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Colloid and Polymer Science
Kolloid-Zeitschrift und Zeitschrift für
Polymere

ISSN 0303-402X

Colloid Polym Sci
DOI 10.1007/s00396-020-04767-5



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Synthesis of polymeric surfactant from palm oil methyl ester for enhanced oil recovery application

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Received: 27 November 2019 / Revised: 28 September 2020 / Accepted: 4 October 2020
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Abstract

Methyl ester sulfonate (MES) is an anionic surfactant derived from natural oils. Polymers are large molecules composed of many repeated units that increase viscosity as a mobility control. Therefore, polymer and surfactant can be reacted into one substance as an alternative for enhanced oil recovery (EOR) application. The principle of this research is to graft sulfonate groups from MES into the polymer chain. Based on the experiments, the best result of polymerization was obtained at a mole ratio of 1:0.3 MES to acrylamide. Based on the interfacial tension (IFT) measurement, the IFT value decreased from 8.6 to 2.3 mN/m before and after the addition of polymeric surfactant respectively. The synthesis of polymeric surfactant obtained a yield of 1384.79%. Polymeric surfactant is potential candidates to change the initial oil-wet state of the quartz surface to water-wet based on wettability alteration study. According to thermal analysis and emulsification behavior, this polymeric surfactant was thermally stable under the desired reservoir temperature and was able to emulsify crude oil. The adsorption study showed that the adsorption onto the rock surface increased when the polymeric surfactant concentration was increased in the system. Core flooding experiments showed an increase in oil recovery in different concentrations of polymeric surfactant. Although the IFT value of polymeric surfactant is not very low, it has the potential as an alternative surfactant for EOR applications.

Keywords Enhanced oil recovery · Interfacial tension · Methyl ester sulfonate · Polymeric surfactant

Introduction

Enhanced oil recovery (EOR) is one of the advanced oil recovery techniques to maximize oil production in a reservoir that has decreased production but still has oil reserves. One of the well-known EOR technologies is using surfactants. The main function of surfactants is to reduce interfacial tension and wettability alteration. The situation in Indonesia is that reserves and oil production have declined by 10% every year, while the level of oil consumption has increased by an average of 6% per year.

According to the Ministry of Energy and Mineral Resources, oil production showed an increasing trend from month to month. As of June 30, 2016, the average production of petroleum was 834.4 thousand barrels per day (bpd). On

July 30, 2016, the average oil production rose at 834.7 thousand bpd [1].

In the condition of lack of oil and gas resources, oil production by primary recovery could no longer be carried out. Primary recovery is a conventional step to inject gas or water into oil reservoir for the objective of delaying the pressure decrease during oil production [2]. The second stage of oil recovery in which an external fluid such as water injection (Water flooding) or gas injection (Gas flooding), is injected into the reservoir through injection wells located in rock that has fluid communication with production wells [3]. Tertiary recovery usually named EOR can be used to recover additional oil. EOR presents fluids that decrease viscosity and improve flow. These fluids could consist of gases that are miscible with oil such as nitrogen or carbon dioxide, oxygen, air or steam, gels, polymer solutions, surfactant-polymer (SP) mixture, alkaline-surfactant-polymer (ASP) formulations, or microorganism formulations [4]. The primary and secondary recovery methods are able to recover oil with an average of one-third of the oil in the reservoir. But by applying tertiary recovery (EOR), production could reach 40–60% oil in the reservoir [4].

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Petroleum sulfonate is one of the most commonly used primary surfactants for EOR technology. This surfactant is pricey and non-biodegradable. To reduce the cost of surfactant production, much attention has been focused on oleochemicals derived from agriculture as raw materials. One type of potential surfactant that will be developed is methyl ester sulfonate (MES) which can be obtained from vegetable oils such as coconut oil, palm oil, and soybean oil for industrial detergent [5] or phosphate-free detergent powders [6, 7]. More attention has grown in using MES, in mixture with other anionic surfactants, in laundry powders, and in markets where soap-based products are widely used, in combination with soap [8]. Because of its mildness to skin and mucous membranes, MES can be used for shampoo, facial cleanser (cosmetic and personal care) [9] [10], and dishwashing applications [11]. Methyl ester sulfonate derived from natural oil for EOR application has been synthesized by several researchers [12–14].

Methyl ester sulfonates exhibit good dispersion characteristics and detergency, especially in hard water. MES can be produced from sulfonation by reacting methyl esters and NaHSO_3 . The use of NaHSO_3 as a sulfonating agent refers to Farn [10] who synthesized amphoteric surfactant alkylamphohydroxypropylsulfonate using epichlorohydrin. The reason of using Al_2O_3 as a catalyst is because it is suitable for both acidic and basic conditions and has reducing properties [15].

Palm oil consist of approximately 50% unsaturated fatty acids, with 40.5% oleic acid (C18:1) and 10.1% linoleic acid (C18:2) [16]. It means that palm oil contains enough double bonds which are potential to be sulfonated into MES.

Polymeric surfactant which can be synthesized from MES is able to overcome several problems in conventional ASP (alkali-surfactant-polymer) flooding without reducing its efficiency. However, because of the different properties, such mixtures are able to separate into two phases in a flow stream. Other problems can result in the loss of surfactant to reservoir rock surface by adsorption because of the attraction of surfactant to rock-water interface [17] or to the unsuitability between surfactant and polymer, yielding in the decline of polymer properties, such as adsorption, aggregation, and diffusion performance in porous media [18]. Moreover, even ASP flooding has demonstrated to successfully increase oil recovery in the field, the existence of the strong base has baneful effects on polymer performance. In many cases, more polymer is requisite to reach the desired viscosity [19].

The principle of polymeric surfactant synthesis is to insert sulfonate groups into the polymer chain. Research conducted by Ye et al. [20], namely the synthesis of poly [acrylamide-acrylic acid-N-(4-butyl) phenylacrylamide], is the basis for synthesizing polymeric methyl ester sulfonate (PMES)/polymeric surfactant through polymerization. Therefore, polymerization was carried out by varying the mole ratio of surfactants to polymer for reducing IFT and viscosity control. The

polymeric surfactant combines the interfacial properties of surfactant with the high viscosity of polymer so that it reduces the water/oil interfacial tension and simultaneously increases the viscosity of the aqueous solution [21]. According to Berger and Christie [22], the IFT value of surfactants for EOR must reach 10^{-3} mN/m. Raffa et al. [23] has also summarized that the IFT for EOR ranges from 10^{-2} to 10^{-3} mN/m. However according to Raffa et al. [23], it is very difficult to get a very low IFT value for polymeric surfactant, and only ranges from 0.1 to 15 mN/m; thus, the assumption that the lower IFT produces higher oil recovery is a too simplistic assumption. Based on Yu et al. [24] research, a very low IFT does not always get higher oil recovery. Therefore, higher IFT values also can be considered for EOR applications.

