Polyhydroxybutyrate for Improved Oil Recovery: A Literature Review

Norrulhuda Mohd Taib¹, Norfarisha Achim, Zulkafli Hassan

Faculty of Chemical Engineering, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia 1 E-mail: norrulhuda74@salam.uitm.edu.my

ABSTRACT

In this study the role of polymer flooding as one of the most efficient processes to enhance oil recovery (EOR) is discussed. Polyhydroxybutyrate (PHB) is a bio-based polymer that has potential application for use in polymer flooding. This polymer is reviewed with particular emphasis on the effect of concentration, shear rate, salinity, hardness and temperature on polymer viscosity. Initial findings showed that PHB owned higher resistant as compared to mechanical degradation and thermal stability of HPAM as well as XG.

Keywords: polymer flooding, partially hydrolyzed polyacrylamide, xanthan gum, polyhydroxybutyrate and rheology

INTRODUCTION

The most commonly applied chemical enhanced oil recovery technique is polymer flooding. Traditional waterflooding requires management of substantial volume of injected and produced water. Polymer flooding on the other hand minimized the requirement of water injected and water produced. The most obvious and significant mechanism of polymer flooding is improving the sweep efficiency by reducing relative permeability of water

 (k_{rw}) relative to oil permeability (k_{r0}) . This will decrease disproportionate permeability reduction and reduce viscous fingering. It also has been suggested that the viscoelastic behavior of polymers will also improve displacement efficiency. The two commonly use polymers in EOR application are synthetic partially hydrolyzed polyacrylamide (HPAM) and biopolymer xanthan gum (XG).

The traditional polymers rely on physical entanglement and chain extension for viscosity enhancement. The carboxylate group of HPAM cause chain expansion due to repulsion of the ionic group thus promoting higher solution viscosity. Normally, oilfield operation used high molecular weight polymers which promotes high viscosity at a given polymer concentration. HPAM has shown good performance for low salinity reservoir but imposes some limitation at high salinity reservoir and in shear degraded condition. High shear rate near wellbore or during pumping cause breakage of polymer backbone resulting in viscosity reduction. Viscosity of HPAM is also reduced in increased salinity and hardness. This situation happened due to shielding of ionic groups which reduces repulsion and cause chain contraction. Presence of high concentration of divalent ions can cause HPAM precipitation. Remaining HPAM in the oilfields produced water lead to difficulty in water-oil separation. As a result, treatment cost for produced water will be expensive due to high concentration of HPAM in waste water.

In contrast to HPAM, XG is a rigid polysaccharide that is insensitive to salinity and divalent ions concentration. Its strong ability to increase shear viscosity together with excellent stability in mechanical degradation condition and high temperature makes it suitable for EOR. Not only for flooding purpose, XG is also used as a drilling fluid because it is not prone to shear degradation. However, usage of XG may cause injectivity problem due to remaining cellular debris from manufacturing process. XG is also susceptible to biodegradation and expensive. Generally, HPAM is efficient for usage at increasing viscosity of up to about 1% mass of NaCI while XG is more efficient in higher salt concentration [1]. Both polymers suffer viscosity loss at higher temperature.

The main concerns related with polymer flooding are the effects of temperature and salinity of formation water on stability of the polymer solution. New advancement in polymer flooding technology produced

new polymers which able to withstand harsh environment. However, these polymers are still in development phase and has no field documented. Many polymers are sum in development phase and has no nerd documented. Many
oil reservoirs contain connate water with high concentration of NaCI and divalent ions. Usage of biodegradable polymer solves waste management issues concerning and is relatively less expensive when compared to synthetic polymers. Demands for biopolymer such as polyhydroxybutyrate (PHB) are increasing. The potential for PHB as plugging agent for soil remediation and enhanced oil recovery (EOR) application has been studied [2]. Findings showed that among other biopolymers usage, PHB demonstrated best plugging effect which can reach more than billion-fold permeability reduction. As for EOR, injecting PHB as gel solution into high permeability "thief" zones is one of practical method to improve sweep efficiency. However, few publications have reported plugging with intracellular polymers such as PHB especially for EOR application. on reservoirs comain connaie water with high concentration of NaCl and This review examines the use of \mathbb{F}_{p} polymer flooding and includes synthesis and includes synthesis and includes synthesis and includes synthesis and include synthesis and include synthesis and include synthesis and

> This review examines the use of PHB for polymer flooding and includes synthesis and rheology.

