mode was changed to oscillatory. The specific viscosity was used to express viscosity change with time of the system while doing the measurement. The specific viscosity, $\eta_{sp,}$ is defined as:

$$\eta_{sp} = (\eta - \eta_0) / \eta_0 \tag{3.1.2}$$

where η_0 is the viscosity of the solvent and η is the apparent viscosity. The best determination technique of the gelation time was found to be the point at which the elastic and viscous modulii are independent of frequency (ω) or time. However, they used the cross-over point to determine the gelation time which gave close results to the frequency independent technique. A second order rate equation for the gelation kinetics was proposed by Vogelsberger et al. (2000) :

$$\frac{1}{C_p(t)\text{ total}} + \frac{1}{C_p \text{ at } t = 0} = K_c \ t \tag{3.1.3}$$

where $C_p(t)$ total is the total concentration of all particles in solution at any time t, $C_{p,\ t=0}$ is the initial concentration of the particles in solution and K_c is the rate constant of the coagulation process. They were able to relate viscosity, gelation time (t_g), K_c t and the activation energy of gelation through a linearized expression.

Shchipunov et al. (2002) studied the phase behavior and rheological properties of an alignate gel. Their system consisted of an anionic polysaccharide (alignate) cross-linked with calcium (introduced into solution as $CaCO_3$). The effect of adding more polymers on the gel strength was studied in terms of G′. The additions of extra polymer to the gelling solution lead to what is known as syneresis (excessive hydrolysis), which leads to an increase in the volume of solution that lowered the density of the crosslinks. The storage modulus, G′ was found to decrease due to the previously mentioned phenomenon.

Tayal et al. (1999) studied the changes in rheological properties due to microstructural changes of a guar polysaccharide polymer crosslinked with borate. The molecular weight of the polymer was measured using GPC (gel permeation chromatography) technique during the degradation of the polymer. The molecular weight was linearly related to time through the following model:

$$1/M(t) = 1/M_0 + kt \qquad (3.1.4)$$

The solution-gel transition of silica alkoxides was studied by Ponton et al. (2002). The alkoxides groups are first replaced by OH^- through hydrolysis reaction forming reactive (=Si-OH) groups. Then, these groups condense to form the gel structure. An acid (like HF, HCl or HNO_3) was utilized as a catalyst for hydrolysis. G' was found to level out when the reaction is complete. For the determination of the gelation time, they found that the cross-over point, G_c, occurs at longer times with increasing frequency. At the gelation time, the following relation was used to predict the relaxation exponent, n:

$$G''/G' = \tan(n\,\pi/2) \qquad (3.1.5)$$

Then, a power law relaxation modulus was proposed. The model proposed was:

$$G(t) = S\,t^{-n} \qquad (3.1.6)$$

where S is gel strength, t is time and n is the relaxation exponent found in the previous equation. High concentrations of the cross-linking monomer decreased the gelation time. Gelation time was correlated to temperature through an Arrhenius-type equation:

$$t_g = c \exp(E_a/RT) \qquad (3.1.7)$$

where E_a is the activation energy of polymerization, R is the gas constant and T is temperature.

Mortimer et al. (2001) studied the rheological behavior of mixed isomers of methyl substituted aminophenol cross-linked with a Lewis acid initiator BF_3. They related viscosity to molecular weight distribution of a polymer. Moreover, gelation time determination from G_c was found to be accurate only for systems with relaxation exponents of 0.5 in equation 2.23.They studied the kinetics of the reaction in terms of conversion of the polymer which was measured using DSC (differential scanning calorimetry). The proposed model of the conversion change with respect to time was:

$$P = A + B\, t^C \qquad (3.1.8)$$

where P is the conversion of the polymer, t is reaction time; A; B and C are constants. Viscosity measurements were used to measure the gelation time. This was done by extrapolating the viscosity vs. time curves to the infinite viscosity regimes. Then, those gelation times were correlated to temperature through Arrhenius type equation.

3.2 Chemistry of the Organically Cross-linked Polymer System (OCP)

In this research, the rheological properties of an organically cross-linked polymer (OCP) gel will be studied. The polymer consists of a polyacrylamide and a t-butyl acrylate (PAtBA) while the organic cross-linker utilized in this system is polyethyleneimine (PEI). This gelling polymeric system was developed in 1999. The polyacrylamide and the t-butyl acrylate are copolymers of an acrylamide and an acrylate ester where the ester provides the mask cross-linking site (Hardy et al., 1999). The PAtBA is prepared at very low degree of hydrolysis so that the cross-linking reaction relies on the PAtBA itself instead of relying on the chemistry of the cross-linker. The hydrolysis of the PAtBA under acidic conditions is shown in the following reaction, which is fast at low pH. At higher temperatures, the thermolysis of the ester group can occur. This thermolysis (dominant at high pH and temperature) results in the formation of iso-butene as shown in Reaction 2.

Using the PEI as a cross-linker has two advantages. First, the PAtBA-PEI bonds are thought to form as a result of a nucleophilic attack by the amine nitrogen from the PEI on the carbonyl group from the t-butyl acrylate as shown in Reaction 3.

It should be mentioned that this reaction (Reaction 3) does not require thermolysis or hydrolysis to take place on the cross-linking site. The other advantage of using PEI as a cross-linker is that PEI is not susceptible to hydrolysis, which will help the PEI to propagate deeper into the treated zones. As shown in reaction 3, the cross-linking bond is a covalent bond between a carbonyl carbon of the PAtBA and amine nitrogen of the PEI. This covalent bond is expected to give rise to the thermal stability of this system.

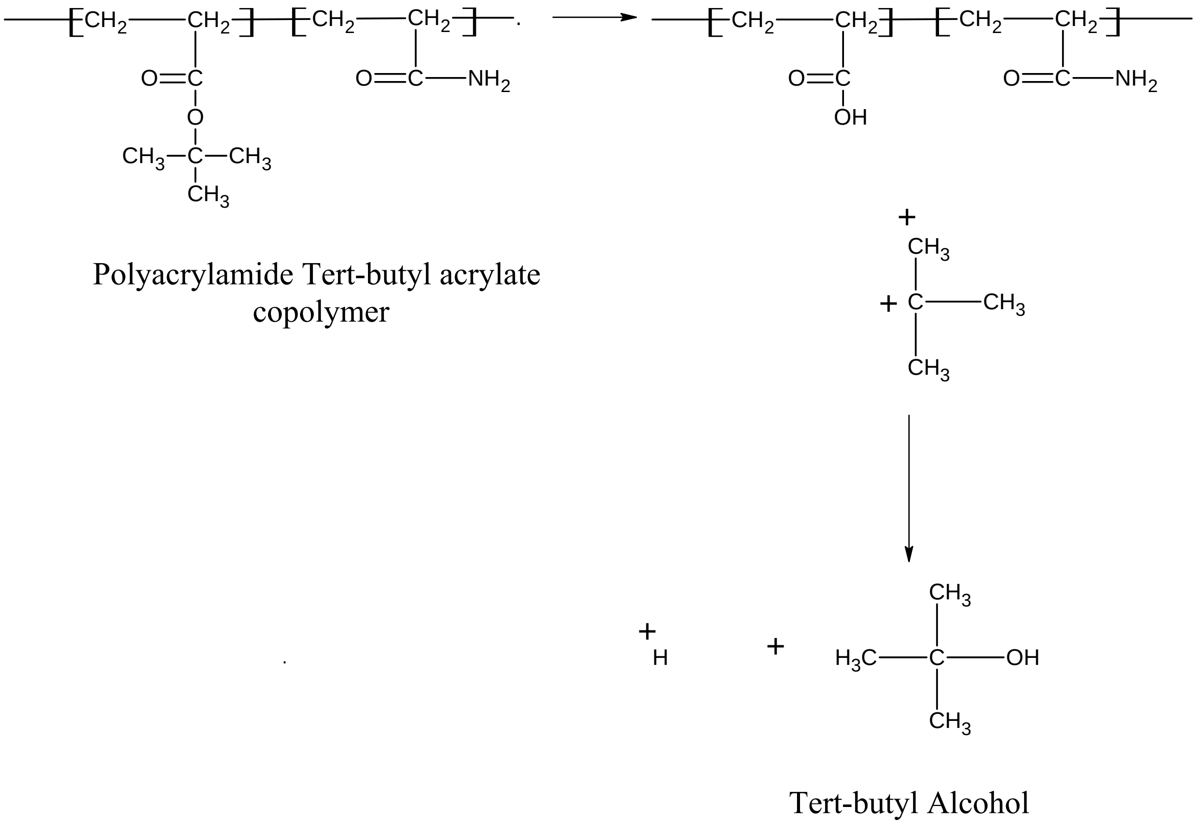


Figure 3.2.1: (Reaction 1) Hydrolysis of the PAtBA polymer

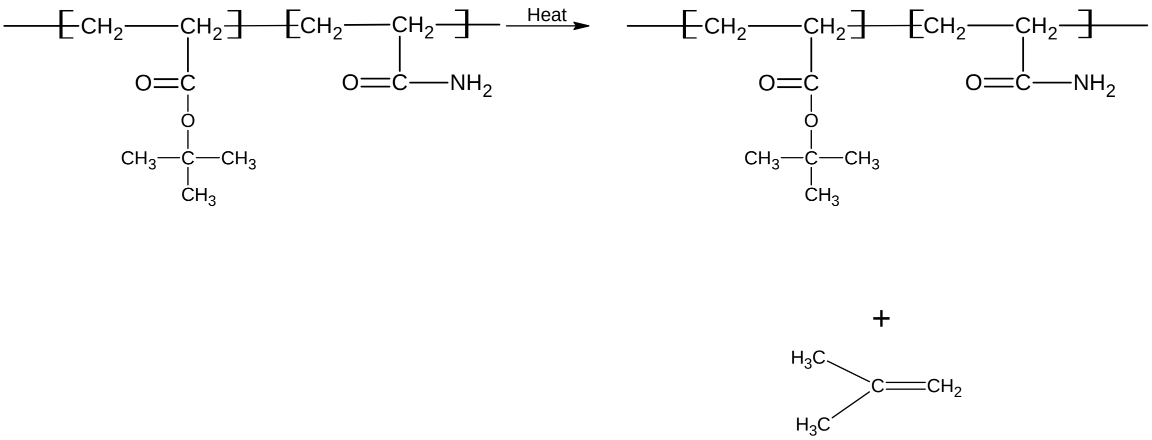


Figure 3.2.2: Thermolysis of the PAtBA polymer

The mentioned three reactions (hydrolysis, thermolysis and nucleophilic attack) are all proposed mechanisms of the PAtBA-PEI cross-linking reaction. However, to ensure the formation of the strong covalent bond, which should be studied, one should run all experiments at a temperature less than 100^oC with all reactions taking place in less than 20 hours. The following facts indicate that the above conditions ($T < 100\,^oC$ and reaction times < 20 hours) ensured that only the covalent bond is studied (Hardy et al., 1999):

1. All hydrolysis and thermolysis products of the polymer are cross-linkable with metallic cross-linkers
2. Alkaline hydrolysis of polyacrylamide solutions is slow at $100\,^oC$
3. PEI/PAtBA solutions are high pH solutions
4. The gelation time of a pH 10.5 solution of 10% PAtBA + 0.5% Zr^{4+} heated to $100\,^oC$ was 40 hours

.

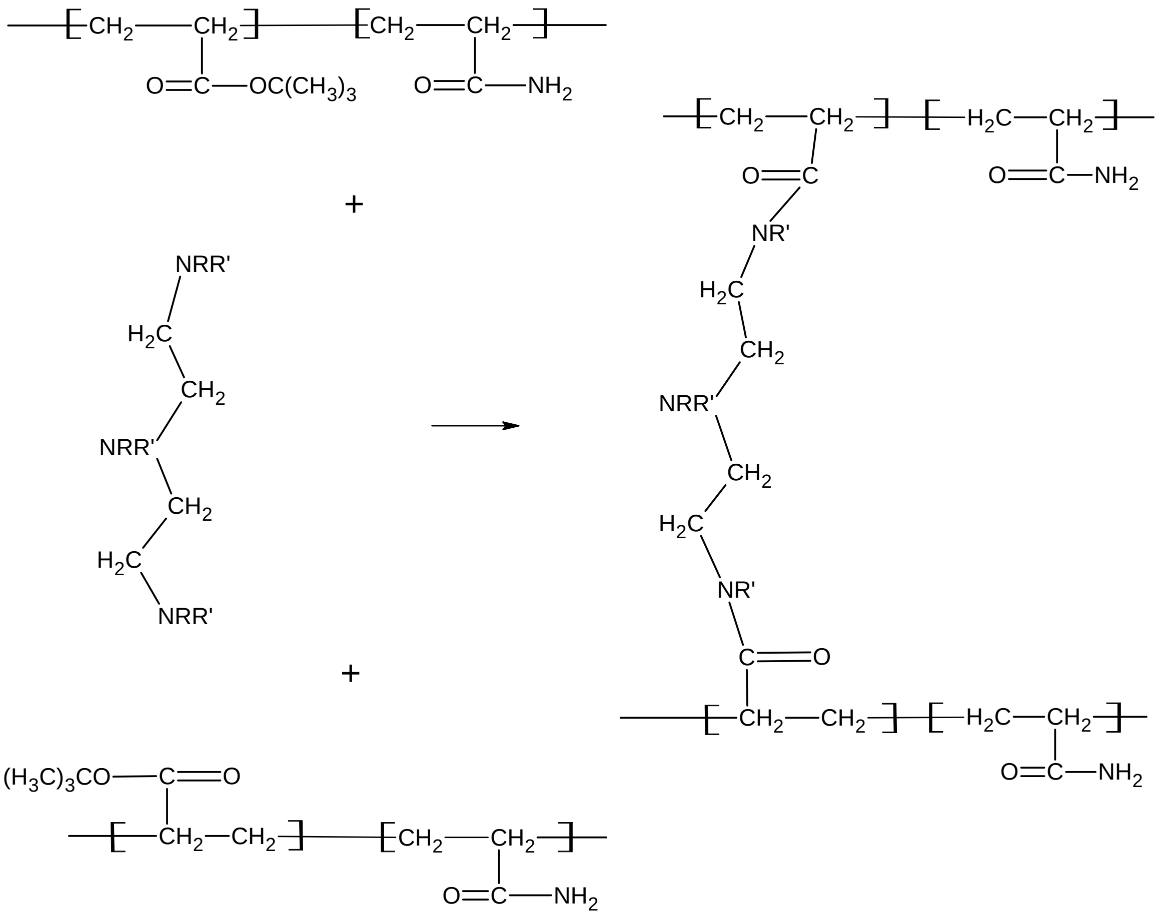


Figure 3.3.3: Cross-linking of PAtBA with PEI

The OCP system to be studied was found to be stable at temperature levels as high as 160 ^oC and at high pH values (Hardy et al., 1998). Due to these characteristics, the penetration depth of this OCP system was found to be eight times higher than that of Cr-polyacrylamide gelling system (Hardy et al. 1998).

Chapter 4

Results and Discussions

4.1 A Rheokinetic Study of an Organically Cross-linked Polymeric Gel Used for Water Shut-Off Treatments

4.1.1 Abstract

Polyacrylamide-based gels are used in many water shut -off treatments. In this study, an organically cross-linked polymeric gel was examined. The kinetics parameters of the gelation reactions were studied using steady shear viscometry. The activation energy was found to be 28,334 and 27,579 cal/mol for deionized mixing water and field mixing water, respectively. Avrami equation was used to obtain the reaction rate constant and order. . The reaction order was to found to be within 10% difference between 5.83 and 5.23. The reaction rate temperature dependence was $k = 2*10^{65} \exp(60,835/T)$. The addition of salts to the mixing water was found to increase the gelation time. Divalent cations delayed the cross-linking reaction more than monovalent cations. On the other hand, higher polymer and cross-linker concentrations reduced the gelation time. The effects of initial pH, and mixing rate on the gelation time were also examined in details.

4.1.2 Introduction

As petroleum reservoirs mature, water cut increases. The cost of handling, separating and disposing produced water is high. Moreover, problems such as scale, corrosion, emulsion and sand production can arise as a result of excessive water production (Reddy et al., 2003). It is estimated that for each barrel of oil, an average of three barrels of water are produced and disposing this water costs $40 billion every year (Seright et al., 2003). Therefore, it is essential to minimize water production. Several techniques are available for water shut-off including mechanical and chemical methods. The choice of the method depends on the candidate. Advantages that polymer gels have over other techniques include lower costs (no rig is needed) and deep placement through the control over the gelation time (Hutchins et al., 1996).

Water-soluble polymers such as polyacrylamides and polysaccharides have been studied as a means for water shut-off since 1950s (Prud'homme et al., 1983). In high temperature applications, the resulting gel should be thermally stable at the reservoir high temperature. At temperatures more than 100^oC, polyacrylamide polymers exhibit hydrolysis and oxidative degradation of the polymer chains (Moradi-Araghi et al., 1987). Moreover, at temperatures more than 75^oC, when multivalent cations are present in high concentrations, over cross-linking occurs resulting in expulsion of water out of the gel structure due to a shrinkage in gel volume (gel syneresis) (Moradi-Araghi and Doe, 1984). Cross-linkers are classified as either organic or metallic. In metallic cross-linking, carboxylate groups resulting from the thermal hydrolysis of the polymer chain further react with the metallic cations forming ionic bonds. Unfortunately, these bonds are unstable at high temperatures (Moradi-Araghi, 2000). Chromium is the most commonly applied metallic cross-linker, however, one main disadvantage of the chromium-based cross-linkers is their toxicity, especially those that contain Cr^{+6} (Nasr-El-Din et al., 1998). Another concern with inorganic cross-linkers is their short gelation times at temperatures higher than 60^oC (Lockhart, 1992; Albonico et al., 1994).

At high temperature reservoirs, more stable systems are needed. It is possible to have thermally stable base polymers and cross-linkers. The polymer thermal stability can be improved by adding a monomer into the polymer structure that will minimize thermal hydrolysis (Moradi-Araghi et al., 1987). Lowering the polymer molecular weight is also reported to enhance thermal stability of water shut-off polymers (Moradi-Araghi., 2000).

Organic cross-linked polymers (OCP) are known to have good stability at elevated temperatures. This is because of the covalent bonds formed between the polymer and the cross-linker (Moradi-Araghi, 2000). There are several organic cross-linkers reported in the literature such as phenol and formaldehyde (Moradi-Araghi et al., 1994). The formaldehyde reacts with water to form methylene glycol that will further react with phenol producing methylol phenols. Methylol phenols will then react with the polyacrylamide via covalent bonding forming the three dimensional gel structure (Moradi-Araghi et al., 1993). Another route could be the reaction of the methylene glycol with the polymer producing a compound that will then react with the methylol phenols to form the gel (Falk, 1984). These gels were reported to be stable at temperatures up to 300^{o}F (Moradi-Araghi, 1993). However, they are not environmentally friendly (Moradi-Araghi et al., 1994). Hence, the need for safer alternatives arises. One way is to use precursors of phenol and formaldehyde such as phenyl acetate and hexamethylenetetramine (HMTA) that thermally hydrolyze in-situ forming phenol and formaldehyde, respectively. More compounds were reported to be alternatives for phenol such as aspirin, furfuryl alcohol and aminobenzoic acid. These gels showed good thermal stability at high temperatures up to 250^{o}F (Moradi-Araghi, 1994).

A co-polymer of acrylamide and t-butyl acrylate (PAtBA) cross-linked with polyethylene imine (PEI) was examined in this study. It was selected because it is stable at high temperatures (Hardy et al., 1999) and the temperature of Saudi Arabian reservoirs can reach 300-320^{o}F (Nasr-El-Din et al., 2004). Moreover, the PEI cross-linker has a low toxicity and was approved for food contact in the USA (Reddy et al., 2003). Several papers examined the ability of this gel system to reduce permeability of reservoir cores (Hardy et al., 1999, Hoek et al. 2001; Alqam et al. 2001; Zitha et al. 2002).

For a successful water shut-off treatment, the gelling solution should be of a low viscosity that makes the solution pumpable using coiled tubing (CT). Moreover, gelation times should be long enough in order to avoid premature gelation. Also, gelation time will be a function of gel composition, temperature, and water TDS. While mixing the gel in the field, applied shear on the gel before pumping can affect the polymer and/or the cross-linker structures and eventually the gelation kinetics. Therefore, the objectives of this study were to investigate the effects of the following parameters on the gelation time of the OCP: temperature, TDS of mixing water, mixing rate, initial pH, polymer concentration and cross-linker concentration. Steady shear viscosity measurements were used to determine the gelation time.

4.1.2 Experimental Studies

4.1.2.1`Materials

The gelling solution consisted of a co-polymer of polyacrylamide and t-butyl acrylate (PAtBA) cross-linked with an organic cross-linker, polyethylene imine (PEI). Both chemicals were received in a liquid form and were used without further purification. The activity of PAtBA was measured by precipitation in pure ACS grade isopropanol (Taylor and Nasr-El-Din, 1994). Then, thermogravimetric analysis (TGA) was performed for the polymer and the cross-linker and the activities were found as 35, 23 wt%, respectively. All gel compositions are reported in terms of the concentration of the active chemical present in the sample received.

Mixing waters with three salinity levels were used. These were deionized water, seawater and field mixing waters. Seawater and field mixing waters were filtered using 0.45 μm filter papers. Chemical analyses of these waters are given in Table 4.1.1.