The polymeric surfactant synthesis for EOR applications was carried out by K. A. Elraies et al. [19]. Sodium methyl ester sulfonate (SMES) was made using chlorosulfonic acid as the sulfonating agent from castor oil methyl ester which had previously been made and investigated by K. A. Elraies et al. [25]. Monomer acrylamide was reacted with sodium methyl ester sulfonate (SMES) to synthesize polymeric surfactant. The results showed that the viscosity and interfacial tension performance of polymeric surfactant were an excellent candidate for chemically enhanced oil recovery application. Connecting SMES to polymer chains to produce PMES offers many benefits. The presence of both surfactants and polymers as a single component makes PMES easier to handle, especially in offshore applications. Moreover, being a polymeric surfactant a single component instead of a mixture, this approach should also have the benefit of preventing the separation into two phases that might occur in a flow stream for conventional surfactant-polymer (SP) mixtures [19, 26, 27]. Furthermore, polymeric surfactant is able to avoid loss of some components during the flooding processes or unwanted interactions [26].

Meanwhile, Babu et al. [28] synthesized polymeric methyl ester sulfonate (PMES) from castor oil. The sulfonation agents and monomers used are the same with Elraies et al. [19]. The variations carried out were the concentration of PMES solution, the weight ratio of SMES to acrylamide, the addition of NaCl on SMES, and the time of equilibrium of the surfactant. The results showed that PMES was able to reduce interfacial tension up to 10^{-2} to 10^{-3} mN/m at the right concentration so that the polymeric surfactant is a suitable candidate for chemical flooding in increasing oil recovery because its viscosity is higher than that of SMES surfactants.

The schematic representation of the proposed chemical reaction for synthesized polymeric surfactant (PMES) is illustrated in Fig. 1. There are two possibilities for producing free radicals in the surfactant chain, which are the breakdown of the -OH bond or cleavage of C=C (unsaturation) bond. Because -OH bond polarity is higher than C=C bond, there are more free radicals for grafting on -OH site than in the breaking of C=C unsaturation bond. In fact, the

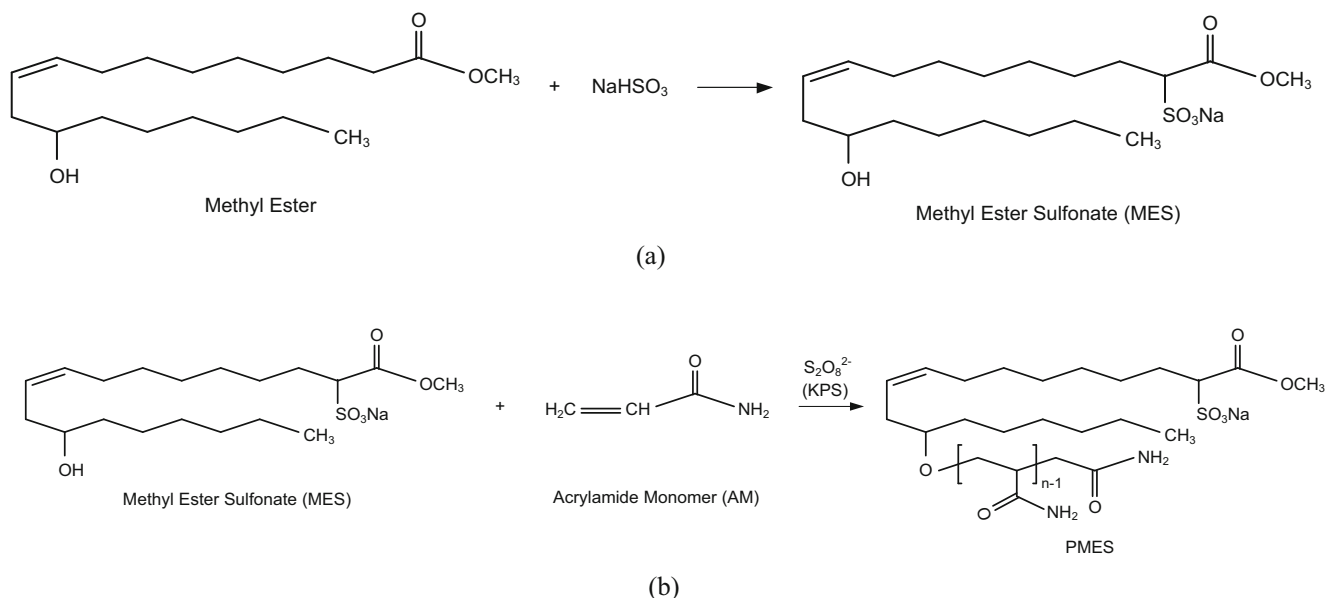


Fig. 1 a Reaction of MES synthesis. b Reaction of PMES synthesis

polyacrylamide chain formation occurs in the hydroxyl substituents ($-\text{OH}$) of surfactants (MES) rather than the unsaturated bond of the surfactant [29].

Du et al. [30] have done research about alkaline flooding by mixture of NaOH and NaCl at 0.5% respectively on crude oil with sand-pack flooding models. The best IFT result was obtained 0.064 mN/m with 26.7% recovery. Performance of MES-based *Jatropha* oil for EOR application has been done by Elraies et al. [25]. It has a good surface activity, reducing the interfacial tension between the MES solution and crude oil from 18.4 to 3.92 mN/m. Meanwhile, the research conducted by Kumar et al. [31] complements the research by Elraies et al. [19] and Babu et al. [28]. The effectiveness of polymeric surfactant/PMES for oil recovery was examined by measuring the physiochemical properties of aqueous solutions, decreasing IFT values, wettability alteration, and rheological behavior. The result showed that the IFT value between crude oil and PMES solution in water decreased from 2.74 to 0.37 mN/m in absence and presence of 2.5 wt% NaCl respectively. Core flooding experiments were carried out in a sand-pack system (40–60 mesh size in the cylinder of $L = 45$ cm, $d = 3.5$ cm, porosity 29%, permeability, k (Darcy) = 4.57) to study EOR efficiency using polymeric surfactant and produce more than 26% OOIP recovery after water flooding [31].