DISCUSSION

Background A. Background

One of the biodegradable polymers that received strong interest is polyhydroxyalkaonate (PHA). Common PHA monomer is Poly-3 hydroxybutyrate (PHB). PHB is a linear polyester of D(-)3-hydroxybutyric acid which was first discovered in bacteria by Lemoigne in 1925. Figure 1 shows general structure of PHB. One of the biodegradable polymers that received strong interest is polyhydroxyalkaonate (PHA). Generally and the polyhydroxyalkaonate (PHA). Generally and the polyhydroxyalkaonate (PHA). Generally and the polyhydroxyalkaon α hydroxyalkaonale (PHA). Common PHA monomer is Poly-3-hydroxyalkaonale (PHA). Common PHA monomer is Poly-3-

Figure 1: General Structure of Polyhydrobutyrate (PHB) [3] **Figure 1: General Structure of Polyhydrobutyrate (PHB) [3]**

PHB become an attractive to common plastic due to its properties including complete biodegradability, good resistance to water and thermoplastic. Since PHB is produced by bacterial fermentation, it has high purity where it results in high degree of crystallinity (almost 80%). However, PHB produced by bacterial fermentation as commodity polymer is limited due to high production cost about (4US\$/kg) which is four fold higher than petroleum derived plastic (<1 US\$/kg) [4]. Many efforts have been dedicated to reduce production cost of PHB which is about 50 % cost comes from raw material cost [5]. Large scale of PHA production used glucose and fructose as main carbon source. Application glucose as substrate contributed to high material cost and it contains low carbon source thus leading to low yield of PHA production. Other available option for PHA biosynthesis is by focusing on utilizing industrial wastes. It is a valuable approach of using these wastes as it helps in reducing cost of sludge handling. Unfortunately, due to high contain of chemical oxygen demand (COD) and biochemical oxygen demand (BOD) and low yield of PHA hinder its successful commercialization of PHA.

Plant oil including soybean oil, palm oil, olive oil, sunflower oil and coconut oil has shown great potential as carbon source for PHA production. Issues arise when plant oil used in biopolymer production as it is unethical, wasteful and may cause imbalance to food supply. To mitigate these problems, an alternative substrate for PHB production is jatropha oil. Finding from [6] reported that about 87% of PHB were accumulated via fermentation of *cupriavidus necator* H16 by using jatropha oil. Jatropha oil is a potential renewable resource as jatropha plantations are non-edible oil, highly resistant to pest and drought, relatively low cost and yield high amount of oil.

Physical Properties

The PHB is a biocompatible thermoplastic, biodegradable and highly viscous polymer. The pure properties of PHB are shown in Table 1.

Table 1: Properties and Features of P(3HB) [7]

Another possible way to improve PHB mechanical properties is via blending with other polymer with better mechanical properties. The first paper in the research field of blends containing PHB with other biodegradable synthetic polymers appeared in 1988. Depending on the miscibility of the two polymers, modification of physical properties such as density, crystallinity and glass temperature can occur thus resulting in formation new polymer with new thermal and mechanical properties. Miscibility between PHB with poly(P-dioxanone) [3], polyvinyl acetate [8], polypropylene [9], polycaprolactone nanocomposites [10] and polyethylene oxide (PEO) [11] have been investigated. Among the listed blend polymer, PEO was selected due to its excellent miscibility and biocompatibility with PHB. They found out that PHB/PEO blends are miscible in the melt as well as in the amorphous state. In addition, PEO is a hydrophilic, nondegradable thermoplastic and is approved for biomedical applications. Good miscibility of PHB/PEO was found at 10, 75 and 90% of PHB content while partially miscible at middle PHB content of 25 and 90% [12].

Rheology

The rheological properties of polymer systems under reservoir conditions have been recognized as one of the most important factors governing success of polymer flooding. The key parameter to improve mobility ratio between water and oil is polymer viscosity. This review focuses on rheological properties of HPAM, XG and PHB polymer. However, there exist only a few studies that explore the rheological properties of PHB/PEO blends [11]. The effects of polymer concentration, shear rate, salinity, hardness and temperature to polymers viscosity solutions are presented below.

