

# Investigating the Various Control Factors on Gelation Time and Gel Strength of Graft Copolymer Gel System to Enhance Oil Recovery from Heterogeneous Reservoirs

Charles Boakye\* and Vikas Mahto

Department of Petroleum Engineering, Indian Institute of Technology (IIT-ISM),  
Dhanbad-826004, Jharkhand, India  
E-mail: charlesboakye81@gmail.com

**Abstract**—The economic need for oil and gas in recent decades has made it more imperative for researchers to delve much into various techniques required to improve productivity in mature oil fields. The primary objective of this present work is to develop a polymer gel for profile modification job to maximize the oil recovery in heterogeneous reservoirs. Basically, xanthan gum grafted polyacrylamide (PAAm-g-XG) copolymer was synthesized by free radical polymerization and confirmed by Fourier Transform Infrared spectroscopy (FTIR) analysis. The grafted copolymer attained was cross-linked with Chromium (III) acetate to form a rigid stable gel with the help of Sydansk's gel strength coding. The impacts of various parameters for example graft copolymer concentration; cross-linker concentration and temperature were studied by the bottle test method. Sand pack flooding experiment was also performed to investigate the plugging capability of the grafted copolymer gel in a simulated heterogeneous reservoir.

**Keywords:** Cross-linker, enhance oil recovery, gel strength, permeability reduction, gelation time.

## 1. Introduction

In the process of water flooding, water sweeps through more permeable sections leaving back oil in low permeability channels leading to low oil recovery and early water breakthrough. Polymer gel treatment which reduces the permeability of high permeability zones is by all account a therapeutic measure as a result of its potential to improve sweep efficiency and increase oil production [1–3].

Cross-linked polymer gel treatments typically focus on the reservoirs with channelling, heterogeneity and fractures caused by driving water which is one of the significant issues related to the economics of the oil industry [1,2,4]. Accordingly, the development of cost-effective gel suited to different oilfields will be advantageous for these drawbacks. Conformance control techniques as shown in figure 1 are generally used to reduce unreasonable production of water in high permeable zones [5–8]. In-depth profile control includes sealing high permeable zones by the injection of plugging

agents such as cement, polymer gel system, etc. Moradi-araghi [9], expressed that when these plugging agents are legitimately set, they can cause any chasing fluids such as water/surfactant to divert into the un-swept low permeability areas, and then increase additional oil recovery[9–11].

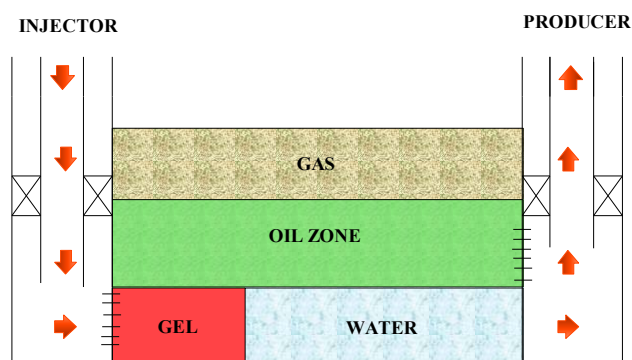


Figure 1: Profile modification job by in-situ gel system

As of late, polyacrylamide cross-linked with either inorganic or organic cross-linkers gels has been the most commonly used agent for profile modification jobs. Inorganic cross-linkers include Cr (III), Al (III) and Zr+4 and have been mostly utilized to crosslink partially hydrolyzed polyacrylamide. Inorganically cross-linked gels result from the ionic bonding between the negatively charged carboxylate groups and the multivalent cation [12,13].

For conformance control processes, the selection of a polymer gel system strongly depends on reservoir conditions such as temperature, hardness, salinity, and the pH of the water used for the preparation of the gelant [13].

The gelation of the polyacrylamide with chromium (III) acetate system was studied by Terry et al. [14] trying to give valuable information. They studied the impacts of the concentrations and types of reactants on the gelation time. It

was determined that the gelation time decreases with the increasing polymer,  $\text{Cr}^{3+}$ , and reducing agent concentrations. Kolnes et al [15] as well have developed a correlation between the reaction temperature and the gelation time for a polyacrylamide with chromium (III) acetate gel system.