Based on the above comparison, the use of MES and PMES surfactants can reduce the IFT value. Even though the value is not ultralow but it has the potential to be used in EOR applications.

Previous researchers synthesized MES from palm kernel, stearin [32], and palm oil [9] with SO_3 gas but they did not carry out the polymerization into polymeric surfactant. Other researchers synthesized polymeric surfactant from castor oil with chlorosulfonic acid as the sulfonating agent [19]. Based on the literature above, the synthesis of polymeric surfactant

from palm oil methyl ester and NaHSO_3 had never been done before. The research to synthesize polymeric surfactant (PMES) from copolymerization between palm oil-based MES and acrylamide monomer needs to be done in order to obtain a very small interfacial tension (IFT) value and as a viscosity control. It is also expected to prevent corrosion problems and scaling handling difficulties in emulsified liquid treatment on the EOR application [33]. Corrosion and scaling are frequent troubles in field application of ASP [34–36].

An earlier paper written by Jirui et al. [37] mentions the corrosion and scale problems that happened during the ASP flood in Daqing field. A strong alkali has a harmful effect on polymer performance, and in many cases, more polymer is needed to attain the desired viscosity [38]. A high alkaline concentration can reduce polymer viscosity, thus more polymer will be needed to get the adequate viscosity which in turn increased cost [33, 39]. In ASP field tests, scaling and corrosion problems due to the use of alkali damaged the lifting system and thus shortened the average pump-checking period, causing in increased workload for maintenance. Beside scaling and corrosion, ASP flooding creates a strong emulsification resulted in many produced liquid treatment problems. Strong emulsification arose in ASP flooding industrialization tests of South-5 zone and North-1 East zone, and it was difficult to separate between oil and water [36].

Experimental

Materials

Palm oil methyl ester, sodium bisulfite (NaHSO_3), aluminum oxide (Al_2O_3) 99% p.a, sodium hydroxide (NaOH) p.a,

methanol (CH_3OH) 98% p.a, potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$) p.a, acrylamide monomer p.a, Merck Germany, acetone p.a.

Experimental procedure

The research of polymeric surfactant synthesis was carried out in two stages. The first stage was the synthesis of MES by reacting palm oil methyl ester with sodium bisulfite. The second stage was the synthesis of polymeric surfactants. The variation was by adjusting the mole ratio of MES to acrylamide monomers (AM). Afterwards, the synthesized PMES were tested on some parameters. Characterization included viscosity, IFT values, yields, and contact angle. In addition, functional groups were determined by FTIR and H-NMR.

Experimental procedure of MES synthesis

The synthesis of MES was done by reacting palm oil methyl ester and NaHSO_3 with a mole ratio of 1:2 into a reactor equipped with condenser and heater. Al_2O_3 1.5% was added to the reactor as a catalyst, then the mixture was heated with a hotplate stirrer at 100 °C and constant stirring for 210 min. Furthermore, precipitation and filtration were needed to separate solids. The liquid was purified by adding 35% methanol at 55 °C for 60 min. After that, 30% of NaOH was added for neutralization until pH 6–8. The last process was methanol evaporation with a rotary evaporator to obtain pure MES.

Experimental procedure of polymeric surfactant synthesis

Ten milliliters of 1.23% potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$) was made using distilled water and the pH was adjusted to 9–10 by NaOH solution. The surfactant solution was made by dissolving a number of MES in 80 mL of distilled water. In addition, a number of acrylamide monomers were also dissolved in 10 mL of distilled water. The polymerization was carried out by inserting the MES solution into monomer solution while adding the $\text{K}_2\text{S}_2\text{O}_8$ initiator. These solutions were stirred under atmospheric condition and heated using a hotplate in the reactor which was connected to the condenser at 60 °C temperature for 90 min. Then, the raw product was purified with acetone by separating funnel. The upper liquid layer was separated and then evaporated from the remaining acetone with rotary evaporator to obtain pure polymeric surfactant (Figs. 2 and 3).

The yield (% wt) of the polymeric surfactant for each experiment was calculated by the following equation [40]:

$$\text{Yield (\%wt)} = \frac{\text{Mass of polymeric surfactant}}{\text{Mass of acrylamide monomer}} \times 100\% \quad (1)$$

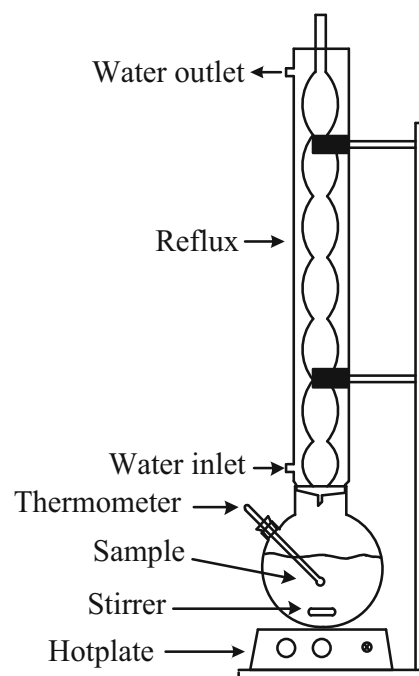


Fig. 2 Experimental equipment scheme

Product analysis and performance testing

Methyl ester was tested quantitatively by gas chromatography (GC) and other important parameters also. The MES and polymeric surfactant product was tested for viscosity and IFT. The yield of polymeric surfactant was calculated using Eq. 1. Polymeric surfactant product was tested for FTIR, H-NMR, contact angle, thermal analysis, emulsion behavior, and adsorption analysis. Finally, polymeric surfactant performance was tested using the sand-pack column equipment for core flooding experiments.

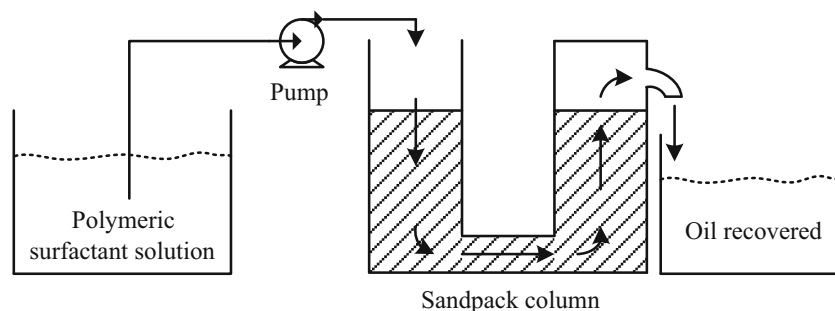
Results and discussion

Analysis of palm oil methyl ester as raw material

Methyl esters are fatty acid esters obtained by esterification of fatty acids using methanol. However, the most common reaction to obtain fatty acid methyl ester (FAME) is transesterification between triglycerides (fats or oils) and methanol. In this study, methyl ester from palm oil is used to synthesize polymeric surfactants. The composition of palm oil methyl ester can be seen from Table 1.

