

Synthesis, characterization and solution properties of polyacrylamide based ternary copolymerization modified nano silica nanocomposites for EOR

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Abstract

In this work, a series of polymer nanocomposites (AAS/KS) of acrylamide (AM)/ acrylic acid (AA)/ sodium p-styrenesulfonate (SSS)/ 3-Methacryloxypropyltrimethoxysilane (KH570) modified nano-silica were successfully synthesized via in situ polymerization. The ¹H nuclear magnetic resonance spectroscopy (¹H NMR) confirmed the successful synthesis of AAS/KS, the morphology of KH570 modified nano-silica (KS) and AAS/KS polymer nanocomposites were observed by scanning electron microscope (SEM). And thermal gravimetric analysis (TGA) showed that the AAS/2.0 wt% KS had better temperature tolerance than pure polymer (AAS), also the solution properties of temperature-resistance, salt-tolerance, shear resistance and viscoelasticity proved the better oil displacement performance in high temperature and high salt reservoirs. Furthermore, the oil recovery of AAS/2.0 wt% KS is 9.9% higher than that of the water flooding processes during the enhanced oil recovery experiment in laboratory. All results indicated that the AAS/2.0 wt% KS polymer nanocomposite had tremendous potential application for enhancing oil recovery.

Keywords: Polyacrylamide based ternary polymeride, Modified nano-silica, Nanocomposites, In situ polymerization, Enhancing oil recovery.

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I. INTRODUCTION

In recent years, with the increasing demand for energy, the exploitations of oil resources have drawn more and more attentions. In order to meet the energy needs, various methods of enhancing oil recovery (EOR) have been developed. Chemical enhanced oil recovery (CEOR) is an interesting topic, because it is beneficial to develop heavy oil, unconventional oil and remaining oil [1,2]. Among the CEOR technologies, polymer flooding is widely used at home and abroad. Because the polymer solution with high viscosity can improve the mobility ratio and enlarge the swept volume, thereby the water-soluble polymer have attracted great interest from researchers due to their huge potential properties and wide applications in oil exploitation [3-5].

Among all of the water-soluble polymer systems, the polyacrylamide (PAM) and partially hydrolyzed polyacrylamide (HPAM) are widely used in the polymer flooding technology of oil fields. Due to the water-soluble polymers have a great capability of thickening and increasing the viscosity, which causes a decrease in water/oil mobility ratio, and increasing the sweep area, so as to enhance oil recovery [6-8]. However, many new problems and limitations appears in the application of traditional polyacrylamide in most oil reservoirs of high-temperature and high-salinity conditions [9]. At high temperature, the amide group (-CONH₂) is easy to hydrolyze, which leads to the viscosity of polymer decrease rapidly. The hydrolysate usually form precipitates at high salinity, which sharply reduces the viscosity of the polymer [10]. 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 [11,12]. Therefore, various of functional groups were introduced into PAM to obtain excellent performance. Such as

the sulfonic acid group, hydrophobic monomer, organic/inorganic materials, etc. has become a research hotspot [13-15].

Sodium p-styrenesulfonate (SSS) is a special polymer monomer, which shows better temperature resistance and salt resistance. So, SSS is introduced into PAM to enhance the temperature and salt resistance. The poly (vinyl acetate-dibutyl maleate-acrylic acid-sodium p-styrenesulfonate) copolymer emulsion was prepared by Gong et al. [16], which powerfully proved that SSS had great salt tolerance and good thermal resistance. The amphiphilic polymer of sodium p-styrenesulfonate and dodecyl methacrylate with temperature and salt resistance was synthesized by Peng et al. [17]. Bai et al. prepared poly (acrylamide-sodium p-styrenesulfonate-*N,N'*-dimethyl octadecyl allyl ammonium bromide) to enhance oil recovery in high temperature and high salinity Oilfield [18]. Therefore, the addition of SSS into the acrylamide-based copolymer matrix is beneficial to improve its heat resistance and salt resistance.

