Egyptian Journal of Chemistry

http://ejchem.journals.ekb.eg/

Radiation-Induced Polymerization of Thermo-Responsive Polymers and Comprehensive Characterization for Improved Performance

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Abstract

Early water breakthrough with high water cut through highly conductive thief zones is a prevalent problem in many water-flooded oil reservoirs. Smart polymers that are sensitive to temperature changes, also known as thermo-responsive polymers, e.g., polyethylene glycol (PEG) have great advantages over conventional polymers that can be exploited to solve the problem of conductive thief zones. Thus, this study aims at designing and synthesizing a thermo-responsive polymer using Gamma Ray Induced radiation with good tolerance against high temperature, and high salinity reservoir conditions with feasible and economic synthesis procedure for application in Egyptian oil reservoirs. That is a combined use of polyacrylamide and/or polymethacrylamide together with the selected thermo-responsive polymer (PEG) (3000 ppm polymer concentration) could achieve a viscosity of about 2.8 cp at 90°C under 200,000 ppm salinity conditions. The thermo-gravimetric analysis as well as the viscosity temperature profiles, confirmed that the polymer composite can maintain its thermal stability up to 105°C. The FT-IR spectrum confirmed that the polymer components were well-blended with each other and produced a homogeneous polymer with enhanced characteristics.

*Keywords:*CEOR; Thermo-responsive polymers; LCST; Heterogeneous reservoirs; Gamma radiation

1. Introduction

Enhanced Oil Recovery (EOR) refers to the utilization of various procedures to recover additional oil from a reservoir beyond the primary and secondary methods. These procedures include chemical flooding (polymer, surfactant, alkaline or combination) [1-6], gas flooding (carbon dioxide) [7], and thermal injection (steam or in-situ combustion) [8]. Among these methods, there has been a great interest in the oil industry for the use of polymer solutions in recovery techniques. When the efficiency of water injection becomes poor due to water breakthrough or high water-cuts, polymer flooding at this case is a very attractive candidate [9-11]. Attia et al have long been involved in EOR [5,12-17] by introducing several probe indexes to characterize the rock typing, water saturation, barriers and production zones, together with extensive investigations on the permeability, wettability resistivity of rocks towards better understanding of the optimum operating conditions with an aim to maximize the oil production. Polymers can improve the vertical and areal sweep efficiency by reducing the fingering effect and improving the sweep of the injected fluid through the reservoir[18]. The success of polymer flooding in enhancing oil recovery is closely related to changes in relative permeability. So, accurate determination of relative permeability is very crucial in order to optimize the

performance of polymer flooding [15]. Actually, low polymer concentration in the displacing fluid can reduce its mobility and eventually enhance the mobility ratio (Eq. 1) to be equal to or less than 1 which is a favorable condition in immiscible flooding operations:

$$M = \frac{\lambda w}{\lambda o} = \frac{\mu w/kw}{\mu o/ko} \qquad (1)$$

where k, μ, λ, are the effective endpoint permeability, viscosity and the mobility, respectively, and the subscripts o and w refer to water and oil [19].Thus, if the mobility ratio is equal to or less than 1, the mobility of water (the displacing phase) will not be higher than that of oil (the displaced phase) a uniform conformance profile will be achieved, and water breakthrough will be delayed. In the same context, Izgec& Shook [20] also mentioned that the main cause of conformance problems in petroleum reservoirs is the inconsistent flow of the injected fluids as a result of reservoirs' heterogeneity in terms of permeability. These conformance problems lead to excessive water production and consequently affect the productivity index of the wells. Thus, various approaches are introduced to mitigate conformance problems, which are mainly based on increasing the flooding fluid viscosity and decreasing the permeability of thief zones (high permeable zones) to achieve favorable mobility ratios and consequently to enhance sweep efficiency.

One of the most used polymers in polymer flooding is polyacrylamide, however several researchers have reported its instability under the conditions of high temperature and high salinity reservoirs. The mechanism of polyacrylamide degradation was explained by Uranta et al [21] in view of the excessive hydrolysis of the polymer at high temperatures (above 75°C) in the presence of salts, which eventually reduces the hydrodynamic volume of the polymer followed by a major reduction in its viscosity. Accordingly, various novel tailor-designed polymers have been synthesized, in recent years, to withstand the harsh reservoir conditions, including Thermo-Responsive polymers. Thermally activated particles or Thermo-Responsive polymers are types of smart polymers that are sensitive to temperature changes. That is, below a specific temperature, so-called Lower Critical Solution Temperature (LCST),

these polymers are completely dissolved in the solvent, but above the LCST they become more hydrophobic, and a solution-gel transition occurs followed by an increase in viscosity [22]. Such property of the LCST is of great benefit in the polymer flooding operations if effectively exploited and tailored.

1.1 Types and properties of thermo-responsive polymers

Cong et al [23] investigated the thermo-response of poly(N-isopropyl acrylamide) (PNIPAM) through synthesizing a tri-block of PNIPAM and poly(N-Vinylpyrrolidone) (PVP). PNIPAM based hydrogels are among the most investigated thermo-responsive hydrogels in view of its LCST which is close to body temperature (32°C), so it was extensively investigated in medical fields [24]. However, Cong et al [23] reported that PNIPAM has slow thermo-responsive behaviour due to the formation of hydrophobic and dense layer at the hydrogel's surface as a result of collective water molecules diffusion in the process of thermal transition or volume phase transition, which occurs at the LCST. Thus, in their work they introduced PVP block to PNIPAM which enhanced the thermal response rate by improving the polymer porosity, incorporation of more amorphous polymer structure in addition to the formation of PNIPAM networks with specific architectures. All these changes helped in enhancing the thermo-responsive behaviour of PNIPAM hydrogel. This can be of great importance in polymer flooding projects using thermo-responsive polymers, as those three mentioned parameters can be adjusted to achieve the required response rate through the flooding project. The synthesis of the PNIPAM-PVP-PNIPAM tri-block was done through reversible addition-fragmentation chain transfer polymerization/ macromolecular design via the interchange of xanthate (RAFT/MADIX) process.

