

# Synthesis and Evaluation of Xanthan-G-Poly (Acrylamide) Co-Polymer for Enhanced Oil Recovery Applications

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## Research Article

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## Abstract

Xanthan is a natural biopolymer, which grafted with vinyl monomers through typical free radical initiation and applied in enhanced oil recovery (EOR) techniques. Application of xanthan in oil reservoirs suffer from microbial and thermal degradation under harsh petroleum reservoir conditions. In this research, xanthan grafted with poly (acrylamide) polymer in the presence of potassium per sulfate as a water-soluble initiator. Structure determination occurs by different spectroscopic techniques involving (FTIR) spectroscopy and nuclear magnetic resonance (<sup>1</sup>H-NMR). Assessment of polymer solution rheology occurs as a function of mechanical, chemical and thermal degradation at simulated reservoir conditions. Flooding tests carried out through unconsolidated sand packed model.

**Keywords:** Xanthan; Chemical flooding; Enhanced oil recovery and Polyacrylamides

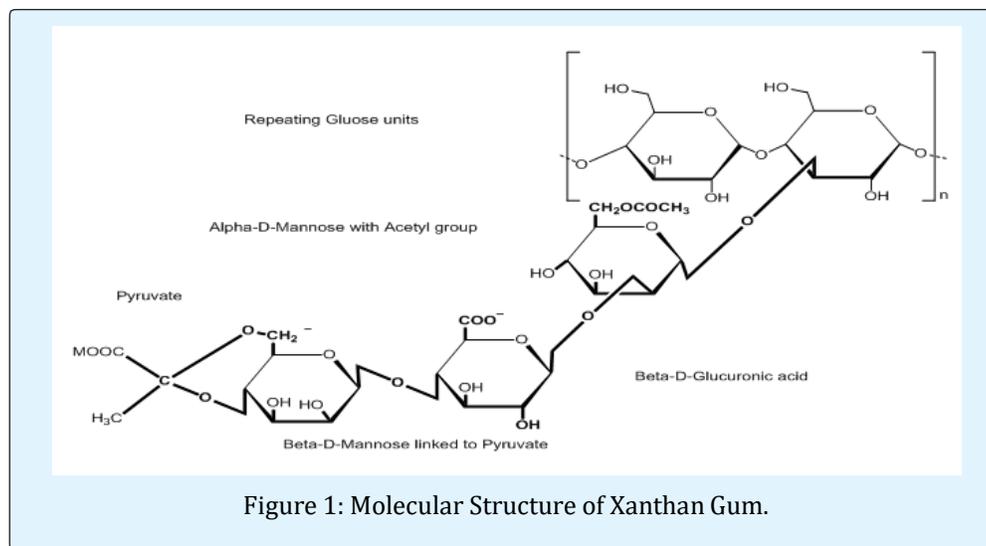
## Introduction

Currently, chemical flooding through sandstone reservoirs acquire more attention due to incremental energy demand [1], and giant residual oil in fossil reservoirs after primary and secondary recovery [2]. Enhanced oil recovery (EOR) by biopolymers including starch and xanthan gum is a promising practice, since they are low-priced, plentiful and environmentally friendly applicants [3-8]. Xanthan gum is a heteropolysaccharide macromolecule produced by the microbial

action of *Xanthomonascampestris* through fermentation of glucose or fructose with a protein supplement and an inorganic source of nitrogen. Its main chain as shown in Figure 1 consist of glucose units arranged in a helical structure, where branches fold in, along the backbone. The side chain consists of alpha-D-mannose that contains an acetyl group, beta-D-glucuronic acid, and a beta-D-mannose terminal unit, linked to a pyruvate group. Alternate glucoses have a short, three-sugar branch consisting of a glucuronic acid sandwiched between two mannose units. Thus, the overall repeating structure is a

pentasaccharide. The terminal mannose has attached pyruvate group and the mannose adjacent to the main chain may have an acetyl group attached to C<sub>6</sub>. The glucuronic and pyruvic acid groups give xanthan gum a highly negative charge. The presence of anionic side chains on the xanthan gum molecules enhances hydration, where xanthan gum soluble in cold as well as hot water, and has very high molecular weight (2 - 50 × 10<sup>6</sup> g/mol). Moreover, xanthan gum is compatible with most surfactants and other injection fluid additives used in

tertiary oil recovery formulations due to; 1) Xanthan gum has excellent viscosifying criteria, as it could significantly increase the viscosity of the injected brine at very low concentrations even in high salinity reservoirs; 2) resistant to shear degradation, exhibit pseudo-plastic behavior; 3) stable over large ranges of pH and less sensitive to mechanical shearing, elevated salinity and to divalent ion concentration (hardness) than hydrolyzed polyacrylamides (HPAM) owing to its rigid polysaccharide chains.