As we all know, the application of nano silica in EOR has been paid more and more attention by researchers. Because the nano silica has the very small size, large surface area, high surface energy and the abundant surface hydroxyls. Due to these outstanding properties of nano silica, it is introduced into the polymer to improve its thermal stability, temperature resistance, salt tolerance, viscoelasticity and the capacity of oil displacement, etc. [19-21]. 3-Methacryloxypropyltrimethoxysilane is a silane coupling agent with alkenyl and long alkyl chains. Therefore, the molecule of KH570 can both modify nano-SiO₂, and form water-soluble hydrophobically associating polymer during monomer polymerization. In a word, all the advantages are beneficial to improve the comprehensive properties of the polymer. Consequently, the KH570 modified nano-SiO₂ polymer nanocomposites has a great contribution to EOR.

In this work, we synthesized a novel polymer nanocomposite (AAS/KS) based on acrylamide (AM)/ acrylic acid (AA)/ sodium p-styrenesulfonate (SSS)/KH570 modified nano-silica (KS). The AAS/KS polymer nanocomposite was characterized by ¹H nuclear magnetic resonance spectroscopy (¹H-NMR), thermal gravimetric analysis (TGA), and scanning electron microscope (SEM). The thickening performance, temperature resistance, salt resistance, shear resistance and viscoelasticity of samples were studied. Also, the oil recovery of AAS/2.0 wt% KS is 9.9% higher than that of the water flooding processes during the enhanced oil recovery experiment in laboratory. All of these outstanding performances proved that AAS/KS polymer composites would be very promising to EOR.

II. EXPERIMENTAL

A. Materials

The unmodified sodium montmorillonite (Na-Mt) with a cationic exchange capacity (CEC) of 100 mmol/100 g was supplied by the Huai An Saibei Technology Co. Ltd., Zhangjiakou, China. Sodium chloride (NaCl, 98%), Calcium chloride (CaCl₂, 96%), sodium hydroxide (NaOH, 96%), ammonium persulfate ((NH₄)₂S₂O₈, 98%), sodium hydrogen sulfite (NaHSO₃, 98%) and absolute ethanol (CH₃CH₂OH, 99.7%) were brought from Tianjin Fuchen Fine Chemical Research Institute, Tianjin, China. Acrylamide (AM, 98%), Acrylic acid (AA, 99%), tetraethyl orthosilicate (Si (OC₂H₅)₄, TEOS, 99.5%), acetone (CH₃COCH₃, 99.5%), *N,N*-dimethylformamide (DMF, 99.5%) were provided by Tianjin Guangfu Fine Chemical Research Institute, Tianjin, China. Ammonia solution (NH₃, 28% aqueous solution) were purchased by Shanghai Aladdin Biochemical Technology Co., Ltd, Sodium p-styrenesulfonate (SSS, 98%) was obtained from Shanghai Macklin Biochemical Co., Ltd., Shanghai, China. *N,N'*-Methylenebisacrylamide (MBA, 99%), 3-Methacryloxypropyltrimethoxysilane (KH570, 97%) were purchased from Aladdin Biochemical Co., Ltd., Shanghai, China.

All of them were analytical grade, and deionized water was used for all experiment.

B. Methods

a) Preparation of SiO₂ nanoparticles and modified by KH570

SiO₂ nanoparticles were prepared by Stöber method[22,23]. The TEOS was added to the mixed solution of ammonia, ethanol and water drop by drop. Then this mixture was reacted at room temperature for 4 hours. After the reaction, it was centrifuged in ethanol for three times and dried in a vacuum oven at 70 °C for 24 h.

The previously prepared SiO₂ nanoparticles were added into a three-necked flask (500 mL) which contained the mixture solution of ethanol and water. Then ultrasonic dispersion for 30 min. After, the KH570 was dropped in the flask under continuous vigorous stirring, the catalytic agent of aqueous ammonia was necessary. A molar ratio of SiO₂ nanoparticles and KH570 was 18:1. Then the reaction was in nitrogen at 50 °C for 12 h. After the reaction, the modified SiO₂ nanoparticles were washed with anhydrous ethanol and dried in a vacuum oven at 50 °C for 24 h. The final product was white solid, which was called KS. The synthetic process was showed in Figure 1.