Grafted copolymers of polyacrylamide and polysaccharides, for example, carboxymethyl cellulose, xanthan gum, guar gum, and so forth have pulled in more consideration as advanced polymeric materials that can withstand different demerits for polymeric gel materials for profile modification. The oil business widely use xanthan gum for enhanced oil recovery jobs since it is a drag reducing agent with good shear stability [16–18].

In this research, PAAm-g-XG copolymer was synthesized by grafting polyacrylamide chains onto xanthan gum backbone by free-radical polymerization and characterized by Fourier transform infrared (FTIR) analysis. The grafted copolymer attained was cross-linked with Chromium (III) acetate to form a rigid stable gel with the help of Sydansk's gel strength coding. The effects of different parameters such as graft copolymer concentration; cross-linker concentration and temperature were studied by the bottle test method. Sand pack flooding experiment was also performed to investigate the plugging capability of the grafted copolymer gel in a simulated heterogeneous reservoir (sand pack flow experiment).

## 2. Experimental Work

### 2.1. Material Used

Sodium chloride (NaCl) salt was procured from the Rankem Ltd., India. Xanthan gum was obtained from Rankem Ltd. India. Potassium persulphate (Extra pure) and Acrylamide (AAM) was purchased from Loba Chemi, India. Chromium (III) acetate and hydroquinone (HQ) was procured from the Central Drug House (P) Ltd., India. Hydrochloric acid was purchased from Nice Chemical Pvt., Ltd., India; sodium hydroxide was purchased from S. D. Fine-Chem. Ltd., India, to adjust the pH of the gel solution.

### 2.2. Synthesis and Characterization of Graft Copolymer

Polyacrylamide grafted xanthan gum was synthesized by free radical polymerization process as chemically illustrated in figure 2, following previous writings with few modifications [16–18]. The reaction took place under a nitrogen atmosphere with potassium persulfate as an initiator. Initially, 2 grams of xanthan gum was dissolved in 200 ml of distilled water in the three-necked round bottom flask under a temperature of  $65^\circ\text{C}$  which was maintained by an oil bath. Xanthan gum was continuously mixed for 1 hour at 500 rpm using magnetic stirrer under a nitrogen atmosphere; afterwards, a desired amount of acrylamide was dissolved in 20 ml distilled water in a different beaker and injected slowly to the already mixed xanthan gum solution. The mixture was allowed to mix

continuously at  $65^\circ\text{C}$  for another 3 hours. At this stage, 0.05g of potassium persulphate dissolved in 5 ml of distilled water was added to the homogeneous solution, and the reaction continued for another 1.5 hours at the same temperature and constant stirring speed. The whole reaction was terminated with 5ml of hydroquinone solution ( $2.56 \times 10^{-5} \text{ mols}$ ) and the nitrogen gas was detached. Afterwards, the reaction mixture was allowed to cool at room temperature ( $27^\circ\text{C}$ ), and the product was precipitated with acetone. The filtered product was finally washed with excess methanol and water solution (30:20) so as to remove any impurities and homopolymer using soxhlet extraction. Afterwards, it was dried in a hot air oven for 24 hours at  $60^\circ\text{C}$ ; it was further powdered by mortar and pestle and sieved through a 125-micron mesh screen.

The sample was further characterized using Fourier transform infrared spectrometric analysis. The IR spectra of the xanthan gum, polyacrylamide, and the grafted copolymer were recorded on PerkinElmer FT-IR spectrometer (model spectrum Two; PerkinElmer Inc. Waltham, MA, USA) using KBr pellets, and range from  $400 - 4000 \text{ cm}^{-1}$ .