Grafting of vinyl monomers on xanthan [9] carried out by different initiators like ammonium and potassium persulfate [10, 11]. Some literature reported about grafting of vinyl monomers [12] such as acrylamide, acrylic acid, vinyl methacrylate and 2-acrylamido-2-methyl-1-propane-sulfonic acid (AMPS) on xanthan, and then applied as chemical flooding agent in EOR process [13-23]. In this research, xanthan gum grafted with poly (Acrylamide) through free radical polymerization. Grafting of acrylamide [24] on xanthan enhance its rheological properties [25]. Assessment of rheological and solution criteria carried out as a function of mechanical, chemical and thermal degradation [26, 27]. Flooding results through unconsolidated sand packed model at simulated reservoir conditions, indicate that the synthesized polymer can be regarded as an effective chemical flooding agent [1].

## Experimental

### Materials

Commercial xanthan gum; Acrylamide (AM ≥ 97%); acetone ≥ 97% ethanol ultra-pure; Potassium persulfate

(KPS ≥ 99 %). All chemicals supplied by Sigma-Aldrich excluding xanthan purchased from commercial source.

### Characterization and Equipment

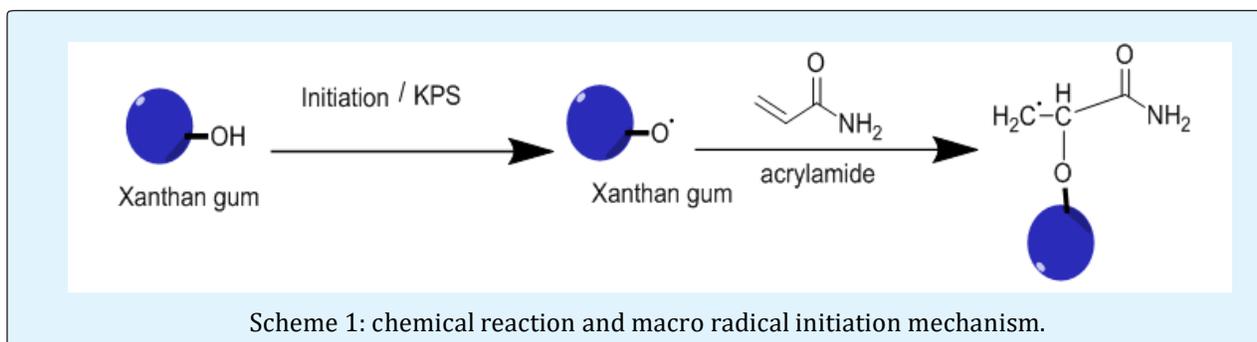
<sup>1</sup>H-NMR spectrum carried out with a BrukerEMX420MHz NMR spectrometer after accumulating 32 scans, using D<sub>2</sub>O as a solvent and tetramethylsilane (TMS) as internal standard. FTIR spectrometric analysis carried with KBr pellets on American FTS-3000 infrared spectrometer in the optical range 400–4000 cm<sup>-1</sup>. Rheological measurements carried out on Brookfield programmable DV-II+ viscometer. Viscosity of solutions investigated with respect to shear rate, salinity and temperature [1].

### Synthesis

In a three-neck 250 ml flask equipped with condenser, thermometer and nitrogen inlet/outlet, 16.9 gm of Acrylamide completely dissolved in 200 ml of deionized water. To this mixture, add 1.6 gm of xanthan gum and 0.491gm of KPS and stir at for 30 minute under nitrogen blanket until complete dissolution. Adjust the temperature at 60 °C, where the polymerization reaction

proceed for 10 hours. After cooling, the viscous polymeric gel precipitated by ethanol, then soxhlet extraction with acetone for 24 hour at 60 °C, then crushed and stored on

silica gel bed. The chemical reaction illustrated in scheme 1.