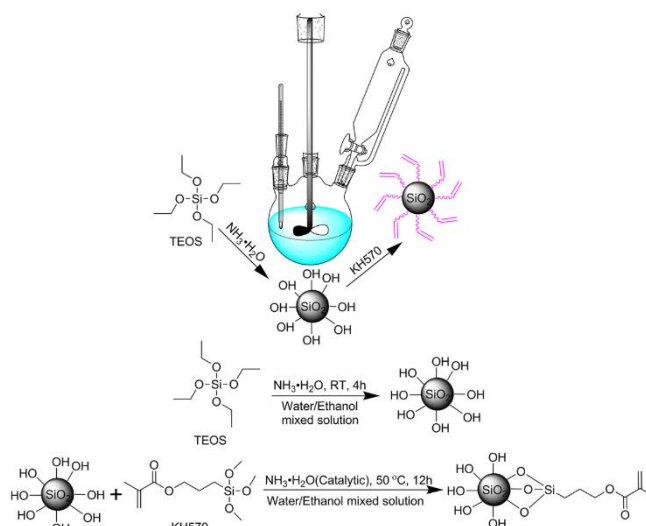


Figure 1. The synthetic process of SiO₂ nanoparticles and modified by KH570.

b) Preparation of AAS/KS nanocomposite

AAS/KS was synthesized by in situ polymerization of aqueous solution. Firstly, a mixture of (0 – 1.000 g) KH 570 modified nano-SiO₂ (KS), 12.532 g AA and 100 g deionized water were added into a 250 mL three neck-flask. Then ultrasonic dispersion for 1h at 50 °C. After that, put into 18.798 g AM, 1.667 g SSS, 0.333 g MBA and continuously stirring for 1h. Secondly, the pH value of the above mixed solution was adjusted to 8-9 by NaOH solution. Thirdly, a certain amount of (NH₄)₂S₂O₈ and NaHSO₃ (molar ratio 1:1, 0.3 wt%) as the initiator were dropped into the reaction solution with stirring under nitrogen atmosphere, after further reacted at 50 °C for 12 h, the obtained samples were washed with absolute ethyl alcohol and water (volume ratio 9:1) several times to remove residual monomers and initiator. Finally, the gel sample was cut into pieces and dried under vacuum environment at 75 °C for 24 h. The final product was ground and sieved with a 200-mesh screen (74 μm eye size), which was called as AAS/x wt% KS (x=1.0, 2.0, 3.0). Pure polymer was prepared by the above process without the presence of

KS, which was called as AAS. The synthetic process of samples was shown in Figure 2.

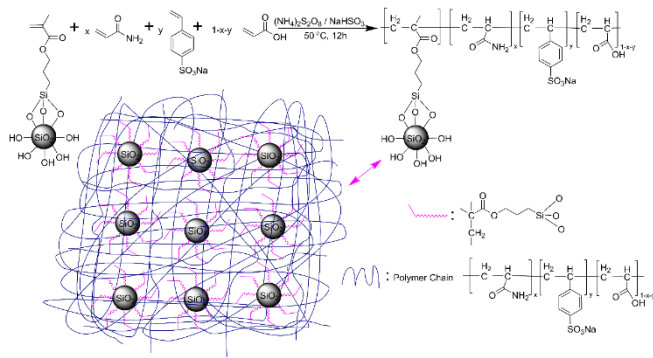


Figure 2. The synthetic process of AAS/modified nano-SiO₂ nanocomposites.

C. Measurements

a) Characterization

The ¹H NMR experiment was performed on a Bruker ASCEND-400 NMR spectrometer. The thermal gravimetric analysis was determined by a NETZSCH analyzer (STA409PC, Germany), under a N₂ flow rate of 140 cm³/min, the samples were heated from 40 °C to 900 °C with the heating rate of 10 °C /min. The size and morphologies of nanocomposite samples were obtained by scanning electron microscope (SEM, SU8010, Japan).

b) Viscosity measurement

The viscosities of nanocomposites under different concentration, temperature, salinity were measured with a Brookfield DV-II + Pro viscometer, and the rotor speed was 60 rpm. The shear resistance of samples at 0-1000 s⁻¹ and the dynamic rheological behavior at 0-10 Hz were evaluated by HAAKE RS600 controlled rheometer.

c) EOR tests in laboratory

The enhanced oil recovery tests were carried out to verify the effects of the AAS/2.0 wt% KS polymer nanocomposite in enhancing oil recovery. The temperature and the back pressure were maintained at 50 °C and 1500 psi, respectively. The detailed experimental procedures were as follows:

- (1) The core was saturated with synthetic brine (4973 mg/L) and then crude oil was injected into the core until no water went out from the outlet.
- (2) Water flooding was conducted at a flow rate of 0.5 mL/min until the moisture content reached 98%.
- (3) 0.2 PV polymer slug was injected into the core, followed by extending water flooding until the moisture content reached 98%.

