

Article

Aqueous Hybrids of Silica Nanoparticles and Hydrophobically Associating Hydrolyzed Polyacrylamide Used for EOR in High-Temperature and High-Salinity Reservoirs

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Abstract: Water-soluble polymers are known to be used in chemically enhanced oil recovery (EOR) processes, but their applications are limited in high-temperature and high-salinity oil reservoirs because of their inherent poor salt tolerance and weak thermal stability. Hydrophobic association of partially hydrolyzed polyacrylamide (HAHPAM) complexed with silica nanoparticles to prepare nano-hybrids is reported in this work. The rheological and enhanced oil recovery (EOR) properties of such hybrids were studied in comparison with HAHPAM under simulated high-temperature and high-salinity oil reservoir conditions (T : 85 °C; total dissolved solids: 32,868 mg·L⁻¹; [Ca²⁺] + [Mg²⁺]: 873 mg·L⁻¹). It was found that the apparent viscosity and elastic modulus of HAHPAM solutions increased with addition of silica nanoparticles, and HAHPAM/silica hybrids exhibit better shear resistance and long-term thermal stability than HAHPAM in synthetic brine. Moreover, core flooding tests show that HAHPAM/silica hybrid has a higher oil recovery factor than HAHPAM solution.

Keywords: silica nanoparticles; hydrophobically associating polyacrylamide; rheological properties; enhanced oil recovery

1. Introduction

Among various enhanced oil recovery (EOR) methods, polymer flooding (PF) has been considered an attractive alternative to conventional water flooding because of its high potential for recovering more oil from reservoirs [1–3]. In the PF process, water-soluble polymers added into the injection water can increase the viscosity of water phase, simultaneously improve the mobility ratio, and enlarge the swept volume, leading to higher oil recovery efficiencies [3–5].

Partially hydrolyzed polyacrylamide (HPAM) is the most widely used water-soluble polymer and has been successfully employed in tertiary oil recovery worldwide [4–7]. However, the main problem of HPAM in the oilfield application is its poor heat tolerance and salt resistance performance, which limit its applications in the high-temperature and high-salinity oil reservoirs [8], such as the Class III reserve of the Shengli Oilfield in China where the temperature is above 85 °C and the salinity (total dissolved solids, TDS) is higher than 30,000 mg·L⁻¹ in which the total amount of Ca²⁺ and Mg²⁺ exceeds 800 mg·L⁻¹. In such a hostile environment, the amide groups of the HPAM undergo extensive hydrolysis into carboxylic acid units at elevated temperature [9–11], and the hydrolyzed products precipitate when they come in contact with divalent cations such as Ca²⁺ and Mg²⁺, commonly present in oil reservoir brines. In addition, the interaction of metal ions such as Na⁺ and K⁺ in the oilfield brines largely shields the mutual repulsion from the carboxylic groups along the HPAM skeleton, leading to the polymer coils to collapse and the hydrodynamic volume to decrease, ultimately lowering the solution viscosity [12,13]. Furthermore, another major limitation of HPAM is its flow-induced mechanical degradation because of its shear-thinning behavior. As a synthetic polymer, molecular chains of HPAM will be cut off when polymer solution passes through the pump, pipeline, perforation, and porous medium at high speed, so the viscosity of polymer solution will be greatly reduced [14–17]. The poor shear stability of HPAM solution hinders its efficiency in the EOR process.

To obviate the limitations of HPAM, many laboratories have been active in developing HPAM with improved thermal stability, shear stability and salinity tolerance. Hydrophobically associating polymers containing a small proportion of hydrophobic groups in the form of pendent side chains or terminal groups has been of increasing interest in improved oil recovery [18]. For instance, hydrophobically associating polyacrylamides (HAPAMs) can be prepared by copolymerization of acrylamide with thermostable and salt-tolerant monomers onto the HPAM backbone to enhance the thermal stability of the products [19–21]. However, the main portion in HAPAM is still the acrylamide segment which shows poor long-term thermal stability and salt tolerance. Meanwhile, increasing molecular weight of HPAM (maximum 35 × 10⁶ g·mol⁻¹ to date) can achieve higher viscosity retention; nevertheless, this will bring about easier mechanical degradation and the plugging of the smaller pore throat in low-permeability oil reservoirs [1,14]. Recently, our laboratory developed hydrophobically associating partially hydrolyzed polyacrylamide (HAHPAM) by copolymerization of acrylamide (AM), sodium acrylate (NaAA) with *N*-(4-benzoyloxy)-acrylamide and dimethylamino-ethyl methacrylate (DMAEMA). *N*-(4-Benzoyloxy)-acrylamide acts as the rigid chain in the copolymer and apparently restricts the level of mechanical degradation to some extent, exhibiting better shear stability than HPAM. However, like its precursor HPAM, the thermal stability and salt tolerance of HAHPAM are still poor in high-temperature and high-salinity environments on account of the amide groups in the

molecular skeleton. Therefore, how to improve the thermal stability and salt tolerance is of vital importance for the application of HAHPAM in EOR processes.

The addition of nanoparticles can be used to manipulate the optical, thermal, magnetic, and electric properties of polymers [22,23]. Compared with pure polymers, the polymer composite materials containing silica nanoparticles may exhibit more satisfactory thermal stability, toughness and strength owing to the effect of physical adsorption such as hydrogen bond formation [24,25]. Meanwhile, water-soluble polymers such as poly (N-isopropyl acrylamide) (PNIPAM) can form a protective layer around particles and effectively control the rheological properties by reinforcing the mechanical properties of polymer networks [26]. Without polymerizing the monomer in a suspension of inorganic particles, hybrid networks can also be obtained by gentle mixing of silica nanoparticles in aqueous solutions of a copolymer having reactive side chains with inorganic nanoparticles [27,28]. The strong interactions between PNIPAM and silica are generally attributed to the formation of hydrogen bonds between the amide groups of NIPAM and silanol functionalities on the nanoparticle surface. Based on these preliminary results, it is concluded that silica nanoparticles can effectively interact with water-soluble polymers which have carbonyl groups and act as physical crosslinkers between macromolecules, reinforcing the polymer structures and improving the mechanical properties of the polymers. Hence, the amide groups in HAHPAM molecule show the possibility of interacting with silanol groups at the surface of silica, and the poor thermal stability and salt tolerance are expected to be improved to some extent. However, to the best of our knowledge, there are no papers about the application of silica nanoparticles in improving temperature tolerance, salt tolerance, and shear resistance of hydrophobically associating polyacrylamide, and no HAHPAM/nanoparticle hybrids used for EOR have been reported to date.