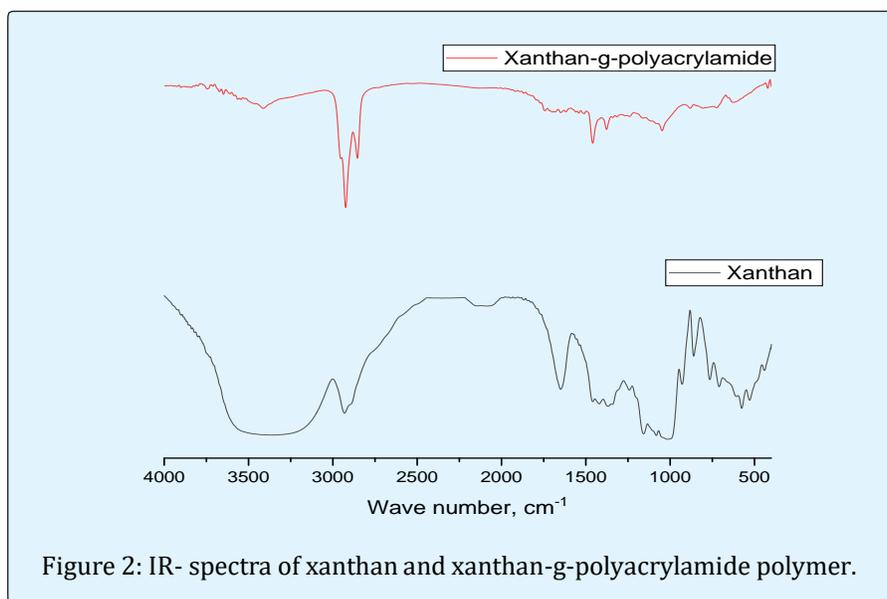
### Polymer Flooding through Unconsolidated Sand Packed Model

Flooding runs performed through unconsolidated sand packed linear model, where flooding conditions and model properties stated according to our previous work [1]. Sand cleaned and evacuated regarding to the standard cleaning procedure then saturated with brine solution for 12 days followed by oil soaking, after that, brine flooded until oil cut terminated (i.e. oil cut <1%) [28]. Solution of the prepared copolymer flooded at simulated reservoir temperature of 60 °C, followed by brine flooding until expelled oil ceased in the effluent [29]. Recovered oil quantity calculated on volume foundation.

### Results and Discussions

### Structure Spectroscopic Analysis

Infrared spectrum of **Xanthan gum** (Figure 2) as reported in literature Faria S, de Oliveira Petkowicz CL, de Morais SAL, Terrones MGH, de Resende MM, et al. [30] shows absorption peaks at 3200-3450  $\text{cm}^{-1}$  due to the (O-H) axial deformation and 2850-2950  $\text{cm}^{-1}$  due to symmetric and asymmetric stretching vibrations of (C-H) group in methyl and methylene groups. The bands at 1710  $\text{cm}^{-1}$  due to C=O stretching vibration, while bands near to 1530-1650  $\text{cm}^{-1}$ , due to axial deformation of (C-O) of enols. IR spectra of **Xanthan-g-polyacrylamide** (Figure 2) show characteristic peaks at 1459  $\text{cm}^{-1}$  assigned to (C=O) of amide group (O=C-NH<sub>2</sub>). Absence of vinyl groups characteristic bands indicate that polymerization occurs successfully. Absorption peaks at 3412  $\text{cm}^{-1}$  attributed to the stretching vibrations of (-NH<sub>2</sub>) group.



**$^1\text{H-NMR}$  spectrum of Acrylamide monomer** (Figure 3a) shows chemical shifts at  $\delta$  (ppm) = 6.83 (s, 2H,  $-\text{CONH}_2$ ); 6.37 (q, 1H,  $-\text{CH}=\text{CH}_2$  terminal vinyl group), 5.72-5.88 (dd, 2H,  $-\text{CH}=\text{CH}_2$  terminal vinyl group).  **$^1\text{H-NMR}$  spectrum of xanthan** (Figure 3b) display chemical shifts at  $\delta$  (ppm) = 1.33 (s, 3H, terminal  $-\text{CH}_3$  group of pyruvate); 2.04 (s, 3H, terminal  $-\text{CH}_3$  group of acetyl group in  $\alpha$ -D-mannose); chemical shifts at  $\delta$  (ppm) = 2.1- 4.9 correspond to  $(-\text{OH} \ \& \ -\text{CH}_2)$  groups of anhydro glucose units of xanthan [31]. **The  $^1\text{H-NMR}$  spectrum of Xanthan-g-polyacrylamide** (Figure 3c) display chemical shifts at  $\delta$  (ppm) = 6.78-6.86 (s, 2H,  $-\text{CONH}_2$ ); 6.37 (q, 1H,  $-\text{CH}=\text{CH}_2$  terminal vinyl group), 5.72-5.88 (dd, 2H,  $-\text{CH}=\text{CH}_2$  terminal vinyl group). Absence of chemical shift at  $\delta$  (ppm) = 7.1 related to vinyl bond ( $-\text{CH}=\text{CH}_2$ ) indicates complete monomers polymerization[1, 32]. Chemical shift of vinyl group from 5.72-6.37 in acrylamide monomer to 1.32 & 4.3 in Xanthan-g-polyacrylamide polymer confirm that acrylamide grafted with xanthan gum.

