Journal of Molecular Liquids 263 (2018) 118–124

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Experimental research of high strength thermally stable organic composite polymer gel

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ARTICLE INFO

Article history:
Received 24 January 2018
Received in revised form 28 April 2018
Accepted 30 April 2018
Available online 01 May 2018

Keywords:
Silica dioxide
Surfactant
Composite gel
Enhanced oil recovery

ABSTRACT

Polymer gel has been successfully applied for enhanced oil recovery (EOR) in heterogeneous reservoirs. A novel composite polymer gel was developed based on amphiphilic polymer, resorsinol/hexamethylenetetramine, silica dioxide (SiO_2) and surfactant under the conditions of temperature from 60 °C to 100 °C and total salinity of 51,984 mg/L, Ca^{2+} 3308 mg/L and Mg^{2+} of 1820 mg/L. It was characterized in terms of gelation time, gel strength, morphology, long term thermal stability and effect of pH. The effect of different component concentrations in the properties of bulk gelation was investigated. The microstructure of the conventional (organic) gel and novel composite gel were studied by electron scanning microscopy (SEM), which provides insight into the mechanism of gel strength. The organic polymer gel was compared with the composite gel. The gelation time and gel strength was studied varying the concentration of nanoparticles, cross linker and polymer. The gel strength was evaluated by vacuum pump method. The composite gel was prepared by using organic cross linker and addition of $SiO_2$with surfactant, showed prominent results and proved to be of good strength with optimum concentration of SiO_2. The composite gel also showed good thermal stability with negligible syneresis at 60 °C for 90 days at pH = 8.0–8.5, which showed that composite polymer gel results in better thermal stability than conventional polymer gel and can be successfully injected into heterogeneous reservoirs for EOR.

1. Introduction

Water flooding is one of the most effective way to improve the oil recovery. The wide application of water flooding for decades leads towards water breakthrough, which is a major problem being faced by oil industry during tertiary recovery. It has been increasingly a serious issue for oil industry to reduce the water and gas breakthrough problem. The heterogeneous and low permeable reservoirs leads to difference of fluid mobility, Gas channeling and other problems [1–4]. It also results in poor sweep efficiency of oil whereas the increment of water production is observed [5]. To overcome early breakthrough problem, several chemical methods including polymer flooding, injecting foams, particle system, and gel system have been widely applied in oil fields [6,7]. Among these polymer gels have been extensively used in mature reservoirs due to its selectively plugging capacity, easy preparation and good profile control ability [8,30]. Polymer gel has proved to be an effective and widely applied technique in profile control, water plugging treatment therefore has been applied in heterogeneous reservoir conditions to mitigate the problem of water and early gas breakthrough [9]. In spite of gaining vital importance it has some limitations at high salinity and high temperature [10].

Gelling fluid is usually composed of polymer and cross linker. It is injected into water producing layer or dominant channels, then the gel is formed with time. In these cases, it improves oil recovery with plugging water channels and enhancing swept volume of water flooding [11]. The gelling solution has proved to be an effective method for water shut-off in mature oil reservoirs [12]. There are two kinds of cross linkers, which are being used nowadays for preparing polymer gel (i) organic (ii) in-organic. However, the gels produced through inorganic cross linkers typically have lower thermally stability, resulting in over cross linking or syneresis in high temperature reservoirs [13]. The organic crosslinking reaction involves the formation of covalent bonds between amide groups of the polymer and the cross linker, which usually forms a good stable gel in high temperature reservoirs [14,15]. So the organic cross linkers has gained wide importance of researchers. Within organic cross linkers, there are various phenolic compounds among them resorcinol and hexamethylenetetramine (HMTA) achieved the maximum degree of strong bulk gelation because of number of cross-linked clusters between resorcinol and HMTA reached the highest degree achieved by any other phenolic compounds [16].

Although the polymer gel has wide application, even though it needs some enhancement for good thermal stability, gel strength, controllable

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https://doi.org/10.1016/j.molliq.2018.04.146
0167-7322/

gelation time and other problems under harsh reservoir conditions [17,18]. The polymer gel which is prepared by using cross linker of HMTA and resorcinol in the ratio of 1:4 has good thermal stability, gel strength than other cross linkers because of less toxicity than phenol and formaldehyde [19,20]. Because of some limitation in harsh reservoirs as discussed earlier, the nanotechnology has emerged in the oil and gas industry. In nanotechnology the nanoparticles have recently shown promising effects in solving many problems in oil industry [35]. The nanoparticles have also proved to be better results in harsh reservoirs for improving the recovery of oil in recent years and for enhancing the gel strength, good thermal stability and other properties [32]. Uses and application of nanoparticles have been studied by several researchers. Whenever doing the EOR process the injection of water is very high and normally we use sea water or river water as the base fluid for injecting the chemicals materials (such as surfactant, nanoparticles or polymer) into oil reservoirs [33,34]. There are various nanoparticles being used in for research among them silica dioxide (SiO_2) has shown prominent effect, the compatibility and strengthening property of SiO_2 has been studied and reported by several researchers. Recently the use of surfactant with nanoparticles in recovery has being gaining vital importance for researchers. The phenomenon of specially designed surfactant/polymer for EOR has been studied and resulted in better thermal stability for heterogeneous reservoirs [25,40].