In this work, silica nanoparticles were introduced into HAHPAM solution to form HAHPAM/silica nano-hybrids in brine. Reported here are the rheological behaviors and core flooding results of these hybrids in simulated high-temperature and high-salinity oil reservoirs, investigating the effect of silica nanoparticles on the thermal stability, shear resistance and EOR. For comparison, HAHPAM was also tested under the same experimental conditions.

2. Results and Discussion

2.1. Rheological Behaviors of HAHPAM Solution and HAHPAM/Silica Hybrids

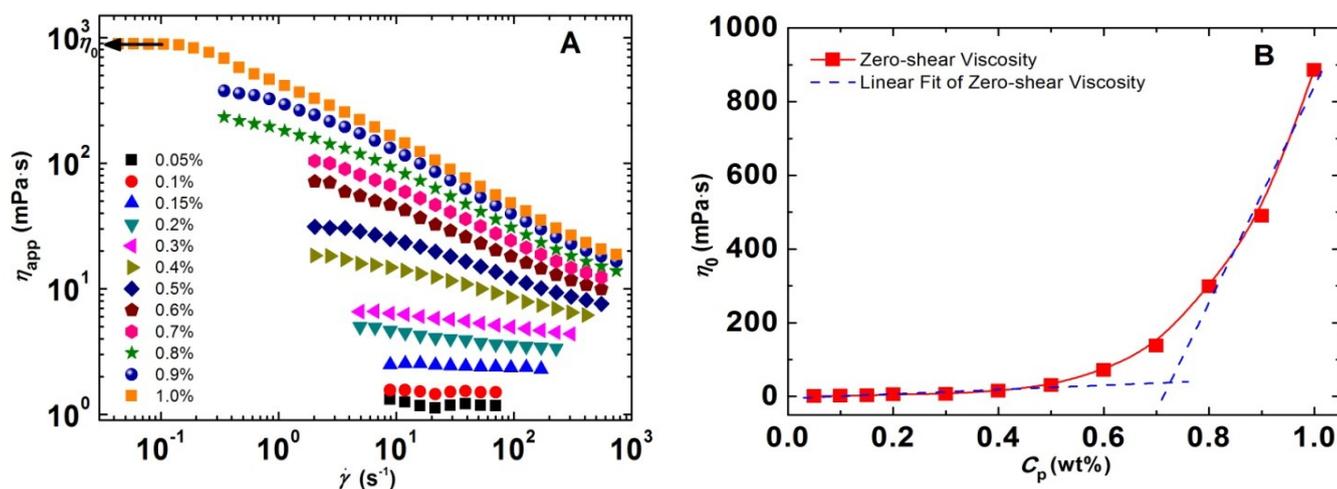
The rheological properties of an injected chasing fluid have an important effect on oil-displacing efficiency in the chemical flooding process. The additional increase of viscosity precludes viscous fingering so that volumetric sweeping is expanded; the oil displacement efficiency is enhanced due to the microscopic deformation of the long-chain molecular structures so that the residual oil can be hauled out in dead ends or pore throats and on the rock surface [29]. It is well accepted that the rheological behaviors such as apparent viscosity of the polymer solution play a crucial role in displacing less viscous oil in the EOR process [30–32]. Therefore, it is necessary to investigate the rheological properties of the samples before a flooding test.

2.1.1. Concentration Dependence of HAPAM

In order to study the pure effect of silica nanoparticles on the HAHPAM solutions, strong hydrophobic associations caused by C12-tailed dimethylaminoethyl methacrylates in the HAHPAM molecule should be avoided. The polymer concentration is fixed below the critical association concentration (CAC) for the purpose of obtaining HAHPAM/silica hybrids without any intermolecular hydrophobic associations. Therefore, the concentration dependence of HAHPAM was studied first so as to determine the CAC.

Figure 1A shows the concentration-dependent flow curves of HAHPAM brine solutions between 0.05 wt% and 1.0 wt% at 85 °C. When the polymer concentration (C_p) is lower than 0.4 wt%, the HAHPAM brine solutions behave as Newtonian fluids, that is, their viscosity is independent of shear rate, while at higher polymer concentrations, the flow curves are composed of two parts: Newtonian behavior at low shear rates and shear-thinning response with increasing shear rates. In the Newtonian fluid region, the zero-shear or plateau viscosity (η_0) can be obtained by extrapolating the shear rate to zero. The variation of η_0 as a function of polymer concentration at 85 °C is plotted in Figure 1B, where the two parts can be separated at around 0.73 wt%. Below this concentration, η_0 increases linearly with increasing polymer concentration; above 0.73 wt%, η_0 increases drastically. This suggests that 0.73 wt% is the CAC of HAHPAM brine solution, above which intermolecular hydrophobic associations play a major role in the solution.

Figure 1. (A) Apparent viscosity plotted as a function of shear rate for various concentrations of HAHPAM and (B) zero-shear viscosity (η_0) plotted as a function of polymer concentration for HAHPAM in brine (TDS = 32,868 mg·L⁻¹, [Ca²⁺] + [Mg²⁺] = 873 mg·L⁻¹, $T = 85$ °C).