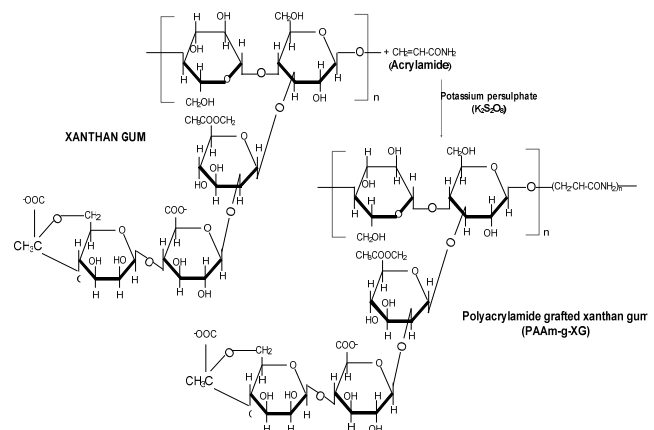


Figure 2: The synthetic process of polyacrylamide grafted xanthan gum

### 2.3. Preparation of the Graft Copolymer Gel

Initially, the synthesized graft polymer (4000 ppm – 12000 ppm) was prepared by gradual addition of the polymer to NaCl solution (30,000 ppm), and the mixture was allowed to age without stirring at room temperature for 24 hours until a homogeneous dispersion was obtained (Solution A). Fresh cross-linker solutions (1000 ppm – 4000 ppm) were prepared by adding chromium (III) acetate to brine solution in a different beaker (solution B).

Then, solution A and B were mixed and homogenized by constant stirring using a magnetic stirrer to obtain the gelant solution. The pH of gelant was maintained using 0.1M NaOH and 0.1M HCl solutions. The obtained gelant solution was taken in a glass tube and kept in a hot air oven at the desired temperatures ( $70^\circ\text{C}$ – $110^\circ\text{C}$ ) for the determination of the gel

strength and gelation time, the bottles were inspected visually at regular time intervals by tilting the bottle against gravity. The time for the formation of a stiff gel was taken as the gelation time.

**2.4. Measurement of Gelation Time and Gel Strength**

The bottle testing method used as an experimental technique provides a semi-quantitative measurement for the determination of the gelation time and the gel strength tends to be attributed as an advantageous and cheap technique to study the gelation kinetics [19,20]. Argabright et al [8] expressed the gel strength in an alphabetic code of A to J as shown in table 1. From the table, code A indicates that the final viscosity is the same as the viscosity of the original gelant solution. And at a gel strength of J indicates that there is no deformation on the gel surface after tilting against gravity. In this study, the gel strength was taken as code J at an experimental temperature of 80°C.



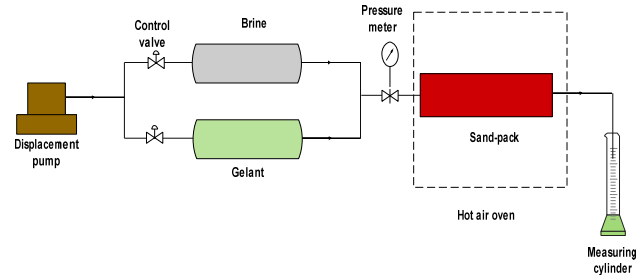
**Figure 3: Bottle test experiment for gel strength and gelation time**

**Table 1: Sydansk’s gel strength grade code and gel description**

CODE	GEL DESCRIPTION
A	No detectable gel formed
B	Highly flowing gel
C	Flowing gel
D	Moderately flowing gel
E	Barely flowing gel
F	High deformable non-flowing gel
G	Moderately deformable non-flowing gel
H	Slightly deformable non-flowing gel
I	Rigid gel
J	Ringing rigid gel

**2.5. Sand Pack Flow Experiment**

Sand pack flow experiment was used to determine the plugging capability after in-situ gelation of the graft copolymer gel. Sand pack of length 45 cm, a diameter of 3.5 cm and the sand grain size of 300 -700 microns were used in this experiment. Figure 4 shows the experimental setup of the flooding experiment.