The major unsaturated methyl ester from palm oil samples are methyl oleate (C18:1) 29.93% and methyl linoleic (C18:2) 6.38% while other methyl ester composition is small. In addition, the number of bonds can be seen from the iodine number of 44.75% wt. The double bonds (C=C) or –OH in the sample are expected to be sulfonated by NaHSO_3 (Table 2).

Fig. 3 Sand-pack column apparatus



The effect of MES to acrylamide mole ratio on polymeric surfactant viscosity

As explained above, polymeric surfactants can combine high viscosity of polymers with the interfacial properties of surfactants thus it can reduce water/oil interfacial tension and increase the viscosity of aqueous solutions simultaneously [21]. Based on Fig. 4, it shows that the viscosity of polymeric surfactant tends to increase with the increasing number of monomers. This is because more monomers results in more polymer chains that are attached to the MES. The highest viscosity of 5.86 cP was obtained at a mole ratio of 1:0.5 and almost equal with 1:2 (5.75 cP). The viscosity of MES is 4.14 cP, this value is lower than the viscosity of polymeric surfactant, it makes sense because MES has not been reacted with monomers which causes an increase in viscosity.

Polymeric surfactant can increase the viscosity. It is similar like polymer which is an important part of the ASP flooding. Polymer is mainly used to increase the viscosity of the injection system and thus improve the mobility ratio [33].

The effect of MES to acrylamide mole ratio on IFT values and yield

Based on Fig. 5, there is a rise in the IFT value of polymeric surfactant along with the increasing amount of acrylamides. The value of IFT increases drastically from 1:0.3 to 1:0.5 with 2.3 and 4.68 mN/m respectively. Afterwards, the IFT values

increases slightly until 5.31 mN/m at 1:2 mol ratio. Therefore, the IFT value declines as the surfactant to acrylamide mole ratio increases. The same result was obtained from Elraies et al. [19]. It shows the aggregative properties of the attached sulfonated group to the polymer chains. More surfactant is being attached to the polymer backbone as the surfactant to acrylamide ratio increases, and thereby lower IFT values are obtained.

When compared to the IFT value between PMES and MES, the IFT value of MES is higher (4.8 mN/m) than that of PMES (mole ratio MES:AM 1:0.3).

The previous research combining surfactant-polymer (SP) or alkali-surfactant-polymer (ASP) flooding have several problems such as mixtures often separate into two phases in a flow stream. Other problems inflict the loss of surfactant to reservoir rock surface by adsorption because of the attraction of surfactant to rock-water interface [17]. The other drawbacks can cause decrease of polymer properties, such as adsorption, aggregation, and diffusion performance in porous media because of the incongruity between surfactant and polymer [18]. Some research proved that ASP flooding effectively increases oil recovery in the field; the existence of the strong base has baneful effects on polymer performance. In many cases, additional polymer is required to achieve the desired viscosity [19]. Thus, polymeric surfactant can be solution to overcome those drawbacks.

According to Cao and Li [21], a polymeric surfactant has combination properties between the high viscosity of a polymer and the interfacial property of a surfactant that reduce the interfacial tension of water/oil and increase the viscosity of the aqueous solution simultaneously.

Based on research by Yu et al. [24], it showed that there is not a simple correlation between reducing the IFT and oil recovery. Although the resulting IFT is not very low, when

Table 1 Composition of palm oil methyl ester

No.	Type of FAME	Concentration (% wt)
1	Methyl laurate	0.13
2	Methyl myristate	1.11
3	Methyl palmitate	56.26
4	Methyl palmitoleate	0.21
5	Methyl stearate	5.15
6	Methyl oleate	29.93
7	Methyl linoleate	6.38
8	Methyl linolenic	0.83

Table 2 Analysis of important parameters of palm oil methyl ester

Density (kg/m ³)	865.60
Viscosity (mm ² /s)	4.74
Cloud point (°C)	17.40
Iodine number (% wt)	44.75
Oxidation stability (h)	17

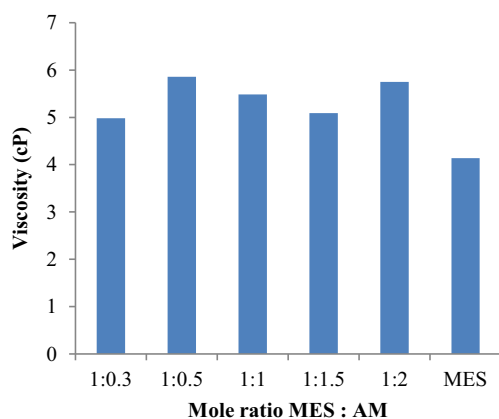


Fig. 4 The effect of MES to AM mole ratio on polymeric surfactant viscosity

compared to Yu et al. [24] with SP mixture at almost the same IFT value, it has 10% incremental recovery.

The yields obtained in polymeric surfactant synthesis drops sharply as the number of monomers increases from mole ratio of 1:0.3 to 1:1 with 1384.79 and 455.3% respectively. After that, the yield declines gradually until 216.28% at mole ratio of 1:2. According to Fig. 5, the best mole ratio is obtained at a ratio of 1:0.3, because it has the lowest IFT value and the highest yield.

Based on the results, a decrease of IFT value from 8.6 to 2.3 mN/m is obtained between crude oil and formation water. Figure 6 shows a visualization of IFT measurements between crude oil and formation water using IK27 Spinning Drop Tensiometer. Figure 6 a and b show IFT visualization without adding PMES and with adding 1% PMES into crude oil-formation water mixture respectively.