The artificial sandstone core was employed for the experiments, and the basic parameters were listed in Table 1. Table 2 presented the composition of synthetic brine used in the experiments. The oil recovery ratio was calculated according to the literature [24,25], which was given in equation (1):

$$EOR = E_T - E_W \quad (1)$$

where EOR was the enhanced oil recovery using polymer solution (%), E_T was the total oil recovery in total flooding process (%), and E_W was the oil recovery of water flooding (%).

Table 1. Basic parameters of artificial sandstone cores.

Core	Length (cm)	Diameter (cm)	Porosity (%)	Permeability (mD)
1#	7.76	3.82	20.64	1121

Table 2. Composition of the brine.

Composi tion	Na Cl	K Cl	Ca Cl ₂	MgCl ₂ ·5 H ₂ O	NaS O ₄	NaH CO ₃	Tot al
Concentr ation (mg/L)	24 84	15	55	135	70	2214	49 73

III. RESULTS AND DISCUSSIONS

A. ¹H-NMR spectra

The ¹H-NMR spectra of AAS/2.0 wt% KS with D₂O as solvent was shown in Figure 3. In the ¹H-NMR spectra, the strong peak at 4.70 ppm represented the deuterium in D₂O. The triplet peaks at 1.17-0.95 ppm (2, 7) and double peaks at 2.12-1.90 ppm (1, 6) corresponded to the protons of -CH- and -CH₂- in AM and AA of polymer backbones, respectively. The single peak at 1.50 ppm (12) was the characteristic peak of -CH₃ in tri-polymer. The peaks at 2.30 ppm (11) was attributed to -CH₂- of KH570 in polymer backbones. All the peaks at 3.75-3.24 ppm (15,14,13) were the -CH₂- in the side chain of KH570. The small peak located at 6.81 ppm (3) was due to the proton of -NH₂ in side chain. The chemical shift at 7.61 ppm (10) and 7.25 ppm (9) were attributed to the protons of the benzene backbones, and the peaks at 6.01 ppm (4) and 5.50 ppm (5) were the characteristic peak of -CH₂-, -CH- in the side chain of benzene ring [26]. The weak peak appeared at 8.26 ppm (8) was due to the proton of -COOH of AA. Therefore, the ¹H-NMR spectrum further proved that the desired product was successfully prepared.

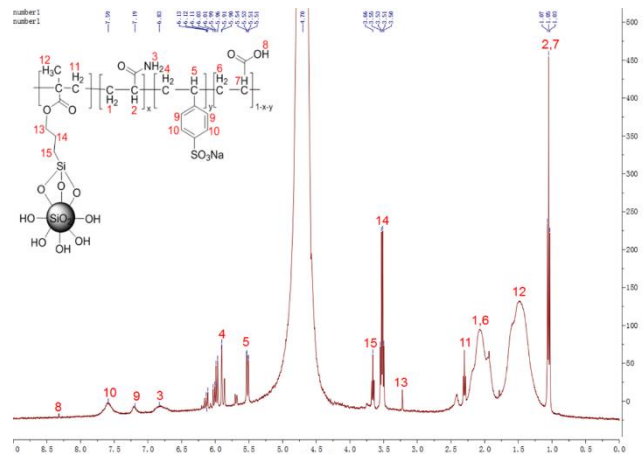


Figure 3. ¹H-NMR spectra of AAS/2.0 wt% modified nano-SiO₂ in D₂O.

B. SEM Analysis

The SEM pictures of prepared KS, pure polymer (AAS) and AAS/2.0 wt% KS polymer nanocomposites were shown in Figure 4. It could be seen in the Figure 4 (a) that the average grain diameter of KS is 30 nm. And it was good for spalling crude oil adhered in the micropores of underground strata. It was observed that the two samples presented the perfect network morphology, and the interconnected skeletons and cavities could be seen in the samples. Compared with the pure polymer AAS, the network of AAS/2.0 wt% KS nanocomposite was much more compact. It was obvious that the skeleton was much stronger, the cavities was less and smaller. The compact structure could be ascribed to the introduction of KH570 modified nano-SiO₂. The perfect network structure indicated that the AAS/2.0 wt% KS polymer nanocomposite was robust, and it could exhibit good comprehensive properties, such as viscosity, high temperature-tolerance, great salt-resistance, good shear-resistance and viscoelasticity. Due to these outstanding properties, the AAS/2.0 wt% KS polymer nanocomposite could enhance oil recovery.