The effect of various salts on the gelation time was examined in detail. Salts examined included: NaCl, KCl, $CaCl_2.2H_2O$, $MgCl_2.6H_2O$ and $FeCl_3.6H_2O$. All salts were ACS grade. Dead oil was filtered using a 0.45 μm filter paper to remove suspended solids and water. The viscosity and density of this oil were measured as 3.3 mPa.s and 0.873 g/cm^3 at room temperature, respectively.

4.1.2.2 Gelation Mechanism

The most interesting aspect about the chemistry of this system is the control of the cross-linking reaction. Generally, controlling the gelation reaction is achieved by monitoring the exposure of the carboxylate groups through the degree of hydrolysis, which is defined as the number of carboxylate groups per the total number of amide, and carboxylate groups. However, at reservoir conditions when the pH and temperature change significantly, it becomes difficult to control degree of hydrolysis. Moreover, repulsion forces between carboxylate groups start to increase resulting in a significant increase in viscosity, which might become a disadvantage while pumping and placing the solution.

Table 4.1.1: Chemical Analysis of Mixing Waters

Variable	**Field Water**	**Seawater**
Ca	126	592
Mg	53	2,304
Na	228	19,325
K	14	730
Cl	361	31,106
SO_4	233	4,108
HCO_3	171	183
TDS[2]	1,186	58,348
pH	7.8	7.9

1. All concentrations are in mg/l
2. Total dissolved solids (TDS) was determined by addition

The PAtBA polymer has a very low degree of hydrolysis and hence weak interactions with the cross-linker through the carboxylate sites are minimized and also diminished at temperatures greater than 105°C (Hardy et al., 1998). Another control approach is via the chemistry of the cross-linker by adding ligands that delay the formation of the active cross-linker. For example, formaldehyde and phenolic sources are added to form the active materials (resole-type) that will crosslink polyacrylamides (Moradhi-Araghi et al., 1993). Also, aldehydes are added as their acetal derivatives that hydrolyze to expose the aldehyde for polymer cross-linking (Avery et al., 1988). Therefore, the need for better-controlled and stable types of sealants rose.

Previous papers discussed the chemistry of the PAtBA-PEI system (Morgan et al., 1997; Hardy et al., 1998;1999). We present a summary of the information published. The ester groups (R-COO-R') on the PAtBA polymer provide masked cross-linking sites. These groups either hydrolyze or thermolyse according to pH and temperature. At low pH and temperatures, the ester groups hydrolyse forming partially hydrolyzed polyacrylamide (PHPA) and t-butyl alcohol (Figure 1).

On the other hand, they thermolyse at high temperatures and pH conditions producing PHPA and isobutene as shown in Figure 2. After the breakage of the ester groups, carboxylate sites are formed. The carbonyl carbon (C in CO) acts as an electrophone due to its lower electronegativity compared to the carbonyl oxygen (O in CO). An imine nitrogen from the PEI (nucleophile) attacks the electrophilic carbonyl carbon forming a covalent bond, which is stable at high temperatures (Figure 3). This system is known to be thermally stable at temperatures up to 160°C (Hardy et al., 1998).

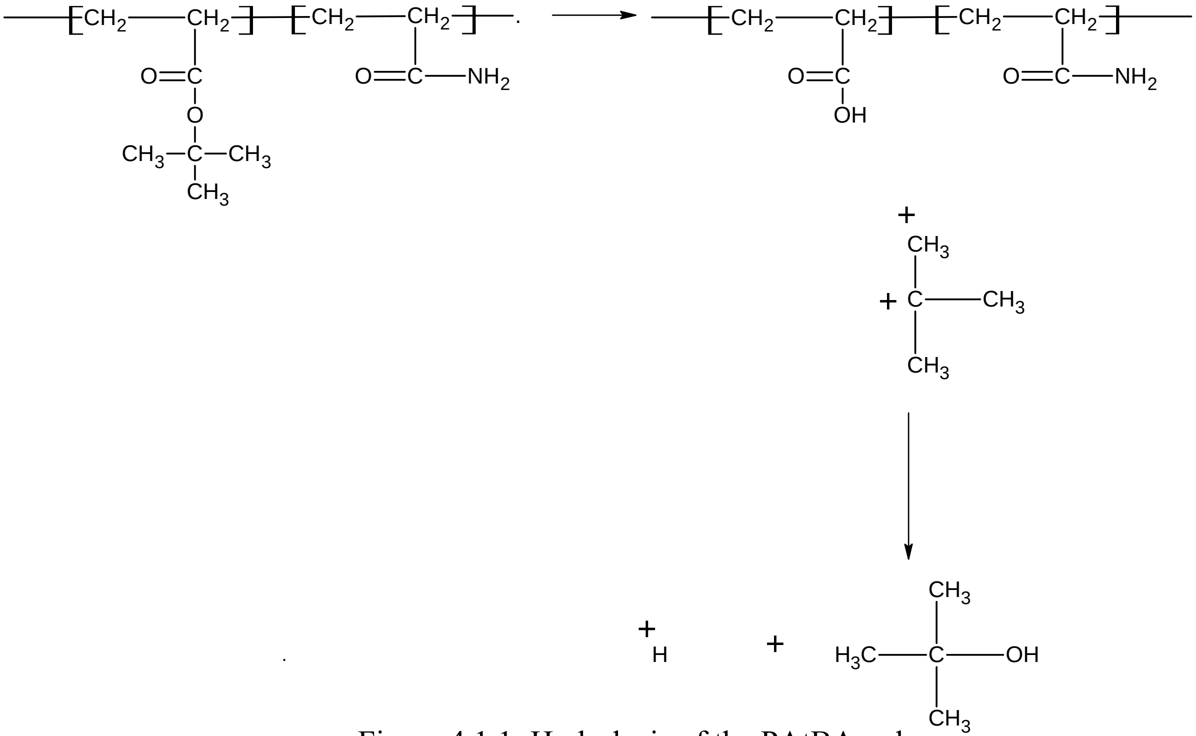


Figure 4.1.1: Hydrolysis of the PAtBA polymer

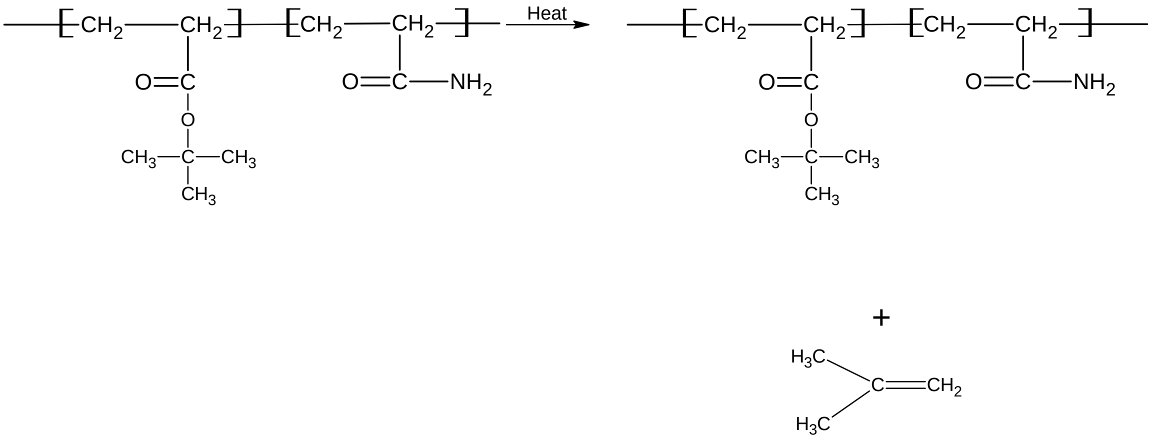


Figure 4.1.2: Thermolysis of the PAtBA polymer

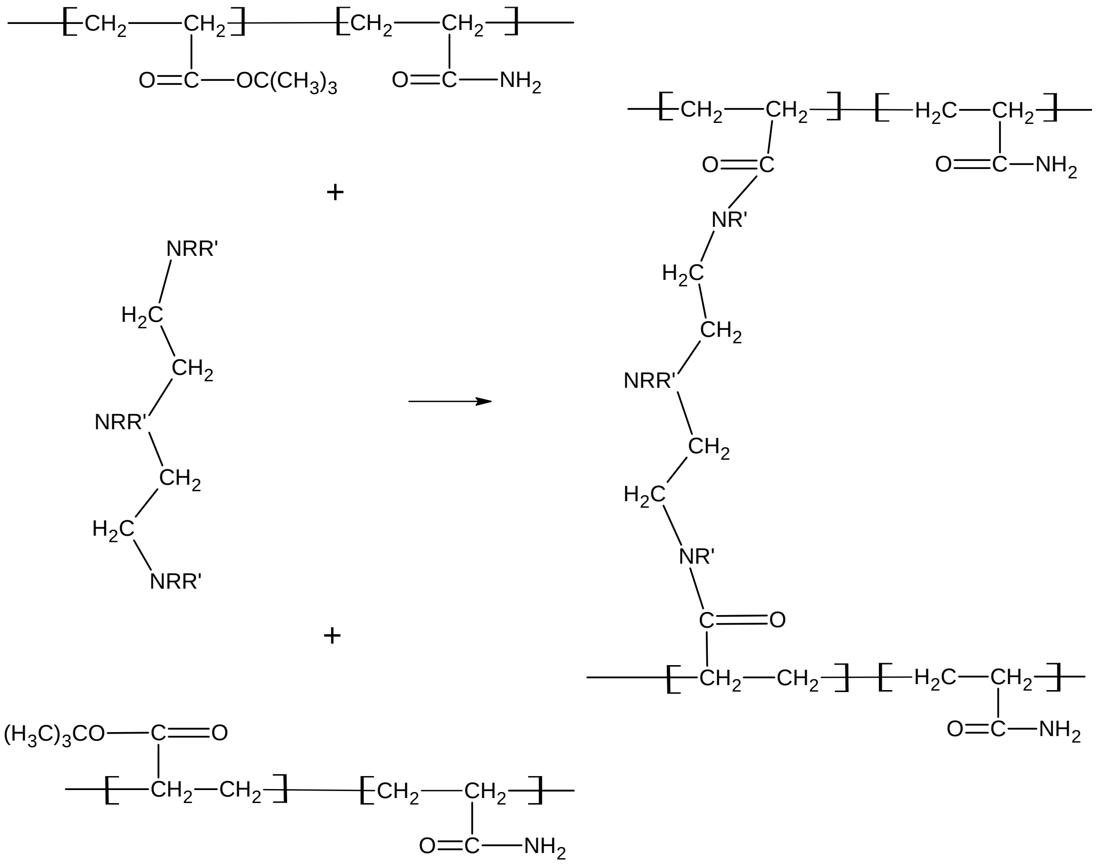


Figure 4.1.3: Cross-linking of PAtBA with PEI

4.1.2.3 Measurements of the Gelation Time

Several definitions of the gelation time are reported in the literature. When the time to target a certain viscosity is taken as the gelation time (Terry et al., 1981; Mijovic et al., 1993), then the operator must account for maximum pumping pressures since some operational limitations may occur. This will take place when the fluid becomes unpumpable due to high viscosity. Another definition is the time needed to target specific gel strength (Sydansk 1990). The experimentalist will visually follow the bulk motion of the gel in a small test tube. This may be applicable when the gelation times are short enough to be observed. In this study, the gelation time is defined as the point at which the slope of the tangent to the viscosity vs. time curve goes through a sharp increase (Figure 4.1.4). This point corresponds to the start of the gel network formation (Hardy et al., 1998).

Steady shear measurements were performed using a Brookfield viscometer (PVS type). Couette geometry of outer and inner radii of 3.4 and 3.8 cm, respectively was used. Viscosity measurements during gelation were made at various temperatures up to 135^{o}C at a shear rate of 8.52 s^{-1} unless otherwise stated. In order to prevent sample evaporation, nitrogen gas was used for pressurizing the system up to 300 psig. Table 2 gives the parameters tested and their ranges.

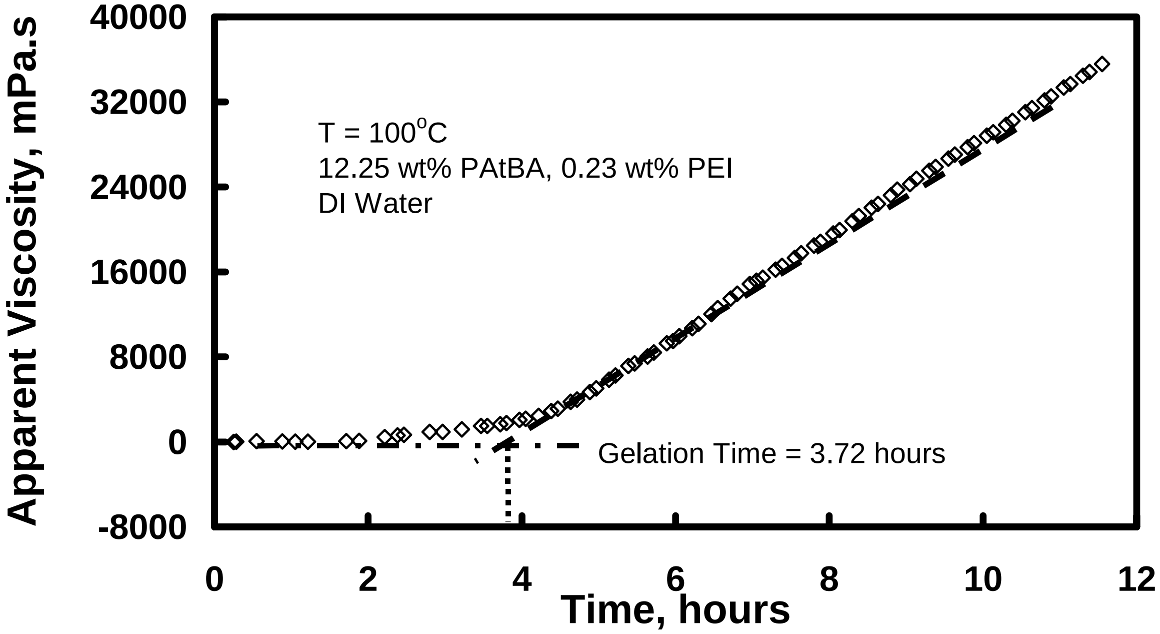


Figure 4.1.4: Gelation Time Determination

Table 4.1.2: Parameters Examined

Parameter	**Range**
Temperature	**80 -150°C**
Polymer Concentration	**7.58 - 14.58 wt%**
Cross-linker Concentration	**0.23 – 0.69 wt%**
TDS of mixing water	**0 - 58,348 mg/l**
Mixing Rate	**8.52 - 255.6 s^{-1}**
Initial pH	**3 – 12**

4.1.3 Results and Discussion

4.1.3.1 Gelation Kinetics

As the gel network starts forming, the viscosity of the gelling solution builds up. Therefore, it is possible to follow gelation reaction with viscosity measurements. Steady shear viscometry is reported in the literature for measuring reaction parameters (Mortimer et al., 2001) using Avrami-type equation, which is defined as:

$$X = 1 - \exp(-kt^n) \qquad (4.1.1)$$

where X = Fractional conversion, -
k = Reaction rate constant, 1/hour^n
t = Time, hours
n = Reaction order, -

The fractional conversion, X, is defined as follows:

$$X = \frac{\eta(t) - \eta_0}{\eta_{\max} - \eta_0} \qquad (4.1.2)$$

where

$\eta(t)$ = Viscosity at time t, mPa.s
η_0 = Initial viscosity at time t=0, mPa.s
η_{max} = Maximum viscosity measured by viscometer, mPa.s

In the original Avrami equation (Avrami, 1939; 1940), X, is defined as the ratio of crystals formed at a time t divided by the maximum amount of crystals that can be formed. In the present study, however, the increase in the viscosity of the solution at a time t, [η(t)- η_o], is proportional to the concentration of x-links formed due to the reactions between the polymer and the cross-linker (Figure 4.1.3). The maximum attainable increase in viscosity, [η_{max} - η_o], represents 100% conversion of reactive sites into cross-links. Hence, the two mechanisms of gel growth due to cross-linking reactions and crystal formation during crystallization are qualitatively similar. Therefore, the use of the Avrami-type equation is a reasonable approximation to the gelation process.

In equation 4.1.1, it is assumed that when the gel reaches the maximum measurable viscosity, the fractional conversion is unity. To demonstrate the use of the Avrami equation in the present gelling system, viscosity data were generated for a gelling solution that contained 12.25 wt% PAtBA and 0.23 wt% PEI. The field mixing water was used to prepare this gelling solution. The viscosity data was converted into fractional conversion, which was plotted as a function of the natural logarithm of time, Figure 4.1.5.

The gelling reaction order was found to be ranging within 10% (from 5.83 at 135°C to 5.23 at 120°C) at the three temperatures examined. This variation is accepted as an experimental error. It should be noted that the reaction order extracted from rheological measurements is not in the range of first to second order as expected for many chemical reactions. The reason is that the classical reaction orders are based on the direct measurements of concentrations of the reactants and/or products. This is not the case in viscosity measurements where the concentration dependence of viscosity is not simple. Also, in the presence of abundant amount of water depends on the concentration of active cross-linking sites of PEI and molecular weight of the polymer.

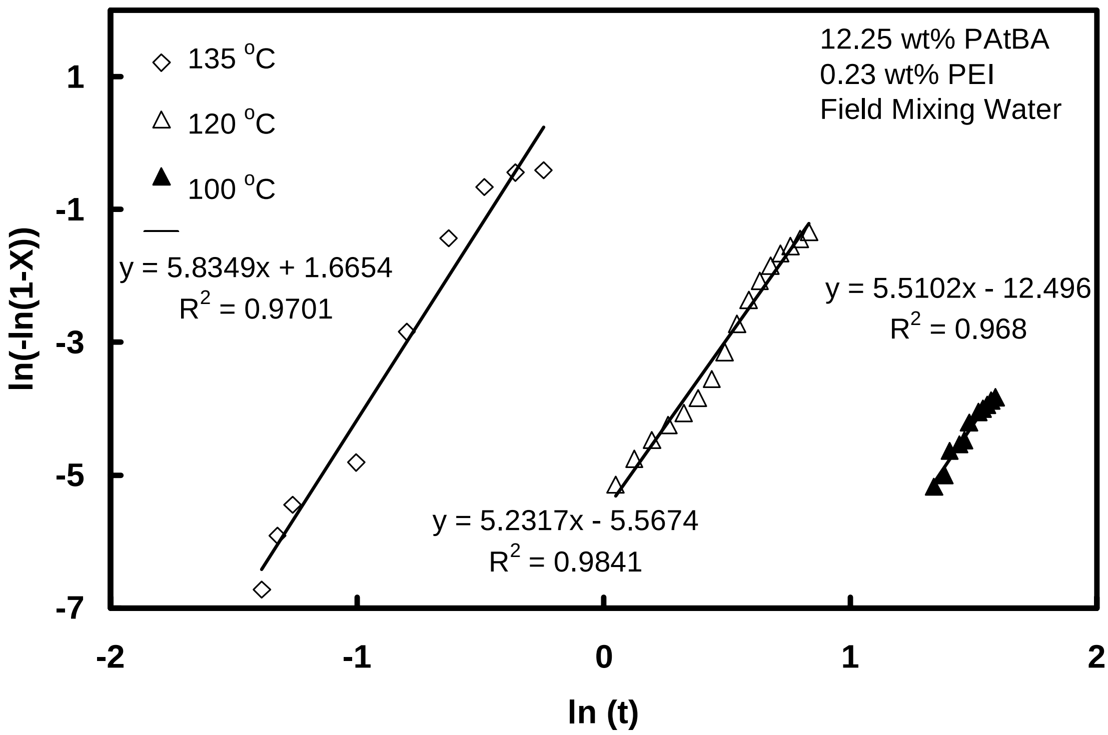


Figure 4.1.5: Prediction of reaction rate constant and order in field mixing water

Therefore, the concentration dependency of viscosity is embedded in the rheologically measured reaction order and rate constants. This may explain the higher reaction order. The effect of temperature on the reaction rate can be expressed using Arrhenius law as follows:

$$k = k_0 \exp(-E_a / RT) \tag{4.1.3}$$

where k = Reaction rate constant (units), (mol/L)$^{1-n}$/Second where n=reaction order.
k_o = Frequency factor
E_a = Activation energy, cal/mol
R = Universal gas constant, cal/mol °K
T = Absolute temperature, °K

Figure 4.1.5 below shows the Arrhenius plot for the k dependence on temperature. The k values were extracted from Avrami equation. The activation energy was found to be 120,880 cal/mol.

4.1.3.2 Effect of Temperature on the Gelation Time

Figure 4.1.7 shows the viscosity evolution obtained at various temperatures for gelling solutions that contained 12.25 wt% PAtBA, 0.23 wt% PEI. Distilled water was used to prepare these solutions. It should be mentioned that these solutions did not form a gel after six days at room temperature. The viscosity of the gelling solution increased somewhat. This is mainly due to the lack of carboxylates groups on the polymer chain. This observation highlights a very important characteristic of this system.