FTIR measurement results

Based on the results, the polymeric surfactant which produced at a mole ratio of 1:0.3 has the lowest IFT value. Furthermore,

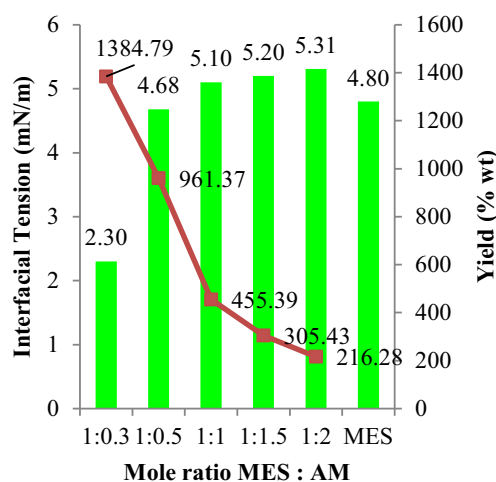


Fig. 5 The effect of MES to acrylamide (AM) mole ratio on IFT values

the polymeric surfactant was tested qualitatively using FTIR spectrophotometry to see the functional groups of the product. The results of FTIR testing can be seen in Fig. 7.

Based on Fig. 7, an absorbance peak of 1741 cm^{-1} showing a typical C=O stretching of an ester compound is seen on the IR spectrum. A CH bending in accordance with asymmetrical bending vibration band of methyl group presents at the peak of 1450 and 1359 cm^{-1} . The $-\text{CH}_3$ group is at the peak of 2856 – 2922 cm^{-1} . The sulfonate group (S=O) is present at the wave number of 1240 – 1010 cm^{-1} . In addition, it is estimated that the change in absorbance peak from 2922 to 3466 cm^{-1} is caused by the attachment of acrylamide to MES surfactants; they are primary and secondary amides because of the N-H stretching. At the peak of 1579 cm^{-1} , the presence of N-H (amide group) because of the vibration stretching C=O is seen. Based on the IR spectrum collected by FTIR, it indicates the presence of sulfonate and amide groups, so it is confirmed that the polymeric surfactant has been formed.

H-NMR measurement results

H-NMR measurement to confirm the polymerization of anionic surfactant (MES) was also done. The spectrum is depicted in Fig. 8.

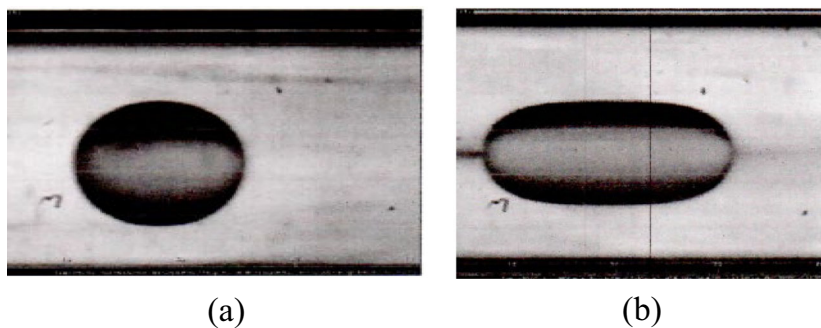
The characteristic resonances attributed to the polymeric surfactant structure are observed at $\delta = 3.650$ ppm for ester (R-COO-CH₃), $\delta = 2.273$ – 2.302 ppm for sulfonate (R-SO₃Na), and $\delta = 5.315$ – 5.341 ppm for amide (R-CO-NH₂). The chemical shifts resulted from the two protons of alkenes' double bond (R-CH=CH-CH₃) is represented at approximately $\delta = 1.588$ – 2.040 and three protons of alkynes' triple bond (R-C≡C-CH₃) at $\delta = 2.160$ ppm. The presence of double and triple bond proves that there is no addition of monomer chain into it. The hydrophobic group of polymeric surfactant is seen in the chemical shift of alkanes R-CH₃ and R-CH₂-R at $\delta = 0.850$ – 0.878 ppm and $\delta = 1.237$ – 1.358 ppm respectively.

Contact angle measurement results

Some effective ways to identify the proper surfactant for enhanced oil recovery by chemical flooding are IFT and contact angles measurement. Contact angle is important for wettability of rock surface and alteration [41, 42], which exhibits the degree of wetting when a solid and liquid interact. Small contact angles ($< 90^\circ$) correspond to high wettability, while large contact angles ($> 90^\circ$) correspond to low wettability [43].

Contact angle of polymeric surfactant solution was measured by using the Phoenix 300 contact angle analyzer. The effect of polymeric surfactant on wettability alteration mechanism is determined by measuring contact angles of crude oil-surfactant interface [28]. In this experiment, a drop of polymeric surfactant was placed in contact with a rock oil-wet

Fig. 6 IFT measurement results **a** without PMES, **b** with PMES



surface. The rock surface was made by hydrophilic SiO_2 glass (quartz). Contact angle between quartz surface and crude oil was determined in the presence of polymeric surfactant solution.

Polymeric surfactant has a very promising result in terms of wettability alteration by reducing contact angles drastically. The initial state of the quartz was oil-wet. By the utilization of polymeric surfactant, the oil-wet surface gradually changed to water-wet state which is preferential need for enhanced oil recovery application. Figure 9 represents the contact angle behaviors of polymeric surfactants with time. The initial contact angle was found to be 66.3° . After 10 min, the contact angle decreases to 25.47° and it goes to less than 10° after certain time (Fig. 10).

The initial contact angle of polymeric surfactant is higher due to the nature of viscous solution of the sample. As the polymeric surfactant is viscous in nature, therefore, the

formation of thin film on the surface is stable which helps to offer a higher contact angle at the beginning [28].

The polymeric surfactant solutions were successful to change from the oil-wet quartz surface to water-wet because the contact angle less than 90° which represent high wettability. Figure 9 depicts the images of polymeric surfactant solution drops on the oil-wet quartz surface with elapse of time.

Thermal analysis

The thermal analysis of the polymeric surfactant was obtained using a simultaneous thermal analysis (STA) Linseis instrument. Approximately 20.1 mg of sample was heated in an open platinum crucible from 30 to 600°C with heating rate of $10^\circ\text{C}/\text{min}$ under nitrogen atmosphere at a flow rate of 26.7 mL/min. The sample was hold at 600°C for 5 min and continued to heat until 900°C under oxygen atmosphere at the