**Figure 4: Setup diagram for sand pack flooding studies**

At first, the core holder was packed with sand, and oil and brine solution were injected at constant pressure to evaluate the relative water and oil permeability using the Darcy equation. A while later, 0.3 pore volume of the graft copolymer gel solution was injected and the sand pack was kept in a hot air oven at 80°C until the gel was formed, with the help of bottle testing the sand pack was kept for 3 days. Then, oil and brine solution was again flooded at a constant flow rate until the pressure and produce fluid reached a stable condition. Water production and pressure values were recorded to evaluate the plugging rate and the resistance factors for oil and water respectively following the equations below [10];

$$F_{rrw} = \frac{\lambda_{w1}}{\lambda_{w2}} = \frac{k_{w1}\mu_{w2}}{k_{w2}\mu_{w1}} = \frac{k_{w1}}{k_{w2}} \tag{1}$$

$$F_{rro} = \frac{\lambda_{o1}}{\lambda_{o2}} = \frac{k_{o1}\mu_{o2}}{k_{o1}\mu_{o1}} = \frac{k_{o1}}{k_{o2}} \tag{2}$$

$$RRF = \frac{F_{rrw}}{F_{rro}} \tag{3}$$

$$\eta = \frac{k_{w1} - k_{w2}}{k_{w1}} \times 100\% \tag{4}$$

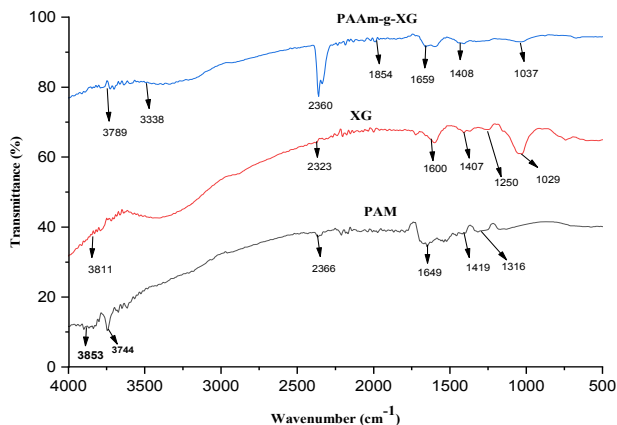
Where  $F_{rrw}$  is the water residual resistance factor;  $F_{rro}$  is the oil residual resistance factor;  $\lambda_{w1}$  and  $\lambda_{w2}$  are water mobility before and after the gel treatment respectively;  $\lambda_{o1}$  and  $\lambda_{o2}$  are oil mobility before and after the gel treatment respectively;  $k_{o1}$  and  $k_{o2}$  is the oil permeability before and after the gel treatment respectively. RRF and  $\eta$  are the residual resistance factor and the decrease in permeability respectively. The viscosities remain the same during the entire experiment, thus  $\mu_{w1} = \mu_{w2}$  and  $\mu_{o1} = \mu_{o2}$ .

These above parameters were used to characterize the plugging capability of the graft copolymer gel.

**3. Results and Discussions**

**3.1. Fourier Transform Infrared Spectrometric Analysis**

The FTIR spectra of Polyacrylamide-g-xanthan gum, xanthan gum and polyacrylamide are shown in figure 5. These spectra are consistent with previous writings [16–18].



**Figure 5: FTIR spectra of Pam, xanthan gum and polyacrylamide grafted xanthan gum**

The spectrum of xanthan gum shows broadband at  $3811\text{ cm}^{-1}$ , a typical stretch for the OH group. A band relating to stretching of the CH group shows up at  $2323\text{ cm}^{-1}$ . Bands at  $1600$  and  $1407\text{ cm}^{-1}$  represent stretching of the carbonyl (C=O) ester of acetyl groups and asymmetrical stretching of C=O for the carboxylate group, respectively. The polysaccharide likewise displayed a band at  $1250\text{ cm}^{-1}$ , ascribed to angular deformation of  $\text{CH}_3$  groups, and another  $1029\text{ cm}^{-1}$ , due to stretching of the CO bond.