The thermal stability of PNIPAM is not assessed at high temperatures (> 80°C), thus it is not the best choice for reservoirs having temperatures much higher than its LCST. Other thermo-responsive polymers are reported to have properties more compatible with chemical enhanced oil recovery (CEOR). For example, Badi [25] introduced Polyethylene Glycol (PEG)-based polymers with

LCST above 100°C in aqueous solutions, due to its amphiphilic characteristics, for use in high temperature reservoirs. However, no application of the polymer using this high LCST have been witnessed in the literature due to the rare applications that need a polymer with this high LCST [26-28].Thus, it is always copolymerized with other constituents to lower its LCST to be compatible with many applications. The attractive point in PEG-based polymers is that their LCST is easily tuned by varying the length of EG units. Indeed the ranges of LCST of the PEG based polymers in the work of Badi [25] was between 7°C and 90°C, which allows its use in various reservoir temperatures. He also reported that the polymerization of PEG based macro-monomers can be achieved via most of polymerization techniques including cationic, anionic, ring opening metathesis, group transfer polymerization, free radical polymerization, coordination polymerization, catalytic chain transfer polymerization, as well as reversible deactivation radical polymerization processes. One of the most attractive PEG-based thermo-responsive polymers is the poly[oligo(ethylene glycol) dimethacrylate] (POEGDMA) which was synthesized and investigated by Suljovrujic et al. [29]. They performed the polymerization through High Energy Radiation technique where gamma radiation breaks the carbon-carbon double bonds to initiate the polymerization. This technique has many advantages over other chemical processes including the ease of process control, no need for cross-linkers and initiators and relatively low run cost and low waste generation [30]. The work of Suljovijic et al. [29] produced a series of POEGDMA hydrogels by varying the feed ratio between monomers and solvents. The values of the LCST of the polymers was between 19 to 75°C, approximately, based on the number of Ethylene Glycol (EG) units in each polymer.

Another important family of thermo-sensitive polymers (called poloxamers) was studied by Zarrintaj et al. [31]. Poloxamers (also known as Pluronic) are among a unique group of synthetic copolymers structured as tri-blocks, where a hydrophobic chains of poly(propylene oxide) (PPO) are sandwiched between two chains of poly(ethylene oxide) (PEO) which are hydrophilic. The cloud point of this tri-block is easily tuned by varying the number of PO and EO units. the cloud point can range from 14°C to more than 100°C, where the more the percentage of EO units in the tri-block the higher the cloud point. The rheology of amphiphilic polymeric solutions (such as Pluronic) is more complex than that of conventional polymers as their hydrophobicity is dependent on the conditions of the test especially temperature [32]. That is at high temperatures above the LCST the polymers are more hydrophobic than at temperatures lower than LCST. Thus, the flow behaviour of poloxamers vary from Newtonian to viscoelastic and up to unstable rheological behaviours. For aqueous solutions of poloxamers with concentrations between 13-19 wt%, they behave like Newtonian fluids, whereas at higher temperatures, above LCST, their behaviours change to thermoplastic gels' having yield stress [33]. At even higher temperatures, i.e., near to gel temperature, a shrinkage in the PEO shells occurs because of dehydration followed by a collapse of the gel structure. The gelling temperature can be recognized by a sudden increase in viscosity, or when yield stress appears [31].

1.2. Applications of Thermo-responsive polymers in EOR

The introduction of thermo-responsive polymers in the oil and gas fields especially in the EOR applications started in 1997 by the use of a BP idea which was taken to a freshly organized research committee informally named "MoBPTeCh", which included BP, Mobil, Cheveron and Texaco, and later Naclo Company joined to serve as a chemical manufacturer and finally the committee included Chevron, BP and Naclo. The developed thermo-responsive polymer was commercially named "Bright Water". The technology patent is assigned to Naclo[34]. The development of the technology started by investigating the effect of reducing the permeability of the "*thief zones*" to direct the injected water into un-swept zones, with lower permeability and high saturation of oil through simulation. They also concluded that the temperature gradient (the temperature difference between the injected water and the reservoir temperature) could be used as the trigger or activator of the thermo-responsive polymer [34]. Then, in the next stage, they performed a laboratory design for the chemical, which resulted developing a submicron particle that significantly expands and its viscosity increases when the activation temperature is reached, just as the behaviour of thermo-responsive polymers [34]. The first successful project with "Bright Water" was in 2001,

and since then, the technology was used in various reservoirs with high heterogeneities in permeability. By July 2009, the technology has been applied in 26 oil fields partially or totally owned by BP, with a success rate of about 80% [34].

The property of solution to gel transition present in thermo-responsive polymers as well as the ability to tune the transition temperature can be of great advantage in polymer flooding projects for several reasons:

(i)   Firstly, the problem of thermal degradation can be eliminated as we can tailor a polymer with a LCST near each reservoir temperature, and

(ii)   Secondly, there is no need for especial pumping equipment to inject this polymer as its viscosity is low at normal conditions and it increases in-situ after reaching its transition temperature (LCST).

In heterogeneous reservoirs with great permeability variation between the layers, water flooding as well as conventional polymer flooding operations often face a great problem where most of the injected fluid (more than 90% in many cases) is directed to the thief zones (layers of higher permeability) and leaving the other layers un-swept. Thus, thermo-responsive polymers can be very effective (in terms of cost and time) in the operations of shutting these thief zones in heterogeneous reservoirs. This is due to the low viscosity of the fluid (containing the thermo-responsive polymer) during its (fast) injection, which then reach its LCST after occupying the thief zones and turned into gel to completely shut this layer or reduce its permeability as required. Then a water slug can be injected until another layer act as a thief zone, so another shutting operation can be easily repeated with a thermo-responsive polymer slug and so on until all the layers are swept and shut in.

Izgec and Shook [20] discussed a simulation model to investigate the aforementioned technique of using thermo-responsive polymers or so-called "Temperature Triggered Submicron Polymers" in EOR operations. The model was built by Akanni[35],where he examined a 2-layer reservoir with high contrast in permeability and with range of

oil/water viscosities between 1 and 10000 cp. This revealed that the optimum case to use such polymers, was obtained for high permeability contrast between layers, and that it is better to place the Temperature triggered particles near the producer for a better conformance control.

Okeke & Lane [36] initiated a research to evaluate how effective thermo-responsive polymers can be used in blocking the thief zones within a reservoir to divert the flow to un-swept areas, thus they introduced mathematical models to simulate the injection and placement of such polymers. They developed various models to perform sensitivity runs of various reservoirs' conditions and characteristics, then they performed an economic analysis study. Models were also developed for water flooding and polymer flooding projects to compare them with the used thermo-responsive polymers. However, they showed that polymer flooding was more economical than thermo-responsive polymers in terms of incremental oil produced.