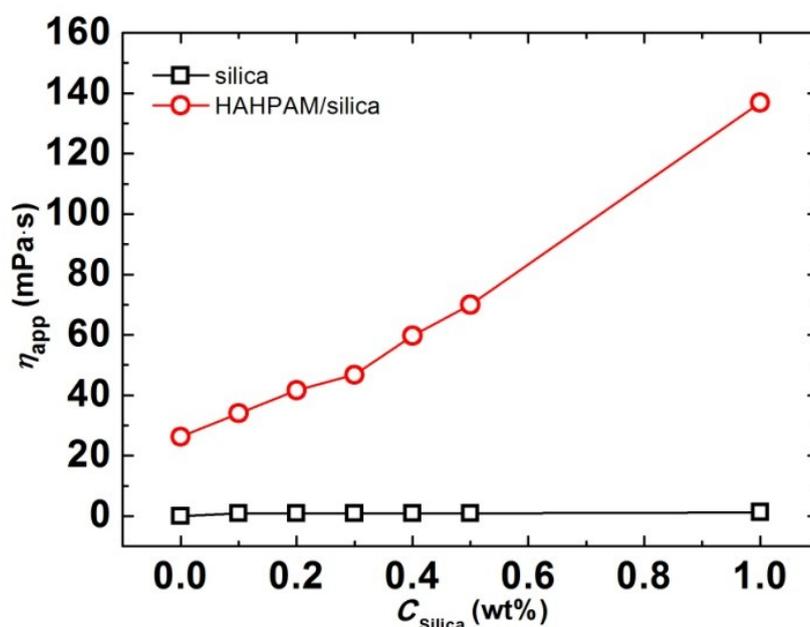
2.1.2. Effect of Nanoparticle Loading on Steady Rheological Behaviors of HAHPAM/Silica Hybrids

Intermolecular hydrophobic associations may play against the interaction between HAHPAM and silica nanoparticles, thus, rheological behaviors of HAHPAM/silica hybrids were studied at a fixed polymer concentration of 0.5 wt% (<CAC).

Presented in Figure 2 is the dependence of silica concentration on the brine solution viscosity of HAHPAM/silica hybrids at 85 °C. It is apparent that the viscosity of hybrid systems is enhanced

gradually with increasing silica concentration under high-temperature and high-salinity conditions. For example, the apparent viscosity (η_{app}) increases from 26.3 mPa·s to 136.9 mPa·s with addition of 1.0 wt% silica nanoparticles. It is worth noting that the viscosity of silica suspension remains just a few mPa·s, independent of the concentration used (Figure 2). Thus, the viscosity enhancement of the hybrid system cannot be regarded as a superposition of the viscosity of HAHPAM solution and that of the silica suspension.

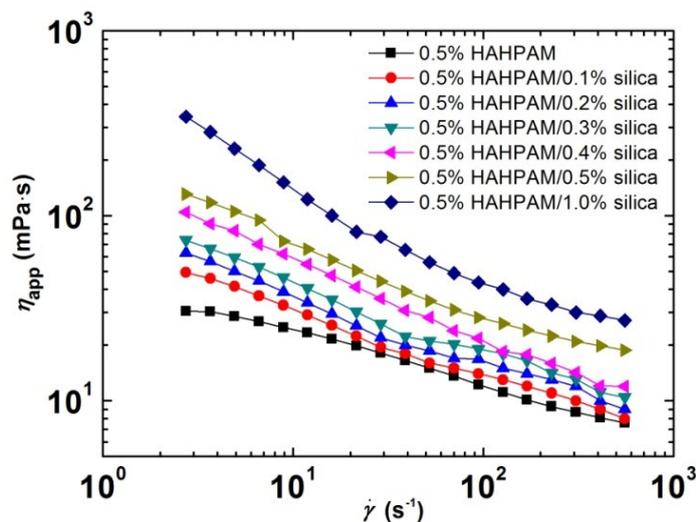
Figure 2. Dependence of apparent viscosity on silica nanoparticle concentration for HAHPAM/silica hybrids in brine and silica suspension (TDS = 32,868 mg·L⁻¹, [Ca²⁺] + [Mg²⁺] = 873 mg·L⁻¹, $T = 85\text{ }^{\circ}\text{C}$, $\dot{\gamma} = 10\text{ s}^{-1}$, $C_p = 0.5\text{ wt}\%$).



Compared in Figure 3 are the flow curves of pure HAHPAM brine solution and HAHPAM/silica hybrids with different silica concentrations at 85 °C. It is found that the samples revealed non-Newtonian shear-thinning behavior. With the increase of the shear rate (from 2.0 s⁻¹ to 550 s⁻¹), the viscosity of HAHPAM/silica hybrids obviously dropped. However, shear viscosity of the hybrids apparently increases with addition of silica nanoparticles. For example, the viscosity of “0.5% HAHPAM/0.5% silica” at 550 s⁻¹ is nearly three times larger than that of 0.5% HAHPAM solution at 85 °C. These results indicate that HAHPAM/silica hybrids have better shear resistance than HAHPAM solution under high-temperature and high-salinity conditions.