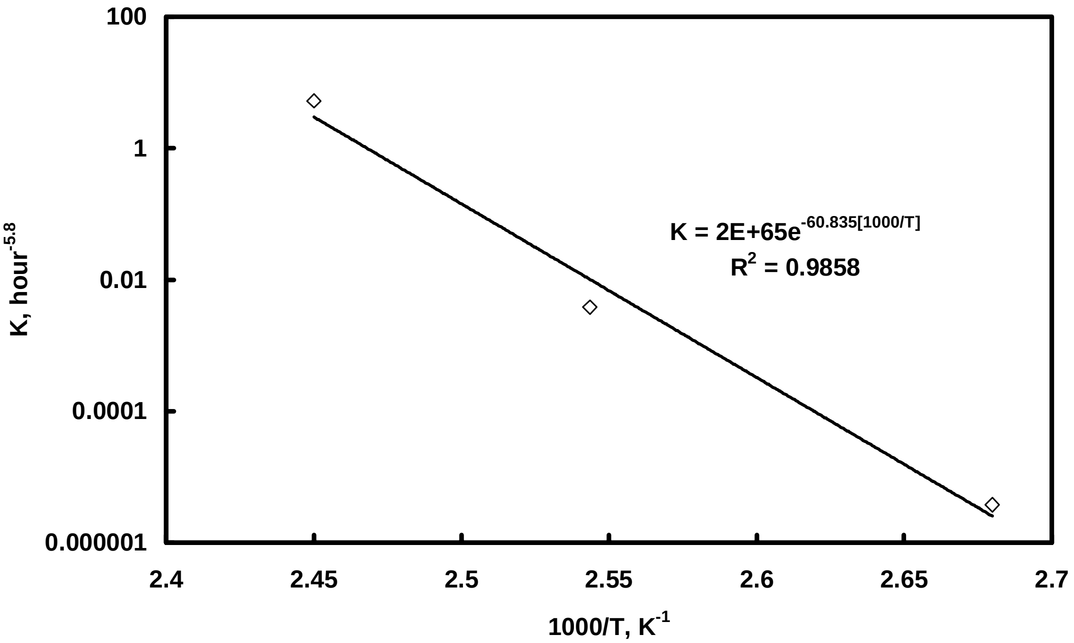


Figure 4.1.6: Reaction Rate Constant Dependence on Temperature

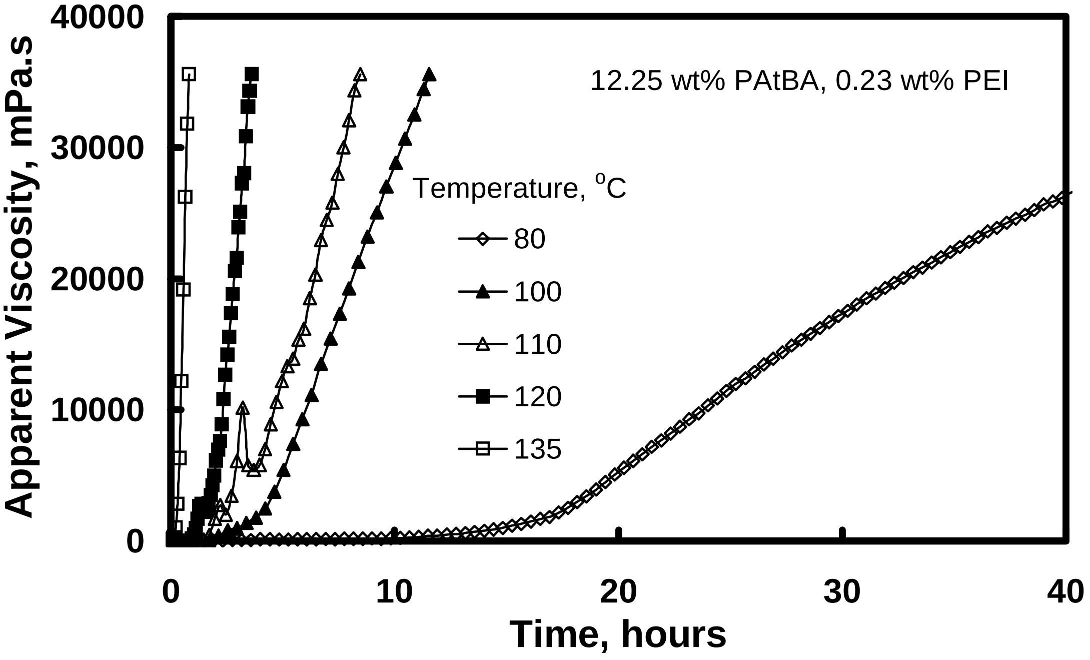


Figure 4.1.7: Viscosity Evolution of 12.25 wt% PAtBA, 0.23 wt% PEI at Various Temperatures in Distilled Water

If this system is mixed in the field and more time is needed for any operational problem, it will not gel in the mixing tank, and can be pumped into the target zone. Another important point is that the gelation time is very short at very high temperatures like 150°C. A suitable preflush can be used to cool down the formation, and extend the gelation time as needed.

At a temperature of 80°C, the gelation time was nearly 15 hours. The gelation time decreased with temperature. This reflects the endothermic nature of the gelation reactions. The results shown in Figure 6 indicate that the ester groups of the polymer did not thermolyse at temperatures less than 80°C and hence it took longer times for gelation. The gel formed at lower temperatures was physically weak. It is most likely that the temperature at which the ester group breaks is between 80 and 100°C at a shear rate of 8.52 s^{-1}. The effect of temperature on the gelation time can be presented using Arrhenius-type equation, as follows (Jurinak et al., 1991):

$$GT = M \exp\left({}^{E_a}\!\big/_{RT}\right) \tag{4.1.4}$$

where GT = Gelation time, hours
M = Frequency factor, hours

From Equation 4.1.4, a plot of the natural log of GT vs. 1/T should give a straight line with a slope of E_a/R and an intercept of ln M.

Figure 4.1.8 shows Arrenhius plot for gels prepared in field mixing water. The gelation time can be presented using Equation 4.1.4. The activation energy was found to be 27,579 cal/mol with a frequency factor of $7*10^{-16}$ hours for field mixing water.

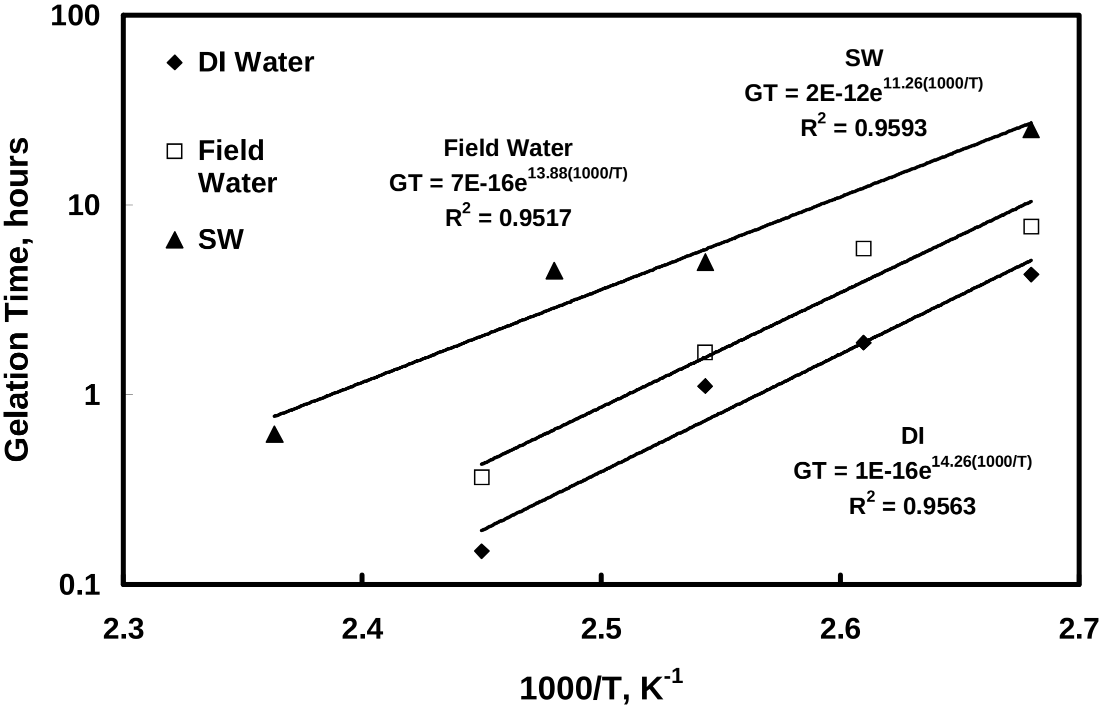


Figure 4.1.8: Activation energy for 12.25 wt% PAtBA, 0.23 wt% PEI in various mixing waters

This value has the same order of magnitude as those obtained for other gelling systems given in Table 4.1.3. It is clear that increasing salinity reduced the activation energy. Addition of salts lowered the activation energy in an exponential manner. The relationship obtained is $E_a = 25{,}102\exp((-4E-6)TDS)$ with r^2=0.9924.

4.1.3.3 Effect of Mixing Water on the Gelation Time

Gels can be prepared in the field using fresh water, aquifer water or even seawater. These waters have different chemical compositions. Therefore, it is of interest to measure the gelation time for gels prepared in deionized water, field mixing water and seawater (Table 4.1.1). Figure 4.1.9 shows the viscosity evolution for gelling solutions that contained 12.25/0.23 wt% PAtBA/PEI and prepared in the three waters. Viscosity measurements were conducted at 120°C and a shear rate of 8.52 s^{-1}. The gelation time or the gel prepared in deionized water was an hour. The gelation time for the gel prepared in the field mixing water was 1.5 hours. It took nearly three hours or the gel prepared in seawater to start the gelation process. The rate of viscosity buildup was much slower than those noted with the other two waters.

It is clear from the data shown in Figure 4.1.9 that increasing the salt content of the mixing water has resulted in increasing the gelation time and reducing the rate of viscosity build up. These results can be explained as follows. The initial degree of hydrolysis of the polymer is very low (less than 0.1 mol%) and its ester content is nearly 5 mol% (Dalrymple, 2004). At high temperatures, the ester groups will hydrolyze into carboxylate groups (Figure 4.1.2), which carry negative charges.

Table 4.1.3: Activation Energies for Various Gel Systems

Gelling System	Activation Energy, cal/mol
Colloidal Silica (Iler, 1979)	12,000 to 15,000
Colloidal Silica (Jurinak et al., 1991)	16,000 to 20,000
Sodium Silicate/Urea (Nasr-El-Din & Taylor, 2004)	28,800 to 32,200
Polyacrylamide/Cr^{+3} (Jordan et al., 1982)	15,000 to 19,000
Polyacrylamide/Glyoxal (Han et al., 1997)	16,700
PAtBA/PEI (present work)	22,373 to 28,343

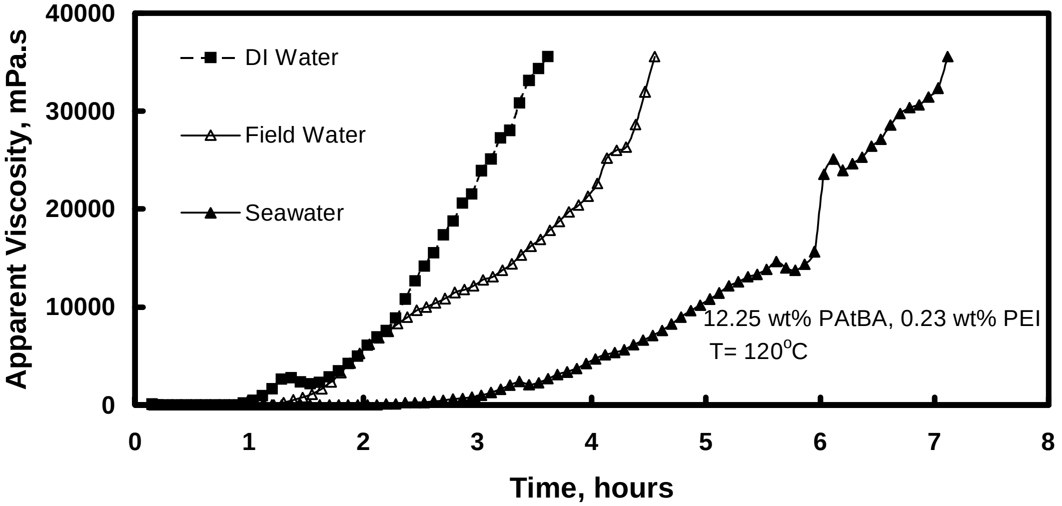


Figure 4.1.9: Viscosity Evolution Using Various Mixing Waters

The repulsive forces between the negative charges will increase the length of the polymer chains. As a result, the carboxylate groups will be more accessible to the cross-linker molecules. This explains the gelation process in deionized water, which started after one hour. On the other hand, the concentrations of mono and divalent cations in seawater are high (Table 4.1.1). These cations shield the negative charges available on the carboxylate groups and, as a result, the polymer chains collapse (Nasr-El-Din et al., 1991; Kontturi et al., 1996). Consequently, the carboxylate groups are no longer available to the cross-linker molecules. The gel in this case will take much longer period of time to form. The most important aspect of the results shown in Figure 4.1.9 is that the gelation time should be measured for gel prepared in the field mixing water. Using different type of water can cause serious errors in determining the gelation time. This can lead to premature gelling during pumping the gelling solution and subsequent operational problems. The gelation time for gelling solutions that contained 12.23 wt% polymer and 0.23 wt% PEI prepared in the field mixing water and seawater was measured as a function of temperatures. Arrhenius-type plots were prepared for these gels as shown in Figure 4.1.8. The activation energy of the gelation reaction in the field mixing water was found to be 27,579 compared to 28,334 cal/mol for the deionized water (Table 4.1.4).

This was also observed for a polyacrylamide/Cr^{+3} system (Jordan et al., 1982). This suggests that salts affect cross-linking chemistry only in terms of an increase in induction period that delays the reaction. Also, we visually observed a difference in the strength of gels prepared in distilled water and those in high salinity waters. That is due to shielding of some of the active cross-linking sites on the polymer chain by cations.

Table 4.1.4: Kinetic Parameters of OCP Gel Using Various Mixing Waters

TDS, mg/l	Activation Energy, cal/mol	Frequency Factor, hours
DI water	28,334	$1 * 10^{-16}$
1,186	27,579	$7 * 10^{-16}$
58,348	22,373	$2 * 10^{-16}$

4.1.3.4 Effect of Monovalent Cations on the Gelation Time

The effect of mixing water on the gelation time was significant. It was decided to examine the effects of mono- and divalent cations on the gelation time separately. Various gelling solutions were prepared and various amounts of sodium chloride were added such that the final polymer and cross-linker concentrations were 12.25 and 0.23 wt%, respectively. The gelation time was measured at 8.52 s^{-1} and a temperature of 120°C. Figure 4.1.10 shows the effect of sodium ion concentration on the gelation time. The gelation time significantly increased by the addition of 5,000 mg/l of sodium ions. The gelation time increased with increasing sodium ion concentration and reached 14 hours at 50,000 mg/l of sodium ions. Figure 4.1.10 also shows that the effect of potassium ion on the gelation time was similar to that of the sodium ions. We noticed that gels prepared in field mixing water and seawater were visually weaker than those prepared in distilled water.

4.1.3.5 Effect of Divalent Cations

The effect of adding divalent cations was also investigated. Figure 4.1.11 shows that Ca^{+2} and Mg^{+2} delayed the cross-linking reaction even more than the K^+ and Na^+. In order to compare monovalent to divalent cations, Figure 4.1.11 is generated where it shows that Ca^{+2} delayed the reaction more than K^+. That was due to the double charge present on Ca^{+2} compared to K^+.

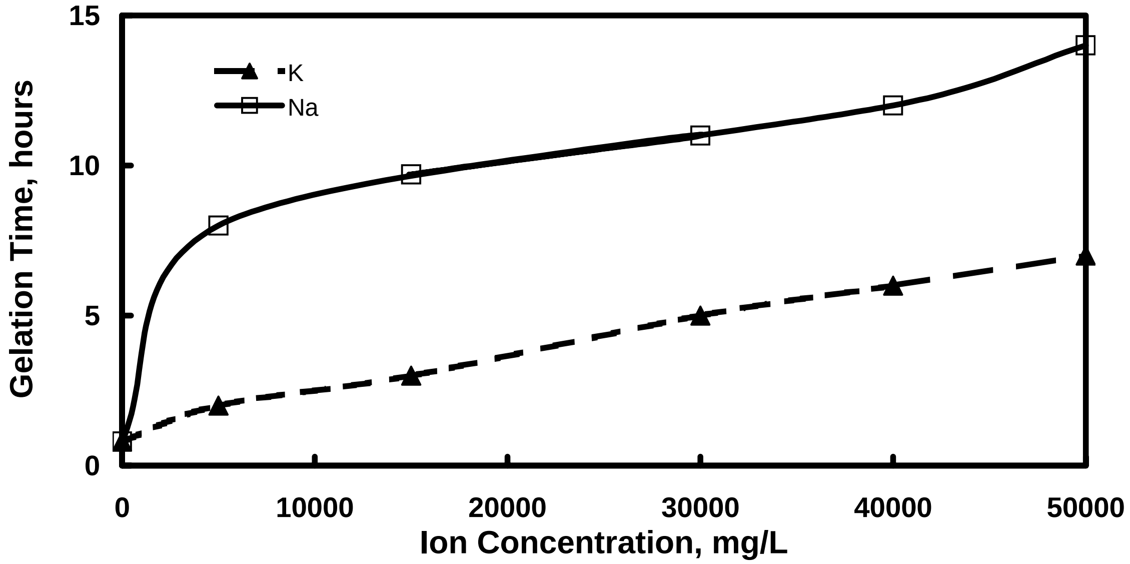


Figure 4.1.10: Effect of Monovalent Cations Concentration on Gelation Time

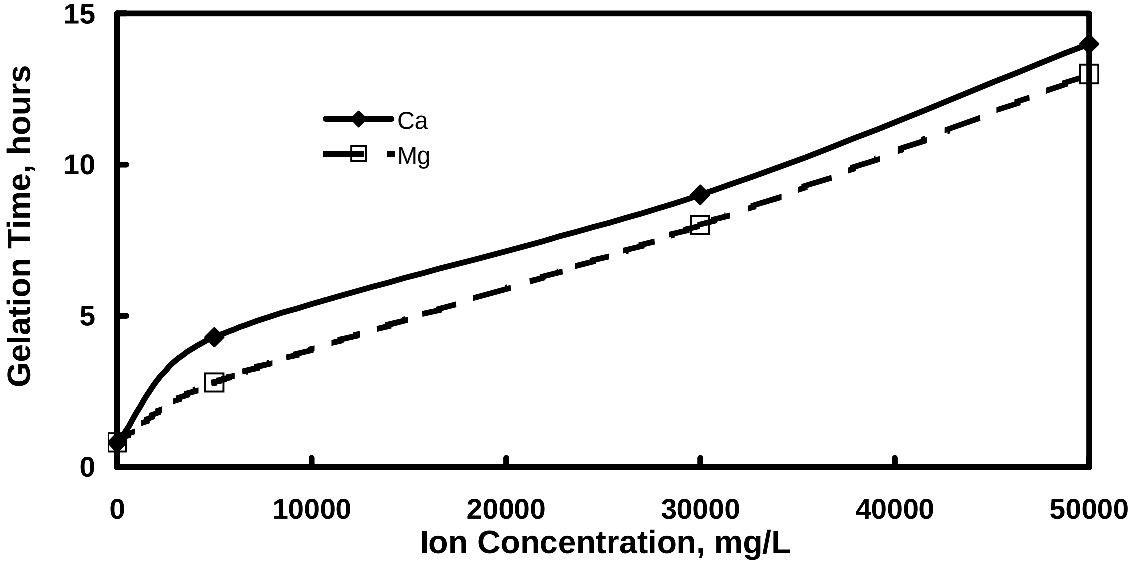


Figure 4.1.11: Effect of Divalent Cations on the Gelation Time

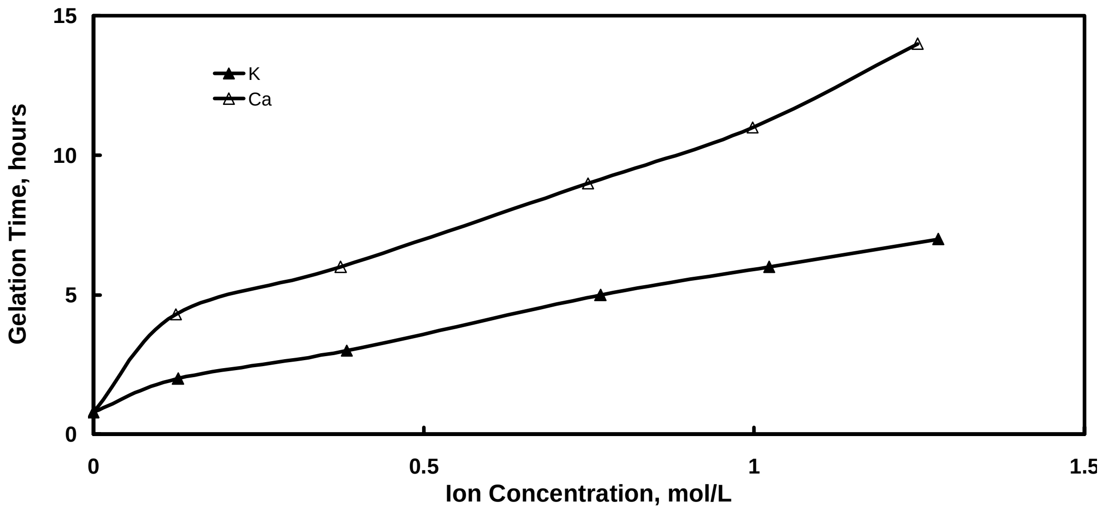


Figure 4.1.12: Comparison of Monovalent to Divalent Cations

4.1.3.6 Effect of Polymer Concentration on the Gelation Time

The effect of polymer concentration was examined by measuring viscosity at different polymer concentrations. Figure 4.1.13 shows viscosity evolution curves for four different polymer concentrations at 120°C with 0.23 wt% PEI prepared in the field mixing water. It can be seen that as polymer concentration increases, the gelation time decreases. Hardy et al. (1999) noted a similar trend at 95°C.