Therefore the organic/inorganic cross-linked polymer gel has gained wide importance for good blocking ability, gel strength and improves sweep efficiency in heterogeneous reservoirs [21]. This is organically cross linked polymer gel, can also be used for long term thermal stability by having the properties of organic and in-organic polymer gels. It has been studied by various researchers for water shut-off treatments and increasing the sweep efficiency from low permeable areas to increase the oil recovery [22].

In this research a novel composite polymer gel is proposed for better thermal resistivity, plugging efficiency, high strength. This composite gel is composed of polymer, cross linker, SiO_2 and surfactant. In this novel composite gel, the polymer used is amphiphilic polymer because it can withstand the harsh reservoir conditions and is better salt resistant polymer than other polymers like HPAM. The structure of amphiphilic (PADC) polymer is shown in Fig. 1, which was synthesized in our lab [36,37]. In the structure the variables x, y, z are the molar ratio of each monomer used in polymer. The polymer is added with cross linker whereas SiO_2 is used as strengthening material with surfactant for the formation and enhancement of composite gel. The composite polymer gel is evaluated in laboratory and has proved to be of better thermal stability, gel strength with negligible or no syneresis for about 90 days. The gel strength of novel composite gel is compared with conventional organic gel. The optimum concentration of SiO_2 is evaluated in laboratory for better results of composite gel.

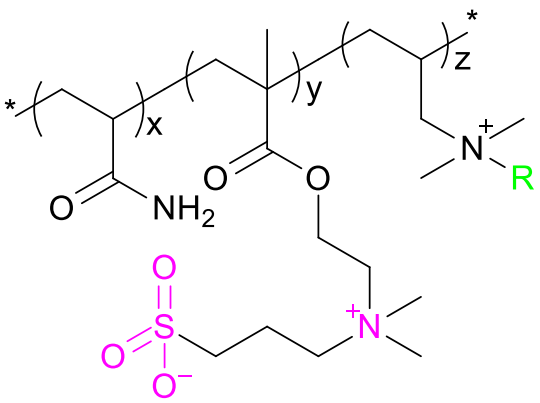

Fig. 1. Chemical structure of PADC polymer.

2. Materials and methods

2.1. Materials

The PADC polymer used in this experiment is synthesized in our lab with the addition of appropriate amount of monomer in amphiphilic polymer [36,37]. The cross linker was prepared using HMTA and resorcinol purchased from Sinopharm Chemical Reagent Co. Ltd. with the purity 99.0%. The SiO_2 used was purchased from Aladin Chemical Reagent Co. Ltd. The surfactant used is petroleum sulphonate with 30% effective content, its name is KD. The formation water of Jidong Oilfield was used for all experiments, which was prepared with deionized water. The compositional analysis of the formation brine is shown in Table 1.

2.2. Preparation of bulk gel

The bulk gel solution was prepared by mixing 0.6 wt% of PADC polymer which was prepared by using IKA stirring machine at the speed of 700 rpm for 4 h. The composite polymer gel was prepared as follows. Firstly, 0.6 wt% of PADC polymer was added into brine and stirred at high speed of 500 rpm for 4 h, after stirring for 4 h. Then, the 0.6 wt% polymer was diluted to the required concentration of (0.3 wt%, 0.4 wt% and 0.5 wt%) at room temperature. Next, prepare separately the solution of SiO_2 using concentration of 5.0% and surfactant using concentration of 0.5%. Then, the SiO_2 solution and surfactant solution was diluted to required concentrations. The solution of silica dioxide and surfactant is then added to the solution of polymer and cross linker and stirred for 5 min to get the gelant solution prepared. The stirring speed is 150 rpm in this experiment.

The conventional gel was prepared by mixing 0.6 wt% of PADC polymer. That was prepared by using IKA stirring machine at the speed of 600 rpm for 4 h. The polymer prepared was further diluted to the required concentration of 0.3 wt%, 0.4 wt% and 0.5 wt% at room temperature. After that, the polymer was mixed with the cross linker in 1:1 and stirred for 5 min to prepare the gelant solution.

Finally, about 25 mL of each conventional and composite gelation solution was injected into an ampoule tubes through tygon tubing and then the ampoule tube was sealed at the neck. The gelling reaction was initiated by heating the gelant solution in an oven.

2.3. Preparation of cross linker

The cross linker is prepared in two steps

(1) The hexamethylenetetramine can decompose formaldehyde slowly under high temperature and acidic conditions.

$$(CH_2)_6N_4 + 6H_2O \xrightarrow{H^+} CH_2O + 4NH_3$$

(2) Then the formaldehyde can react with resorcinol to form hydroxymethyl resorcinol.

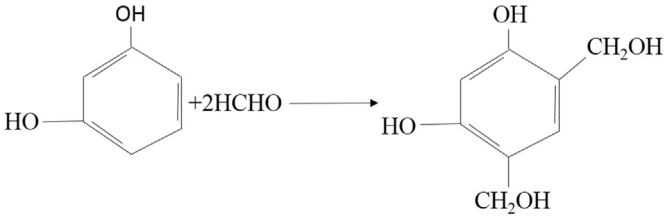

Table 1
Composition of formation water of Jidong Oilfield.

Ions	$Na^+ + K^+$	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}	HCO_3^-
Concentration Total (mg/L)	13,039 51,984	3308	1820	28,950	222	314