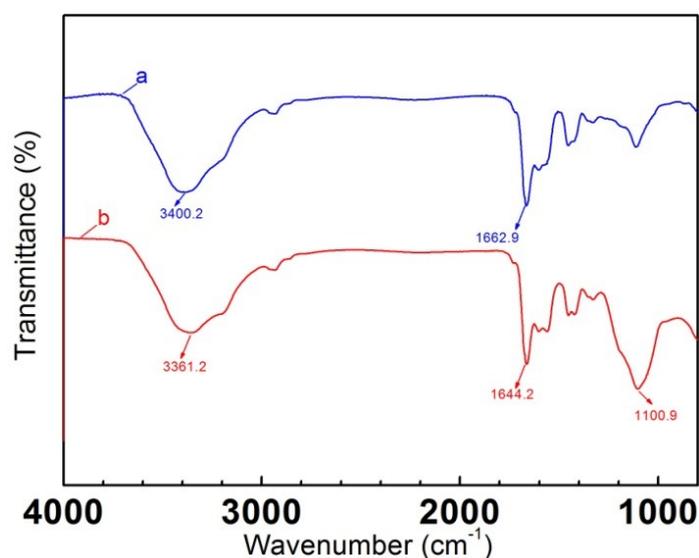
Similar to the formation of hydrogen bonds between the amide groups of NIPAM units and the silanol functions at the surfaces in the PNIPAM/silica system [27,28], the incremental viscosity and better shear resistance of HAHPAM/silica hybrid are also attributed to the strong interactions between HAHPAM and silica particles caused by the formation of hydrogen bonds between the amide groups of HAHPAM and the silanol functions of silica. With increasing concentration of silica, the fraction of amide groups interacting with the nanoparticles becomes stronger, consequently, the movement of polymer chains is limited, and the hydrodynamic volume increases, resulting in the increase of the brine solution viscosity and shear viscosity of the HAHPAM/silica hybrid.

Figure 3. Apparent viscosity plotted as a function of shear rate for HAHPAM/silica hybrids in brine with different silica loading ($TDS = 32,868 \text{ mg}\cdot\text{L}^{-1}$, $[\text{Ca}^{2+}] + [\text{Mg}^{2+}] = 873 \text{ mg}\cdot\text{L}^{-1}$, $T = 85 \text{ }^\circ\text{C}$, $C_p = 0.5 \text{ wt}\%$).



FT-IR spectroscopy was employed to check if there are some hydrogen bonds formed between silica and the polymer. As depicted in Figure 4, the peaks in the wavenumber range from 900 to 4000 cm^{-1} are nearly the same for both HAHPAM (A) and HAHPAM/silica hybrid (B). HAHPAM shows strong stretching vibration peaks at 3400.2 cm^{-1} and 1662.9 cm^{-1} attributing to the amino group and carbonyl group of the amides, respectively. However, in HAHPAM/silica hybrid the amide peaks are shifted to lower wave numbers (3361.2 cm^{-1} and 1644.2 cm^{-1}), showing a substantial red shift. Meanwhile, a new peak appears at 1100.9 cm^{-1} in the spectrum of the hybrid sample, which is ascribed to the Si–O–Si asymmetric band stretching vibration. These results illustrate the formation of hydrogen bonds between the amide groups of the polymer and the silanol functions of the silica particles.

Figure 4. Comparison of FT-IR spectra of (A) 0.5% HAHPAM and (B) 0.5% HAHPAM/0.5% silica.

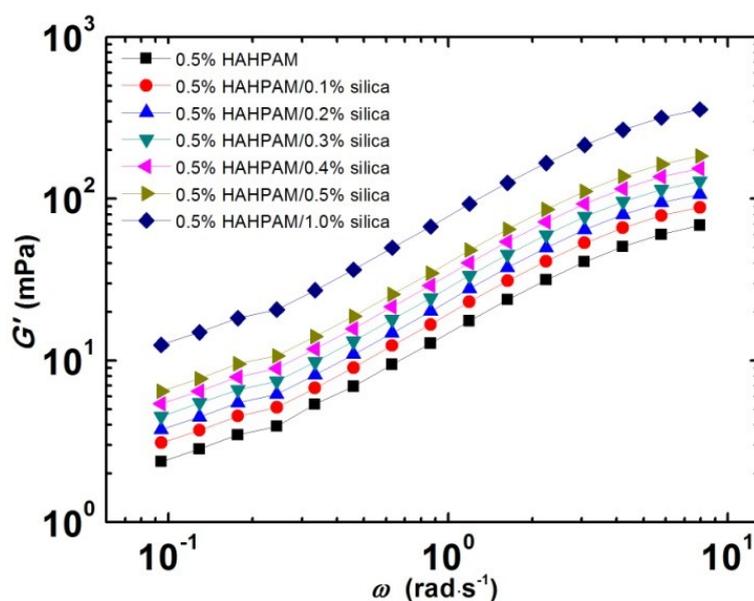


2.1.3. Effect of Nanoparticle Loading on Dynamic Rheological Behaviors of HAHPAM/Silica Hybrids

Viscoelastic properties of polymer solutions are used extensively to gain insight into the structure and conformation of polymers in solution, and elastic modulus (G') also plays an important role in increasing oil recovery [33]. Thus, dynamic rheological experiments of HAHPAM brine solution and HAHPAM/silica hybrids were performed at 85 °C as well.

Figure 5 shows the plots of elastic modulus (G') as a function of oscillatory shear frequency (ω) for HAHPAM brine solution and HAHPAM/silica hybrid in brine at 85 °C. For all the samples, G' is a strong function of the frequency and increases gradually over the entire range. With addition of silica nanoparticles, G' of the hybrids is higher than that of HAHPAM solution, indicating the nanoparticles increasingly influence the elastic properties of the polymers. These results suggest that HAHPAM/silica hybrids undergo microstructural changes and they have the ability to increase the oil recovery factor in high-temperature and high-salinity oil reservoirs because of the increased elastic modulus. In the HAHPAM/silica hybrid, effective interactions between the amide groups of HAHPAM and the silanol functions of silica occurred, so the structure of HAHPAM is strengthened and the elasticity of the hybrid becomes more pronounced, even though the temperature and salinity are very high.

Figure 5. Storage modulus (G') plotted as a function of angular frequency (ω) for HAHPAM/silica hybrids in brine with different silica loading (TDS = 32,868 mg·L⁻¹, [Ca²⁺] + [Mg²⁺] = 873 mg·L⁻¹, $T = 85$ °C, $C_p = 0.5$ wt%).