As the polymer concentration increases, the number of carboxylate groups increases, which will increase the rate of gel formation and reduce the gelation time. This behavior is the same as that noted with polyacrylamide/Cr^{+3} gels (Prud'homme et al., 1983). Higher polymer concentrations can eliminate the effects of high salinity levels as shown in Figure 4.1.14.

4.1.3.7 Effect of Cross-linker Concentration on the Gelation Time

Figure 4.1.15 shows the apparent viscosity as a function of time at various cross-linker concentrations and 120°C. These gelling solutions were prepared in the field mixing water with 12.25 wt% PAtBA. Increasing the loading of the cross-linker increases the number of imine groups, and reduces the gelation time.

The gelation time showed an exponential dependence on cross-linker concentration according to GT=0.24 exp(2.6[cross-linker]). Shorter gelation times at higher salinity levels can be obtained by adding more cross-linker as shown in Figure 4.1.14. However, adding too much cross-linker can result in syneresis (Eggert et al., 1992), which is the reduction in

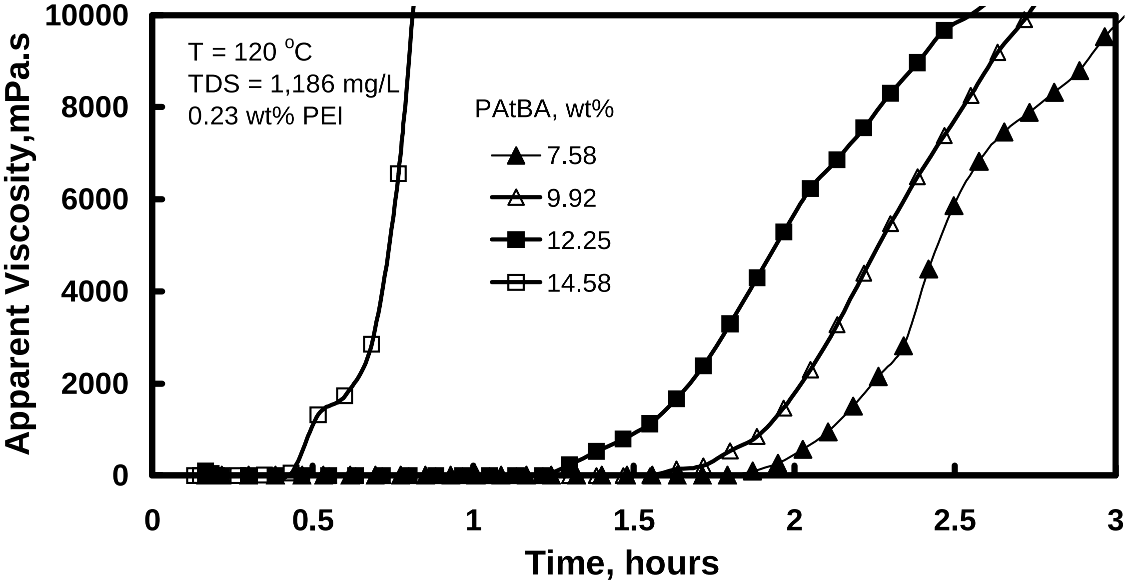


Figure 4.1.13: Viscosity Evolution at Different Polymer Concentrations

gel volume forcing water to leave the structure. Syneresis was noted with all mixing waters at cross-linker concentration of 0.69 wt%. Precipitation occurs with seawater only.

4.1.3.8 Effect of Initial pH on the Gelation Time

Initial pH value is a key factor since it has a strong effect on the polymer hydrolysis. In a field application, the solution pH may change a little due to the presence of contaminants present in mixing tanks.

Also, the solution pH may change upon the contact with the formation. The gelling solutions were prepared as described in the experimental section and the pH was adjusted by adding either 1.0 N NaOH or 15 wt% HCl before loading sample into the viscometer (Figure 4.1.17). Nothing was added to the sample with pH=8.32. Lowering the initial solution pH to 3.05 produced a fast gelation at the beginning represented in a sharp increase in viscosity. After an hour, the viscosity decreased gradually until it reached a plateau of 7,000 mPa.s. The gel formed in this case was weak and easily deformed by shear.

At pH = 8.2, the gelation time was 1.5 hours. The gel formed was a strong one, and did not break by shear. A similar behavior was noted at pH = 11.9. However, the gelation time was more that two hours. This increase in gelation time is most likely due to the presence of sodium ions that were introduced to the gelling solution with the addition of sodium hydroxide. The most important conclusion that can be inferred from these results is that the gelation mechanism depends on the initial pH of the solution.

4.1.3.9 Effect of Mixing Rate on the Gelation Time

In a typical field application, the gel solution is mixed at the surface then pumped into the formation. In order to examine the effect of mixing on the gelation time, gelling solutions

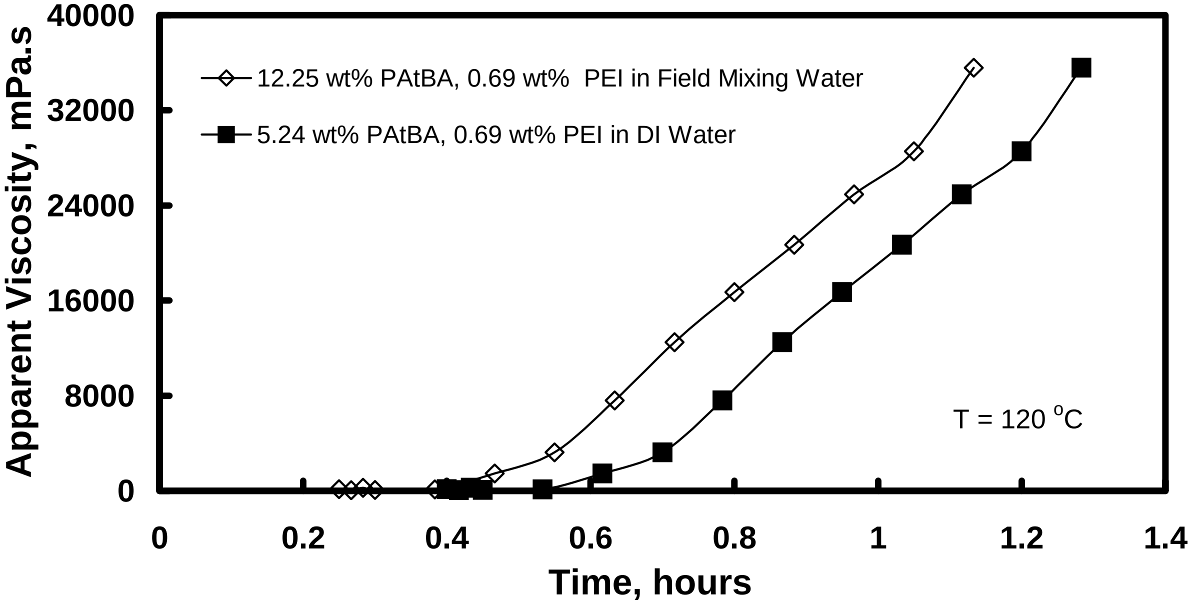


Figure 4.1.14: Elimination of TDS Effects by Adding More Polymer

were prepared at room temperature then, various shear rates were applied for 30 minutes. Finally, the apparent viscosity was measured for each solution at 8.52 s^{-1} after heating to 120°C. Figure 4.1.18 shows the results obtained from these tests. Mixing the gelling solution at high shear rates produced a weak gel in a shorter period time.

This is a strong indication that mixing at higher rates may produce weaker gels due to breakup of network structure.

4.1.3.10 Effect of Contaminants

In a typical field application, the chemicals are mixed in large steel tanks that may contain corrosion products. In order to investigate the effect of contaminants on the gelation time, $FeCl_3.6H_2O$ was added to gelling solutions that contained 12.25 wt% PatBA and 0.23 wt% PEI in distilled water such that the final gel contained 1,000 mg/l of Fe(III), 250 and 100 mg/L. The apparent viscosity was measured as a function of time at 120°C as shown in Figure 4.1.19.

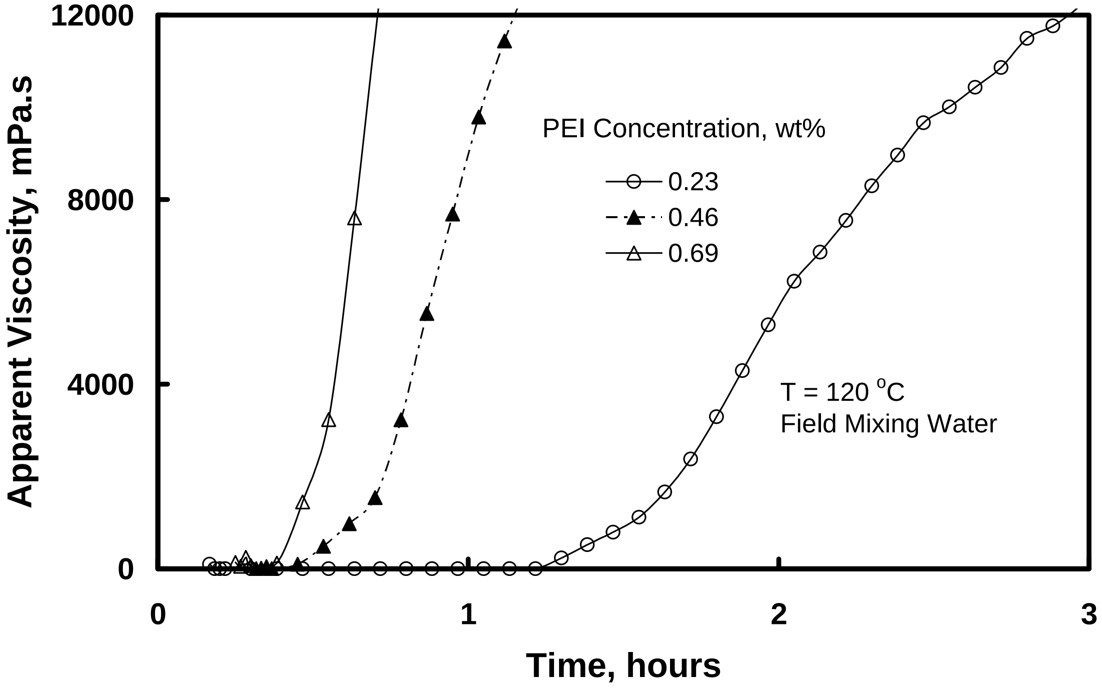


Figure 4.1.15: Effect of cross-linker Concentration on Viscosity Evolution

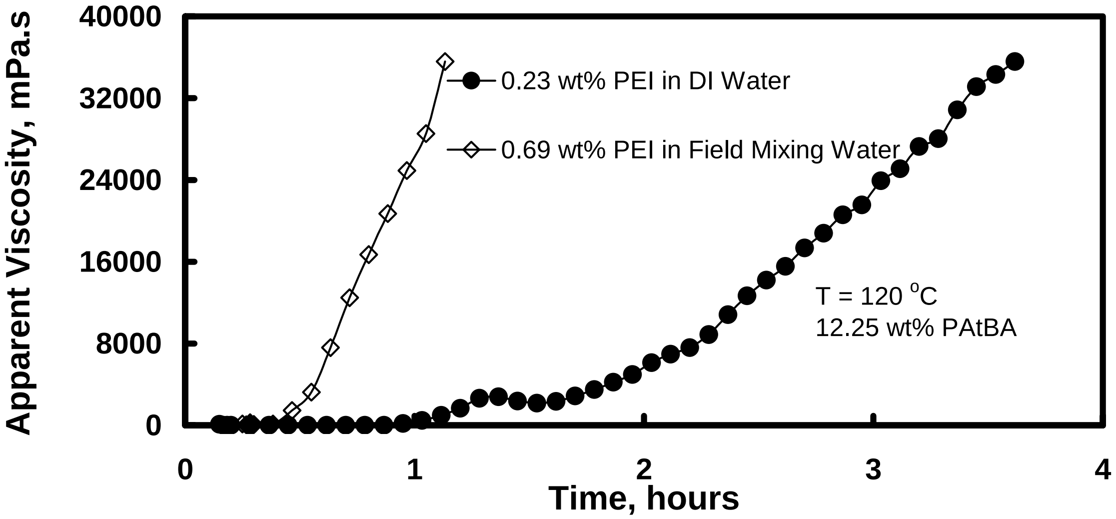


Figure 4.1.16: Elimination of Salinity Effects by Adding More Cross- linker

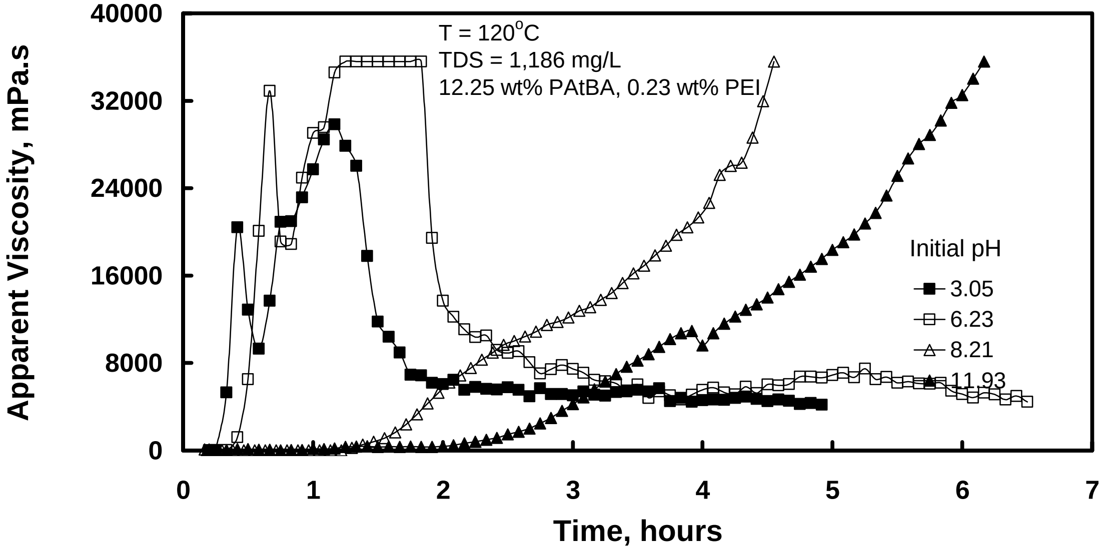


Figure 4.1.17: Effect of Initial pH on Viscosity Evolution

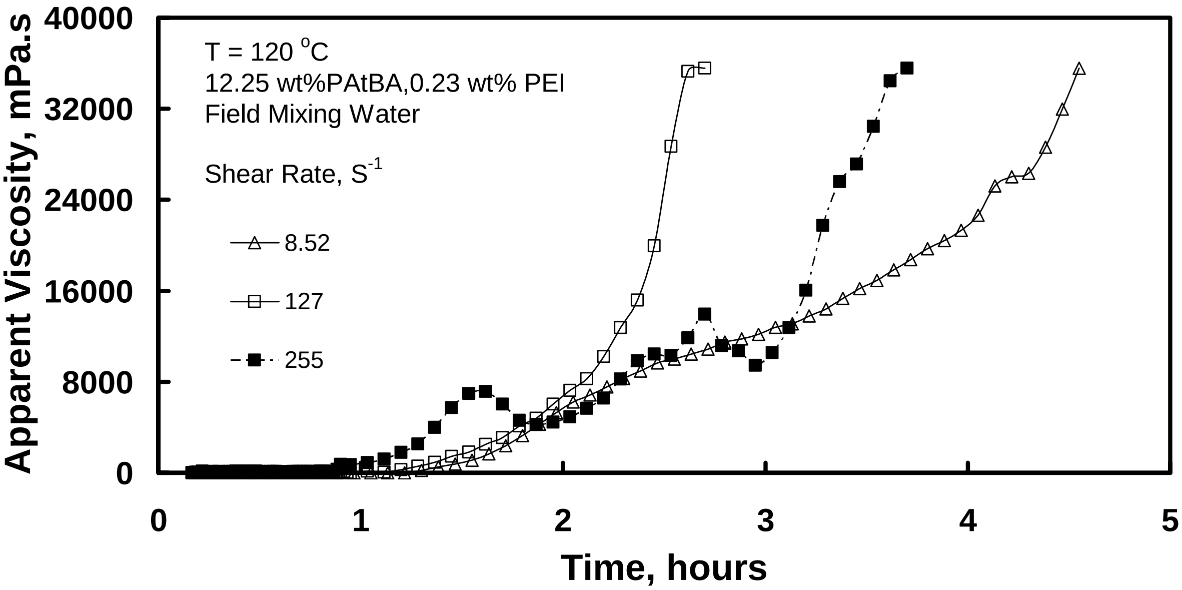


Figure 4.1.18: Viscosity Evolution After Various Preshear Rates in Field Mixing Water

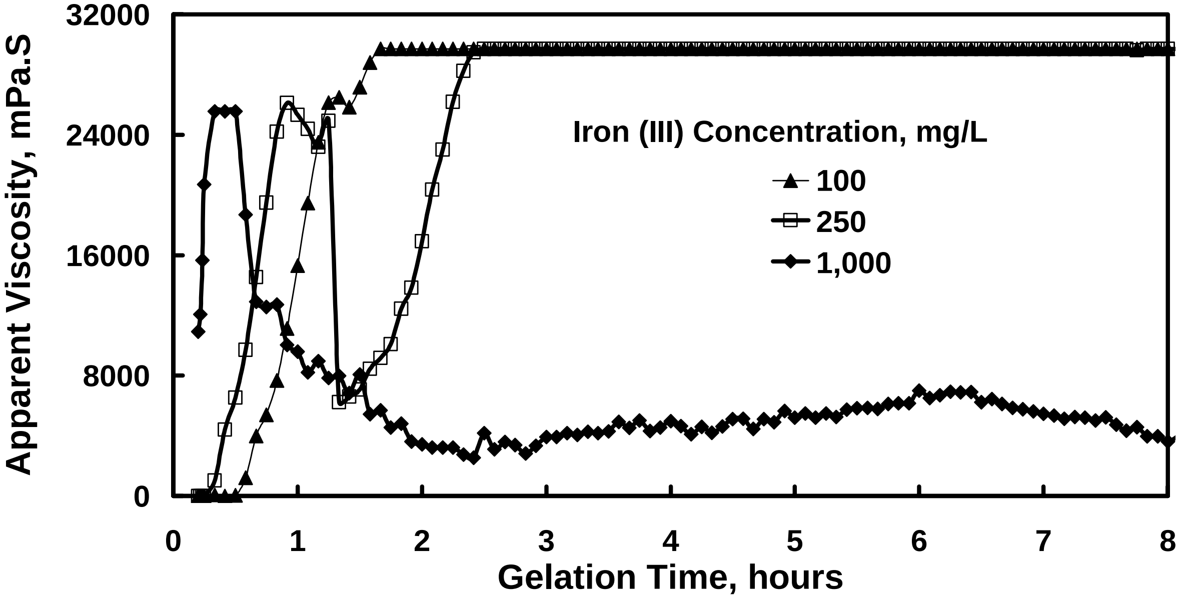


Figure 4.1.19: Viscosity Evolution at Various Iron Concentrations

At 1000 ppm Fe, viscosity built up immediately at room temperature. Then, it broke when heated to 120oC and did not form gel again. This means that Fe(III) strongly shielded active cross-linking sites on the polymer chain. On the other hand, a more stable structure was formed with 100 ppm Fe. It was also possible to produce gel with 250 ppm Fe(III) although it was less stable than the 100 ppm Fe(III) sample. Hence, contaminants in field mixing tanks can cause gel formation at ambient conditions.

4.1.3.11 Compatibility

Gelling solutions (5.25 wt% PAtBA, 0.69 wt% PEI) prepared in seawater formed a precipitate upon heating to 100^{o}C under a pressure of 500 psig for 12 hours. Solids were filtered and then analyzed using XRD technique. The solids were found to contain 97% NaCl and 3% KCl. Scanning electron microscope indicated the formation of calcium carbonate and magnesium oxide.

4.1.4 Conclusions

1. Higher temperatures increased the rate of gel structure formation and hence shorter gelation times were noticed.
2. Activation energy of PAtBA/PEI gelling system was calculated as 28 kcal/mol in deionized water. Addition of salts lowered the activation energry in an exponential manner. The relationship obtained is $E_a = 25{,}102\exp((-4E-6)TDS)$ with r^2=0.9924.
3. The reaction order was within 10% of 5.83. This value is high reflecting the inclusion of rheological, kinetic and molecular weight effects into it.

4. Gelation time was lowered by increasing polymer and/or cross-linker concentration.
5. Gelation time decreased with the increase of the rate of mixing; however, high mixing rates resulted in the breakup of the gel.
6. Salts were found to increase gelation times. Divalent cations have more effect on gelation time than monovalent cations.
7. Initial pH showed a strong influence on the fluid viscosity of the gel. Higher viscosities were obtained at high initial pH values. At acidic conditions, the gels formed were weaker than those at alkaline pH.
8. The presence of high iron concentration (1000 ppm Fe(III)) can will result in an immediate increase in viscosity which will hinder pumping the gelling solution. Moreover, the gel formed will be weak.