Polymer concentration

Most of previous core flooding studies on polymer flow via porous media used polymer concentration up to maximum 1,500 ppm [13]. This is because polymer with high concentration have better controlled of mobility ratio thus leads to an effective swept efficiency caused by more conducive in driving crude oil. They also stated that viscosity is a strong function of polymer concentration. Viscosity of polymer drastically increased with concentration when above the critical overlap concentration. Flow characteristic of high concentration of HPAM was investigated by [14]. From the study, they found out that due to chemical absorption and retention and mechanical trapping, some of high concentration polymer will remain in reservoir making permeability of reservoir became low due to increase fluid flow resistance. As a result, permeability of porous medium decline resulting from greater residual resistance and this may lead to improve oil recovery. Results also showed that HPAM with concentration of 3,500 mg/L improved recovery about 25.9% which is much higher than 1,000 mg/L improved 17.4%. It is certain that increased polymer concentration leads to increased oil recovery. The effect of XG concentration was well fitted by power law and the results was showed in [15]. It is clear that XG concentration increased with consistency index (k) as consequence of structure development. In contrast, flow behaviour index (n) decreased with concentration indicating progressive increase in shear-thinning nature. Similar conclusions were reported in [11] where shear viscosity PHB80 is much higher than PHB100 (pure PHB).

Shear rate

Polymers used in EOR process is shear-thinning fluids in a viscometer whose apparent viscosity decreased at high shear rate inside reservoir. From injectivity perspective, shear-thinning behavior of polymer is beneficial because near injection well, viscosity is lower due to higher shear rate thus promote more favorable injectivity. Within reservoir, viscosity of polymer increased at declining shear rate resulting desired mobility control. As fluid moves radially out from the well, very low shear rates on the order of 1 to 10s-1. Normally, operator accepts viscosity loss of 10 to 20% but higher loss can compromise the project itself [16]. Several early papers identified that the HPAM is more susceptible towards mechanical degradation than XG in both fields and laboratory test. In term of viscosity loss, XG showed less reduction compared to HPAM due to rigidity of polysaccharide chain cause it less affected towards mechanical degradation even at high shear rate. Studies confirmed that XG demonstrated better resistant to mechanical degradation by experiencing about 19% reduction of viscosity at pressure gradient of 24,600 psi/ft [17]. Studies investigated by [11] showed that viscosity of PHB/PEO blend was reduced with increasing shear rate similar to other polymeric system. Viscosity of pure PHB is much lower than PHB/ PEO blend at low shear rate.

Salinity

Another challenge that imposes polymer flooding applicability is salinity of formation water. Most of worldwide reservoir is high salinity reservoir such as in Kuwait. By enhancing the performance of polymer under high salinity, it will unlock the trapped oil and thus improved the oil discoveries. With increasing of salinity, viscosity of polymer reduced. Increased salt concentration cause repulsive forces between polymer chains reduced and due to charge of screening effect, the chain coils up. As a result, hydrodynamic radius of polymer chain becomes smaller and viscosity of polymer solution decreased. Tian *et al* investigated performance of various HPAM consists of (1,400 million, 2,000 million, 1,800 million salt resistant HPAM, 800 million temperature-salt resistant polymer and 600 million) at different salinity (5,000, 10,000 and 15,000 mg/L)[18]. They examined that normal HPAM (1,400 million) was experiencing more reduction of viscosity after addition of NaCI than salt-resistant HPAM. Finding showed that when salinity is less than 5,000 mg/L NaCI, salt resistant polymer is best to use while when salinity is between 5,000 to 15,000 mg/L, temperature-salt resistant polymer. The influence of NaCI composition (0, 10 and 20%) on the viscosity of XG and guar gum were also examined by [19]. They found out that XG is more susceptible to addition of salt which led to viscosity reduction while viscosity of guar gum increased with salinity. They also claim that XG/guar gum mixtures may minimize viscosity loss but high composition of guar gum was needed. Since PHB is widely used in food packaging industries makes the effect of salinity towards PHB is rarely being reported.

Hardness

Existence of metal ions in the produced water greatly reduces polymer viscosity and further impact in displacement efficiency. Interaction of divalent ions such as Mg^{2+} and Ca^{2+} shields mutual repulsion from carboxylic

group of HPAM structure resulting polymer collapse caused hydrodynamic volume reduced thus lowering the solution viscosity. Low polymer viscosity caused low residual resistance coefficient. The influence of specific ion such as Ca^{2+} , Mg^{2+} , Al^{3+} , Fe^{2+} and S^2 on HPAM viscosity was reported in [20]. Based on experimental results, these authors showed that all specific ions listed above except Al^{3+} demonstrated negative effect on HPAM viscosity while Al^{3+} graph trend display increasing viscosity. At beginning, trivalent ion showed the same action with divalent ion. Unfortunately, Al^{3+} ions can crosslink with HPAM result in extending molecular weight and space stretching. The effect of iron ion on HPAM solution was further studied by [21]. In the process of preparing HPAM solution, usually water used contains of much iron ion. Plus, pipeline which have been used for many years to convey water probably corrode and experience aging coating and this condition may cause iron ion travelled together with water when it flows through. Presence of iron ion within HPAM solution makes HPAM degrade thus destroying its structure resulting in viscosity reduction. From his studies, he reported that HPAM viscosity is not significant at low concentration of Fe^{3+} . He claimed that high Fe^{3+} concentration crosslinked with HPAM and thus formed type of gel. At this point, viscosity loss is significant. When cations added into XG solution, the viscosity decreased was significant and further addition of ions to the system resulted in less impact on its viscosity. However, study of hardness effect to PHB solution was limited thus hinder its review.