The effectiveness of conventional polymer flooding over thermo-responsive polymer in the work of Okeke & Lane [36] was assigned to several reasons. Although the properties of thermo-responsive polymers look more efficient and economical in blocking the thief zones, the design of such polymers is very critical. That is if the polymer is not properly tailored in terms of LCST to fit the reservoir temperature, the process will fail. This is because the LCST should be designed to be reached when the polymer has occupied the whole thief zone from the injector to the producer and not before that to make sure that the thief zone was effectively shut in. Moreover, the design of thermo-responsive polymer projects should be performed upon an effective and accurate thermal simulations to the thermal fronts between injectors and producers, and this may not have been done in their work.

Divers et al. [19] used various samples of thermo-responsive polymers to assess their properties and performance for use in extreme conditions of Oman Oil Fields. The characterization of polymers was based on their thermal stability, rheology, and flow in porous media. Firstly, the rheological properties of the polymers were investigated in dynamic and stationary modes. The polymers were grouped into two categories, first category included polymers to be used in the South fields where the reservoir temperature is 60°C and the second category was for

polymers to be used in the North fields where the temperature is 90°C. It was concluded that as the temperature increases, higher concentrations of polymers are needed to achieve the same viscosity. In thier research, concerning thermal stability, four polymers were chosen to perform long-term thermal stability tests while controlling the amount of O_2 present and in the presence of hydrogen sulfide gas (H_2S). The samples used for the South fields showed no thermal degradation under all conditions, while the samples used for the North fields showed the same behaviour except for samples aged under anaerobic conditions there was a 20% degradation. This is interesting as the conventional HPAM cannon work in temperatures higher than 75°C due to its excessive hydrolysis above this temperature which eventually results in a decrease in its hydrodynamic volume followed by a decrease in the viscosity of the solution. For the core flooding tests, there was a problem in the transportation of the polymers in low permeability cores. Thus, the molecular weight as well as the LCST of the polymers should be accurately-tuned to be compatible with low permeability zones.

Khamees et al. [37] built a model to investigate the effect of slug size and concentration, reservoir heterogeneity, reservoir wettability, cross-flow among layers, thief zones locations, treatment initiation time, reservoir initial temperature, brine salinity, and activation of LCST on the Bright Water (a type of Thermo-Responsive polymer). The results of their study are outlined here:

- As the polymer concentration increases, the recovery factor increases.
- Short injection time with high polymer concentration is better than long injection time with low polymer concentration.
- As the reservoir heterogeneity increases, the incremental oil recovery increases.
- The optimum value of cross flow was 0.1. Nevertheless, a model with lower value of cross flow and high permeability contrast showed a better performance than a model with higher cross flow value and lower permeability contrast.
- Water-wet models showed better results over the oil-wet model in terms of water cut, where the water cut was higher in the oil-wet model was higher than that of the water-wet model.

- No difference when the location of the thief zones was at the lower or upper of the model. However, when the thief zone was in the middle location, better results were obtained.
- To achieve better treatment performance, unfavorable mobility ratio should be the case at the start of the project.
- The earlier the initiation of the treatment, the better obtained results.
- As the initial reservoir temperature decreases, the recovery factor increases (but this is because the same grade of bright water was used for both models, however for higher reservoir temperatures another grade with higher activation temperature should be used to achieve the same results, and this is the essence of the thermo-responsive polymers as their activations temperatures which are the LCST is tunable and be tailored for every reservoir condition).
- The best reduction in the thief zones' permeability occurred at an activation temperature of 150°F.

Maddinelly et al. [38]evaluated the performance of novel types of thermo-responsive polymers in polymer-flooding operations through core flooding tests. The selected rock type for the flooding test was Clashach sandstone. Differential pressure monitoring was used to assess the injectivity requirements of the thermo-responsive polymer. The LCST of the polymer was around 70°C. The permeability reduction upon reaching the LCST was evaluated by measuring the relative permeability to water before and after the flooding to find the residual resistance factor which was equal to 4 in this case. Generally, the tested polymer appeared to be appropriate when sufficient shear resistance, low viscosity and reduction in permeability is required, however the reduction in permeability in the core folding test was not adequate as no simulation models was run to assess the optimum polymer properties required for this case.

Li et al. [39] investigated the performance of two novel thermo-viscosifying polymer named SAV-A and SAV-T, compared to a conventional EOR polymer (PT2500), in three reservoir conditions,

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i.e.,

(i)   Reservoir 1: 85°C, 29000 mg/L
        NaCl, 1000 mg/L Mg^{2+} + Ca^{2+},
(ii)   Reservoir 2: 105°C, 190020 mg/L
        NaCl, 10000 mg/L Mg^{2+} + Ca^{2+},
        and
(iii)   Reservoir 3: 120°C, 190020 mg/L
        NaCl, 10000 mg/L Mg^{2+} + Ca^{2+}.

Their work concluded that the two thermo-viscosifying polymers showed a thermo-responsive behavior only at concentrations above 0.2 wt% when heated along a temperature gradient between 20°C to 80°C, while salinity is being increased from 32000 to 220000 mg/L, while PT2500 showed a thermo-thinning behaviour under the same conditions. As long as the thermal stability is concerned, the thermo-viscosifying polymers (TVPs) were better than PT2500. Moreover, the TVPs' propagation through porous medium was smooth. Recovery efficiencies obtained from the TVPs were higher than that of PT2500, especially at higher reservoir temperatures with lower concentrations used for TVPs than PT2500.

Chen et al. [40] developed a thermo-sensitive polymer to work as a water shut off agent with a compact structure and high plugging strength to plug the high permeability zones (thief zones). The performance of the polymer and its potential in field applications was evaluated and tested through various laboratory tests and the results were as follows. Firstly, the viscosity of the polymer at room temperature (injection temperature), was 34.5 cp, which allows easy flow of the polymer through the completion tools (e.g., gravel pack and screen pipe), and then it is activated in the reservoir when its temperature reaches the LCST and an in-situ gelation occurs. This is a great advantage of the thermo-responsive polymers over conventional ones, as the viscosity while injection is low which allows the operation to be done with the same pumping equipment for the water flooding, then an increase in the viscosity occurs in the reservoir after reaching the LCST of the polymer.