4.1.5 Acknowledgments

The authors would like to acknowledge Saudi Aramco for permission to publish this work. Thanks are also due to Ali Al-Aamri for his help some of the experimental work. Members of the Analytical Support Division at the R&DC of Saudi Aramco are appreciated for the analysis of water samples and TGA analysis. Also, the authors would like to acknowledge the support of KFUPM. Mr. E.D. Dalrymple is acknowledged for many useful discussions.

4.1.6 References

Albonico, P., Baritone, M., Lockart, T.P., Causin, E. and Rossoi, E., 1994. New polymer gels for reducing water production in high-temperature reservoirs. SPE 27609 presented at the European Production Operations Conference and Exhibition held in Aberdeen, Scotland, March 15-17.

Alqam, M.H., Nasr-El-Din, H.A. and Lynn, J.D., 2001. Treatment of super k-zones using gelling polymers. SPE 64989 presented at the SPE International Symposium on Oilfield Chemistry held in Houston, TX, February 13-16.

Avery, M.R., Wells, T.A., Chang, P.W. and Millican, J.P., 1998. Field evaluation of a new gelant for water control in production wells. SPE 13201 presented at the Annual Technical Conference and Exhibition held in Houston, TX, October 3-5.

Avrami, M., 1939. Kinetics of phase change. I. General theory. J. Chemical Physics, 7, 1103-12.

Avrami, M., 1940. Kinetics of phase change. II. Transformation-time relations for random distribution of nuclei. J. Chemical Physics, 8, 212-24.

Dalrymple, E.D., 2004, Personnel communication. November 2004.

Eggert, R.W., Willhite, G.P. and Green, D.W., 1992. Experimental measurement of the persistence of permeability reduction in porous media treated with xanthan/Cr(III) gel systems. SPE Res. Eng. J., 7(1) 29-35.

Han, M., Muller, G. and Zaitoun, A., 1997. Gel formation of polyacrylamide in the presence of glyoxal for water control application. Polymer Gels and Networks, 5, 471-480.

Hardy, M.B., Botermans, C.W., Hamouda, A., Valda, J. and John, W., 1999. The first carbonate field application of a new organically cross-linked water shutoff polymer system. SPE 50738 presented at the SPE International Symposium on Oilfield Chemistry held in Houston, TX, February 16-19.

Hardy, M.B., Botermans, C.W. and Smith, P., 1998. New organically cross-linked polymer system provides competent propagation at high temperatures in conformance treatments. SPE 39690 presented at the SPE/DOE Symposium on Improved Oil Recovery held in Tulsa, OK, April 19-22.

Hoek, V., Botermans, C.W. and Zitha, P.L.J., 2001. Full blocking mechanism of polymer gels for water control. SPE 68982 presented at the SPE European Formation Damage Conference held in The Hague, The Netherlands, May 21-22.

Hutchins, R.D., Dovan, H.T. and Sandiford, B.B., 1996. Field applications of high temperature organic gels for water control. SPE 35444 presented at the SPE/DOE Symposium on Improved Oil Recovery held in Tulsa, OK, April 21-24.

Jordan, D.S., Green, D.W., Terry, R.E. and Willhite, G.P., 1982. The effect of temperature on gelation time for polyacrylamide/Cr(III) systems. Soc. Pet. Eng. J., 22(4), 463-471.

Jurinak, J.J., Summers, L.E. and Bennett, K.E., 1991. Oilfield applications of colloidal silica. SPE Prod. Eng. J., 6(4) 406-412.

Kontturi, K., Mafe, S., Manzanares, J.A., Svarfvar, B.L., and Viinikka, 1996. Modeling of the salt and pH effects on the permeability of grafted porous membranes. Macromolecules, 29, 5740-46.

Lockhart, T.P., 1992. A new gelation technology for in-depth placement of Cr^{+3}/polymer gels in high-temperature reservoirs. SPE 24194 presented at the SPE/DOE Eighth Symposium on Enhanced Oil Recovery held in Tulsa, OK, April 22-24

Mijovic, J., Kenny, J.M. and Nicolais, L., 1993. Comparison of kinetic and rheological evaluation of gel time for an amine epoxy system. Polymer, 34 (1) 207-209.

Moffit, P.D., Moradi-Araghi, A., Janway, V.R. and Young, G.R., 1996. Development and field testing of a new low toxicity polymer cross-linking system. SPE 35173 presented at the Permian Basin Oil & Gas Recovery Conference held in Midland, TX, 27-29 March.

Moradi-Araghi, A. and Doe, P., 1987. Hydrolysis and precipitation of polyacrylamides in hard brines at elevated temperatures. SPE Res. Eng. J., 2(2) 189-198.

Moradi-Araghi, A., Bjornson, G. and Doe, P.H., 1993. Thermally stable gels for near-wellbore permeability contrast corrections. Advanced Technology Series, **1,** No.1, 140-145.

Moradi-Araghi, A., 1994. Application of low-toxicity cross-linking systems in production of thermally stable gels. SPE 27826 presented at the SPE/DOE Ninth Symposium on Improved Oil Recovery held in Tulsa, OK, April 17-20.

Moradi-Araghi, A., 2000. A review of thermally stable gels for fluid diversion in petroleum production. J. Pet. Sci. Eng., 26 (1-4) 1-10.

Mortimer, S., Ryan, A.J. and Stanford, J.L. 2001. Rheological behavior and gel-point determination for a model Lewis acid-initiated chain growth epoxy resin. Macromolecules, 34, 2973-80.

Nasr-El-Din, H.A., Taylor, K.C., 2004. Evaluation of sodium silicate/urea gels used for water shut-off treatments. Submitted for publication in J. Pet. Sci. Eng.

Nasr-El-Din, H.A., Al-Driweesh, S.M., Al-Muntasheri, G.A., 2003. Field application of HCl-formic acid system to acid fracture deep gas wells completed with super Cr-13 tubing in Saudi Arabia. SPE 84925 presented at SPE International Improved Oil Recovery Conference held in Kuala Lumpur, Malaysia, 20-21 October.

Nasr-El-Din, H.A., Bitar, G.E., Bou-Khamsin, F.I., Al-Mulhim, A.K. and Hsu, J., 1998. Field application of gelling polymers in Saudi Arabia. SPE 39615 presented at the SPE/DOE Improved Oil Recovery Symposium held in Tulsa, OK, April 19-22.

Nasr-El-Din, H.A., Hawkins, B.F. and Green, K.A., 1991. Viscosity behavior of alkaline, surfactant, polyacrylamide solutions used for enhanced oil recovery. SPE 21028 presented at the SPE Symposium on Oilfield Chemistry held in Anaheim, CA, February 20-22.

Okasha, T.M., Nasr-El-Din, H.A. and Al-Kudair, W.S., 2001. Abatement of water production from upper Permian gas wells in Saudi Arabia using a new polymer treatment. SPE 68152 presented at the SPE Middle East Oil Show held in Bahrain, March 17-20.

Prud'homme, R.K., Jonathan, U., Poinsatte, J.P. and Halverson, F., 1983. Rheological monitoring of the formation of polyacrylamide/Cr^{+3} gels. Soc. Pet. Eng. J., 23(5) 804-808.

Reddy, B.R., Eoff, L., Dalrymple, E.D. and Brown, D., 2003. Natural polymer-based compositions designed for use in conformance gel systems. SPE paper 84510 presented at the SPE Annual Technical Conference and Exhibition held in Denver, CO, October 5-8.

Seright, R.S., Lane, R.H. and Sydansk, R.D., 2003. A strategy for attacking excess water production. SPE Prod. Fac. J., 18(3) 158-169.

Stahl, G.A. and Schulz, D.N., 1998. Water-soluble polymers for petroleum recovery. Plenum Press, New York, 299-312.

Stavland, A. and Jonsbraten, H.C., 1996. New insight into aluminum citrate/polyacrylamide gels for fluid control. SPE 35381 presented at the Tenth SPE/DOE Symposium on Improved Oil Recovery held in Tulsa, OK, April 21-24.

Sydansk, R.D., 1990. Acrylamide-polymer/chromium (III)-carboxylate gels for near wellbore matrix treatments. SPE 20214 presented at the SPE/DOE Symposium on Enhanced Oil Recovery, Tulsa, OK, April 22-25.

Taylor, K. and Nasr-El-Din, H.A. 1994. Acrylamide copolymers: A review of methods for the determination of concentration and degree of hydrolysis, J. Pet. Sci. Eng., 12, 9-23.

Terry, R.E., Huang, C.G., Green, D.W., Michnick, M.J., and Willhite, G.P., 1981. Correlation of gelation times for polymer solutions used as sweep improvement agents. SPEJ, 21(2) 229-235.

Vasquez, J., Civan, F., Shaw, T.M., Dalrymple, E.D., Eoff, L. Reddy, B.R. and Brown, D., 2003. Laboratory evaluation of high-temperature conformance polymer systems. In: SPE 80904 presented at the SPE Production and Operations Symposium held in Oklahoma City, OK, 22-25 March.

Ward, J.S. and Martin, F.D., 1981. Prediction of viscosity for partially hydrolyzed polyacrylamide solutions in the presence of calcium and magnesium ions. Soc. Pet. Eng. J., 21(5) 623-631.

Zitha, P.L.J., Botermans, C.W., v.d. Hoek, J. and Vermolen, F.J., 2002. Control of flow through porous media using polymer gels. J. Applied Physics, 92 (2) 1143-1153.

4.2 Viscoelastic Properties of an Organically Cross-linked Water Shut-Off Polymeric Gel

4.2.1 Abtsract

This is the first study that investigates the viscoelastic properties of an organically cross-linked polymeric gel used in water shut-off treatments. A copolymer of acrylamide and t-butyl acrylate was cross-linked with polyethylene imine. The effect of various parameters was also addressed. It was observed that the increase in salt concentration reduces the gel ultimate elasticity. Also, the increase in cross-linker concentration was found to enhance the elastic nature of the gel. A maximum elastic modulus of 3.4 kPa was achieved with a polymer concentration of 12.25 wt% and a cross-linker concentration of 0.92 wt%. However, higher concentrations of cross-linker reduced the final gel strength. The gelation temperature was found to influence the cross linking mechanism of this system. It was observed that below 100^{o}C, the gel network was weak and its strength showed substantial increase at temperatures higher than 120^{o}C. It is postulated that the removal of the ester group is the main reason for this increase. The gel lost 53% of its elastic modulus after one month of ageing at 150^{o}C, which is typical of local reservoirs.

4.2.2 Introduction

Polymeric gels are obtained by cross-linking high and/or low molecular weight polymers with a suitable cross-linker. Recent work showed that a combination of both levels can enhance the mechanical and thermal properties of the gel (Sydansk et al., 2004). These materials exhibit a wide range of rheological properties. This makes them suitable for a variety of applications including controlled drug recovery, soft contact lenses and gelatin foods (Kesavan et al., 1992). In the oil industry, larger water handling facilities are needed when water cut in produced oil and gas increases. This may reach to a level where production from a certain well is no longer economical. Gels are utilized to minimize this water production. They are injected as a solution and then cross-linked at reservoir conditions into a 3-D structure. This structure should be strong enough to withstand the high reservoir temperatures and pressure gradients. Partially hydrolyzed polyacryalmides (PHPA) are the most widely applied type of polymeric gels. They can be cross-linked either organically or inorganically. Organically cross-linked polymers are known to have a higher thermal stability (Hardey et al., 1998). Rheological testing of water shut-off gels was reported in the literature from two aspects. The first aspect is the kinetics study in which the time needed to form the 3-D structure is measured; hence, gelation parameters are extracted. This is done by both steady shear measurements (Al-Muntasheri et al., 2004) and oscillatory shear measurements (Prud'homme et al., 1983). The other aspect is the measurement of the gel strength. This is done via testing the gel ability to reduce permeability of treated cores using core flooding experiments (Okasha et al., 2001; Reddy et al., 2003; Vasquez et al., 2003). The elastic properties were obtained using dynamic rheological measurements (Liu et al., 2000 & Nijenhuis et al., 2002).

A copolymer of acrylamide and t-butyl acrylate (PAtBA) cross-linked with polyethylene imine (PEI) was used in this study. It was chosen for its stability at high temperatures and its low toxicity (Hardy et al., 1998). Experimental investigation of this system was previously reported in the literature. Hoek et al. (2001) conducted core flooding experiments with this gel and a reduction in permeability was reported. Also, the gel got displaced from the porous medium when the applied pressure drops exceeded a critical pressure (the pressure at which the gel starts to yield). When the permeability of the cores (porous rock) increases, lower pressure drops are needed to yield the gel. At low polymer concentrations, no polymer adsorption was observed. These observations were made for sandstone cores with clay content ranging from 0.9 to 7.3 wt%.

Alqam et al. (2001) tested the ability of these gels to reduce permeability of fractured cores. Their results on carbonate core showed a reduction in permeability from 2,116 to 0.135 mD at 200°F and 3,500 psi. The gel strength was found to increase with increasing gel age. Zitha et al. (2002) performed theoretical analysis of the yield behavior of this type of gels. Their study focused on the displacement of the gel from the porous media as a three-stage process. First, the compression of the porous media and the gel was analyzed. Then, the microscopic flow within the gel system before the yield point was addressed. Finally, the macroscopic flow beyond the yield point during which gel displacement occurs was examined. The theoretical work was compared to the experimental data of Hoek et al. (2001). They found that the critical yield stress scales like the square root of the energy of the cross-links, which is represented mathematically as follows:

$$P_c \approx \frac{\sqrt{n\varepsilon Y l_0}}{R^2} \tag{4.2.1}$$

where P_c = critical yield pressure
n = number of cross-links in a gel sample
ε = energy to break a single crosslink
Y = Young modulus
l_o = cylinderical pore length

During the gel compression stage, the pressure was found to increase exponentially. Also, gel strength was a function of gel composition, temperature, and water TDS. The objective of this study is to investigate the effect of different parameters on the viscoelastic properties of this system. These parameters include: salinity, gel composition, temperature, and gel age. It should be noted that most of the literature on the system under investigation was limited to conference publications of the Society of Petroleum Engineers.

4.2.3 Experimental Procedures

4.2.3.1 Dynamic Mechanical Analysis

In the oil industry, steady shear viscosity is usually measured in couette geometry. However, steady shear measurements are not good for the analysis of rheological behavior of structured viscoelastic fluids. The steady shear data produced from such methods is impossible to reproduce (Clarket, 1979). This irreproducibility is due to a couple of reasons. The first is the Weissenberg effect, which is known as die-swell effect. This phenomenon is simply a fluid climbing up a rotating shaft (climbing out of the containing cup). This is due to the presence of normal stresses generated in the fluid. In other words, the presence of tension forces in the tangential direction pulls the fluid towards the rotating rod overcoming the centrifugal force (Bird et al., 2002). The other reason why simple steady shear measurements are not reproducible, if used to predict the rheological behavior of such viscoelastic fluids, is the resistance of the fluid to flow created by the semi-structured nature of a cross-linked fluid. Researchers since late 70s and till now (Clark, 1979; Liu et al. 2000) used dynamic mechanical analysis (DMA) techniques for rheological studies of viscoelastic fluids.

In the DMA technique, a sinusoidal shear strain (or shear stress) is applied and the resulting stress (or strain) is measured. The use of these oscillatory rheological measurements was reported in the literature to monitor the gelation without affecting the

3-D structure of the gel and to minimize effects on cross-linking rates (Prud'homme et al., 1983). In controlled strain rheometers, the governing equation of applied strain, γ, is

$$\gamma = \gamma_0 sin(\omega t) \tag{4.2.2}$$

where γ_0 is the shear strain amplitude applied while ω is the frequency of the strain wave. The measured stress wave τ is described by:

$$\tau = \tau_0 sin(\omega t + \delta) \tag{4.2.3}$$

where the phase angle δ is zero for elastic solid and 90^o for a Newtonian fluid. Hence, whenever the tested material is viscoelastic, the phase angle will lie between zero and 90^o. In the case of a controlled stress rheometer, stress is applied and strain is then measured. The expressions for the applied stress and the measured strain are similar to equations 2 and 3, respectively. For the sake of analysis, the stress wave is usually separated into two waves with the same frequency. One of those two waves is the elastic component, τ', which is in phase with the strain wave. The second wave is the viscous component wave, τ'', which is 90^o out-of-phase.

The elastic modulus, G', is defined by the following equation:

$$G' = \frac{\tau'_0}{\gamma_0} \tag{4.2.4}$$

where τ'_0 is the maximum component of the elastic stress.

The loss modulus, G'', is defined as follows

$$G'' = \frac{\tau''_0}{\gamma_0} \tag{4.2.5}$$

G' and G'' are related to the phase angle through the following equation:

$$tan(\delta) = \frac{G''}{G'} \quad (4.2.6)$$

The complex modulus, $|G^*|$ is defined by:

$$|G^*| = \sqrt{G''^2 + G'^2} = \tau_0 / \gamma_0 = \eta^* \omega \quad (4.2.7)$$

where η^* is the complex viscosity which is related to the dynamic viscosity, η', and η'' by:

$$\eta^* = \sqrt{\eta' + \eta''} \quad (4.2.8)$$

4.2.3.2 Materials

Properties of the polymer and the cross-linker are shown in Table 4.2.1. Detailed discussion about the chemistry of this system is reported elsewhere (Morgan et al., 1997; Hardy et al., 1998 & 1999). Basically, the ester group on the t-butyl acrylate provides a mask that breaks at high temperatures. This breakage will produce cross-linking sites on the polymer chain. Field water was filtered using 0.45 μm filter papers.

Chemical analysis and physical properties of these waters are given in Table 2. Laboratory brines were prepared by dissolving the needed amounts of salts in deionized water. $MgCl_2.6H_2O$, KCl, NaCl and $CaCl_2.2H_2O$ salts were used to prepare synthetic lab brines. All salts were ACS grade. All samples were prepared in filtered field water, unless otherwise stated.

Table 4.2.1: Properties of the Polymer and Cross-linker

Variable	Polymer	Cross-linker
pH	3	12
Specific gravity	1.06	1.05
Active content, wt%	35	23

Table 4.2.2: Chemical Analysis of Field Mixing Water

Parameter	Field Water
Ca	126
Mg	53
Na	228
K	14
Cl	361
SO_4	233
CO_3	171
TDS^2	1,186
pH	7.8

In addition, all gelants were prepared at room temperature. Then, the samples were transferred to a high temperature high pressure cell. No stirring was applied while heating the samples in the cell. Finally, dynamic shear measurements were performed at room temperature using ARES rheometer. All samples were given the same thermal history and then tested under the same conditions. The active content of the polymer and the cross-linker was measured by TGA as 35 and 23 wt%, respectively. All solutions were prepared by adding the polymer to the mixing water while applying gentle stirring. Then, the cross-linker was added drop wise while stirring fast enough for micro gels not to form and without entrapping gas bubbles.

All concentrations are reported in wt% of active material in the gelant solution. Gelation experiments were conducted in a high temperature high pressure cell (batch reactor) at 150^{o}C. After sample loading, nitrogen gas was used to pressurize the system to 500 psig for 12 hours and the temperature was kept at 150^{o}C using a temperature controller. The sample volume was 30 mL.

4.2.3.3 Instrument

All rheological measurements were performed in a controlled strain ARES rheometer equipped with a force rebalance transducer (0.02-1000 g.cm torque). Frequency sweep tests were performed in the range 0.1 to 100 rad/s on 25 mm dia cone and plate geometry. The cone angle was 1^{o} and the truncated gap was 48 μm. All tests were conducted at room temperature (23.5^{o}C). Gelled samples were placed on the lower plate and the upper plate was brought slowly to the 48 μm gap. Dynamic measurements were performed at 5% strain at which the material response was in the linear viscoelastic range.

4.2.4 Results and Discussion

4.2.4.1 Effect of Polymer Concentration

Figure 4.2.1 shows the elastic modulus, G', measured in the frequency range ω= 0.1-100 rad/s. These measurements were conducted on gelled samples containing polymer concentrations of 12.25, 9.92, 7.58 and 5.24 wt%. In order to simulate field conditions, filtered field water was used to prepare these solutions. In general, gels with higher polymer concentrations exhibited higher values of G'. The highest polymer concentration produced the highest G' value (500-700 Pa depending on ω). This value is much higher than those reported in the literature for other water shut-off systems (Liu et al., 2000, Thurston et al., 1985 & Kakadjian et al., 1999). The maximum G' value reported by Kakadjian et al. (1999) for a HPAM/Cr^{+3} acetate, with sodium lactate as a retarder, was 210 Pa. This indicates the unique elastic nature of this organically cross-linked system.

On the other hand, G' is a very weak function of ω since it showed a plateau over a wide range of ω. This indicates the rubbery nature of these materials (Macosko, 1994). Also, similar behavior is previously reported by other researchers for polymeric gels (Liu et al., 2000; Grattoni et al., 2000; Kakadjian et al., 1999; Prud'homme et al., 1983 & Thurston et al., 1985) .The slope of log G' vs. log ω was less than 2 for all samples. This value is a characteristic of a cross-linked network (Nijenhuis et al., 2003).

