

# **A REVIEW ON POLYMER FLOODING IN ENHANCED OIL RECOVERY UNDER HARSH CONDITIONS**

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## **ABSTRACT**

Polymer flooding is a commercially verified technology to enhance the recovery of residual oil from oil reservoirs. Polymers are used to increase the viscosity of the displacing phase. Accordingly, they resulted in a significant reduction in the mobility ratio between the water and oil. Due to the decrease in the mobility ratio, the sweep efficiency will significantly increase compared to water flooding. This paper aims to provide a comprehensive review on thermal and chemical stability and the rheological properties of various water-soluble polymers used in sandstone and carbonate reservoirs. The properties of conventional and novel water-soluble polymers applied in enhanced oil recovery (EOR) are discussed along with their limitations. Moreover, field and laboratory core flooding data of different water-soluble polymers are presented. This review covers current research studies on the application of polymer flooding to high-temperature and high-salinity reservoirs. It also provides recommendations for future work on synthesis of novel polymers with higher stability under harsh reservoir conditions.

**Keywords:** Polymer flooding, Hydrophobic polymer, Cationic monomer, Acrylamide, Enhanced oil recovery.

## **1 INTRODUCTION**

Crude oil is an essential material for energy and many petrochemical industries. Due to the increasing demand of energy, it is essential to maximise the recovery from oil reservoirs and increase the exploration activities of new fields. It is estimated that only 30% of original oil in place (OOIP) can be recovered using the conventional oil recovery methods. Enhanced oil recovery (EOR) techniques are considered to recover oil that cannot be produced using the primary and secondary recovery methods. Chemical EOR which involves polymers, surfactants, and/or alkali flooding is considered as one of encouraging EOR methods [1].

In 1960, polymer flooding was proposed as an EOR technique to improve the mobility ratio between the displacing phase (water) and displaced oil. Many studies and field applications were implemented in polymer flooding during 60s-70s. Nowadays, polymer technology is one of the most widely applied mobility control techniques. Water-soluble polymers with high molecular weight are utilised to increase water viscosity and consequently, improve displacement and volumetric sweep efficiencies[2]. Researchers at the Daqing oil field performed a significant number of polymer flooding experiments in a microscopic model which made momentous development in polymer flooding technology[3]. They concluded that polymers' viscoelastic properties can improve volumetric sweep and microscopic displacement efficiencies as it can mobilise residual oil in small pores and oil droplets trapped by capillary forces. However, given a severe reservoir conditions of high temperature and high pressure that exist in many oil reservoirs, new limitations appear with the usage of water-soluble polymers as they must be stable in a saline environment, high concentration of divalent ions, and elevated reservoir temperatures (>70°C) [4].

There are numerous polymers that are commercially used for EOR applications. The most applied polymer in EOR applications is partially hydrolysed polyacrylamide (HPAM), which is a co-polymer of acrylamide and acrylic acid. Many attempts were reported about chemical modifications of the conventional HPAM. In this review, the latest proposed chemical modifications to HPAM have been summarised and their structure-property relationship has been discussed.

## 2 TYPES OF POLYMERS USED IN EOR

### 2.1 Partially hydrolysed polyacrylamide (HPAM)

Water soluble polyacrylamide (PAM) is commercially used for EOR application, is known as partially HPAM, and is composed of a copolymer of acrylamide (AM) and acrylic acid. This polyelectrolyte copolymer has high tendency to interact with solution ions. Due to its flexible polymer chain structure, the viscosity of this polymer is dependent on the ionic strength of aqueous solution [5].

#### *Rheological Properties of HPAM*

The presence of electrolytes in aqueous solution decreases the electrostatic repulsion between the carboxylate groups that exist on the polymer backbone structure. This phenomenon is called “shielding effect” which reduces the existing layer of negative charge that formed due to carboxylate groups [6]. Shielding effect progresses with increasing salt concentration, which cause a significant decrease in electrostatic repulsion between negatively charged carboxylate groups. It was estimated that the viscosity of the polymer solution decreases 10 times of its initial value when the NaCl salt concentration increases with a factor of 10 above 3% [7]. Additionally, the effect of divalent cations is greater than monovalent ions ( $\text{Na}^+$  and  $\text{K}^+$ ) at the same concentration. Accordingly, the salt concentration at which the polymer backbone coils up is lower in the presence of divalent ions [6].

Chang [7] concluded that the hydrolysis rate is significantly affected by the change of temperature and/or pH. The degree of hydrolysis (DOH) increases with an increase in temperature. Accordingly, rapid rate of hydrolysis is observed at 90°C, modest at 70°C, and insignificant at 50°C. According to the rheological study conducted on HPAM polymer sample aged for few days at 100°C, the DOH reached 90%. However, the sample reached 70% when aged for 100 days at 83°C. Moradi et al.[8] , also concluded that HPAM can be applied in EOR applications in the presence of calcium ions up to reservoir temperature of 75°C. They have reported that when water salinity is less than 200 ppm, HPAM can be safely used up to 100°C.