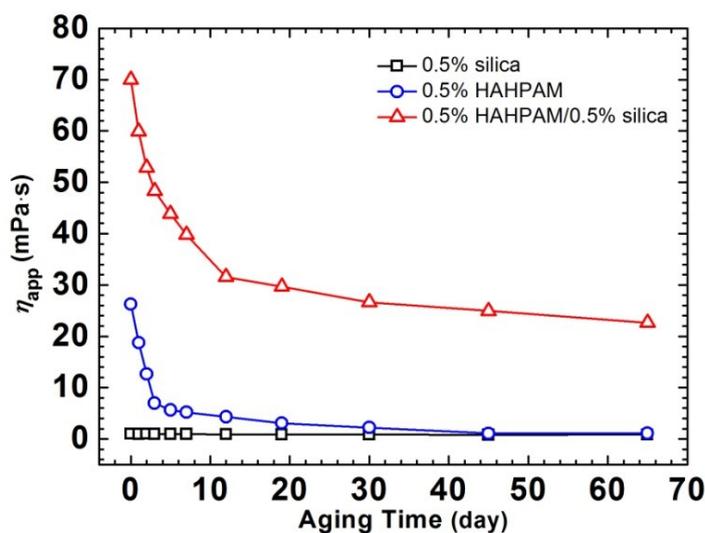


2.2. Long-Term Thermal Stability

In the PF process, polymers have to stay in the high-temperature and high-salinity oil reservoirs for several months before interacting with oil, and the continuous aging of the displacing fluid is detrimental to tertiary oil recovery [14,34]. The remaining viscosity at high temperature represents a primary criterion for any chemicals to be used in hostile environment. Therefore, high-temperature aging is crucial to EOR chemicals, and long-term thermal stability experiment of HAHPAM/silica hybrid samples is necessary.

Figure 6 shows the variation of η_{app} as a function of aging time for the HAHPAM/silica hybrid and HAHPAM brine solution after aging at 85 °C. η_{app} of 0.5 wt% silica suspension remains around 0.9 mPa·s, independent of the aging time. Thus, the viscosity of the HAHPAM/silica hybrid is not the superposition of viscosity of HAHPAM solution and silica suspension. For instance, η_{app} (0 day) of “0.5% HAHPAM/0.5% silica” is 69.96 mPa·s, nevertheless, η_{app} (0 day) of 0.5% HAHPAM solution and 0.5% silica suspension are only 26.28 mPa·s and 0.92 mPa·s, respectively. On the contrary, one can clearly find a sharp reduction in η_{app} for HAHPAM after continuous aging: the initial η_{app} (0 day) is 26.28 mPa·s, but drops down to 4.31 mPa·s after 12 days of aging; *i.e.*, 83.92% of viscosity is lost. There is also a sharp reduction in η_{app} for the HAHPAM/silica hybrid in the first 12 days: its η_{app} decreases from 69.96 mPa·s to 31.55 mPa·s, and the viscosity loss is 54.90%, much lower than that of pure HAHPAM. After 65 days of aging, the remaining η_{app} of HAHPAM brine solution is only 1.11 mPa·s left, while that of the HAHPAM/silica hybrid still has 22.65 mPa·s; therefore, the viscosity retention rate for HAHPAM is only 4.22%, while the hybrid can maintain 33.83%. These results clearly demonstrate that HAHPAM/silica hybrid possesses much better long-term thermal stability over HAHPAM, and the addition of silica nanoparticles will improve the thermal stability of HAHPAM. This difference is mainly ascribed to the physical interactions between silica and HAHPAM which can partially avoid the hydrolysis of amide groups taking place in high-temperature and high-salinity oil reservoirs.

Figure 6. Long-term thermal stability of 0.5% HAHPAM/0.5% silica hybrid in comparison with 0.5% HAHPAM and 0.5% silica (TDS = 32,868 mg·L⁻¹, [Ca²⁺] + [Mg²⁺] = 873 mg·L⁻¹, $\dot{\gamma} = 10 \text{ s}^{-1}$). Both the aging and measuring temperature is 85 °C.



2.3. Oil Displacement Test

Although HAHPAM/silica hybrids show promising potential for chemical EOR in high-temperature and high-salinity oil reservoirs, no core flooding test has been performed yet. Plotted in Figure 7 are the recovery factors, water cut and flooding pressure as a function of injected volume of the sample solutions under the simulated high-temperature and high-salinity oil reservoirs environment. Table 1 shows the core parameters, displacement process and the results of these oil displacement tests. It was found that only 5.44% oil recovery factor by HAHPAM flooding was obtained under these conditions

(Figure 7A), whereas the oil recovery factor of HAHPAM/silica hybrid reached 10.57% (Figure 7B) under the same conditions. The main reason for a relatively high oil recovery factor with the hybrid sample can be ascribed to its improved steady and dynamic rheological properties at high temperature and salinities; that is, the apparent viscosity and elastic modulus increase with addition of silica nanoparticles, thus effectively improving the water-to-oil mobility ratio to produce more oil. Meanwhile, the better shear resistance and long-term thermal stability of the HAHPAM/silica hybrid makes it more suitable to be applied in EOR.

Figure 7. Recovery factor, water cut and flooding pressure plotted as a function of injected volume of the samples: (A) 0.5% HAHPAM and (B) 0.5% HAHPAM/0.5% silica hybrid (TDS = 32,868 mg·L⁻¹, [Ca²⁺] + [Mg²⁺] = 873 mg·L⁻¹; T = 85 °C; injected volume = 30% PV; injected rate = 0.23 mL·min⁻¹).