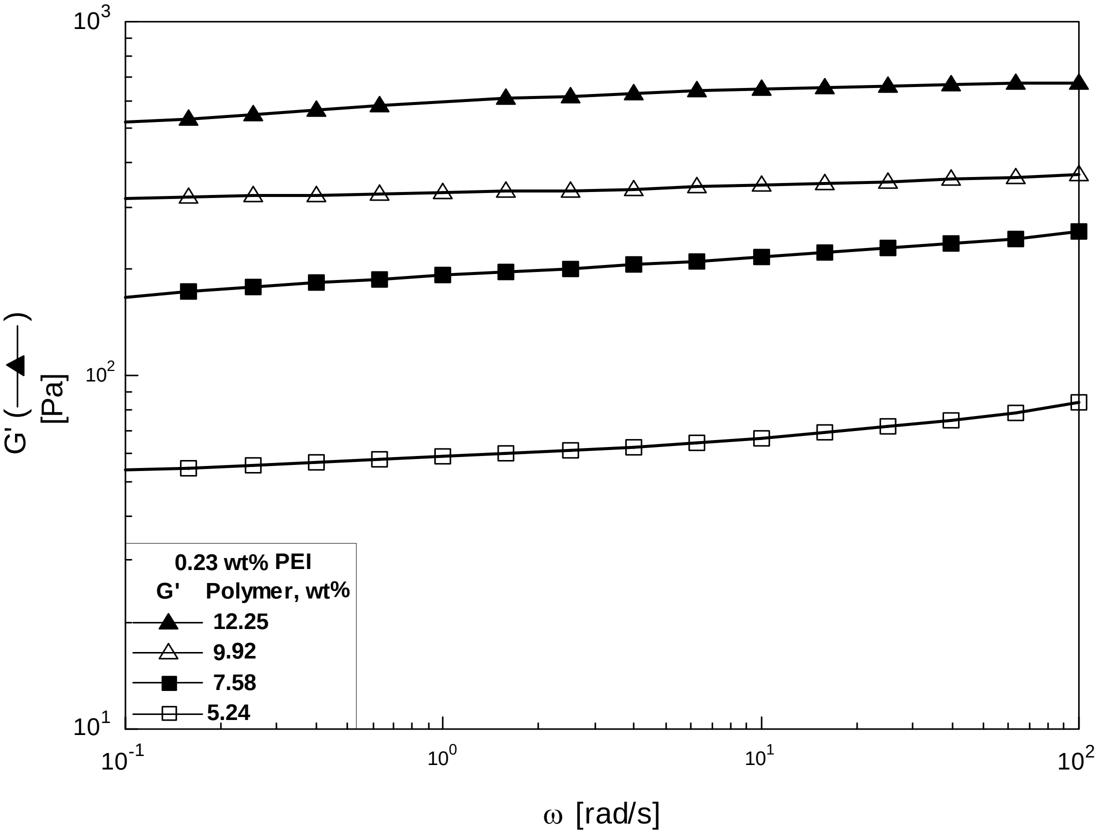


Figure 4.2.1: Frequency Sweep for Different Polymer Concentrations

Also, G' values were larger than G'' over the whole ω-range as shown from Figure 4.2.2. This suggests the formation of a gel network (Michon et al., 1993). The unusual trend for the 12.25 wt% polymer sample in Figure 4.2.2 is due to the high values of G'' at low ω as will be discussed later. This high polymer concentration sample was more sensitive to ω than all other samples.

The previous discussion confirms the formation of an elastic rubbery 3-D structure of rubbery nature and is of a very high elasticity in comparison to other systems.

The data for G'' at different polymer concentrations are given in Figure 4.2.3. G'' was found to increase with polymer concentration especially at low ω. These differences are minimized at higher ω.

At the lowest polymer concentration used in this study (5.24 %), G' showed a different dependency on ω. At the same time, G' values for this concentration were significantly lower than the 7.58 % case. This is unlike the noted trend of samples with 12.25 and 9.92 % polymer concentration. This suggests that the intensity of cross-links is the lowest at this level of polymer concentration. Figure 4.2.4 shows the equilibrium elastic modulus, G_e, and G'' as a function of polymer concentration extracted from Figures 4.2.1 and 4.2.3, respectively. G_e is defined as the plateau modulus. There is a strong dependence of both G_e and G'' on polymer concentration.

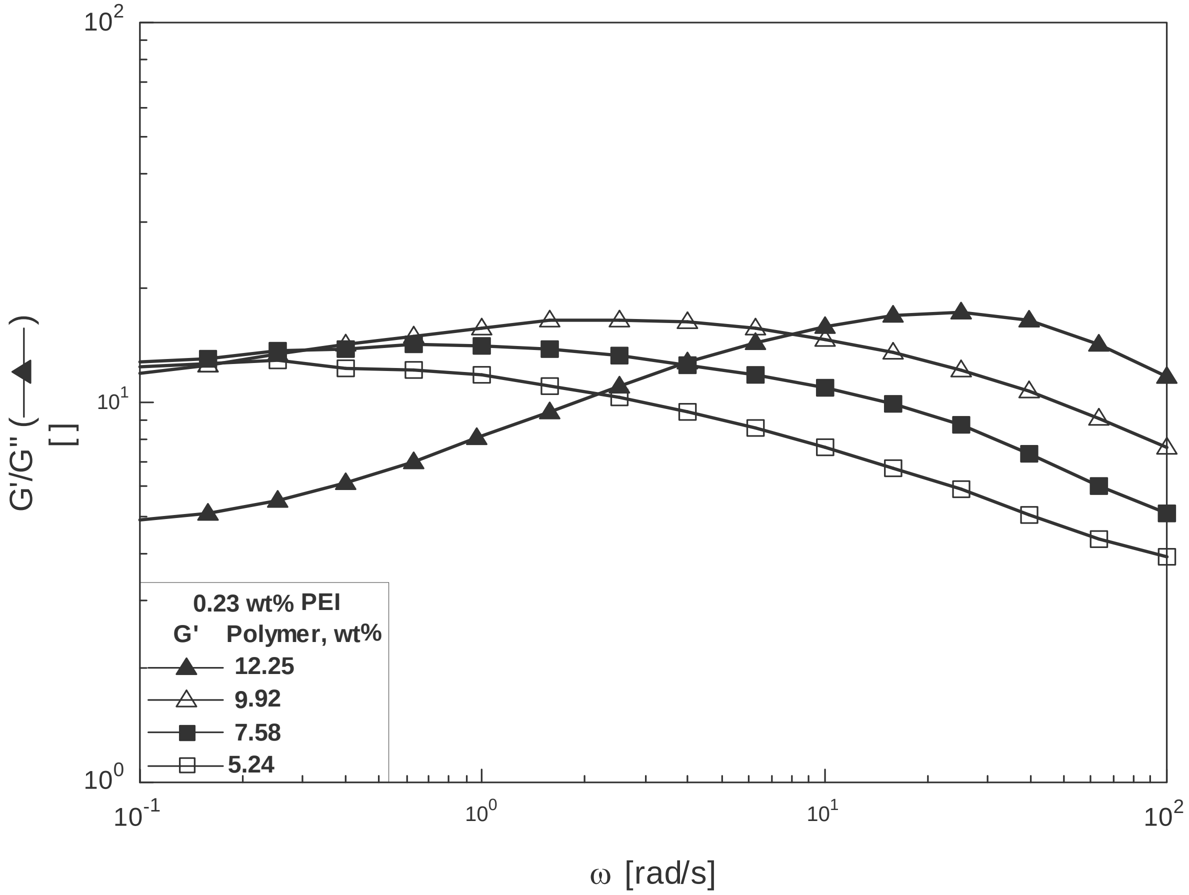


Figure 4.2.2: G'/G'' data as a function of frequency for samples with different polymer concentrations

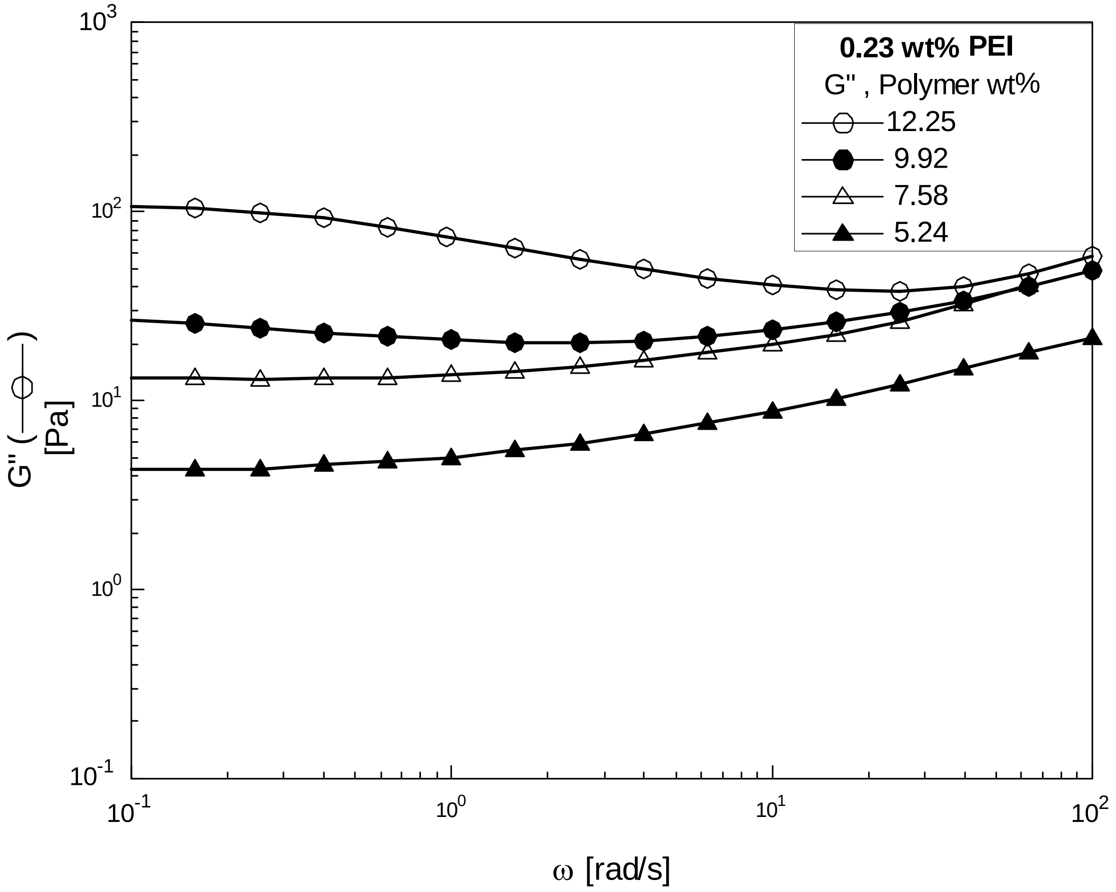


Figure 4.2.3: Effect of polymer concentration on loss modulus

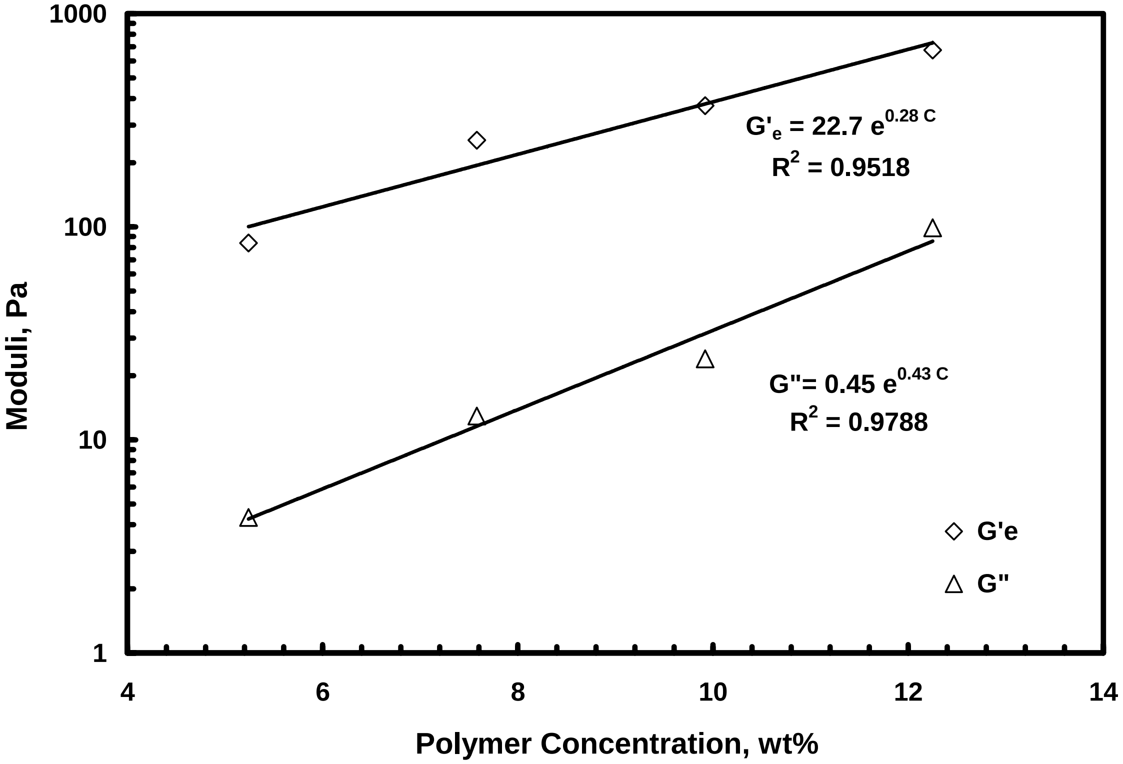


Figure 4.2.4: Equilibrium storage modulus as a function of polymer concentration (ω=0.3 rad/s)

4.2.4.2 Effect of Cross-linker Concentration

Figure 4.2.5 shows equilibrium storage modulus as a function of cross-linker concentration. Namely, 0.23, 0.46, 0.69 and 0.92 % of cross-linker were used. Samples were prepared according to the procedure outlined in the experimental section. All data were typical for rubbery like materials since G' values were independent of ω. G' increased with increasing cross-linker concentration. The maximum G' value was 3.4 kPa measured for the sample with the 0.92 wt% cross-linker. This is more than four times larger than G' for the 0.23 wt% polymer sample.

Therefore, addition of cross-linker results in a proportional increase in the gel elastic nature. However, it is well known that too much cross-linker can lead to syneresis. Syneresis is defined as repulsion of water out of gel structure due to shrinkage in gel volume resulted from over-cross-linking (Moradi-Araghi and Doe, 1984). We visually observed that the sample with the highest cross-linker content was very elastic but had the lowest degree of physical strength (rigid). However, the behavior of this gel in porous media upon compression in real field applications is not yet known.

4.2.4.3 Effect of Gel Age

Figure 4.2.6 shows the equilibrium storage modulus values obtained from frequency sweep tests vs. the gel age for samples containing 12.25% polymer, and 0.23% cross-linker prepared in field mixing water and aged at 150^{o}C. The ageing time (time during which gelling solution was kept at 150^{o}C), was varied from 12 hours to one month.

$G_e^{'}$ decreased with time in an exponential way. The gel lost 53% of its elastic storage modulus after heating for one month; however, the gel has almost stabilized at this value in the first 4 days. The effect of gel age on $G_e^{'}$ diminishes after one month. The storage modulus reached a plateau of 310 Pa**.** However, this is still higher than what was previously published (210 Pa at 25°C by Kakadajian et al., 1999) for water shut-off gelling systems (Liu et al., 2000; Grattoni et al., 2000; Kakadjian et al., 1999; Prud'homme et al., 1983 & Thurston et al., 1985). It is clear that the decay was fast in the first four days, where the gel lost about half of its strength. The gel ageing behavior was well fitted with the relationship $G_e^{'} = 304.91\ e^{\frac{-t}{9.52}}$. The time constant for this process is 9.52 hours.

4.2.4.4 Effect of Gelation Temperature

Four gelling solutions were prepared using field mixing water with 12.25 wt% polymer, 0.23 wt% cross-linker and aged for 12 hours. The ageing temperatures were 100°, 120°, 130° and 150°C. The elastic modulus increased with the increase in temperature as shown in Figure 4.2.7.

This is explained by the fact that the rate of cross-links formation increases due to temperature. It should be noted that the elastic modulus increased by almost a factor of 6 upon heating from 100 to 120°C. This indicates that the cross-linking mechanism of the gel at 100°C is different from that at 120°C. This is likely due to the thermolysis of the ester group on the copolymer chain (Hardy et al., 1998). Our results suggest that this temperature is likely between 100°C and 120°C. Therefore, at 100°C the cross-linking sites were produced due to polymer hydrolysis only. On the other hand, at 120°C, the breakage of the ester group created more sites for cross-linking.

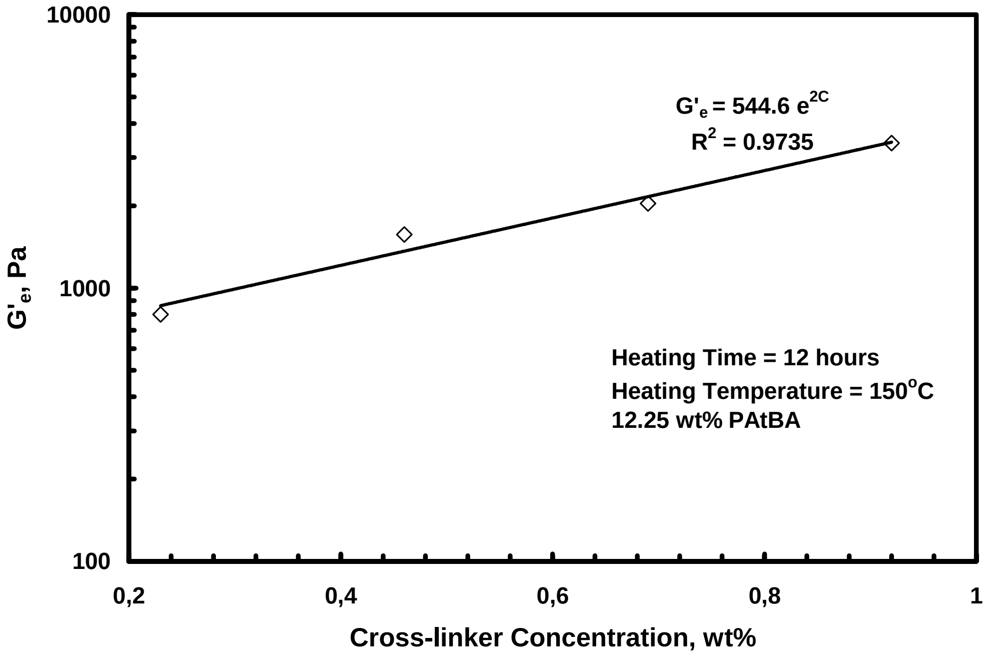


Figure 4.2.5: Equilibrium storage modulus as a function of cross-linker concentration (ω=0.3 rad/s)

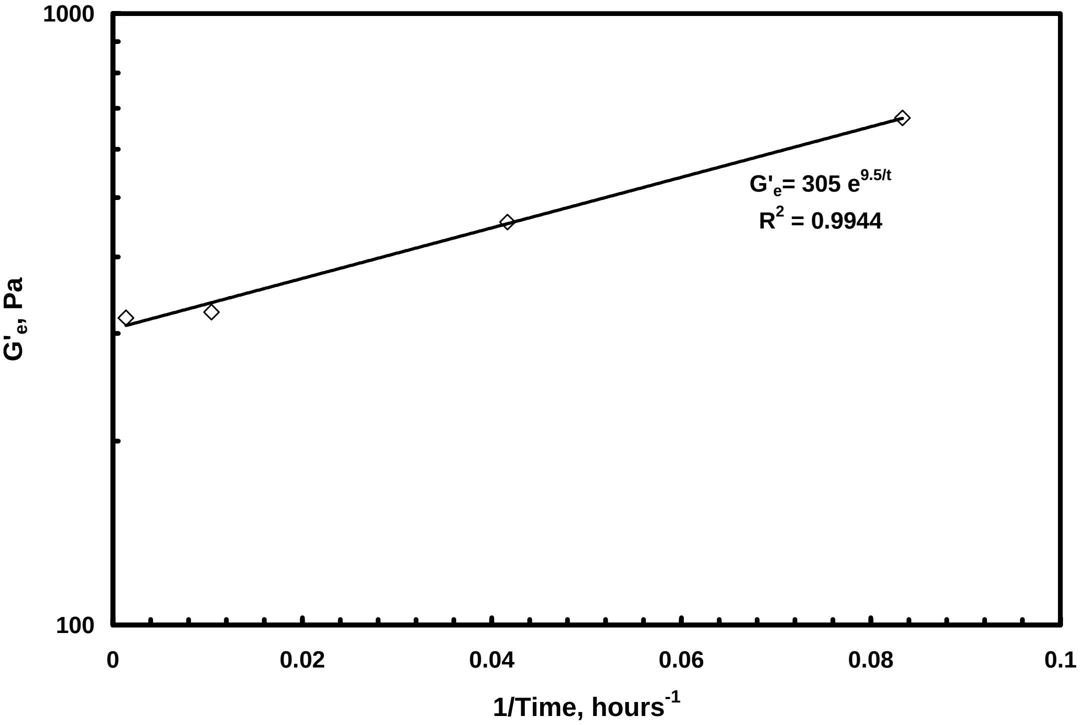


Figure 4.2.6: Equilibrium storage modulus as a function of gel age (ω=0.3 rad/s)