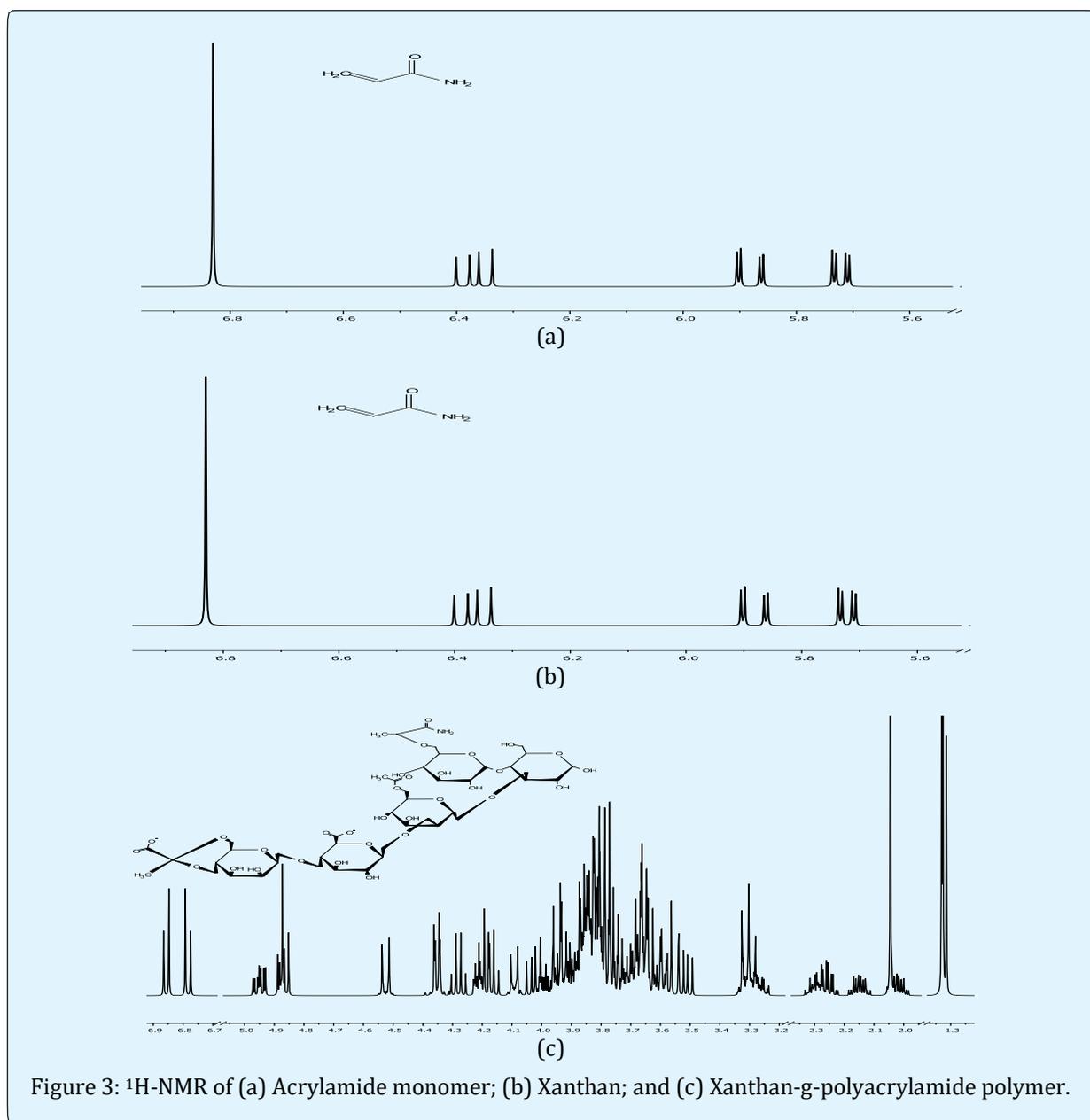


Figure 3:  $^1\text{H-NMR}$  of (a) Acrylamide monomer; (b) Xanthan; and (c) Xanthan-g-polyacrylamide polymer.