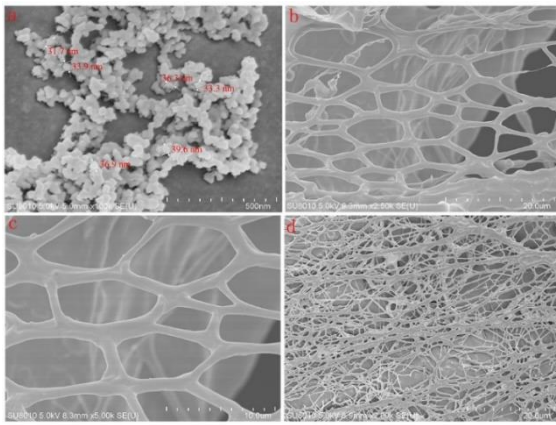


Figure 4. SEM morphologies of (a) KS, (b-c) AAS and (d) AAS/2.0 wt % KS polymer nanocomposite.

C. Thermogravimetric analyses (TGA)

The thermogravimetric analyses curves of pure AAS, AAS/1.0 wt% KS, AAS/2.0 wt% KS, AAS/3.0 wt% KS were showed in Figure 5. From this figure, it could be seen that AAS/2.0 wt% KS presented 10% and 50% weight loss at 262 °C, 667 °C, respectively. And, the pure AAS polymer shows 10% and 50% weight loss at 254 °C and 473 °C, AAS/1.0 wt% KS had 10% and 50% weight loss at 256 °C, 477 °C, and the AAS/3.0 wt% KS had 10% and 50% weight loss at 299 °C, 462 °C. Surprisingly, the temperature of 10% weight loss of AAS/3.0 wt% KS was higher than others. It might be due to the relatively stable intermolecular forces formed by adsorption bridging among the KH570 modified nano SiO₂. However, with the temperature increasing, the intermolecular forces were destroyed. As a result, the weight loss of AAS/3.0 wt% KS decreased rapidly. When the temperature reached 900 °C, the residual mass of AAS/2.0 wt% KS maintained 35.0%, but the residual mass of AAS/1.0 wt% KS and AAS/3.0 wt% KS were 26.5% and 34.8%, respectively. And pure AAS was only 23.3%. Therefore, under the temperature range of 40-900 °C, all these results proved that AAS/2.0 wt% KS displayed higher residual mass and better stability. So the AAS/KS polymer nanocomposites could be used to enhance oil recovery in high temperature reservoir.

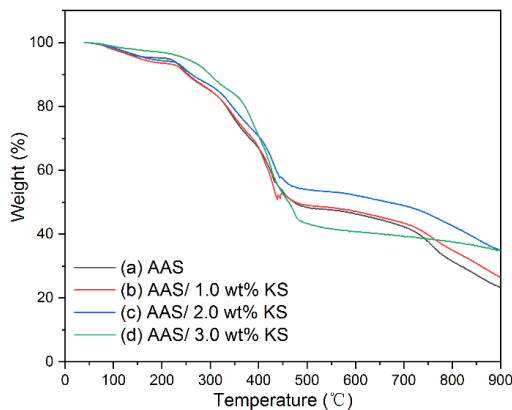


Figure 5. TGA curves of AAS, AAS/1.0 wt % KS, AAS/2.0 wt % KS and AAS/3.0 wt % KS.