Secondly, the polymer was not soluble in water and the characteristics of its phase transition were not changed by the presence of guar gum as a fracturing fluid. Thirdly, the position where the polymer will reach its LCST and its viscosity increases could be determined by the adjustment of the dose of SA-DST, which is the chain transfer agent during polymerization. This is very attractive as the position of thermo-responsive polymer activation is a major factor in determining the success of the project. Fourthly, the plugging strength of the polymer was more than 19.1 MPa and the rate of volume retention was up to 99.13%. The results of field applications were very effective as there was an increase in oil production from 0.08 m^3/day to 5.37 m^3/day.

The importance of thermo-responsive polymers for EOR projects was stated again by others [41,42] as they stated that due to the structure of thermo-sensitive polymers, they are intriguing for EOR applications. They are considered alternate viscosifying agents for circumstances of high temperature and salinity since they have a hydrophilic main chain with hydrophobic side.

The aforementioned merits of the use of thermo-responsive polymers with tuned properties suitable for CEOR, urged us towards the objective of the current study. That is the design and synthesize of a new thermo-responsive polymer is targeted, herein, using radiation-induced polymerization technique (employing gamma-rays source) and explore its thermo-sensitivity for potential application in CEOR under harsh conditions of high temperature and salinities. The advantages of Ionizing Radiation Polymerization are as follows:

- Easy technique for polymerizing various monomers that have high resistivity to polymerization by conventional techniques [43].
- A safe technique, when polymerization involves hazardous compounds such as, organo-chlorine [44,45].
- Allows polymerization to be carried out in the solid state [46,47].
- High polymer purity as the polymer is obtained without by product, where in conventional methods, complicated purification stages are required [48,49].
- Very cheap especially when tons of monomers are to be polymerized.

2. Materials and Methods

2.1. Chemicals

Chemicals' selection was almost the most challenging mission in the work,due to the several aspects that must be considered in such process. Firstly, regarding the thermo-responsive polymer, its should be cheap and commercially-available with LCST suitable for use in a particular oil reservoir. Secondly, the monomers also should be cheap, commercially-available and most important they should have high thermal stability and they should be easily cross-linked with the polymer. Thus, the selection process was achieved through several stages, firstly a review of all the commercially available monomers and polymers and their prices was performed, and accordingly several candidate monomers and polymers were purchased. Finally, through several experiments and sensitivity analyses on the monomers and polymers, the selected monomers were Acrylamide and Meth-acrylamide, and the selected thermo-responsive polymer was poly-ethylene glycol (PEG).

2.2 Samples Preparation

In this work, a total of 48 samples were prepared to investigate the effect of the concentration of each component, i.e., PEG, acrylamide and methacrylamide on the composite viscosity under various operating conditions (i.e., temperature and salinity) to achieve the least possible optimum concentration of each and to test the tenability of the composite's cloud point. The 48 samples are categorized as follows:

- 24 samples for viscosity-sensitivity analyses on the concentrations of acrylamide, meth-acrylamide, and PEG,
- 12 samples for viscosity-sensitivity analyses on salt concentration (salinity),
- 6 samples for testing cloud point tenability, and
- 6 samples for the polymer composite final form.

The base solvent for each sample was deionized water with/without NaCl. All the used chemicals were of analytical grade and were used as-received without any further purification.

2.3. Polymerization

As mentioned above, the aim of this work is to tailor the properties of a thermo-responsive polymer to be used in enhancing oil recovery. This can be achieved by cross-linking the selected thermo-responsive polymer (PEG) with other polymers (in-situ prepared via radiation-induced polymerization) in order to tune its properties as a thermo-responsive polymer, such as, the Lower Critical Solution Temperature (LCST) and thermal stability. The polymerization and cross-linking via radiation-induced polymerization, also known as Ionizing radiation, using Gamma Rays (irradiation dose of 15 kGy obtained at a rate of 2 kGy/h) was performed at the Egyptian Atomic Energy Authority.

2.4 Sensitivity Analyses

After the selection of the components of each polymer-composite, it is the aim to achieve a high polymer viscosity with the lowest concentration. However, before selecting the optimum concentration of the components, it was important, firstly, to perform several sensitivity analyses tests to know the effect of each component separately as well as the effect of the ratios between the components on the viscosity of the polymer in addition to the effect of salinity on the polymerization and viscosity of the polymer. Thus, four sensitivity analyses tests were performed, three analyses for each component and one for salt concentration.

The first sensitivity analysis was performed to know how the acrylamide concentration as well as its ratio to the other two components contributes to the viscosity of the polymer. The experiment consisted of 8 samples, where each sample contained 1% of meth-acrylamide and PEG while the concentration of acrylamide was changed from 500 ppm to 50000 ppm. The experiment was performed using deionized water and the irradiation dose was 15 kGy obtained at a rate of 2 kGy/h.

The second sensitivity analysis was performed to know how the meth-acrylamide concentration as well as its ratio to the other two components contributes to the viscosity of the polymer. The experiment consisted of 8 samples, where each sample contained 1% of acrylamide and PEG while the concentration of meth-acrylamide was changed from 500 ppm to 50000 ppm. The experiment was performed using deionized water and the irradiation dose was 15 kGy obtained at a rate of 2 kGy/h.

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The third sensitivity analysis that was performed to probe the impact of PEG concentration as well as its ratio to the other two components on the viscosity of the polymer blend. The experiment consisted of 8 samples, where each sample contained 1% of acrylamide and PEG while the concentration of meth-acrylamide was changed from 500 ppm to 50000 ppm. The experiment was performed using deionized water and the irradiation dose was 15 kGy obtained at a rate of 2 kGy/h.

The fourth sensitivity analysis was performed to disclose the effect of the salinity on the viscosity and polymerization of the polymer. The experiment consisted of 12 samples, where each sample had the same composition of the three components of the polymer, while the NaCl concentration changed from 500 to 200000 ppm. The experiment was performed using irradiation dose of 15 kGy obtained at a rate of 2 kGy/h.

2.5. Rheological measurements

All samples for sensitivity analysis were tested using the Anton Paar MCR 502 Rheometer, operating under both oscillator and rotational modes at a wide range of temperatures. Additionally, Brookfield viscometer (BROOKFIELD DV – III ULTRA Programmable Rheometer) located in the Egyptian Petroleum Research Institute (EPRI) is used as well.