### Mechanical Degradation

Mechanical degradation of polymer evaluated through studying effect of different shear rates on polymer solution, where shear stress and viscosity versus shear rate reported as shown in Figure 4 [33]. It is obvious that the prepared polymer display shear thinning effect (i.e. pseudo plastic fluids) which is often used by chemical flooding agents [34]. Shear stress calculated through the power law model [35].

$$\Gamma = K\gamma^n \quad (\text{Equation 1})$$

Where, ( $\Gamma$ ) shear stress, Pascal; ( $\gamma$ ) shear rate,  $s^{-1}$ ; ( $k$ ) is the coefficient of flow consistency, ( $Pa \cdot s^{-n}$ ); and ( $n$ ) is the flow behavior index [1]. For pseudo plastic fluids,  $n$  is typically lower than or equal unity ( $n \leq 1$ ). In this study ( $n$ ) calculated to be 0.3091. This indicates that the prepared polymer is a pseudo plastic fluid, which is widely implemented in EOR [1, 34]. Moreover, viscosity slightly decrease by shear rate increase.

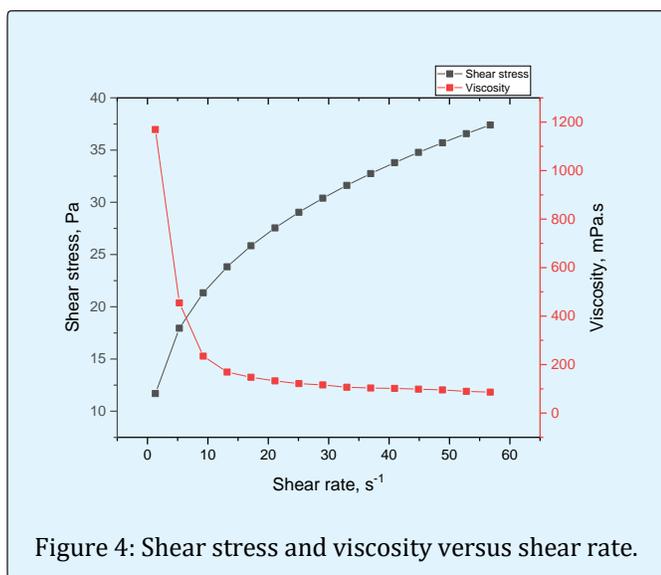


Figure 4: Shear stress and viscosity versus shear rate.

### Chemical Degradation

Polymer solutions subjected to high mineral concentrations during flooding process. This leads to chemical degradation of polymer chains. The prepared polymer assessed at salinity of 75,000 ppm as NaCl equivalent at different shear rates as exhibited in Figure 5. It is found that, polymer exhibit reasonable resistance against chemical degradation and this may resort to increasing of hydrodynamic volumes of the prepared polymer in saline solutions [29] which in turn prevents

the chain from curling, so viscosity reduction decreases [1].

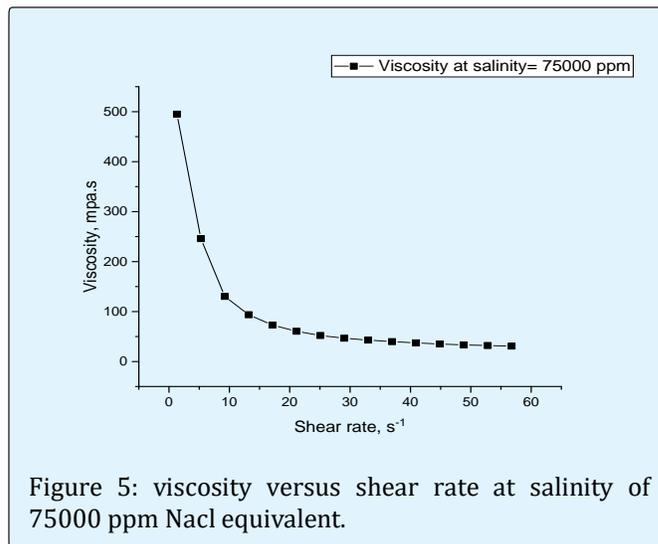


Figure 5: viscosity versus shear rate at salinity of 75000 ppm NaCl equivalent.