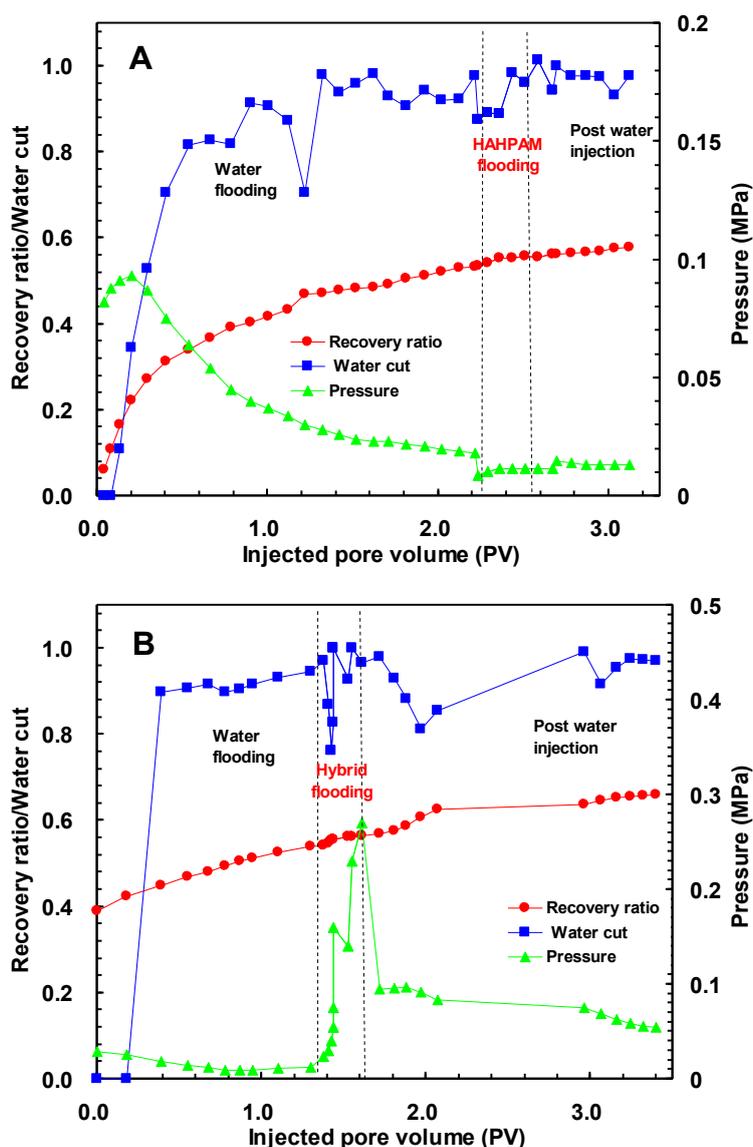


Table 1. Core parameters, displacement process and recovery factors.

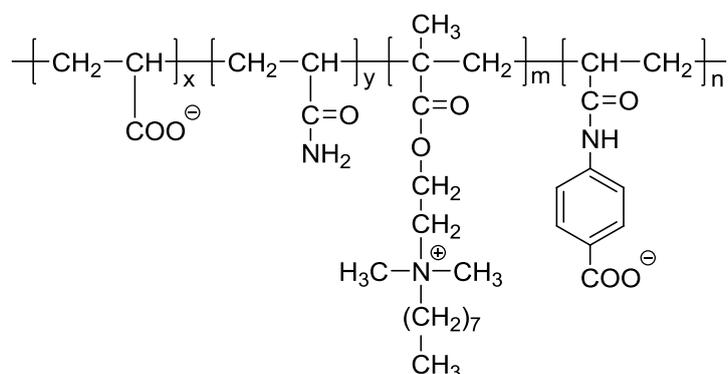
Core No.	Permeability (mDarcy)	Pore volume (cm ³)	Saturated oil (cm ³)	Slug	Slug injected (PV)	Water flooding recovery (%)	Ultimate recovery (%)	Oil recovery factor (%)
1	1497	50.2	42.0	HAHPAM	0.3	52.42	57.86	5.44
2	1498	47.3	38.0	Hybrid	0.3	55.48	66.05	10.57

3. Experimental Section

3.1. Materials

HAHPAM (Figure 8) was prepared via copolymerization of acrylamide (AM) and sodium acrylate (NaAA) with *N*-(4-benzoyloxy)-acrylamide and dimethylaminoethyl methacrylate (DMAEMA). Its viscosity-average molecular weight (M_η) is 8.9×10^6 g·mol⁻¹ determined by an Ubbelohde capillary viscometer. The HAHPAM solutions were prepared by dissolving designed amount of powders into synthetic brine with total dissolved solids (TDS) of 32,868 mg·L⁻¹ and divalent cations ([Ca²⁺], [Mg²⁺]) of 873 mg·L⁻¹. HAHPAM was dissolved under gentle stirring at room temperature.

Figure 8. The molecular structure of HAHPAM ($x = 25.0$ wt%, $y = 74.85$ wt%, $m = 0.1$ wt%, $n = 0.05$ wt%).



The silica powders were obtained from Sigma-Aldrich (St. Louis, MO, USA) and used as received. The suspension of silica nanoparticles was prepared by dissolving defined quantities of silica powders into pure water and finally conditioned at 10 wt%. According to the product specification, the average diameter of these particles is 7 nm, and the corresponding specific area is $S_{spe} = 395$ m²·g⁻¹.

3.2. Preparation of Hybrid Samples

HAHPAM/silica nano-hybrid samples were prepared by mixing silica suspensions with HAHPAM brine solution at the designed recipe rates following a previously-reported procedure for mixing silica nanoparticles with copolymer solutions [35]. The inorganic/organic mixtures were gently stirred for 7 days and left to stand for 3 days prior to the studies. These samples are stable and no visible macroscopic phase separation is observed over time at room temperature.

3.3. Infrared Spectroscopy

The Fourier transform infrared spectra (FT-IR) of HAPAM and HAPAM/silica hybrid were registered in solid state using a KBr pellet method in the transmittance mode. A Nicolet MX-1E FT-IR spectrophotometer (Waltham, MA, USA) was used to record the spectra within the scanning range of 900–4000 cm^{-1} .