### 2.2 Hydrophobically associating polyacrylamide polymers (HAPAMs)

Hydrophobically associating polyacrylamide polymers (HAPAMs) were synthesised by modifying partially HPAM through the incorporation of hydrophobic chain linked with the main hydrophilic backbone. It also synthesised by copolymerisation of a hydrophilic monomer (e.g. acrylamide) with another monomer that contains a hydrophobic group [9]. Due to the unique properties of this polymer, it is considered as a promising candidate for polymer flooding at harsh conditions [10]. Hydrophobic groups that linked with the polymer backbone aggregate and form microdomains. These microdomains are stronger in a block like structure than random one. The distribution of the hydrophobic groups is affected with the surfactant to micelle ratio (SMR). The formation of block-like structure is more likely at low values of SMR, conversely, a random structure is expected at high SMR. List of hydrophobic monomers have been illustrated in Table 1.

#### *Rheological Properties of HAPAMs*

The existence of the hydrophobic groups hinders the polymer solubility. Consequently, the solubility associated limitations are expected if the incorporation rate of hydrophobic groups exceeds a certain limit. This phenomenon has been observed with poly(di-*n*-octylacrylamide-co-acrylamide) in which phase separation is noticed when the incorporation rate of DOAM monomer exceeds 1.2 mol% [11, 12]. Hydrophobic groups with high hydrophobicity yield enhanced polymer thickening capability. Different ways in use to increase the hydrophobicity of the groups including the usage of win-tailed hydrophobes, increased hydrophobic group length and fluorocarbons rather than hydrocarbons.

The critical polymer concentration at which hydrophobic aggregation arise is decreased compared to the classic associating polymers due to the strong interaction forces between the hydrophobic groups with high hydrophobicity,. The hydrophobic groups length is essential for aggregation as short hydrophobe will not form hydrophobic aggregation e.g. DDAM co-monomer. However, increasing the hydrophobicity to very

high-level cause solubility issues. Additionally, it has been proven that the introduction of phenyl containing monomer rises the thermal stability[12].

### 2.3 Ionic modified polyacrylamides

Ionic modified polyacrylamides include polyelectrolyte and polyampholytes copolymers. Polyelectrolytes are those polymers that bear only one charge and involve the cationic and anionic copolymers. Polyampholyte which bears two different charges present at the same polymeric backbone was highly evaluated for EOR applications due to its unique characteristics. The rheological properties of these polymeric systems can be customised by careful molecular design, i.e. the ratio of the different monomers. A list of cationic and anionic monomers is indicated in Table 1.

#### *Rheological Properties of HAPAMs*

Polyelectrolyte polymer displayed high thermal stability and thickening capability in fresh water as it retains repulsive forces between the charged groups present on the polymer backbone. Consequently, it yields the maximum viscosity in fresh water. Nevertheless, in the presence of electrolytes there is a significant decline in its viscosity owing to the decrease in the repulsive forces between molecules, and hence the hydrodynamic volume shrinks. The viscosity of a polyampholytic solution increases with the increase in salinity under certain conditions [13].

In polyelectrolyte polymers, it was observed the type of the charge (e.g. carboxylate or sulfonate anion) influences polymer solubility and the association behaviour. This is not perceived in a zwitterionic polymer. Co-monomers with low charge density (e.g. carboxylate groups) showed stronger association beyond the critical association. However, co-monomers with higher charge density e.g. sulfonate anions have yielded a reverse behaviour. Polymeric systems which contain groups of high charge density are more prone to screen out in high concentration of electrolytes [13].

Table 1. Monomers used to increase acrylamide stability

<b>Hydrophobic monomers</b>	<b>Ref.</b>
N-hexadecylacrylamide (C <sub>n16</sub> -AM)	[14]
Allyl-β-cyclodextrin (A-β-CD)	[15]
Octadecyl dimethyl allyl ammonium chloride (C <sub>18</sub> DMAAC)	[15]
1-(4-dodecyloxy-phenyl)-propenone (DPP)	[9]
N-benzyl-N-octylacrylamide (BOAM)	[16]
Di-N-dodecylacrylamide (DDAM)	[12]
Di- N-octylacrylamide (DOAM)	[12]
<b>Anionic Monomers</b>	
Sodium acrylate (NaA)	[17]
Methacrylic acid (MAA)	[18]
2-(Acrylamido)-dodecanesulfonic acid (AMC <sub>12</sub> S)	[9]
3-(2-(2-Heptadec-8-enyl-4,5-dihydro-imidazol-1-yl)ethylcarbamoyl)acrylic acid (NIMA)	[19]
3-(Diallyl-amino)-2-hydroxypropyl sulfonate (NDS)	[19]
<b>Cationic Monomers</b>	
Acryloylmorpholine (ACMO)	[20]
Dimethylaminoethyl methacrylate (DMAEMA)	[17]
2-(Acrylamido)-2- methylpropyl]trimethylammonium chloride (AMPDAC)	[13]