2.6. Thermogravimetric Analysis (TGA)

Thermogravimetric analysis was performed using DTG-60/60Hin the MICROANALYTICAL Center at Cairo University.

2.7. Fourier Transform Infrared Spectrometry (FT-IR)

FT-IR is the preferred technique for infrared (IR) spectrometry. The obtained spectrum is a representation of the molecular transmission and absorption, and it creates a molecular fingerprint for the sample. The FT-IR tests were carried out in the Egyptian Atomic Energy Authority to ensure the quality of our blend and confirm the presence of the function groups of the components of our polymer.

3. Results and discussion

The results of each set of tests are presented herein for each synthesized polymer composite blend. The rheology tests for the sensitivity analyses, the cloud point analysis, the rheology of the final form samples, as well as the results and interpretation of TGA and IR tests.

3.1. Sensitivity Analyses Results

The first sensitivity analysis was done to test the effect of changing the acrylamide concentration in the polymer composite blend on its viscosity. The viscosities of the tested samples are shown in **Table 1**.

Table 1: Dynamic Viscosities of Acrylamide Sensitivity Samples

Sample No.	Concentration (ppm)			Viscosity (cp)
	Acrylamide	Meth-acrylamide	PEG	
1	500			1.3
2	1000			1.1
3	2000			1.1
4	3000	10000	10000	1.2
5	5000			1.6
6	10000			2.3
7	20000			9.6
8	50000			(gel) Semi-solid

Samples 5-7 show a steep increase in the viscosity. The difference in viscosity between sample 5 and sample 6 is somewhat reasonable, as the acrylamide concentration in sample 6 was twice the concentration in sample 5 and the viscosity of sample 6 was almost 1.5 times that of sample 5. However, there is still another hidden factor as the viscosity was not doubled, so the concentration is not the only factor that affects the composite viscosity.

The difference in viscosity between sample 6 and sample 7 approves that the concentration is not the only contributor to the viscosity as here the acrylamide concentration was also double, but the viscosity increased with a factor of almost 4. The reason for this will be revealed in the next sensitivity analyses.

Sample 8 was semi-solid (gel-like) after polymerization and its viscosity was not measured due to its excessively high value.

The second sensitivity analysis was done to test the effect of changing the meth-acrylamide concentration in the polymer composite composite on the mixture viscosity. The viscosities of the samples are shown in **Table 2**.

Table 2: Dynamic Viscosities of Meth-acrylamide Sensitivity Samples

Sample No.	Concentration (ppm)			Viscosity (cp)
	Acrylamide	Meth-acrylamide	PEG	
9		500		Semi-solid (gel)
10		1000		109.5
11		2000		5.6
12	10000	3000	10000	2.9
13		5000		2.6
14		10000		2.4
15		20000		2.5
16		50000		4.2

Sample 9 was excessively viscous after polymerization and the viscosity of sample 10 was also high, although the concentration of meth-acrylamide was increased.

From sample 11 the viscosity showed a steep drop then kept decreasing slightly till sample 14 followed by a slight increase in samples 15 and 16, despite the excessive increase in concentration for those samples.

3.2. Findings of Acrylamide and Meth-acrylamide Sensitivity Analyses

The results of the two sensitivities (shown above) confirm that the dominant factor that controls the viscosity is the ratio between the acrylamide and methacrylamide concentrations. It is apparent that as the ratio of the acrylamide to the methacrylamide increases, the viscosity steeply increases and as the ratio drops below 1, the change in viscosity becomes very minor. For instance, considering the acrylamide sensitivity in Table 1, for samples 7 and 8 the ratios of acrylamide to meth-acrylamide were 2:1 and 5:1 respectively, and these samples were the start point of a steep increase in viscosity, while for samples 1-6 where the ratios were 1:20, 1:10, 1:5, 1:3, 1:2 and 1:1, the differences in viscosities were negligible. Whereas, regarding the second sensitivity analysis which was done on the meth-acrylamide, the same effect of the ratio between acrylamide and the meth-

acrylamide applies. As in samples 9 and 10 where the ratios were 20:1 and 10:1 respectively, the viscosities were very high, then decreased steeply as the ratio approached 1:1 and less.

These findings are of great economic importance, as the viscosities obtained with excessively high concentrations can be obtained with much lower concentrations just by adjusting the ratios between the acrylamide and the methacrylamide monomers. For example, in sample 8, where the viscosity was excessively high, the ratio of the acrylamide to the meth-acrylamide was 5:1 and the total concentration was 70000 ppm. However, in sample 9, the viscosity was also excessively high with a total concentration of 20500 ppm, but the only difference here is that the ratio of the acrylamide to the meth-acrylamide was 20:1.

The Third sensitivity analysis was done to test the effect of changing the PEG concentration in the polymer composite composite blend on the resultant viscosity. The viscosities of the samples are shown in **Table 3**.

Table 3: Dynamic Viscosities of PEG Sensitivity Samples

Sample No.	Concentration (ppm)			Viscosity (cp)
	Acrylamide	Meth-acrylamide	PEG	
17			500	1.4
18			1000	2.5
19			2000	3.8
20	10000	10000	3000	1.9
21			5000	1.6
22			10000	1.9
23			20000	2.4
24			50000	6.7

In this analysis it is apparent that the PEG concentration has a minor effect on the viscosity of the polymer composite blend and a wider sensitivity analysis with higher accuracy is needed to detect its effect precisely. However, the main role of the PEG in this polymer composite blend lies in its thermo-responsiveness, so it is not expected to provide high viscosities at the ambient temperature, but its role is to maintain or increase the viscosity of the composite at high temperature to avoid the effects of high temperatures in the reservoirs. Thus, the next section will be dedicated to the thermo-response tests for the PEG.

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The Fourth sensitivity analysis was done to test the effect of changing the salinity of the aqueous medium on the viscosity of the polymer composite blend (with fixed concentration for each component). The viscosities of the samples are shown in **Table 4**.