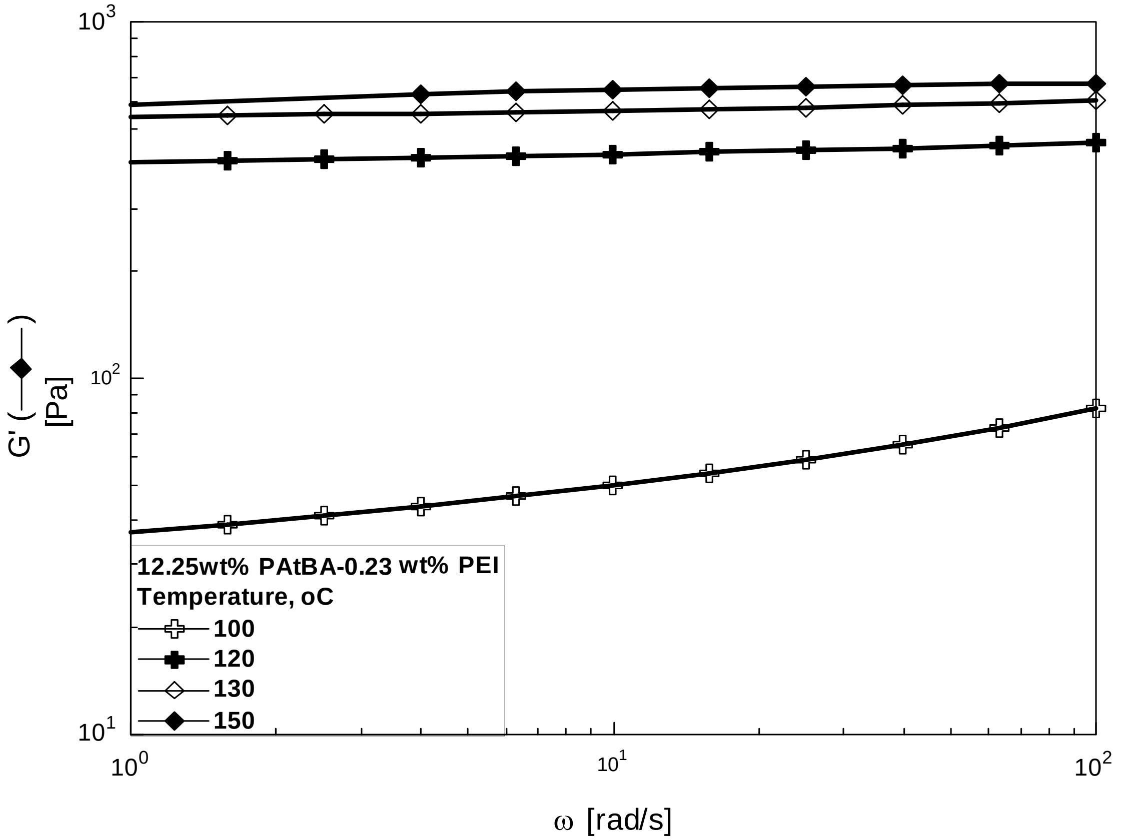


Figure 4.2.7: Equilibrium storage modulus as a function of ageing temperature (ω=0.3 rad/s)

This observation was also noted in a previous work by our group (Al-Muntasheri et al., 2004). We suggested that the temperature was below 100^{o}C and higher than 80^{o}C. The breakage of the ester group at a higher temperature in this case is likely due to the absence of shear during the gelation reaction. Hence, it is likely that the combined effect of shear and temperature enhances the breakage of the ester group and shear might have reduced that temperature.

Also, G' at a constant frequency was plotted in Figure 4.2.8 as a function of the reciprocal of temperature (1/T, K^{-1}). $G_e^{'}$ at 120^{o}, 130^{o} and 150^{o}C, was found to follow Arrhenius behavior($G_e^{'} = c_1 e^{-E/RT}$). The activation energy for this gelation process is 1,089 cal/mol and the pre-exponent is 3,916 Pa. It is clear that the gelation at 100^{o}C follows a different mechanism since it does not fit the Arrhenius behavior followed by data obtained at temperatures above100^{o}C.

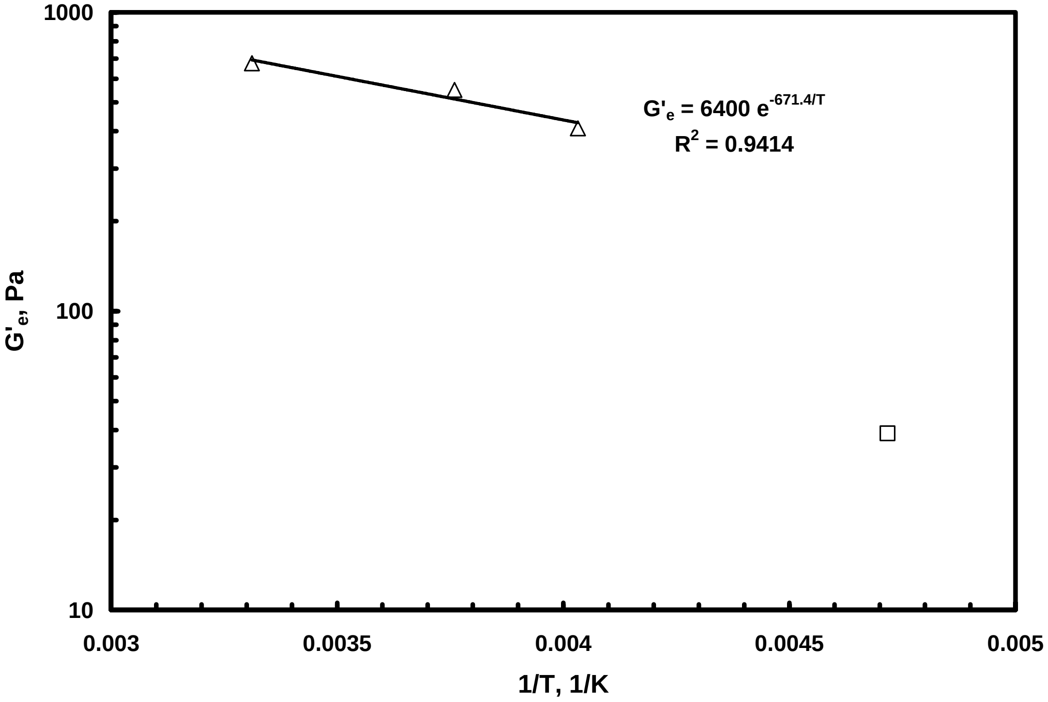


Figure 4.2.8: Fitting of equilibrium storage modulus with ageing temperature (ω=0.3 rad/s)

4.2.4.5 Effect of Salinity

In order to examine the effect of different cations on the elastic behavior of this system, samples containing different amounts of salts were prepared. Figure 4.2.9 shows the equilibrium elastic modulus values for samples containing salt concentrations of 0, 5000 and 50,000 mg/L of Na and K. Samples prepared in deionized water had the maximum storage modulus. Then, the elastic modulus decreased with the increase of the concentration of monovalent. The intensity of cross-links was lowered due to the presence of cations. It was suggested that some of the active cross-linking sites were blocked by these cations. Also, the addition of potassium has resulted in larger values of G_e' compared to those of sodium ion.

This is because of the higher atomic number of potassium; hence, for the same mass concentration, the number of moles of K is lower by a factor of 39/23 (1.7). So, this explains the high elastic modulus of solutions containing K cations. However, the influence of salt diminishes at high concentrations. So, the molar concentration of the salt is not the only factor that controls the elastic modulus and the type of cation is also important. The number of active sites for cross-linking by PEI is inversely proportional to the number of moles (not mass) of the chemical species (K or Na). So, for the same mass concentration of Na and K, the equilibrium modulus, $G_e^{'}$, was higher for K, by a factor of 1.25 at 5,000 mg/L, where less active sites were blocked.

It should be noted that field mixing water had a lower equilibrium elastic modulus, 675 Pa, than the deionized water case (1,025 Pa). The $G_e^{'}$ was fitted with salt content for potassium and sodium through an Arrhenius type equation, $G_e^{'} = C_1 e^{-TDS/C_2}$. The constant C_2 was found to be 10^5 mg/L for both potassium and sodium. The constant C_1 values were 908 and 812 Pa for potassium and sodium, respectively.

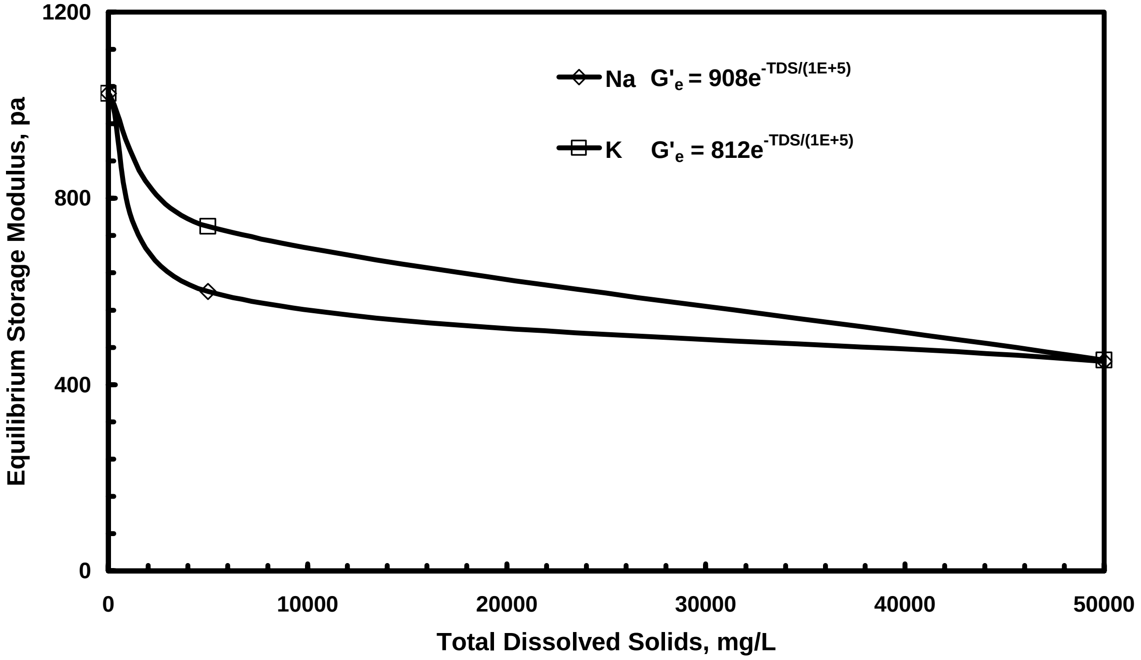


Figure 4.2.9: Effect of monovalent cations on equilibrium elastic modulus

4.2.5 Conclusions

1. The organically cross-linked polyacrylamide gel showed elasticity (600 Pa at 23.5°C) that is much higher than the previously reported values (210 Pa at 25°C by Kakadajian et al., 1999).

2. The elastic modulus showed substantial increase when the gel was heated at temperatures higher than 100°C suggesting the presence of a different mechanism of gel formation at temperatures above 100°C.

3. Both $G_e^{'}$ and G'' showed an exponential dependence on polymer concentration as $G'_e = 50.6e^{0.21C}$ and $G'' = 0.45e^{0.43C}$, respectively.

4. The elastic modulus increased by a factor of 4.8 upon increasing the cross-linker concentration from 0.23% to 0.92%. However, the strength of this gel was low.

5. Addition of salts to the gelling solution reduced equilibrium gel elasticity. $G_e^{'}$ decreased with TDS in an exponential manner. The relationship is $G_e^{'} = 908e^{-TDS/(1E+5)}$ for potassium and $G_e^{'} = 812e^{-TDS/(1E+5)}$ for Na.

6. Also, $G_e^{'}$ decayed at 150°C with gel age in a similar fashion: $G_e^{'} = 304.91\ e^{\frac{-t}{9.52}}$

7. At TDS less than 10,000 mg/L, the influence of monovalent (Na or K) salts was observed to be proportional to their molar concentration.

4.2.6 Acknowledgments

Authors would like to acknowledge the support of KFUPM and Saudi Aramco. Thanks are also due to Ali Al-Amri for his help in some of the experimental work. The ASD of the R&DC of Saudi Aramco are appreciated for the analysis of water samples and TGA analysis.

4.2.7 References

Al Muntasheri, G.A, H.A. Nasr-El-Din and I.A. Hussein "A Rheokinetic Study of an Organically Cross-linked Polymeric Gel Used for Water Shut-Off", Polymer Engineering & Science, submitted, **2004.**

Alqam, M.H., H.A. Nasr-El-Din and J.D. Lynn, "Treatment of Super K-Zones Using Gelling Polymers", SPE 64989 presented at the 2001 SPE International Symposium on Oilfield Chemistry held in Houston, TX, 13-16 February **2001**.

Bird, R. B., W.E. Stewart and E. N. Lightfoot, "Transport Phenomena", 2nd Edition John Wiley & Sons, New York, **2002**.

Clark, P.E., "Stimulation Fluid Rheology- New Approach", SPE 8300 presented at the 54th Annual Fall Technical Conference of the Society of Petroleum Engineers of AIME held in Las Vegas, 23-26 September **1979**.

Grattoni, C.A., H.H. Al-Shraji, C. Yang, A.H. Muggeridge and R.W. Zimmerman, " Rheology and Permeability of Crosslinked Polyacrylamide Gel", Journal of Colloid and Interface Science, 240, 601-607, **2001.**

Hardy, M.B., C. W. Botermans and P. Smith, "New Organically Crosslinked Polymer System Proides Cpmpetent Propagation at High Temperatures in Conformance Treatments", SPE 39690 presented at the SPE/DOE Symposium on Improved Oil Recovery held in Tulsa, OK, 19-22 April **1998.**

Hardy, M.B., C. W. Botermans, A. Hamouda, J. Valda and W. John, "The First Carbonate Field Application of a New Organically Crosslinked Water Shutoff Polymer System", SPE 50738 presented at the 1999 SPE International Symposium on Oilfield Chemistry held in Houston, TX , 16-19 February **1999**.

Hoek, V., C.W. Botermans and P.L.J. Zitha, "Full Blocking Mechanism of Polymer Gels for Water Control", SPE 68982 presented at the SPE European Formation Damage Conference held in the Hague, The Netherlands, 21-22 May **2001**.

Kakadjian, S., Rauseo, O. and Mejias, F., "Dynamc Rheology as a Method for Quantify Gel Strength of Water Shutoff Systems," SPE 50751 presented at the International Symposium on Oilfield Chemistry held in Houston, TX, **February** 16-19, **1999**.

Kesavan, S., Prud'homme, R.K.,"Rheology of Guar and HPG Cross-Linked by Borate," Macromolecules, 25,p. 2026-2032, 1992.

Liu, J. and R.S. Seright, "Rheology of Gels Used for Conformance Control in Fractures," SPE 59318 presented at the SPE/DOE Improved Oil Recovery Symposium held in Tulsa, Oklahoma, **April** 3-5**, 2000.**

Macoskow, C.W.“ Rheology: Principles, Measurements and Applications,” Wiley-Vch, New York, p.175-378, **1994**.

Michon, C., G. Cuvelier and B. Launary,“ Concentration Dependence of the Critical Viscoelastic Properties of Gelatin at Gel Point”, Rheologica Acta 32, 94, **1993.**

Moradi-Araghi, A and P. Doe, P., “Stability of Polyacrylamides in Hard Brines at Elevated Temperatures. SPE 13033, presented at the 59th Annual SPE Conference and Exhibition, Houston, TX, September 16-19, 1984.

Morgan, J.C., P.L. Smith and D.G. Stevens, “Chemical Adaptation and Deployment Strategies for Water and Gas Shut-Off Gel Systems,” presented at the Royal Chemistry Society’s Chemistry in the Oil Industry 6th International Symposium , Ambleside, UK, Apr.14-17, **1997.**

Okasha, T.M, H.A. Nasr-El-Din and W.S. Al-Kudair, “Abatement of Water Production from Upper Permian Gas Wells in Saudi Arabia Using a New Polymer Treatment”, SPE 68152 presented at the 2001 SPE Middle East Oil Show held in Bahrain, 17-20 **March 2001**.

Prud'homme, R.K., U. Jonathan, J.P. Poinsatte and F. Halverson “Rheological Monitoring of the Formation of Polyacrylamide/Cr^{+3} Gels”, SPE Journal p.804-808, 1983.

Reddy, B. R., L. Eoff, E.D. Dalrymple, K. Black, D. Brown and M. Rietjens, “A Natural Polymer-Based Cross-Linker System for Conformance Gel Systems,” SPE Journal, 99, June **2003.**

Sydansk, R.D., Al-Dhafeeri, A.M, Xiong, Y., and Seright, R.S.: "Polymer Gels Formulated with a Combination of High and Low Molecular-Weight Polymers Provide Improved Performance for Water-Shutoff Treatments in Fractured Production Wells," paper SPE 89402 presented at the 2004 SPE/DOE Symposium on Improved Oil Recovery, Tulsa, OK, **April** 17-21, **2004**.

Te Nijenhuis, K., A. Mensert and P.L.J Zitha, “Viscoelastic Behavior of Partly Hydrolysed Polyacrylamide/Chromium(III) Gels”, Rheo Acta, (42), p.132-141, **2003.**

Thurston, G.B., Ozon, P.M., and Pope, G.A.,“ The Viscoelasticity and Gelation of Some Polyacrylamide and Xanthan Gum Solutions,” unsolicited SPE paper, **1985.**

Vasquez, J., F. Civan, T. M. Shaw, E. D. Dalrymple , L. Eoff, B.R. Reddy & D.Brown, “Laboratory Evaluation of High-Temperature Conformance Polymer Systems,” paper SPE 80904 presented at the SPE Production and Operations Symposium held in Oklahoma City, OK, U.S.A., **March** 22-25 **2003**.

Zitha, P. L. J., Botermans C. W., v.d. Hoek, J. and Vermolen, F. J., "Control of Flow through Porous Media using Polymer Gels," Journal of Applied Physics, 92 (2), 1143-1153, **2002**.

Chapter 5

Conclusions and Recommendations

5.1 Conclusions

The gelation kinetics of an organically cross-linked polymeric gel used for water shut-off treatments was investigated. It was observed that higher temperatures increased the rate of gel structure formation and hence shorter gelation times were noticed. Activation energy of PAtBA/PEI gelling system was calculated as 28 kcal/mol in deionized water. Addition of salts lowered the activation energy in an exponential manner. The relationship obtained is $E_a = 25{,}102\exp((-4E-6)TDS)$ with r^2=0.9924. The reaction order was within 10% of 5.83. This value is high reflecting the inclusion of rheological, kinetic and molecular weight effects into it. The effect of gel composition on kinetics was also studied. Gelation time was lowered by increasing polymer and/or cross-linker concentration. Mixing the gelling solution at higher rates lowered the gelation time. However, high mixing rates resulted in the breakup of the gel. Salts were found to increase gelation times. Divalent cations have more effect on gelation time than monovalent cations. Initial pH showed a strong influence on the viscosity build up of the gel. Higher viscosities were obtained at high initial pH values. At acidic conditions, the gels formed were weaker than those at alkaline pH.

To simulate real field conditions, iron was added to gelling solutions. The presence of high iron concentration (1000 ppm Fe(III)) resulted in an immediate increase in viscosity which will hinder pumping the gelling solution. Moreover, the gel formed was weak.

The viscoelastic properties of the gelling system were also investigated. This organically cross-linked polyacrylamide gel showed elasticity (600 Pa at 23.5^{o}C) that is much higher than the previously reported values (210 Pa at 25^{o}C by Kakadajian et al., 1999). The elastic modulus showed substantial increase when the gel was heated at temperatures higher than 100^{o}C suggesting the presence of a different mechanism of gel formation at temperatures above 100^{o}C. Both $G_e^{'}$ and G'' showed an exponential dependence on polymer concentration as $G'_e = 50.6e^{0.21C}$ and $G'' = 0.45e^{0.43C}$, respectively. Moreover, the elastic modulus increased by a factor of 4.8 upon increasing the cross-linker concentration from 0.23% to 0.92%. However, the strength of this gel was low. Addition of salts to the gelling solution reduced equilibrium gel elasticity. $G_e^{'}$ decreased with TDS in an exponential manner. The relationship is $G_e^{'} = 908e^{-TDS/(1E+5)}$ for potassium and $G_e^{'} = 812e^{-TDS/(1E+5)}$ for sodium. Also, $G_e^{'}$ decayed at 150^{o}C with gel age in a similar fashion: $G_e^{'} = 304.91\ e^{\frac{-t}{9.52}}$. The influence of monovalent (Na or K) salts was observed to be proportional to the number of their moles (not mass).

5.2 Recommendations for Future Work

This system showed good elasticity behavior at room temperatures. However, the behavior at high temperatures similar to those encountered at petroleum reservoirs is not known. Hence, it is recommended to use a rheometer that can measure the viscoelastic properties at high temperatures without evaporating the samples. The relationship between the gel network and its elasticity of this system could be a feasible continuation work on this system.

References

1. Albonico P., Bartosek M., Lockart T.P., Causin E. and Rossoi E. , (1994), “New Polymer Gels for Reducing Water Production in High-Temperature Reservoirs”, *SPE 27609*

presented at the European Production Operations Conference and Exhibition held in Aberdeen, U.K., 15-17 March.