### 3 LABORATORY AND FIELD APPLICATIONS OF VARIOUS POLYMER SYSTEMS

The application of polymer flooding in severe reservoir conditions of high temperature and salinity is the actual challenge. HPAM injection in harsh condition requires high concentration due to its poor resistance to

chemical degradation. Consequently, polymers with better stability in higher temperature and saline environment were proposed. Moreover, a summary for the core flooding data of recently synthesised polymers along with incremental oil recovery after applying polymer flooding is illustrated in Table 2. It is clearly shown in Table 2 that polymer flooding is highly applied in sandstone reservoirs.

Table 2. Laboratory Core flooding data of some selected polymers

Polymer	Conc. (ppm)	Porosity (%)	Permeability (mD)	Salinity ppm	Oil viscosity cp	Lithology	T °C	Oil Rec. %	Ref.
HAPM	2000	31.6	2.49	2000	NR	Sand pack	95	10.5	[21]
HAP-4	2000	32.1	2.51	2000	NR	Sand pack	95	28.3	
HAP-CDE	2000	31.2	2.48	2000	NR	Sand pack	95	34.8	
AM-MAA- (C <sub>n16</sub> - AM)	1000	23	7	5000	32	Carbonate	60	10.23	[14]
AM-MAA	1000	23	7	5000	32	Carbonate	60	4.9	
HPAM	2000	35	1.67	21000	NR	Sand pack	80	5.6	[15]
AM-(A-β-CD)- (C <sub>18</sub> DMAAC)	3000	35	1.69	21000	NR	Sand pack	80	11.3	
AM-(A-β-CD)- (C <sub>18</sub> DMAAC)	3000	35	1.72	21000	NR	Sand pack	80	15.5	
HPAM	1000	23.62	7.841	7200	67.4	Sand pack	80	1.31	[19]
AM-AA- NIMA	2000	23.60	7.840	7200	67.4	Sand pack	80	4.18	
AM-AA-NDS- NIMA	2000	23.59	7.838	7200	67.4	Sand pack	80	4.80	
HPAM	500	32.12	1.7356	NR	45.6	Sand pack	65	6.23	[9]
AM- AMC <sub>12</sub> S- DPP	500	35.33	1.8223	NR	45.6	Sand pack	65	11.26	
AM- AMC <sub>12</sub> S- DPP	1500	33.56	1.7769	NR	45.6	Sand pack	65	15.67	

Polymer flooding has been widely applied in numerous oil fields. China is a leading country in applying EOR projects and it has the largest oil field “Daqing” where polymer flooding has been highly applied[3]. Tables 3 summarises some recent polymer flooding field applications [22]. HPAM is widely applied in field applications even though the presence of many new polymers have been synthesised and characterised by laboratory evaluation.

Table 3. List of polymers applied in various fields

Field	Polymer type	Temp. °C	Salinity ppm	Oil viscosity cp	Incremental oil Recovery (OOIP %)	Ref.
Bohai Bay	HAPAM	98	6071	70	3	[23]
Grimbeek II	HPAM	60	25000- 32000	120	11	[24]
North african field	Acrylamide/ATBS/AA	74	86000	23	10.4	[25]
Supermature Field	HPAM	50	20000	19	5-10	[26]
Brazilian Field	HPAM 30 % acrylate and 70 % acrylamide	50	3800	NR	17	[27]
Palogrande - Cebú Field	HPAM	62	700	9.4	10	[28]
Belayim land filed	Polyacrylamide	76	200000	8	NR	[29]
Pelicon lake	HPAM	NR	26000	25	25	[30]

#### 4. CONCLUSIONS

This review summarises the rheological properties, core flooding data, and field applications of polymer systems that have been applied recently in polymer flooding. These polymers include partially hydrolysed polyacrylamide, hydrophobically associating polyacrylamide and ionic modified polyacrylamides, which comprise anionic, cationic and polyampholyte. The essential parameters that should be considered for polymer flooding include reservoir temperature, formation brine salinity, oil viscosity and formation type. HPAM provide acceptable viscosifying effect if formation water salinity with less than 200 ppm and can be safely used up to 100°C. Hydrophobically modified polymers can yield good viscosification besides high thermal stability due to the formation of hydrophobic microdomains. For harsh conditions, different copolymers have been reported in the literature. The data summarised in this work indicate that most of the recent research is dedicated to synthetic polymers (e.g. acrylamide) especially hydrophobically associating polyacrylamides and most of the rheological evaluation studies have changed from HPAM to novel hydrophobically modified copolymers. However, HPAM is considered to be the most applied polymer especially in sandstone reservoirs due to its low cost.

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