Fig. 7 The infrared spectrum graph in the FTIR measurement

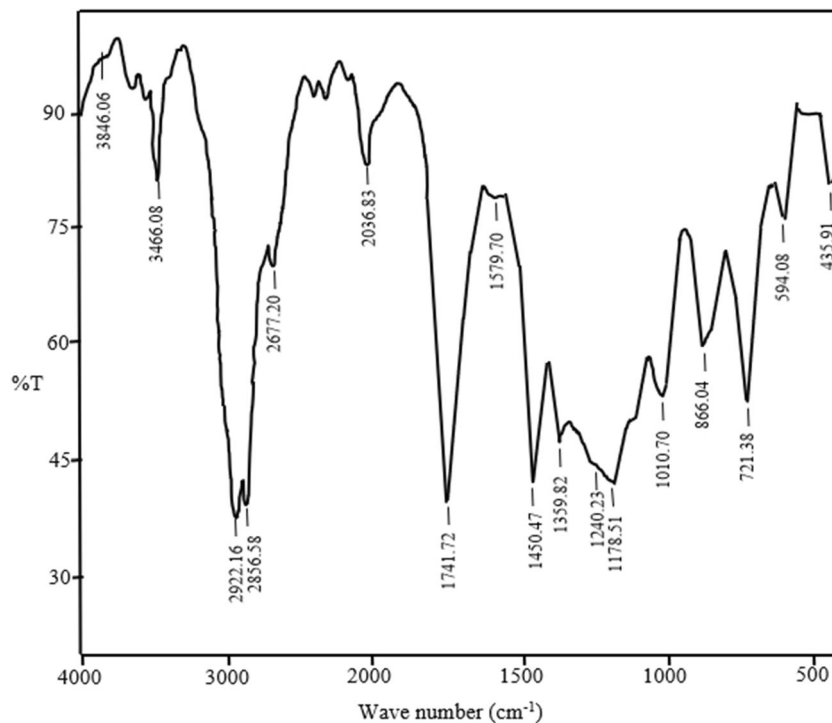
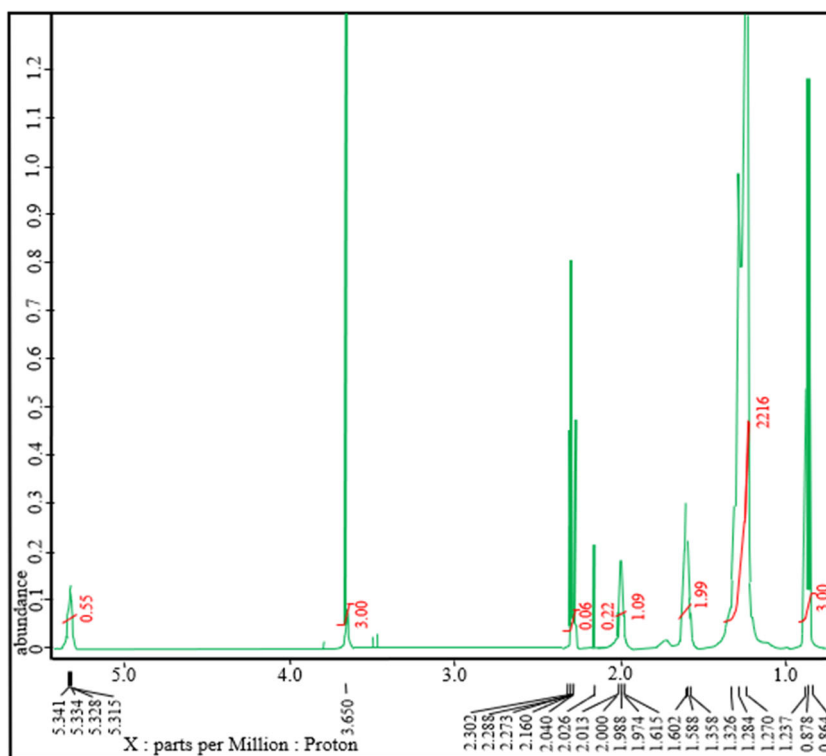


Fig. 8 H-NMR spectrum of synthesized polymeric surfactant



same flow rate. The STA determines changes of weight loss of the polymeric surfactant (PMES) against temperature. Based on the result, the composition of organic compounds in polymeric surfactant consists of 92.5% organic materials and 7.5% combustible matter. The mass loss of polymeric surfactant is drastically decreased from 150 to 600 °C. Whereas from 600 to 900 °C, there was no significant loss of mass.

The STA thermogram of polymeric surfactant can be seen on Fig. 11. At the earlier stage, thermal degradation was happened from ambient to 100 C because of the loss of weakly bonded H₂O molecules. Then, an average of 92.5% mass loss take place dramatically in second region from 150 to 600 °C, showing that polymeric surfactant molecules start to rot of amide group at temperatures more than 100 °C [44, 45]. The final stage of degradation region from 600 to 900 °C indicates a complex thermal degradation, which may result from the condensation of the cyclic amide rings and the residual amide groups [29].

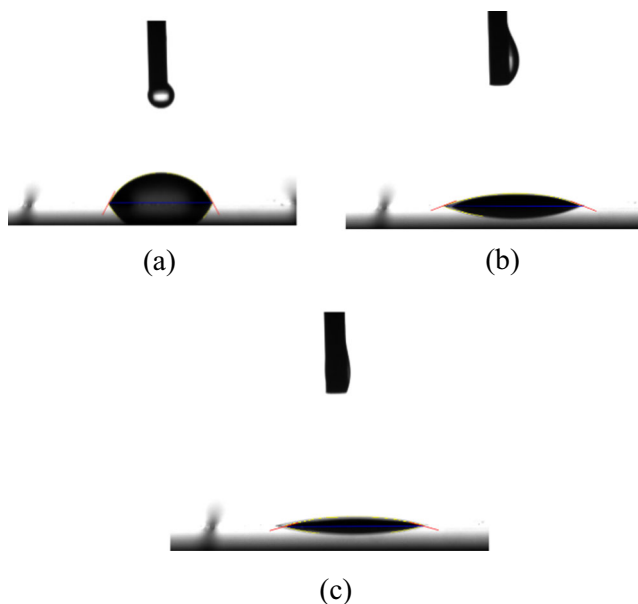


Fig. 9 Images of polymeric surfactant solution drops on oil-wet quartz surface during contact angle measurement. **a** 0 min (initial), **b** after 5 min, **c** after 10 min