### Thermal Degradation

Hydrolyzed polyacrylamides suffer from thermal degradation at harsh reservoir conditions, so polyacrylamide grafted with xanthan to enhance its thermal stability. In this study, the prepared polymer dissolved in distilled water at concentration of  $1.5gL^{-1}$ , then subjected to temperature of  $80^{\circ}C$  at different shear rates as shown in Figure 6. The viscosity decrease slightly above shear rate of  $33.0 s^{-1}$ . This behavior of reasonable thermal stability resort to gelation effect of xanthan by temperature increase [1, 33].

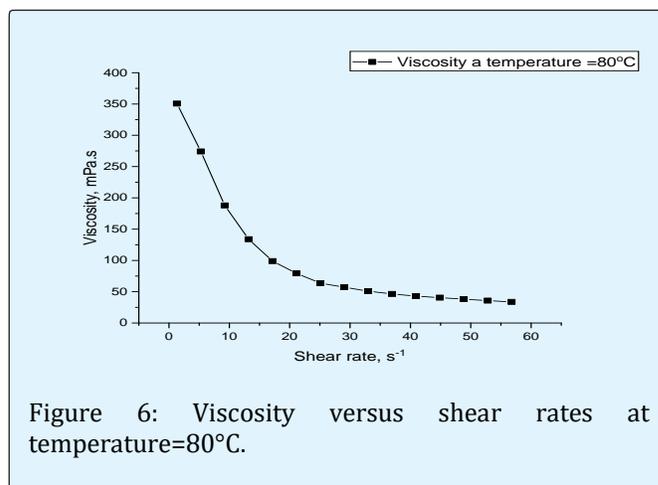
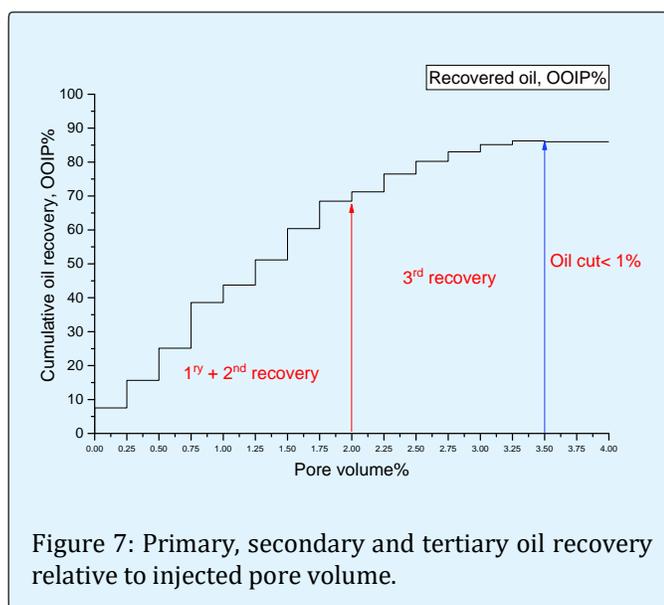


Figure 6: Viscosity versus shear rates at temperature= $80^{\circ}C$ .

## Flooding Experiments

Flooding tests carried out on linear unconsolidated sand packed model as reported previously at temperature of 60°C at polymer concentrations ( $1.5 \text{ gL}^{-1}$ ) [1]. The sand pack saturated firstly with brine followed by oil saturation until water effluent was less than 1%, after that brine flooded until ejected oil cut become less than 1%. At this stage, the recovered oil amount represent primary and secondary oil recovery that, reach to 68% of original oil in place (OOIP). The residual oil amount estimated to be 32% OOIP, and represents tertiary oil recovery. The sand pack flooded with polymer solution at concentration of  $1.5 \text{ gL}^{-1}$ , until oil cut become less than 1%. The recovered oil amount calculated and estimated to be 18% of OOIP as indicated in Figure 7. The obtained results indicate that the prepared xanthan-g-polyacrylamide polymer can be considered as an EOR applicant due to its gelling effect, which increase aqueous phase viscosity and enhance sweeping efficiency, so increase recovery factor.



## Conclusion

Xanthan gum successfully grafted on poly (Acrylamide) polymer through free radical emulsion polymerization. Structure determination proved by spectroscopic analysis. Rheological and solution properties at simulated reservoir conditions including mechanical, chemical and thermal degradation carried out to evaluate the polymer ability as a chemical flooding agent. Flooding tests performed on unconsolidated sand packed model, where the recovery factor reach to 18% of original oil in place

(OOIP). Consequently, this polymer can be considered as an effective EOR candidate.

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