3.4. Rheological Measurements

All rheological measurements were carried out on a Physica MCR301 (Anton-Paar, Graz, Austria) rotational rheometer equipped with a CC27 concentric cylinder geometry. The radii of the measuring bob and the measuring cup are 13.33 and 14.46 mm, respectively. Samples were equilibrated at 85 °C for no less than 10 min prior to experiments. The rheological behavior of samples was determined under both steady and oscillatory shear to obtain the steady and dynamic viscoelastic properties. The temperature was controlled by a Peltier system that provides fast and precise adjustment of the temperature during heating. A solvent trap was used to prevent evaporation of the solvents during measurement.

3.5. Long-Term Thermal Stability Measurement

The samples for long-term thermal stability experiment were prepared in synthetic brine, and the TDS and hardness of the brine are close to those of connate water in the high-temperature and high-salinity condition in the Shengli Oilfield, China. The sample solutions were distributed into 120-mL glass bottles, and then sealed with a cover, followed by placing them into an oven and aged at 85 °C. At consecutive time intervals, the samples were taken out for viscosity monitoring at the MCR rheometer mentioned above.

3.6. Core Flooding Test

The core flooding tests were performed under the simulated high-temperature and high-salinity oil reservoirs in Shengli Oilfield of China, and followed a previously-reported protocol [36]. A steel cylinder with 2.5 cm inner diameter and 25 cm in height was packed with several sizes of silica sand in the model. The porosity of the sandstone core was 32.6%. The density of dehydrated Shengli oil was 0.93 $\text{g}\cdot\text{cm}^{-3}$ and the viscosity was 39.2 $\text{mPa}\cdot\text{s}$ at 85 °C. First of all, the oil had been aged at 85 °C for several days. Then the sand pack was initially saturated with the synthetic brine, followed by injecting the dehydrated and aged Shengli oil to ~70%. The core was then injected with the synthetic brine until the water content was higher than 98% in the output fluid, and the injection of 30% pore volume (PV) of the sample solution was followed. The total oil recovery and the oil recovery by water flooding were calculated, respectively, and the difference between them was the tertiary oil recovery factor by polymer or polymer/silica hybrid flooding. The injection rate of the sample was maintained at 0.23 $\text{mL}\cdot\text{min}^{-1}$, and the cylindrical sand pack was placed in a chamber and heated at 85 °C throughout the test.

4. Conclusions

The effect of silica nanoparticles on the rheological and EOR properties of HAHPAM solutions under simulated high-temperature and high-salinity reservoir conditions were examined. It was found that the apparent viscosity and elastic modulus of HAHPAM solutions increased with addition of silica nanoparticles. The main reason for these results is that silica nanoparticles can interact with HAHPAM molecules by the formation of hydrogen bonds between the silanol functions of the silica and the amide groups in the HAHPAM molecular chain. These interactions can reinforce the polymer structure and increase the viscosity and elasticity. In addition, the oil recovery factor of HAHPAM flooding was 5.44% in the laboratory core flooding test, whereas that of HAHPAM/silica hybrid was 10.57%. Along with their improved shear resistance and long-term thermal stability, the HAHPAM/silica hybrids thus show great potential to enhance oil recovery from hostile oil reservoir environments.

Acknowledgments

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Author Contributions

Dingwei Zhu and Yujun Feng developed the idea of the HAHPAM/silica hybrid and contributed to the discussion of the results. Limin Wei and Biqing Wang prepared the polymer and silica nanoparticles. Dingwei Zhu performed the experiments and wrote the paper. All authors have given approval to the final version of the manuscript.

Conflicts of Interest

The authors declare no conflict of interest.

References

1. Sorbie, K.S. *Polymer-Improved Oil Recovery*; Springer: Boca Raton, FL, USA, 1991; pp. 82–125.
2. Needham, R.B.; Doe, P.H. Polymer flooding review. *J. Pet. Technol.* **1987**, *39*, 1503–1507.
3. Taylor, K.C.; Nasr-El-Din, H.A. Water-soluble hydrophobically associating polymers for improved oil recovery: A literature review. *J. Pet. Sci. Eng.* **1998**, *19*, 265–280.
4. Chelaru, C.; Diaconu, I.; Simionescu, I. Polyacrylamide obtained by plasma-induced polymerization for a possible application in enhanced oil recovery. *Polym. Bull.* **1998**, *40*, 757–764.
5. Wang, W.; Liu, Y.; Gu, Y. Application of a novel polymer system in chemical enhanced oil recovery (EOR). *Colloid Polym. Sci.* **2003**, *281*, 1046–1054.
6. Jung, J.C.; Zhang, K.; Chon, B.H.; Choi, H.J. Rheology and polymer flooding characteristics of partially hydrolyzed polyacrylamide for enhanced heavy oil recovery. *J. Appl. Polym. Sci.* **2013**, *127*, 4833–4839.
7. Mothé, C.G.; Correia, D.Z.; de Fran, F.P.; Riga, A.T. Thermal and rheological study of polysaccharides for enhanced oil recovery. *J. Therm. Anal. Calorim.* **2006**, *85*, 31–36.