Temperature

Polymer flooding in high temperature reservoir showed poor performance as the polymeric solution experienced severe thermal degradation which caused polymer solution to have ineffective sweep efficiency. At elevated temperature, molecules speed became faster and caused contact time with nearest molecules thus resulting in viscosity loss. The relationship between effect of thermal degradation of HPAM polymer solution by measuring viscosity at reference temperature (20°C) before and after solution heating at temperature 40°C with heating duration 9, 15 and 24 hours and 60°C with heating duration 8, 10.5 and 12 hours was investigated by [22]. Finding showed that as heating duration increased, viscosities of HPAM slowly reduced. Similar result was obtained at 40°C with small reduction compared to 60°C of HPAM viscosities. Another studies performed by [23] also agreed with [22] as HPAM polymer solution

is vulnerable for reservoir condition of to thermal degradation when the reservoir temperature is above 60°C and completely lose its viscosity. Plus, the effect of different temperature (50, 70 and 90°C) to 1,500 ppm of HPAM polymer concentration was also studied by [24]. Similar conclusions were reported [23].

The effect of HPAM solution with addition of NaOH at tested condition of 0.5 wt% of NaOH mixed with 1500 ppm of HPAM was examined [25]. The addition of NaOH into HPAM solution significantly increased the viscosity of HPAM caused by ionic strength. Addition of NaOH, caused negative charged of carboxyl groups along HPAM chain to coil up. This repulsion caused increased hydrodynamic radius and viscosity to increase. Studies were conducted by [26] to overcome deficiencies of HPAM by complexing with improved salinity and thermal stability tolerance; erucyl dimethyl amidobetaine (EDAB) under simulated high salinity and temperature oil reservoir (85°C). Composition of HPAM (P)/EDAB (E) were varied consists of $(P_{30}E_{30}, P_{25}E_{25}, P_{10}E_{20}, P_{15}E_{15}$ and $P_{5}E_{25})$. Results obtained showed that $P_{15}E_{15}$ and $P_{10}E_{20}$ exhibited improved long-term thermal stability and salt tolerance. These clearly illustrated that addition of EDAB into HPAM improved thermal stability of HPAM. However, it is necessary to further study the optimum ratio of HPAM/EDAB for economic consideration.

XG viscoelasticity was improved by association with inclusion complexes of EOR surfactant and β-CD to produce self-assembling biopolymer (SAP) network system. Thermal stability of SAP was tested at 90°C and result showed that SAP displayed higher viscosity than XG for 30 days of aging. Studies are currently on going to determine the optimum amount of β-CD and surfactant mix which will result in lowest possible concentration [27]. The influence of temperature to PHB was also studied [28]. The tested temperatures are between 170 to 190°C. Findings demonstrated similar result with HPAM and XG where by at high temperature, high mass loss of PHB was observed. These studies showed that PHB have better thermal stability compared to HPAM and XG. Thermal stability of PHB was also investigated using Differential Scanning Calorimetry (DSC) [29]. Result showed melting point of PHB started at 170 °C.

Choi *et al* successfully developed an in-situ rheological model for high temperature porous media [30]. Through this model, it may minimize

potential problems resulting from underestimation of laboratory calculations compared to in-situ observations. Several conclusions were made including an extra of 500 ppm needs to be added to 1,000 ppm of polymer injected at 120°C to maintain mobility control. Aside from that, reservoir condition of higher than 160°C tends to cause severe polymer viscosity reduction. Reservoir with temperature of 140°C and below was advisable to use low concentration of polymer in order to maintain polymer stability. Additionally, for 160°C and higher, it is not advisable to inject polymer as it accelerates decomposition of polymer.

CONCLUSION

From this research, it can be concluded that viscosity of polymer solution depends strongly not only on shear rate but also on the other parameters such as the polymer concentration, salinity, hardness and temperature. PHB showed better resistant to mechanical degradation and thermal stability compared to HPAM and XG. It was proven that polymer such as HPAM is more affected to salinity and high temperature conditions relative to biopolymers. Better understanding of PHB rheological properties for EOR application is vital as it helps to improve PHB potential as an effective EOR polymer in sweeping the oil.

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