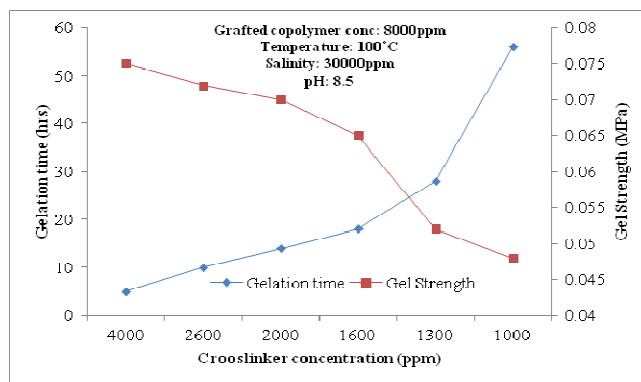
Polyacrylamide indicated bands at  $3853$  and  $3744\text{ cm}^{-1}$ , related with asymmetrical and symmetrical stretching of the NH bond, respectively. The band depicted at  $2366\text{ cm}^{-1}$  speaks to typical stretching of CH bonds. Typical bonds of amide are seen at  $1649$  and  $1419\text{ cm}^{-1}$ , the first corresponding to stretching of the C=O group (amide I) and the second to angular deformity of the  $\text{NH}_2$  group (amide II). The band at  $1316\text{ cm}^{-1}$  was credited to CN bond stretching. The grafted copolymer spectrum exhibited a combination of the bands found in spectra of polyacrylamide and xanthan gum, indicating grafting was effective.

The IR spectra of synthetically grafted polyacrylamide onto xanthan gum indicated broadband at  $3789\text{ cm}^{-1}$  corresponding to the overlapping of asymmetrical OH and NH stretches. The signal delineated at  $3338\text{ cm}^{-1}$  is identified with symmetrical stretching of the NH bond. A peak representing CH bond stretching is seen at  $2360\text{ cm}^{-1}$ , while an extraordinary peak, associated with superposition of the amide I band of polyacrylamide and asymmetrical stretching of carboxylate C=O shows up at  $1854\text{ cm}^{-1}$ . The signal observed at  $1659\text{ cm}^{-1}$  corresponds to amide II. Bands at  $1408$  and  $1037\text{ cm}^{-1}$  represent CN stretching and angular deformation of CH, respectively. Hence, these factors are viable proof for the successful grafting reaction.

### 3.2. Effect of Graft Copolymer and Cross-linker Concentration on Gelation Time and Gel Strength

The bottle test method demonstrates the impact of the grafted copolymer and cross-linker concentration on the gelation time and gel strength, and furthermore their huge impact on the physical properties of the gel. Figure 6 shows the cross-linker concentration versus the gelation time with gel strength and figure 7 also shows that of the graft copolymer concentration.

Figure 6 and 7 depicts that as both the grafted copolymer and cross-linker concentration increases the gel formation reaction increases, which leads to the decrease of the gelation time and increase in gel strength. This implies that there are more cross-linking sites accessible for the quick cross-linking reaction [19,20].



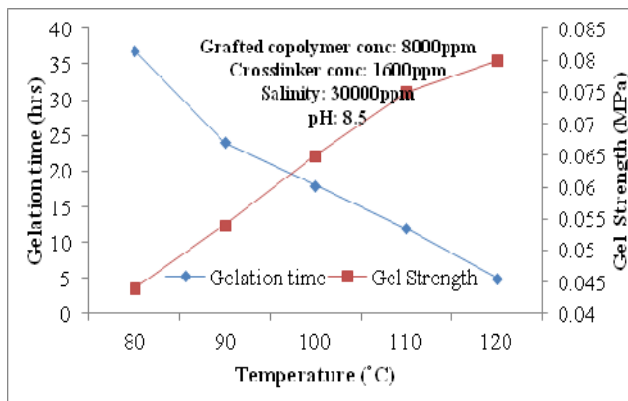
**Figure 6: Effect of cross-linker concentration on gelation time and gel strength**

Copolymer conc. ppm	Gel Strength codes																Gel Strength (MPa)	
	0.5	1	2	3	4	5	7	9	11	18	24	48	168(1week)	1month				
4000	B	B	B	B	C	C	D	D	E	E	F	F	G	G	G	G	G	0.048
6000	B	C	C	C	E	E	E	E	G	G	G	G	H	H	H	H	H	0.053
8000	E	E	F	F	G	G	G	G	H	H	I	I	I	J	J	J	J	0.065
9000	F	F	G	G	G	H	H	H	I	I	I	J	J	J	J	J	J	0.070
10000	G	G	G	H	H	I	I	I	J	J	J	J	J	J	J	J	J	0.073
12000	G	G	H	H	I	I	I	J	J	J	J	J	J	J	J	J	J	0.083