8. Zaitoun, A.; Poitie, B. Limiting conditions for the use of hydrolysed polyacrylamides in brines containing divalent ions. In Proceedings of the SPE International Oilfield and Geothermal Chemistry Symposium, Denver, CO, USA, 1–3 June 1983.
9. Leung, W.M.; Axelson, D.E. Thermal degradation of polyacrylamide and poly(acrylamide-co-acrylate). *J. Polym. Sci. Part A Polym. Chem.* **1987**, *25*, 1852–1864.
10. Yang, M.H. The rheological behavior of polyacrylamide solution. *J. Polym. Eng.* **1999**, *19*, 371–381.
11. Sabhapondit, A.; Borthakur, A.; Haque, I. Characterization of acrylamide polymers for enhanced oil recovery. *J. Appl. Polym. Sci.* **2003**, *87*, 1869–1878.
12. Kheradmand, H.; François, J.; Plazanet, V. Hydrolysis of polyacrylamide and acrylic acid-acrylamide copolymers at neutral pH and high temperature. *Polymer* **1988**, *29*, 860–870.
13. François, J.; Truong, N.D.; Medjahdi, G.; Mestdagh, M.M. Aqueous solutions of acrylamide-acrylic acid copolymers: stability in the presence of alkaline earth cations. *Polymer* **1997**, *38*, 6115–6127.
14. Chauveteau, G.; Sorbie, K.S. Mobility control by polymers. In *Basic Concepts in Enhanced Oil Recovery Process*; Bavière, M., Ed.; Elsevier: London, UK, 1991; Volume 30, pp. 44–87.
15. Mungan, N.; Smith, F.W.; Thompson, J.L.; Sinclair, O.; Gas, C. Some aspects of polymer floods. *J. Petrol. Technol.* **1996**, *18*, 1143–1150.
16. Chang, S.H.; Chung, I.J. Effect of shear flow on polymer desorption and latex dispersion stability in the presence of adsorbed polymer. *Macromolecules* **1991**, *24*, 567–571.
17. Xue, L.; Agarwal, U.S.; Lemstra, P.J. Shear degradation resistance of star polymers during elongational flow. *Macromolecules* **2005**, *38*, 8825–8832.
18. Evani, S.; Rose, G.D. Water soluble hydrophobe association polymers. *Polym. Mater. Sci. Eng.* **1987**, *57*, 477–481.
19. Lu, H.; Feng, Y.; Huang, Z. Association and effective hydrodynamic thickness of hydrophobically associating polyacrylamide through porous media. *J. Appl. Polym. Sci.* **2008**, *110*, 1837–1843.
20. Lu, H.; Feng, Y. Study on associative polymerizable inverse microemulsion. *J. Macromol. Sci. Pure Appl. Chem.* **2008**, *45*, 372–380.
21. Feng, Y.; Billon, L.; Grassl, B.; Khoukh, A.; François, J. Hydrophobically associating polyacrylamides and their partially hydrolyzed derivatives prepared by post-modification. 1. Synthesis and characterization. *Polymer* **2002**, *43*, 2055–2064.
22. Tokarev, I.; Tokareva, I.; Minko, S. Gold-nanoparticle-enhanced plasmonic effects in a responsive polymer gel. *Adv. Mater.* **2008**, *20*, 2730–2734.
23. Xiang, Y.; Chen, D. Preparation of a novel pH-responsive silver nanoparticle/poly (HEMA-PEGMA-MAA) composite hydrogel. *Eur. Polym. J.* **2007**, *43*, 4178–4187.
24. Xia, H.S.; Wang, Q. Preparation of conductive polyaniline/nanosilica particle composites through ultrasonic irradiation. *J. Appl. Polym. Sci.* **2003**, *87*, 1811–1817.
25. Bershtein, V.A.; Egorova, L.M.; Yakushev, P.N.; Pissis, P.; Sysel, P.; Brozova, L. Molecular dynamics in nanostructured polyimide–silica hybrid materials and their thermal stability. *J. Polym. Sci. Part B Polym. Phys.* **2002**, *40*, 1056–1069.
26. Walldal, C.; Wall, S. Coil-to-globule-type transition of poly (*N*-isopropylacrylamide) adsorbed on colloidal silica particles. *Colloid Polym. Sci.* **2002**, *278*, 936–945.

27. Portehault, D.; Petit, L.; Pantoustier, N.; Ducouret, G.; Lafuma, F.; Hourdet, D. Hybrid thickeners in aqueous media. *Colloids Surf. A Physicochem. Eng. Asp.* **2006**, *278*, 26–32.
28. Petit, L.; Bouteiller, L.; Brûlet, A.; Lafuma, F.; Hourdet, D. Responsive hybrid self assemblies in aqueous media. *Langmuir* **2007**, *23*, 147–158.
29. Zhang, Z.; Li, J.; Zhou, J. Microscopic roles of “viscoelasticity” in HPMA polymer flooding for EOR. *Transport Porous Med.* **2011**, *86*, 199–214.
30. Kotlar, H.K.; Selle, O.; Torsaeter, O. Enhanced oil recovery by comb flow: Polymer floods revitalized. In Proceedings of the SPE Oilfield and Geothermal Chemistry Symposium, Houston, TX, USA, 28 February–2 March 2007.
31. Moradi-Araghi, A.; Ahmed, I. *Water-Soluble Polymers (Oil Recovery Applications)*; CRC Press: Boca Raton, FL, USA, 1996; pp. 8638–8655.
32. Wever, D.A.Z.; Picchioni, F.; Broekhuis, A.A. Polymers for enhanced oil recovery: A paradigm for structure-property relationship in aqueous solution. *Prog. Polym. Sci.* **2011**, *36*, 1558–1628.
33. Zhang, L.J.; Yue, X.A. Mechanism for viscoelastic polymer solution percolating through porous media. *J. Hydrodynamics Ser. B* **2007**, *19*, 241–248.
34. Cayias, J.L.; Hayes, M.E.; Schechter, R.S.; Wade, W.H. Surfactant aging-possible detriment to the tertiary oil recovery. *J. Petrol. Technol.* **1976**, *28*, 985–988.
35. Portehault, D.; Petit, L.; Hourdet, D. Synthesis and self assembly processes of aqueous thermoresponsive hybrid formulations. *Soft Matter* **2010**, *6*, 2178–2186.
36. Wang, H.Y.; Cao, X.L.; Zhang, J.C.; Zhang, A.M. Development and application of dilute surfactant-polymer flooding system for Shengli oilfield. *J. Pet. Sci. Eng.* **2009**, *65*, 45–50.

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