Table 3 The thermogravimetric analysis data of samples

	The temperature of 10% weight loss	The temperature of 50% weight loss	The residual mass
AAS	254°C	473°C	23.3%
AAS/1.0 wt% KS	256°C	477°C	26.5%
AAS/2.0 wt% KS	262°C	667°C	35%
AAS/3.0 wt% KS	299°C	462°C	34.8%

D. Viscosification properties of nanocomposites

A certain amount of samples were dissolved into distilled water to obtain different concentrations of sample solutions. Then the apparent viscosity of each sample solution was measured at the temperature of 25 °C. It was clearly seen from Figure 6 that the apparent viscosity raised with the increase of solution concentration. The concentration of AAS/2.0 wt% KS from 2500 to 12500 mg/L, the apparent viscosity changed from 226 to 1050 mPa.s. At equal temperature, the apparent viscosity of AAS/2.0 wt% KS was significantly higher than that of AAS. The addition of KS could enhance the apparent viscosity of the polymer nanocomposites. Nevertheless, when the addition of KS was 3.0 wt%, the apparent viscosity decreased. It may be that the hydrophobicity of the AAS/3.0 wt% KS increased, resulting in the poor water-solubility. In a word, the viscosification property of AAS/2.0 wt% KS made it have significant application to enhance oil recovery.

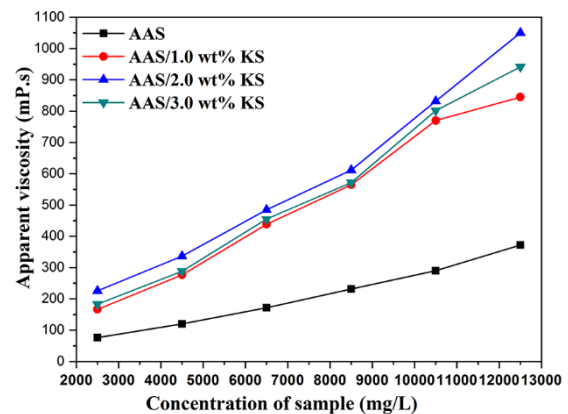


Figure 6. Relationship between apparent viscosity and the concentrations of AAS, AAS/1.0 wt% KS, AAS/2.0 wt% KS, AAS/3.0 wt% KS.

E. Temperature-resistance evaluation

As is known to all, the high temperature could destroy the main chain of polymer and the intermolecular force among polymer chains. Therefore, the molecular framework of polymer was wrecked, resulting in the decrease of apparent viscosity of polymer nanocomposites. The 2500 mg/L of sample solutions were prepared, and the temperature effect on the apparent viscosity of AAS and

AAS/KS solutions could be observed in Figure 7. The results proved that the apparent viscosity of both AAS and AAS/KS solutions decreased with the temperature went up. However, due to the addition of KS made that the polymer nanocomposites exhibited better temperature tolerance. For example, the apparent viscosity of AAS/2.0wt% KS was always higher than other samples under the same conditions. On account of the hydrophobicity of AAS/3.0wt% KS increased, led to the poor water solubility, so the apparent viscosity decreased and the temperature resistance descended. In addition, the SSS with benzene ring was able to resistant high temperature. On the one hand, the benzene ring was the special steady six-membered ring with extremely little ring strain. The decomposition of benzene ring needed enough energy. On the other hand, the steric effect of benzene ring could prevent the rotation of single bond attached to polymer backbone chain. Therefore, the polymer backbone chain was not easy to be broken. The AAS/2.0 wt% KS was applied to enhance oil recovery in the oil field, due to its better performance of high temperature resistance.

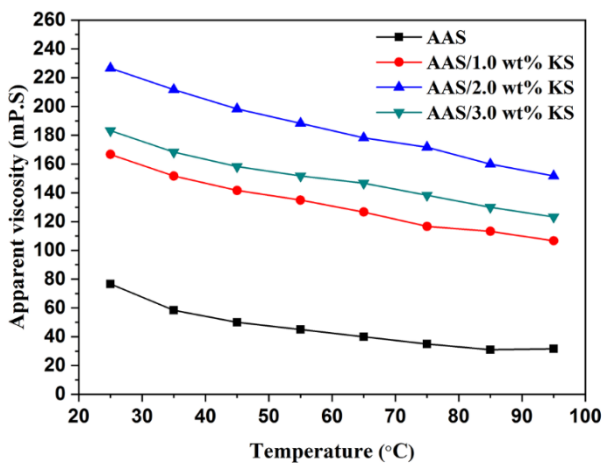


Figure 7. Relationship between apparent viscosity and the temperature-resistance of AAS, AAS/1.0 wt% KS, AAS/2.0 wt% KS and AAS/3.0 wt% KS.