**Figure 7: Effect of grafted copolymer concentration on gelation time and gel strength**

Since the gelant will be injected through wellbore of different reservoir temperatures, it is important to contemplate the effect of temperature on the grafted copolymer gel. It can be seen from figure 8 that gelation time is exceptionally delicate to temperature. The gel strength increases with raised temperature, though the elevated temperature massively lessens the gelation time. This may be because the raised in temperature accelerates the thermal motion between the grafted copolymer and the cross-linker molecules [19,20].



**Figure 8: Effect of temperature on gelation time and gel strength of the PAAm-g-XG gel 3.4. Plugging Capability of the Graft Copolymer Gel**

The results of the sand pack flooding test before and after injection of the grafted copolymer gel from table 2 shows that the studied polymer could reduce the relative permeability of water from 7.6 to 0.08 Darcy. This is because the injection of grafted copolymer gel caused an additional resistance to brine flow, which causes a reduction in water relative permeability.

On the other hand, the reduction in oil relative permeability was also changed from 14.4 to 0.86 Darcy and the percentage permeability reduction was calculated to be 98.85% from equation 4. The residual resistance factor for water ( $F_{rrw}$ ) and oil ( $F_{rro}$ ) was calculated about 86.67 and 16.8 respectively. Therefore, the residual resistance factor ratio of water to oil was 5.16 which indicated the good performance of the grafted copolymer gel in reducing water relative permeability.

**Table 2: The results of sand pack flooding experiment for polyacrylamide grafted xanthan gum gel**

EX P	Before gel injection				After gel injection				RF (%)
	Oil injection		Brine injection		Brine injection		Oil injection		
	Rate (cm <sup>3</sup> / s)	Pressu re (atm)	Rate (cm <sup>3</sup> / s)	Pressu re (atm)	Rate (cm <sup>3</sup> / s)	Pressu re (atm)	Rate (cm <sup>3</sup> / s)	Pressu re (atm)	
1	0.4	0.61	0.45	0.61	0.02	2.24	0.02	0.68	53.5
2	0.7	0.68	0.8	0.68	0.04	2.79	0.04	0.82	56.8
3	1.0	0.75	2.0	0.75	0.09	3.13	0.09	0.95	58.2
Av g	$k_{o1}$ = 14.438 D		$k_{w1}$ = 7.597 D		$k_{w2}$ = 0.0876 D		$k_{o2}$ = 0.859 D		
<b>Sand pack one properties</b>					<b>Plugging capability</b>				
Pore volume 180		Swc = 21.0%			$F_{rrw} = \frac{k_{w1}}{k_{w2}} = 86.67$				
Bulk volume 432.9 cm <sup>3</sup>		Soi = 79.4%			$F_{rro} = \frac{k_{o1}}{k_{o2}} = 16.8$				
Porosity 42%		Sor = 51.0%			$RRF = \frac{F_{rrw}}{F_{rro}} = 5.16$				

Ka = 4.208 D	Mesh size: 300µm – 700µm	$\eta = \frac{k_{w1} - k_{w2}}{k_{w2}} * 100$ = 98.85%
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**4. Conclusions**

In the present paper, xanthan gum was successfully grafted onto polyacrylamide backbone by the free radical polymerization process. The grafted copolymer was characterized by Fourier transfer infrared spectroscopy (FTIR), with the peaks indicating that the polymer was indeed grafted.

The impact of graft copolymer concentration on gelation time and gel strength indicated that with the increase in the graft copolymer concentration the gelation time decreases and the gel strength increases. High cross-linker concentration causes gel syneresis.

The gel formed with the grafted copolymer was sensitive to temperature, as the temperature increases the gelation time reduces and gel strength increases.

In the sand pack experiment, the permeability was reduced after plugging the pack with the graft copolymer gel system. The gelation time and gel strength can be adjusted by engineers in the oil and gas industry during the profile modification treatment with this grafted copolymer gel.

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