Table 4: Sensitivity analysis on NaCl concentration at 12% polymer concentration

Sample No.	Concentration (ppm)			NaCl(ppm)	Viscosity (cp)
	Acrylamide	Meth-acrylamide	PEG		
30	50000	50000	5000	500	116.4
31	50000	50000	5000	1000	86.2
32	50000	50000	5000	3000	78.5
33	50000	50000	5000	5000	91.5
34	50000	50000	5000	10000	73.5
35	50000	50000	5000	30000	57.1
36	50000	50000	5000	60000	66.1
37	50000	50000	5000	100000	92.2
38	50000	50000	5000	125000	110.3
39	50000	50000	5000	150000	114.6
40	50000	50000	5000	175000	142.7
41	50000	50000	5000	200000	206.5
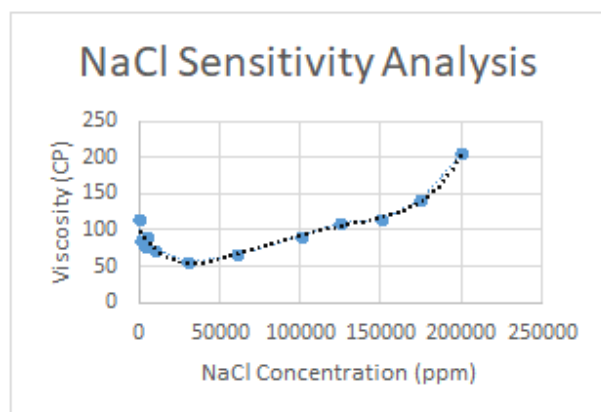
Figure 1: Sensitivity analysis of viscosity of polymer composites (at 12% polymer concentration) prepared at various NaCl concentrations. N. B. 15kGy irradiation dose is used.

From this sensitivity analysis one can conclude that a specific salt concentration opposes polymerization till a specific point then it enhances the polymerization.
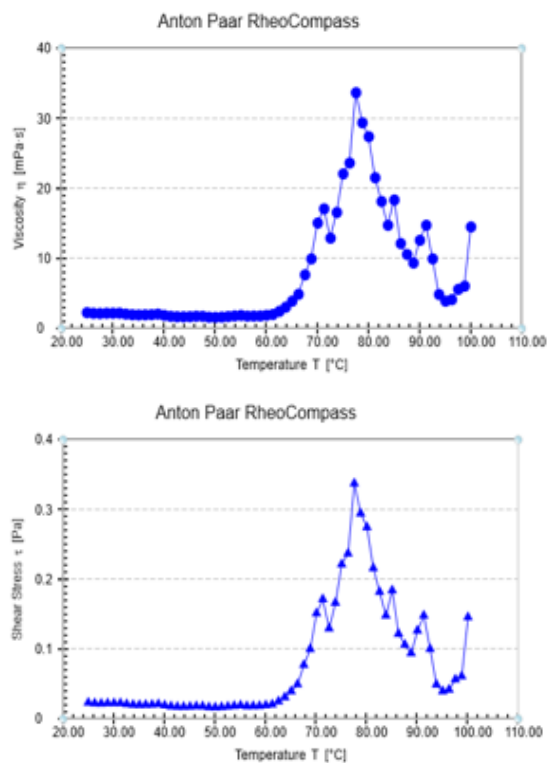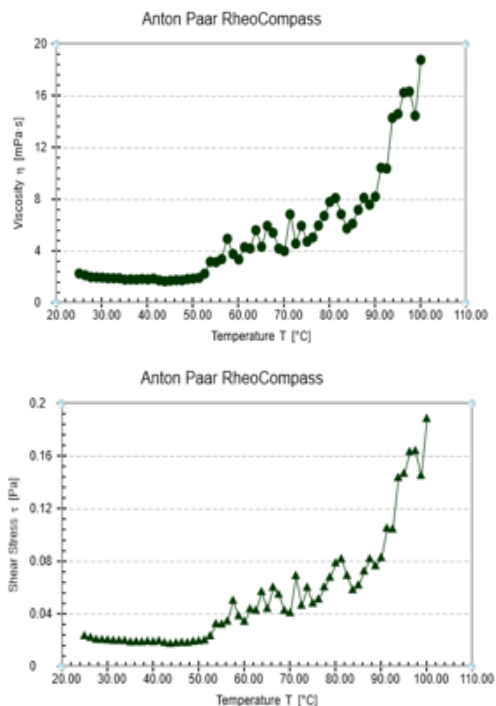
3.3. Cloud Point Tests

This section presents the results of the tests that were performed to check and confirm the presence of thermal response in the PEG-based composite blends and to test the ability to tune its thermo-responsiveness; to change its cloud point temperatures to be applicable in various reservoir temperatures. The cloud point of pure PEG-6000 is above $100\,^{\circ}$C, so it was not easy to perform the cloud point tests at temperatures higher than $100\,^{\circ}$C as the solvent will evaporate and the test must be performed at higher pressures, where the boiling point of the water is $>100\,^{\circ}$C. Thus, for simplicity, Poly(ethylene oxide) PEO (molecular weight 100000) is used to check the tune-ability of the cloud point. PEO-100000 was chosen as it is confirmed from the literature that its cloud point is below $100\,^{\circ}$C and at the same time it is chemically similar to the PEG, so the technique for tuning the cloud points of both chemicals will be apparently the same.

3.3.1. PEO Cloud Points Tuning

The technique for tuning the cloud point of the poly(ethylene oxide) (PEO) was carried out by using sodium sulphate (Na_2SO_4), as it is mentioned in the literature that as the concentration of inorganic salts increases in a thermo-responsive polymer, its cloud point decreases. Thus, we prepared 4 samples of PEO (1 wt.%) with different molar concentrations of (Na_2SO_4) as shown in **Table 5**, then their viscosities against temperature were measured using MCR 502.

Table 5: Tuning PEO Cloud Point

Sample no.	PEO (ppm)	Na_2SO_4 (M)
1	10000	0.1
2	10000	0.2
3	10000	0.3
4	10000	0.4