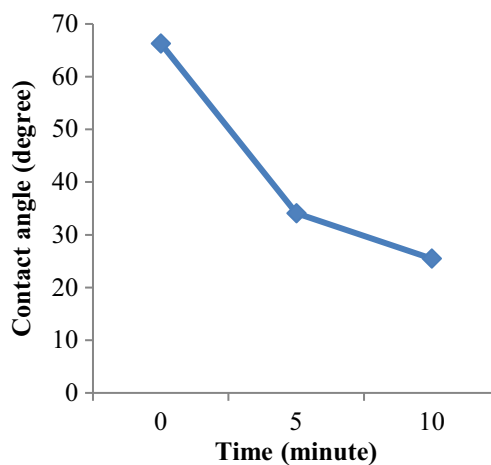
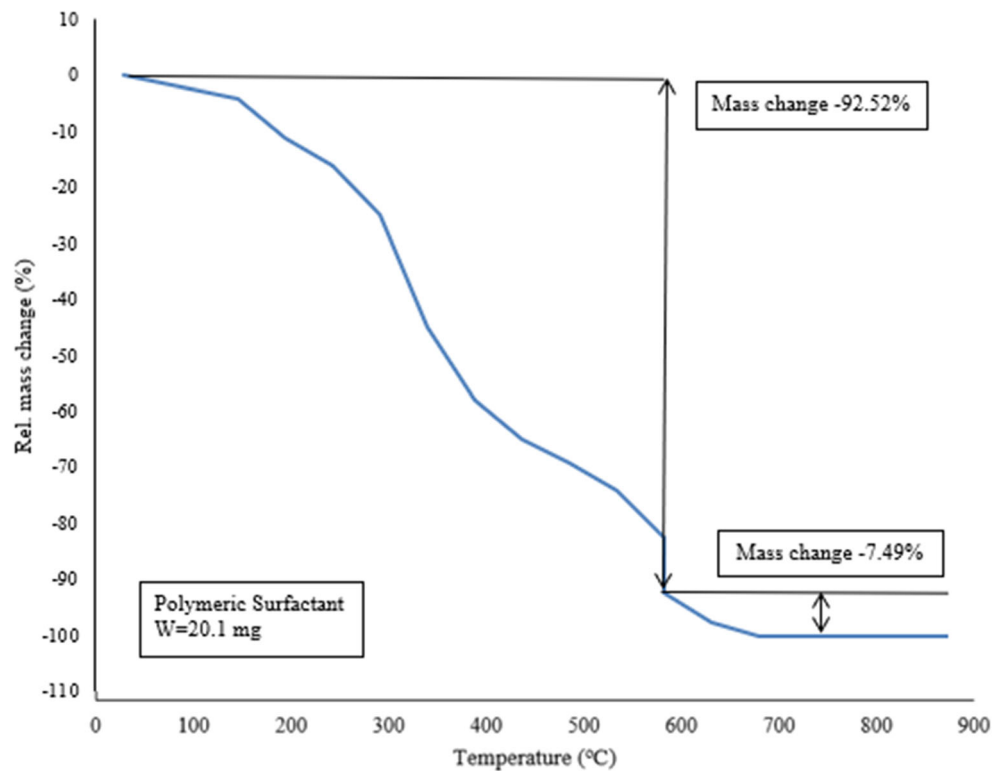


Fig. 10 Variation of dynamic contact angle for polymeric surfactant on oil-wet surface

Fig. 11 STA thermogram of polymeric surfactant sample



According to Taber et al. [46, 47], the reservoir temperature should be lower than 93 °C for ASP projects. The polymeric surfactant retains an average of 98% of their original structure and mass. It can be resumed that the polymeric surfactant is thermally stable under the desired reservoir temperature.

Emulsification behavior

Emulsion study is required in order to check the emulsification properties of the polymeric surfactant for EOR application. The ability of the polymeric surfactant to form emulsion was tested by mixing the polymeric surfactant solution with crude oil at different concentrations. Many surfactants simultaneously form three coexisting liquid phases when mingled with oil and water. The middle phase, which contains diffused oil droplets stabilized by surfactant, is called an emulsion [48]. The homogenous polymeric surfactant solution at different concentrations and crude oil was mixed oil in equal amount (ratio of 1:1).

The creation of emulsion during surfactant flooding is highly useful and also having significant miscibility with the trapped crude oil, important to enhanced oil recovery. Emulsion formation during surfactant flooding reduces the mobility of the aqueous phase and turn the pore level and microscopic channels which leads to increase in oil recovery [48]. Figure 12 exhibits the pictures of

emulsification behavior of polymeric surfactant solution with different concentrations.

Based on Fig. 12, it can be seen that polymeric surfactant solution can emulsify crude oil which is characterized by a cloudy solution at concentration of 5%.

Adsorption behavior

Concentration of polymeric surfactant solution was made from 10,000 to 100,000 mg/L. The grinded rock and sand samples were added to the polymeric surfactant solutions by weight

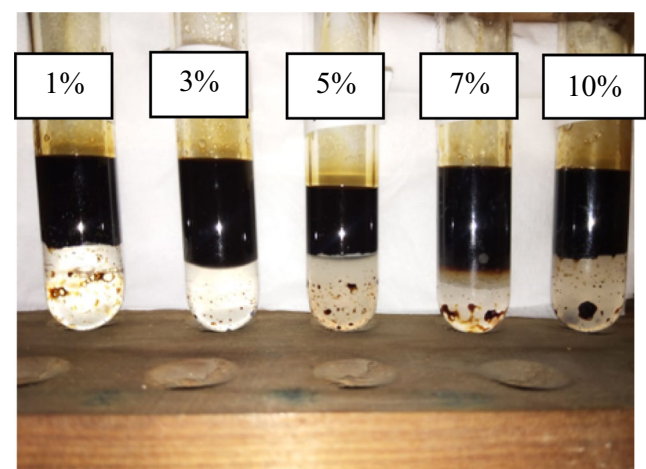


Fig. 12 Photographs of polymeric surfactant solution to solubilize and emulsify of crude oil

ratio of 1:1. The solution was shaken by orbital shaker at 80 rpm and 60 °C for 9 h. Then, the liquid was separated from the solid by a centrifuge and analyzed under UV-visible spectrophotometer (SHIMADZU) to obtain the equilibrium concentration. The UV spectroscopy technique is corresponded with the interaction of light with matter. When a monochromatic light is absorbed by compound, it causes the rise of energy content of the atomic or molecular constituents of the chemical compound. Thus, a peak is acquired at specific wavelength for each compound [49]. The unknown concentration of the polymeric surfactant solution was calculated by using the calibration curve from the surfactant solutions of known concentrations. The initial and final concentration of the polymeric surfactant solutions were used to find the adsorbed amount of adsorbent at equilibrium concentrations (q) by Eq. (2).

$$q = \frac{V(C_i - C_e)}{m} \quad (2)$$

where V is the volume of the polymeric surfactant solution (L) and m is the mass of the adsorbent (g) used in the experimental analysis. C_i and C_e are the initial and final equilibrium concentrations of the polymeric surfactant in the solution (mg/L) respectively.