F. Salt-tolerance evaluation

The salt-resistance of polymer nanocomposites was a significant index in polymer flooding to enhance oil recovery. The concentration of sample solutions is 2500 mg/L, the test temperature is 25 °C, and the results were shown in Figure 8. The apparent viscosity of AAS and AAS/KS solution declined rapidly as the concentration of NaCl or CaCl₂ solution increased from 0 to 6000 mg/L. Because the electrolyte ions (Na⁺, Ca²⁺) shielded the effective charge, and then the electric double layer of polymers were compressed by salt ions, resulting in a reduction of hydrodynamic volume. Due to the addition of KS were able to prevent this effect. So the apparent viscosity of AAS/KS was higher than AAS, resulting in better ability in the improvement of oil recovery.

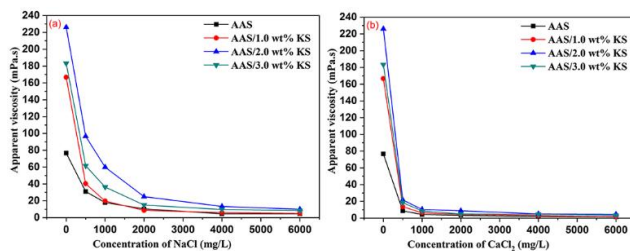


Figure 8. The effect of (a) NaCl solution and (b) CaCl₂ solution on apparent viscosity for AAS, AAS/1.0 wt% KS, AAS/2.0wt% KS and AAS/3.0wt% KS.

G. shear resistance evaluation

The shear resistance was a significant performance of polymer nanocomposite in petroleum engineering. In the process of injection and displacement, the shear force from the pump, pipeline, wellbore, bullet hole and porous media greatly reduced the viscosity of polymer solution, and affected the oil recovery [27]. Figure 9 showed the apparent viscosity of AAS, AAS/1.0 wt% KS, AAS/2.0 wt% KS and AAS/3.0 wt% KS under different shear rate. With the increasing of shear rate, the viscosity of AAS/KS decreased, because polymer chains broke down and network structure destroyed. However, the addition of KS, the polymer skeleton became stronger. In the shear rate range of 0-1000 s⁻¹, the apparent viscosity of AAS/2.0 wt% KS was always higher than others. As a result, the optimal addition of KS in polymer nanocomposites is 2.0 wt%. In short, the AAS/2.0 wt% KS polymer nanocomposite was beneficial to enhance oil recovery.

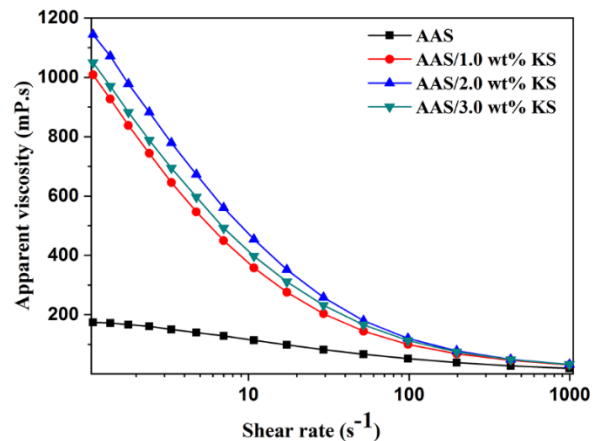


Figure 9. Effect of shear rate on apparent viscosity for prepared sample solutions (solution concentration is 2500 mg/L; T=25 °C).

H. Viscoelasticity of AAS/KS nanocomposites

Viscoelastic polymer solution could improve the oil-displacement efficiency, thus greatly enhancing the crude oil recovery. Therefore, the dynamic rheology was studied, and the change of storage modulus (G') and loss modulus (G'') with frequency were shown in Figure 10. The G' and G'' of AAS, AAS/1.0 wt% KS and AAS/2.0 wt% KS exhibited an upward tendency along with the increase of frequency. Interestingly, the G' and G'' of AAS/2.0 wt% KS was always higher than those of AAS and AAS/1.0 wt% KS, which indicated that AAS/2.0 wt% KS had better viscoelasticity. The stronger the viscoelasticity, the larger the first normal stress and the dragging force on oil film, and the higher the enhanced oil recovery. While the frequency was less than the characteristic frequency (point of intersection), G'' was higher than G', and the viscosity of nanocomposites was predominant. And when the frequency exceeded the characteristic frequency, G' was greater than G'', and the elasticity play a dominating role. The phenomenon could attribute to the KS interacted with the polymer chains, resulting in the network structure of AAS/KS was reinforced and the elasticity of the polymer composite got more significant. As a result, the AAS/KS could be better applied in EOR.