2. Alqam M.H., Nasr-El-Din H.A. and Lynn J.D., (2001), “Treatment of Super K-Zones Using Gelling Polymers”, *SPE 64989* presented at the 2001 SPE International Symposium on Oilfield Chemistry held in Houston, TX, 13-16 February.

3. Aslam S., and Vossoughi S., (1984), “Viscometric Measurement of Chromium (III)-Polyacrylamide Gels by Weissenberg Rheometer”, *SPE/DOE 12639* presented at the 4th Symposium on EOR held in Tulsa, OK, 15-18 April.

4. Avery M.R., Burkholder L.A and Gruenenfelder M.A., (1986), “Use of Cross-linked Xanthan Gels in Actual Profile Modification Field Project”, *SPE 14114* presented at the 1986 International Meeting on Petroleum Engineering held in Beijing, China 17-20 March.

5. Avery M.R., Wells T.A., Chang P.W. and Millican J.P., (1998), “Field evaluation of a new gelant for water control in production wells. *SPE 13201* presented at the Annual Technical Conference and Exhibition held in Houston, TX, October 3-5.

6. Avrami M., (1939), “Kinetics of phase change. I. General theory”, *Journal of Chemical Physics*, 7, 1103-12.

7. Avrami M., (1940), “Kinetics of phase change. II. Transformation-time relations for random distribution of nuclei”, *Journal of Chemical Physics*, 8, pp: 212-224.

8. Batycky J.P., and Milosz G., (1982) “A Study of the Application of Polymeric Gels in Porous Media”, *SPE 10620* presented at the SPE Sixth International Symposium on Oilfield and Geothermal Chemistry held in Dallas, TX, 25-27 January.

9. Bird R.B., Armstrong R.C. and Hassager O., (1987), “Dynamics of Polymeric Liquids”, 2nd Edition *John Wiley & Sons*, New York.

10. Bird R. B., Stewart W.E. and Lightfoort E. N., (2002), "Transport Phenomena", 2nd Edition *John Wiley & Sons*, New York.

11. Chauveteau G., Tabary R. and Kohler N., (1997), "Rheology of Polyacrylamide Systems Under Near-Well Bore Conditions", *SPE 37299* presented at the SPE International Symposium on Oilfield Chemistry held in Houston, TX, 18-21 February.

12. Clark P.E., (1979), "Stimulation Fluid Rheology- New Approach", *SPE 8300* presented at the 54th Annual Fall Technical Conference of the Society of Petroleum Engineers of AIME held in Las Vegas, 23-26 September.

13. Clark P.E., Balakrishnan M. and Sundram L., (1993), "Cross-linking of Hydroxypropyl Guar With Metal Ions", *SPE 25208*, SPE International Symposium on Oilfield Chemistry held in New Orleans, LA, 2-5 March.

14. Cloud J.E., and Clark P.E., (1980), "Stimulation Fluid Rheology (III) Alternatives to The Power Law Fluid Model For Cross-lined Fluids ", *SPE 9332* presented at the 55the Annual Fall Technical Conference and Exhibition of the Society of Petroleum Engineers of AIME held in Dallas, TX, 21-24 September.

15. Dalrymple E.D., (2004), *Personal Communication*, November 16.

16. Eggert R.W., G.P. Willhite and Green D.W., (1992), "Experimental Measurement of the Persistence of Permeability Reduction in Porous Media Treated with Xanthan/Cr(III) Gel Systems," *SPE Reservoir Engineering Journal*, 7(1), pp: 29-35.

17. Farooqui M.A, and Al-Rufaie Y.A., (1995), "Rigless Techniques Enhanced the Effectiveness and Economics of Water Shut-Off', *SPE 39511* presented at the 1995 SPE India Oil and Gas Conference and Exhibition held in New Delhi, India, 17-19 February.

18. Frampton H., (1994), "Chemical Gels for Improved Oil Recovery", R. Soc. Chem. 159, *Recent Advances in Oilfield Chemistry*, pp: 295-310.

19. Free D.L., Frederick A.F. and Thompson J.E., (1978), "Fracturing with a High-Viscosity, Cross-linked Gel-Continuous Fracturing Technique", *Journal of Petroleum Technology*, 119-122, January.

20. Fulleylove R.J., Morgan J.C. and D.G. Stevens, (1996), "Water Shut-off in Oil Production Wells - Lessons from 12 Treatments", *SPE 36211* prepared for the 7th Abu Dhabi International Petroleum Exhibition and Conference held in Abu Dhabi, U.A.E., 13-16 October.

21. Garland T. M., (1996), "Selective Plugging of Water Injection Wells", *Journal of Petroleum Technology*, pp: 1550-1560.

22. Gleasure R. W., (1990), "An Experimental Study of Non-Newtonian Polymer Rheology Effects on Oil Recovery and Injectivity", *SPE Reservoir Engineering Journal*, 481, November.

23. Grattoni C.A., Al-Shraji H.H.,Yang C., Muggeridge A.H. and Zimmerman R.W.,(2001),"Rheology and Permeability of Crosslinked Polyacrylamide Gel", *Journal of Colloid and Interface Science*, 240, pp: 601-607.

24. Han M., Muller G. and Zaitoun A., (1997), "Gel Formation of Polyacrylamide in the Presence of Glyoxal for Water Control Application", *Polymer Gels and Networks*, 5, pp: 471-480.

25. Hardy M., Botermans W., Hamouda A. and Smith P.,(1998), "New Organically Crosslinked Polymer System Provides Competent Propagation at High Temperature in Conformance Treatments", *SPE 39690* presented at the 1998 SPE/DOE Oil Recovery Symposium held in Tulsa, OK, 19-22 April.

26. Hardy M.B., Botermans W., Hamouda A., Valda J. and John W., (1999), "The First Carbonate Field Application of a New Organically Crosslinked Water Shutoff Polymer System", *SPE 50738* presented at the 1999 SPE International Symposium on Oilfield Chemistry held in Houston, TX , 16-19 February 1999.

27. Henning H and Chambon F., (1986), "Analysis of Linear Viscoelasticity of a Cross-linking Polymer at the Gel Point", *Journal of Rheology*, 30(2), pp: 376-382.

28. Hoek J., Botermans W. and Zitha P.L.J, (2001), "Full Blocking Mechanism of Polymer Gels for Water Control", *SPE 68982* presented at the SPE European Formation Damage Conference held in the Hague, The Netherlands, 21-22 May.

29. Hutchins R.D., Dovan H.T. and Sandidford B.B., (1996), "Field Applications of High Temperature Organic Gels for Water Control", *SPE 35444* presented at the 1996 SPE/DOE Tenth Symposium on Improved Oil Recovery held in Tulsa, OK, 21-24 April.

30. Jordan D.S., Don W., Ronald E. and Willhite G.,(1982), "The Effect of Temperature on Gelation Time for Polyacrylamide/Chromium (III) Systems", *SPE Journal*, 463, August.

31. Jousset F., Green D.W., Willhite G.P. and McCool C.S., (1990), "Effect of High Shear Rate on In-Situ Gelation of a Xanthan/Cr (III) System" *SPE 20213* presented at the SPE/DOE Seventh Symposium on Enhanced Oil Recovery held in Tulsa, Oklahoma, April 22-25.

32. Jurinak J.J., Summers L.E. and Bennett K.E., (1991), "Oilfield applications of colloidal silica", *SPE Production Engineering. Journal,* 6(4), pp: 406-412.

33. Kakadjian S., Rauseo O. and Mejias F.,(1999), "Dynamic Rheology as a Method for Quantify Gel Strength of Water Shutoff Systems," *SPE 50751* presented at the International Symposium on Oilfield Chemistry held in Houston, TX, February 16-19.

34. Kesavan S., Prud'homme R.K., (1992), "Rheology of Guar and HPG Cross-Linked by Borate", *Macromolecules*, 25, pp: 2026-2032.

35. Kolnes J., Stavland A. and Ersdal T., (1997), "Effect of pH Gelation Time for Xanthan/Cr (III) Gels", *SPE 37301* presented at the 1997 SPE International Symposium on Oilfield Chemistry held in Houston, U.S, 18-21 February.

36. Kontturi K., Mafe S., Manzanares J.A., Svarfvar B.L., and Viinikka P., (1996), "Modeling of the Salt and pH Effects on the Permeability of Grafted Porous Membranes", *Macromolecules*, 29, pp: 5740-46.

37. Liu J., and Seright R.S., (2000), "Rheology of Gels Used For Conformance Control in Fractures", *SPE 59318* presented at the 2000 SPE/DOE Improved Oil Recovery Symposium held in Tulsa, Oklahoma, 3-5 April.

38. Lockhart T.P., (1991), "Chemical and Structural Studies on Cr^{+3}/ Polyacrylamide Gels", *SPE 20998* presented at the SPE International Symposium on Oilfield Chemistry held in Anaheim, California, 20-22 February.

39. Lockhart, T.P. "A New Gelation Technology for In-Depth Placement of Cr^{+3}/Polymer Gels in High-Temperature Reservoirs", *SPE 24194* presented at the SPE/DOE Eighth Symposium on Enhanced Oil Recovery held in Tulsa, Oklahoma, April 22-24.

30. Lockhart T.P., and Albonico P., (1996), "A New Gelation Technology for In-Depth Placement of Cr+3/Ploymer Gels in High-Temperature Reservoirs", *SPE 24194* presented at the SPE/DOE Eighth Symposium on Enhanced Oil Recovery held in Tulsa, Oklahoma,21-24 April.

31. Macoskow, C. W., (1994), "Rheology Principles, Measurements & Applications" *Wiley-Vch*, New York, pp:175-378.

32. Michon C., Cuvelier G. and Launary B., (1993), "Concentration Dependence of the Critical Viscoelastic Properties of Gelatin at Gel Point", Rheologica Acta ,32, 94.

33. Mijovic J., Kenny J.M. and Nicolais L., (1993), "Comparison of Kinetic and Rheological Evaluation of Gel Time for an Amine Epoxy System", *Polymer Journal*, 34 (1) 207-209.

34. Moffit P.D., Moradi-Araghi A., Janway V.R., and Young G.R.,(1996), "Development and Field Testing of a New Low Toxicity Polymer Cross-linking System", *SPE 35173* presented at the Permain Basin Oil& Gas Recovery Conference held in Midland, Texas,27-29 March.

35. Moradi-Araghi, A., (1991), "Altering High Temperature Subterranean Formation Permeability", *U.S patent 4,994,194*, February 19.

36. Moradi-Araghi A., (1994), "Application of Low –Toxicity Cross-linking Systems in Production of Thermally Stable Gels", SPE 27826 presented at the SPE/DOE Ninth Symposium on Improved Oil Recovery held in Tulsa, OK, 17-20 April.

37. Moradi-Araghi A., (2000), "A Review of Thermally Stable Gels for Fluid Diversion in Petroleum Production", *Journal of Petroleum Engineering and Science*,26 (1-4),pp: 1-10.

38. Moradi-Araghi, A., Bjornson, G. and Doe, P.H., (1993), "Thermally Stable Gels for Near-Wellbore Permeability Contrast Corrections", *Advanced Technology Series*, 1, No.1, pp: 140-145.

39. Moradi-Araghi A., and Doe P.,(1984), "Stability of Polyacrylamides in Hard Brines at Elevated Temperatures", *SPE 13033*, presented at the 59th Annual SPE Conference and Exhibition, Houston, TX, September 16-19.

40. Moradi-Araghi A. and Doe P., (1987), “Hydrolysis and Precipitation of Polyacrylamides in Hard Brines at Elevated Temperatures”, *SPE Reservoir Engineering Journal,* p. 189.

41. Morgan J.C., Smith P.L and Stevens D.G.,(1997), “Chemical Adaptation and Deployment Strategies for Water and Gas Shut-Off Gel Systems,” presented at the Royal Chemistry Society’s Chemistry in the Oil Industry 6th International Symposium , Ambleside, UK, Apr.14-17.

42. Mortimer S., Ryan A.J. and Stanford J.L. Stanford, (2001), “Rheological Behavior and Gel-Point Determination for a Model Lewis Acid-Initiated Chain Growth Epoxy Resin”, *Macromolecules*, 34, pp: 2973-2980.

43. Murthy A.K., and`Muthukumar M., (1987), “Dynamic Mechanical Properties of Poly(γ-Benzyl L- α-Glutamate) Gels in Benzyl Alcohol”, *Macromolecules*, 20, pp: 564-569.

44. Nagra S.S., Batycky J.P., Nieman R.E. and Bodeux J.B., (1986), “Stability of Waterflood Diverting Agents at Elevated Temperature”, *SPE 15548* presented at the 61st Annual Technical Conference and Exhibition of the Society of Petroleum Engineering held in New Orlands, USA, 5-8 October.

45. Nasr-El-Din H.A., Al-Driweesh S.M., Al-Muntasheri G.A., (2003),“Field Application of HCl-Formic Acid System to Acid Fracture Deep Gas Wells Completed with Super Cr-13 Tubing in Saudi Arabia”, *SPE 84925* presented at SPE International Improved Oil Recovery Conference held in Kuala Lumpur, Malaysia, 20-21 October.

46. Nasr-El-Din H.A., Bitar G.E., Bou-Khamsin F.I., Al-Mulhim A.K. and Hsu J., (1998), “Field application of gelling polymers in Saudi Arabia”, *SPE 39615* presented at the SPE/DOE Improved Oil Recovery Symposium held in Tulsa, OK, April 19-22.

47. Nasr-El-Din H.A., Hawkins B.F. and Green K.A., (1991), "Viscosity Behavior of Alkaline, Surfactant, Polyacrylamide Solutions Used for Enhanced Oil Recovery", *SPE 21028* presented at the SPE International Symposium on Oilfield Chemistry held in Anaheim, California U.S.A, 20-22 April.

48. Nasr-El-Din H.A., Taylor K.C., (2004), "Evaluation of sodium silicate/urea gels used for water shut-off treatments. Submitted for publication in *Journal of Petroleum Engineering and Science*, 2004.

49. Oisen E.H., (1986), "Case History: Water Shut-off Treatment in Phosphoria Formation, Hot Springs Country, Wyoming", SPE 15163 presented at the Rocky Mountain of the Society of Petroleum Engineers held in Billings, MT, 19-21 May.

50. Okasha T.M, Nasr-El-Din H.A. and Al-Kudair W.S.,(2001), "Abatement of Water Production from Upper Permian Gas Wells in Saudi Arabia Using a New Polymer Treatment", *SPE 68152* presented at the 2001 SPE Middle East Oil Show held in Bahrain, 17-20 March.

51. Omari A., (1995), "Rheological Study of the Gelation Kinetics of the Scleroglucan-Zicronium System", *Polymer Journal*, Volume 36, 4.

52. Pal R., Yan Y and Masliyah J, (1992), "Emulsions Fundamentals & Applications in the Petroleum Industry, *American Chemical Society*.

53. Ponton A., Warlus S. and Griesmar P., (2002), "Rheological Study of the Sol–Gel Transition in Silica Alkoxides", *Journal of Colloid and Interface Science*, 249, pp: 209-216.

54. Prud'homme R. K., U. Jonathan, J. P. Poinsatte and F. Halverson, (1983), "Rheological Monitoring of the Formation of Polyacrylamide/Cr+3 Gels", *SPE Journal* p.804.

55. Reddy B.R., Eoff L., Dalrymple E.D. and Brown D., (2003), "Natural Polymer-based Compositions Designed for Use in Conformance Gel Systems", *SPE 84510* presented at the SPE Annual Technical Conference and Exhibition held in Denver, CO, October 5-8.

56. Seright, R.S.,(1988), "Placement of Gels To Modify Injection Profiles", *SPE/DOE 17332* presented at the SPE/DOE Enhanced Oil Recovery Symposium held in Tulsa, Oklahoma, 17-20 April.

57. Seright, R.S. and F.D Martin,(1993), "Impact of Gelation pH, Rock Permeability, and Lithology on the Performance of a Monomer-Based Gel", SPE Reservoir Engineering *Journal*, 8 (1), 43-50.

58. Seright R.S., (2000), "Conformance Improvement Using Gels", Technical Proposal Submitted to the U.S Department of Energy and Potential Industrial Participants.

59. Seright R.S., Lane R.H. and Sydansk R.D., (2003), "A Strategy for Attacking Excess Water Production", *SPE Production Facilities Journal*, 18(3) 158-169.

60. Shchipunov Y.A., Koneva E.L. and Postnova I.V., (2002), "Homogenous Alignate Gels: Phase Behavior and Rheological Properties", *Journal of Polymer Science*, Series A, Vol. 44, No.7.

61. Stahl G.A., and Schulz D.N., (1998), Water-Soluble Polymers for Petroleum Recovery. *Plenum Press*, New York, pp: 299-312.

62. Stavland, A. and Jonsbraten H.C., (1996), “New Insight into Aluminum Citrate/Polyacrylamide Gels for Fluid Control”, *SPE 35381* presented at the 1996 SPE/DOE Tenth Symposium on Improved Oil Recovery held in Tulsa, OK,21-24 April.

63. Sydansk R.D., (1990), “Acrylamide-polymer/Chromium (III)-Carboxylate gels for near wellbore matrix treatments. SPE 20214 presented at the SPE/DOE Symposium on Enhanced Oil Recovery, Tulsa, OK, April 22-25.

64. Sydansk R.D., Al-Dhafeeri A.M, Xiong Y., and Seright R.S., (2004), “Polymer Gels Formulated with a Combination of High and Low Molecular-Weight Polymers Provide Improved Performance for Water-Shutoff Treatments in Fractured Production Wells”, *SPE 89402* presented at the 2004 SPE/DOE Symposium on Improved Oil Recovery, Tulsa, OK, April 17-21.

65. Sydansk R.D. and Southwell G.P., (1998), “More Than 12 Years’ Experience With a Successful Conformance-Control Polymer-Gel Technology”, *SPE 49315* presented at the 1998 SPE Annual Technical Conference and Exhibition held in New Orleans, Louisiana, 27-30 September.

66. Tayal A., V.B. Pai and S.A. Khan, (1999), “Rheology and Microstructural Changes During Enzymatic Degradation of a Guar-Borax Hydrogel”, *Macromolecules*, 32, pp: 5567-5574.

67. Taylor K., and Nasr-El-Din H.A., (1994),“Acrylamide Copolymers: A Review of Methods for the Determination of Concentration and Degree of Hydrolysis, *Journal of Petroleum Engineering and Science*, 12, 9-23.

68. Te Nijenhuis K., Mensert A. and Zitha P.L.J.,(2003), “Viscoelastic Behavior of Partly Hydrolysed Polyacrylamide/Chromium(III) Gels”, Rheologica Acta, (42), pp:132-141.

69. Thurston G.B., Ozon P.M. and Pope G.A., (1985),“ The Viscoelasticity and Gelation of Some Polyacrylamide and Xanthan Gum Solutions,” unsolicited SPE paper.

70. Vasquez J., Civan F., Shaw T.M., Dalrymple E.D., Eoff L., Reddy B.R. and Brown D., (2003), “Laboratory Evaluation of High-Temperature Conformance Polymer Systems”, *SPE 80904* presented at the SPE Production and Operations Symposium held in Oklahoma City, OK, 22-25 March.

71. Vogelsberger W., Seidel A. and Fuchs R., (2000), “Contribution to the Determination of Kinetic Parameters of the Sol-Gel Transformation by Rheological Measurements”, *Journal of Colloid and Interface Science*, 230, pp: 268-271.

72. Ward J.S., and Martin F.D., (1981), “Prediction of Viscosity for Partially Hydrolyzed Polyacrylamide Solutions in the Presence of Calcium and Magnesium Ions”, *SPE Journal*, 21(5), pp: 623-631.

73. Wellington S.L., (1980), “Biopolymer Solution Viscosity Stabilization-Polymer Degradation and Antioxidant Use”, *SPE 9296* presented at the Fall Technical Conference and Exhibition of the Society of Petroleum Engineers of AIME held in Dallas, US, 21-24 September.

74. Whitney D.D., Montagomery D.W. and Hutchins R.D., (1996), “Water Shutoff in the North Sea: Testing a New Polymer Gel System in the Heather Field, UKCS Block 2/5” *SPE Production & Facilities Journal*, pp.108.

75. Wibowo W., Gould J.H., Munir A., and David A.R.,(1999), “First Four Water Shut-off Treatment in ONWJ Filed: Design, Execution, Evaluation and Strategy for the Next Treatments”, *SPE 256737* presented at the 1999 SPE Annual Technical Conference and Exhibition of the Society of Petroleum Engineers held in Houston, US, 3-6 October.

76. Winter H. H., and Chambon F., (1986), "Analysis of Linear Viscoelasticity of a Cross-linking Polymer at the Gel Point", *Journal of Rheology*, pp: 367-382.

77. Zitha P.L.J., Botermans C.W., v.d. Hoek J. and Vermolen F.J., (2002), "Control of flow through porous media using polymer gels. J. Applied Physics, 92 (2), pp: 1143-1153.

VITAE

Name: **Ghaithan Ahmad Al-Muntasheri**

Father's Name: **Ahmad Abdullah Al-Muntasheri**

Place of Birth: **Hafr Al-Baten, Saudi Arabia**

Education: **B.S. in Chemical Engineering from King Fahd University of Petroleum & Minerals (KFUPM), Dhahran, Saudi Arabia. June, 2001.**

M.S. in Chemical Engineering from King Fahd University of Petroleum & Minerals (KFUPM), Dhahran, Saudi Arabia. December, 2004

E-mail: ghaithan.muntasheri@aramco.com