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EO Viscosity Against Temperature
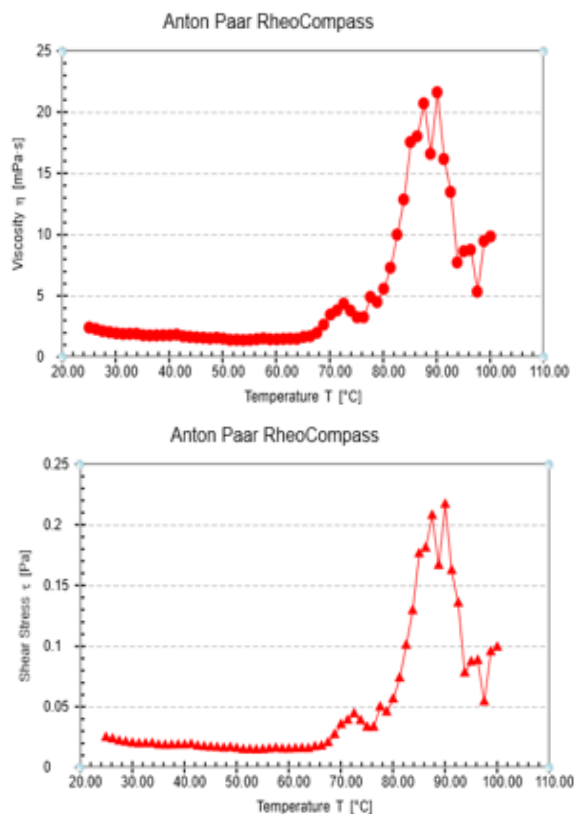
Figure 1: Viscosity-temperature Profile of 10000 ppm PEO in 0.1 M Na$_2$SO$_4$

Figure 3: Viscosity-temperature Profile of 10000 ppm PEO in 0.3 M Na$_2$SO$_4$

Figure 2: Viscosity-temperature Profile of 10000 ppm PEO in 0.2 M Na$_2$SO$_4$
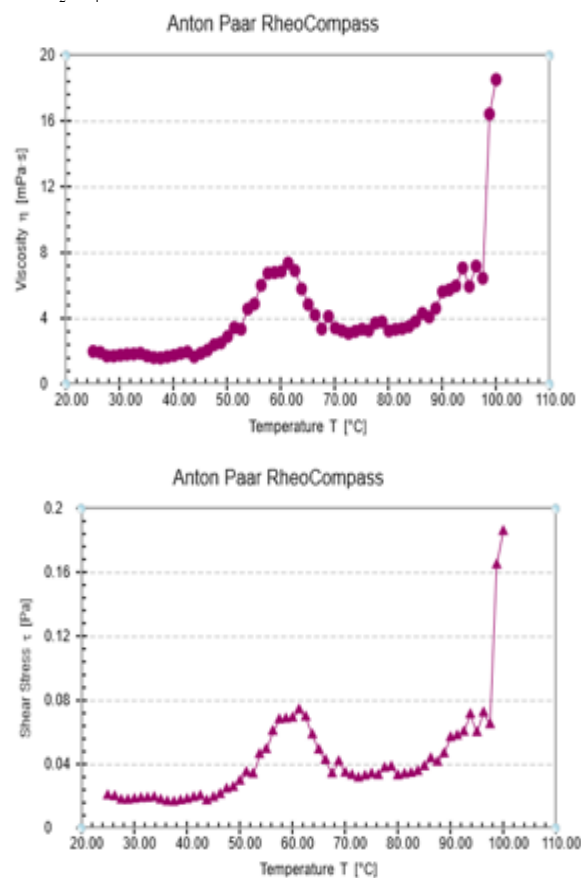
Figure 4: Viscosity-temperature Profile of 10000 ppm PEO in 0.4 M Na$_2$SO$_4$

The Cloud Point for each sample is shown in **Table 6**.

Table 6: The cloud point for each sample

Sample no.	PEO/ppm	Na$_2$SO$_4$/M	Cloud Point (ºC)
1	10000	0.1	68
2	10000	0.2	62
3	10000	0.3	53
4	10000	0.4	44

From these results it is confirmed that the cloud point of PEO (and similarly PEG) can be tuned and tailored for different reservoir temperatures just by varying the concentrations of the inorganic salts. This, phenomenon gives the Thermo-Responsive polymers a great advantage over conventional Polymers in EOR projects. As salinity is one of the greatest challenges and obstacles that degrade the properties of conventional polymers is indeed a requirement for thermo-responsive polymers.
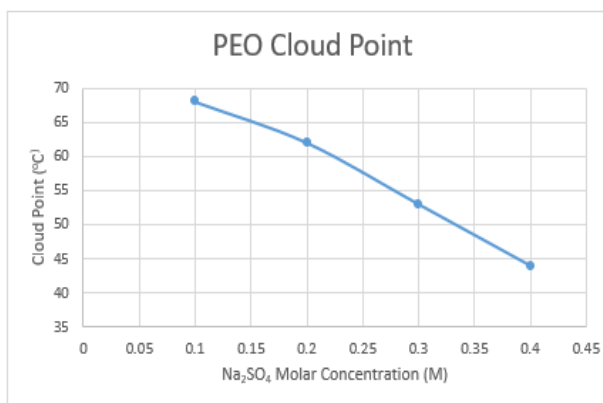
Figure 5: Tune-ability of PEO Cloud Point at 1 wt% PEO concentration

3.4. Cloud point test for the polymer composite

Figure 7 confirms that the cloud point or the thermo-responsiveness still exists after producing the polymer composite with a cloud point around 58 °C.

Finally, after the contribution of the composite's components have been recognized to an acceptable extent, we prepared a sample with a total concentration of 3000 ppm for the polymer composite blend and 200000 ppm of NaCl with a high ratio between the acrylamide and methacrylamide to achieve a high viscosity. The temperature-viscosity profile measured via the

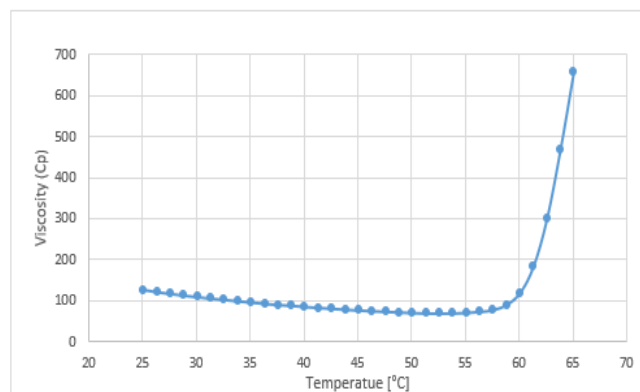Brookfield rheometer of the sample is presented in Figure 8.