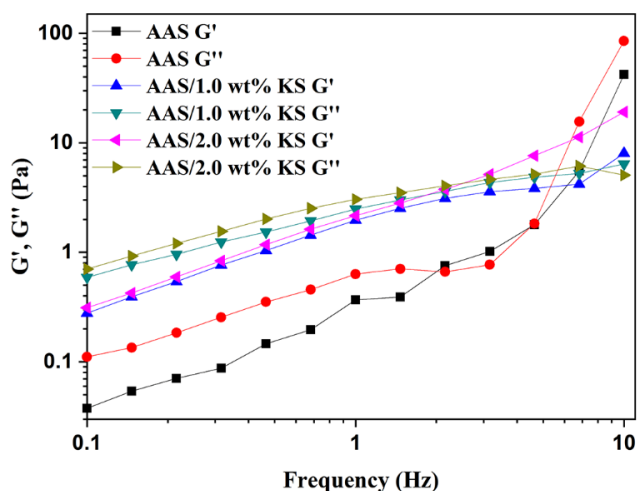


Figure 10. Elastic (G') and viscous (G'') modulus as a function of frequency for AAS, AAS/1.0 wt% KS and AAS/2.0 wt% KS.

I. EOR experiments in laboratory

The EOR capability of AAS/2.0 wt% KS was studied in sandstone cores, and the results were showed in Figure 11 and Table 4. When the moisture content reached 98% in the first water flooding, the oil recovery was E_w (43.8%). As the following water flooding, 0.2 PV polymer flooding and subsequent water flooding could increase the oil recovery to a stable value ($E_T = 53.7\%$). In comparison with the water flooding, the oil recovery increased by 9.9%. The main reason for obtaining higher oil recovery was due to its better temperature-resistance, salt-tolerance, shear resistance and viscoelasticity and so on. All the outstanding properties were attributed to the introduction of KS. All these results showed that AAS/KS nanocomposites had a great potential to enhance oil recovery.

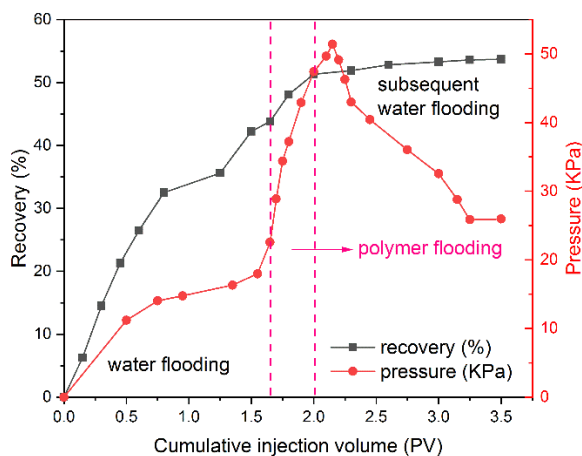


Figure 11. EOR experiments of AAS/2.0 wt% KS in laboratory.

Table 4 EOR of AAS/2.0 wt% KS

Sample	Concentration (mg/L)	E_w (%)	E_T (%)	EOR (%)
AAS/2.0 wt% KS	1000	43.8	53.7	9.9

IV. CONCLUSIONS

A novel of AAS/KS polymer nanocomposites were successfully synthesized by in situ polymerization of AM, AA, SSS, and KH570 modified nano-SiO₂. ¹H-NMR analysis determined the successful synthesis of AAS/KS polymer nanocomposites. The results of

solution performance tests indicated that the introduction of KS improved the properties of AAS/KS polymer nanocomposites. Compared with pure AAS, the AAS/KS nanocomposites exhibited superior performance on aspects of thermal stability, temperature resistance, salt tolerance, shear resistance and viscoelasticity. Furthermore, the 9.9% oil recovery was increased during the EOR tests in laboratory. These results suggested that AAS/KS nanocomposite had great potential application for EOR in high temperature and high salinity oilfield.

V. ACKNOWLEDGMENTS

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