Adsorption behavior of surfactant onto the rock surface is deemed to be a baneful property that takes place as a result of surfactant loss, which causes to high operating cost in the EOR application. This weakens the ability of the surfactant to effectively reduce oil-aqueous IFT and wet the nonwetting oil-wet rock surface. However, the adsorption behavior is important for designing surfactant for chemical flooding [48]. Surfactant molecules are adsorbed at the interface with the higher affinity due to lateral interactions between surface species and alkyl non-polar tails, creating surface aggregates with the increase in the surfactant concentration in the aqueous phase [50].

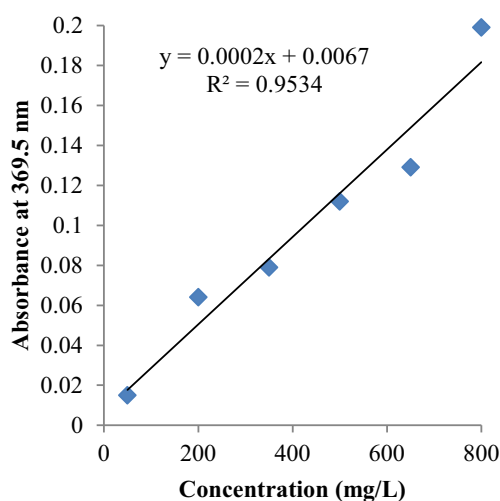


Fig. 13 Calibration curve of surfactant solution at wavelength 369.5 nm

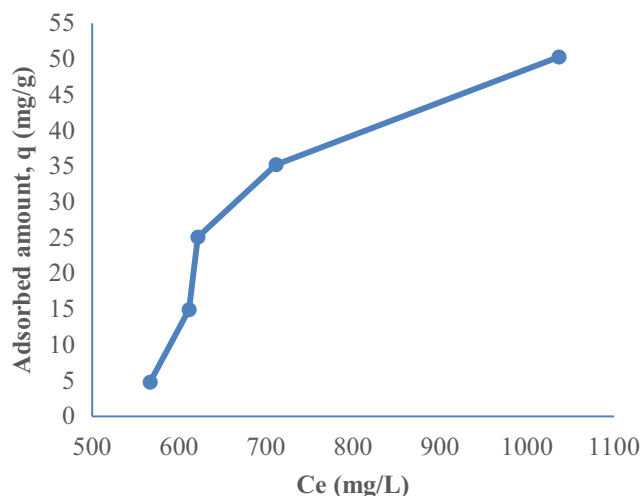


Fig. 14 Adsorption profile of the polymeric surfactant on sandstone rock surface

Based on the experiment, the maximum absorbance was obtained at the wavelength of 369.5 nm. This maximum absorbance was used to plot the calibration curve as shown in Fig. 13. The equation which was resulted from the calibration curve was used to calculate the equilibrium concentration of the polymeric surfactant in the solution (C_e). Finally, q was obtained to find the adsorbed amount of adsorbent at equilibrium concentrations.

According to the experimental data in Fig. 14, the higher the concentration of polymeric surfactant solution is, the more amount of surfactant was adsorbed on to the sample surface. At low surfactant concentration, the molecules of surfactant are enamored to the charge dispersed on the rock surface as electrical double layer (as clarified by Helmholtz 1879, and further improved by Stern in 1924) [51, 52]. This dispersed charge is responsible for appealing the surfactant molecules. The molecules of surfactant start aggregating and creating hemi-micelles at higher surfactant concentration [49].

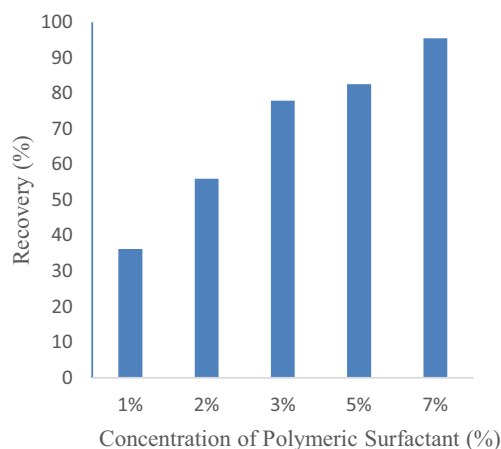


Fig. 15 Performance of polymeric surfactant solution in oil recovery

Core flooding experiments

Polymeric surfactant performance was performed using a core flood test as shown in Fig. 15. Ratio of sandstone to oil in a model of EOR is 1:15. Volumetric flow rate of the pump is 1.83 mL/s. Figure 15 shows the oil recovery performance as a function of different polymeric surfactant concentrations. The percentage of recovery increases sharply as the concentration of polymeric surfactant solution rise also from 1 to 7%. Based on emulsification study above, if the concentration of polymeric surfactant is below 3%, it does not form a good emulsion, but if it is more than or equal to 3%, it is able to emulsify the oil. Therefore, with a 3% concentration, it is able to obtain 77.98% recovery.

Conclusion

The best polymerization to synthesize polymeric surfactant was obtained at a mole ratio of 1:0.3 MES to acrylamide monomer. The polymeric surfactant was able to reduce the interfacial tension (IFT) up to 2.3 mN/m. The synthesis of polymeric surfactant obtained a yield of 1384.79%. Characterization of polymeric surfactant by FTIR and H-NMR proved that the polymeric surfactant was successfully formed in this study. Based on wettability alteration study of oil-wet quartz surface with the polymeric surfactant, it showed that the polymeric surfactant was potential candidates to change from the initial oil-wet to water-wet quartz surface. According to thermal analysis, it showed that the polymeric surfactant was thermally stable under the desired reservoir temperature. Referring to emulsification behavior, it could be concluded that polymeric surfactant solutions were able to emulsify crude oil. When the polymeric surfactant concentration was increased in the system, the adsorption onto the rock surface was also increased due to the more molecules available for adsorption. Flooding experiments showed an increase in oil recovery in different concentrations of polymeric surfactant. Based on the above test results, although the IFT value of polymeric surfactant is not very low, it has the potential as an alternative surfactant for EOR applications.

Acknowledgments The authors would like to express the biggest gratitude to Vilia Kartika Setyaningrum, Erika Wahyu Putri, Wisnu Dwi Pamungkas, Muhammad Waliyuddin Hakim, Reginata Xaviera, Nurfitriyana Mayau, and Felicia Gunawan for all the help and support

Funding The authors received funding from Kemenristekdikti (Ministry of Research, Technology and Higher Education) with contract number 43/AKM/MONOPNT/2019.

Compliance with ethical standards

Conflict of interest The authors declare there are no conflicts of interest.

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