Figure 6: Temperature-viscosity profile of polymer composite blend (10% concentration0 in aqueous solution containing 150000 ppm NaCl.
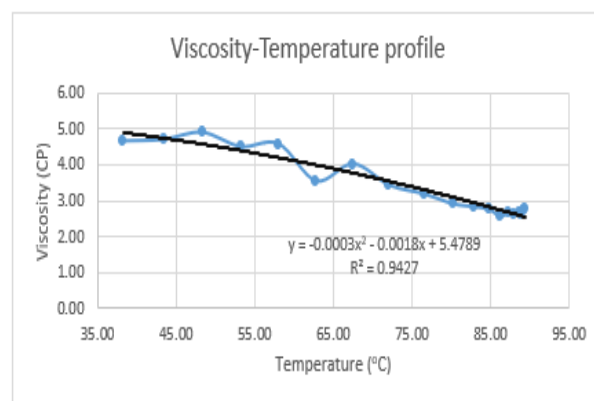

Figure 7: Viscosity-temperature profile of the polymer composite blend (total concentration of 3000 ppm) measured in an aqueous solution containing 200000 ppm NaCl

Thus, we succeeded in achieving a viscosity of about 2.8 cp at 90°C, 200000 ppm salinity and 3000 ppm polymer concentration. However, the thermo-responsiveness did not appear in this experiment, which means that the cloud point is beyond this temperature at this composition, thus further studies should be performed to have a deeper understanding on tuning on the cloud point of this polymer composite.

3.5. Thermogravimetric Analysis

Figure 9 shows the TGA curve that illustrates the thermal decomposition mechanism of the polymer composite blend. The sample was tested in the solution form, so the first mass loss (42.94-104.12 °C) is due to the evaporation of the solvent (water). The second mass loss, stared at 110 °C,

indicates the onset of the polymer decomposition. This confirms the thermal stability of till temperatures < 110 °C, so this polymer can be used in reservoir temperatures just below this value (e.g., up to 105 °C).
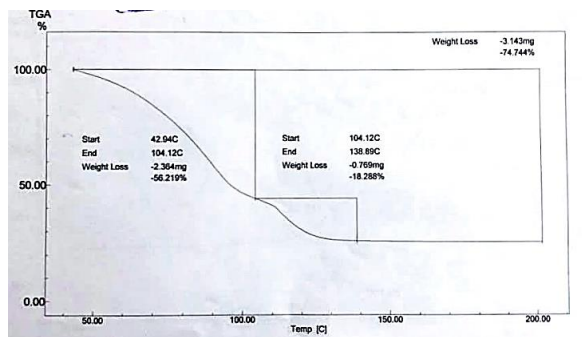

Figure 9: TGA Curve for the decomposition of the polymer composite blend.

3.6. FT-IR analysis

The FT-IR spectrum is obtained for one sample where the polymer composite blend was analyzed to detect the functional groups that exist in its structure. The infrared spectrum of the composite is shown in **Figure10**. The most significant spectral bands present in the region from 400 cm^{-1} to 4000 cm^{-1} were: (3332-3340 cm^{-1} which indicates the presence of the amide group; 1630-1650 cm^{-1}: which indicates the presence of the carbonyl; 590-610 cm^{-1}: Alcohol, out-of-plane bend. The presence of smooth and limited peaks is a good indication that a good blend has been formed between the monomers and the PEG.
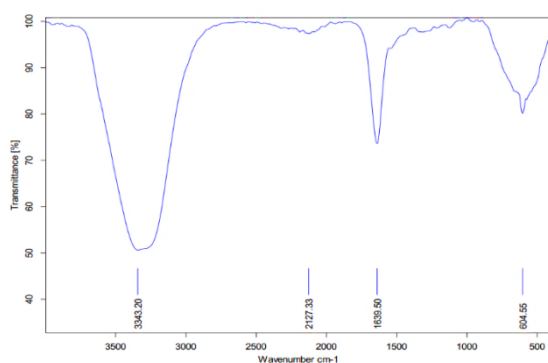

Figure 10: FTIR Spectrum of the Polymer Composite blend

3.7. Economic Feasibility of Induced Radiation Polymerization

In the Egyptian Atomic Energy Authority, the cost to induce 1 ton of a material with 15 kGy of

gamma rays, is around 1300 $, and this does not depend on the material being polymerized. Thus, the cost to induce a ton of water with zero monomer concentration is the same cost of inducing a ton of water with any monomer concentration. Thus, the water (solvent) should be saturated with monomers to polymerize the maximum possible amount in the run. However, there is another way to increase the method's feasibility. As mentioned in the literature, one of the advantages of induced-radiation polymerization is that polymerization can occur in the solid state. Thus, in that case no solvent is needed to polymerize the monomers, and 1 ton of the polymer will cost just 1300$ for polymerization. However, further studies and experiments are needed to test the ability of gamma rays to polymerize the monomers of the proposed polymers in the solid state.

4. Conclusions and Perspectives

Thermo-responsive polymers (e.g., PEG) are among the family of smart polymers that change their properties (e.g., viscosity) upon changing the surrounding environment (temperature and/or salinity). They are water soluble as long as the solution temperature is below the Lower Critical Solution Temperature (LCST), which is different for every type of these polymers. Above LCST, the hydrophobicity of the polymer greatly increases as well as its viscosity. Such a family of polymers have been widely investigated in various fields especially in the medical field for drug delivery applications, however, it was just introduced to the oil and gas field in the EOR applications in 2000.

The main conclusions of the current investigation are:

- A new thermo-responsive polymer composite blend (based on PEG and Acrylamide and Meth-acrylamide monomers) is prepared using radiation induced polymerization.
- 4 sensitivity analyses sets were performed to detect the contribution of each component in the composite separately are carried out to single out the effect of each on the viscosity of the blend.
- A successful blend of the polymer composites (3000 ppm) showed a viscosity of about 2.8 cp at 90°C in an aqueous

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solution containing 200000 ppm NaCl.

- The thermo-gravimetric analysis as well as the viscosity temperature profiles, confirmed that the polymer composite can maintain its thermal stability up to 105 °C.
- The FT-IR spectrum confirmed that the polymer components blended well with each other and produced a homogeneous polymer with enhanced characteristics in terms of viscosity and thermal tolerance.
- Further experiments should be performed to study the ability of gamma radiation to polymerize monomers in the solid as this greatly enhances the economic feasibility of the method.
- As a perspective, various parameters control the efficacy of the proposed system, including the rock typing, porosity, salinity, temperature profile, quality of the oil, …etc. Thus, it is believed that the applicability of the proposed system could be implemented in any reservoir with similar conditions as reported herein in the current investigation. Furthermore, tuning of the LCST of the polymer composite blend is a feasible procedure for a wide application under specific reservoir conditions.

Conflict of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgement

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