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Rheological properties of partiallyhydrolysed polyacrylamide seeded by nanoparticles

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Abstract

This work aims to improve the rheological properties of partially hydrolysed polyacrylamide (HPAM) for enhanced oil recovery by using SiO_2 nanoparticles (NPs).Novel aqueous HAPM based SiO_2nanocomposites were formulated and their rheological properties were investigated under different salinities, temperature and aging time. The results show that the inclusion of silica NPs improved significantly the viscosity and viscoelastic properties of HPAM especially under high temperature and high salinities. The NP/HPAM hybrid showed an impressive thermal stability at T= 80 ºCafter 12 days, and the viscosity reached ~5 times of that HPAM at 0.8w% NP loading. The FT-IR spectra data confirmed that the formation of hydrogen bond between the carbonyl groups in HPAM and the silanol functionalities on the surface of silica NPs, which attributed to the improved performance. The oscillation test indicated that seeding SiO_2 remarkably facilitated the cross links among polymer molecules and made the hybrids more elastically dominant. For a given HPAM concentration, it was observed that there was acritical NP concentration (CNC)which many indicating the absorption status of SiO_2 NPsonto HPAM, and the salinity also affected the viscosity value.

Keyword: Rheology, enhanced oil recovery, chemical flooding, partially hydrolysed polyacrylamide, silica nanoparticles

1. Introduction

Partially hydrolysed polyacrylamide(HPAM) has attracted a great deal of attention in petroleum industry over the last a few decades, ranging from the treatmentof waste water produced from oil extraction[1]and low-grade oil sand[2] to enhanced oil recovery (EOR).[3, 4]For instance, HPAM is widely used as a polymer additive for conformance control in some low temperature oil reservoirs to increase oil recovery rate, which has been tested at the field scale.[5-7]Tobe an effective candidate for EOR, HPAM has to possess the ability to increase significantly the viscosity of the displacing fluid, thus reducing the mobility ratio and improving the sweep efficiency, and be stable with consistent performance under reservoir conditions during the recovery process, which may last a few months.

The critical problem that hinders the successful application of HPAM for EOR applications is the polymer degradation, especially under high temperature and high salinity conditions.[8]As most of the reservoirs that requires EOR have high temperatures, ranging from 60 to 120 °C,[9]HAPM would experience a serious viscosity reduction and decrease the recovery rate. The reduction would be caused by the impairment of hydrophobic effect due to the increased mobility of the polymer chains and the resultantloss of inter-chain liaisons.[10-12]At temperature above 60°C, the acrylamide groups would experience a hydrolysis process to form acrylate[8] or carboxylic[13] groups, which are sensitive to the presence of inorganic salts in the reservoir. As most of the reservoirs that requires EOR are also under high salinity conditions(i.e., >30000 mg/Lor by the API standard, 8 wt% NaCl and 2 wt% $CaCl_2$,equivalent to 1.8 M total ionic strength[14]), the high concentration of saltswould further interact with the formed polyelectrolytes and deteriorate HPAM performance. With the increase of the degree of hydrolysis, HPAM could precipitate from the bulk solution due to the complexes formed between the polymer and divalent cations.[15] In addition, the shielding of the mutual repulsions between carboxylic groups along the HPAM skeleton would lead to the decrease of hydrodynamic volume, resulting in additional viscosity reduction.[16-18] It has been shown thatthe higher salt concentration always corresponds to a lower temperature limit for the applicability of HPAM in EOR processes.[19]

To alleviate the problems mentioned above, a few strategies have been proposed thatcan be categorised as:mobility control, copolymerization, and forming organic /inorganic nanocomposites. For example, Zhong et al.[20,21]showed thatby forming polymerswith sufficiently low mobility numbers, the freshwater polymer bank could displace the oil and brine ahead of it with the minimum mixing in high salinity reservoirs; however the problem of the high temperature deterioration of HPAM was still present. Different functional groups such as the sulfoacid group, annular material, and hydrophobic monomerhave been introduced into polyacrylamide (PAM) for copolymerization[22,23], which could reach similar properties to that for HPAM.[8]

Introducing inorganic nanoparticles (NPs) into HPAM is a recent development. It is expected that properly-engineered NPs could reinforce the intermolecular hydrophobic associations by forming polymer/inorganic nanocomposites hydrogels, and improve the rheological behaviour of polymer solution. In addition, NPs could strengthen the network structure of HPAM, rendering improvedbulk mechanical and thermal properties. To date,a few inorganic constituents have been investigated, which include clay minerals,[24-26] layered double hydroxides (LDHs),[27-29] CNTs[30] and graphene oxide (GO)[31,32] and metal oxide nanoparticles.[33] The dispersion of SiO_2NPs into a HPAM to form ananocomposite hydrogel has been recently investigated. Bhardwaj et al.[33] reported that synthesisedPAM-SiO_2nanocomposites showed improved thermo-resistance and high thermal stability behaviours. Maghzi et al.[34] showed that the viscosity of PAM was increased by introducingSiO_2NPs and the oil recovery efficiency was also 10% higher during a polymer flooding process. However it shall be noted that most of these studies were either focused on the temperature effect or the salinity effect, and experiments were performed in a limited range with insufficient characterisation of NPs and NP-HPAM hybrids.The long term behaviour of the formed nanocomposites(i.e., up to a few weeks)under reservoir-like conditions is also little known.

This work addresses such limitations by conducting a systematic study of SiO_2/HPAMnanocompositesunder high temperature (up to 90^oC) and high salinity (up to 8w% NaCl) conditions, and examine the effect of important parameters such as NP loading, temperature, aging time and electrolyte concentration, on the rheological behaviour.The dynamic viscosity was also studied to clarify the contribution of NPs on the improvement of rheological properties.

2.Experiment

2.1 Material

SiO_2 nanoparticle (12 nm, ≥99.0%in purity) was purchased from Sigma Aldrich Co., LLC. The specific surface area is 150 m^2/g measured by the BET method, and the corresponding specific weight is 2.4 g/ml. Partially hydrolysed polyacrylamide (HPAM) was purchased from Shandong Tongli Chemical Co. Ltd China, which has a molecular weight of 5-22 million g/moland relative density of 1.302 g/cm^3.Sodium chloride (ACS reagent, ≥99.0% in purity) was obtained from Sigma-Aldrich. All of the chemicals were of analytical reagent (A.R.) grade and used as received without further purification.

2.2 Preparation of hybrid sample

SiO_2NPs at different concentrations (0.0, 0.1, 0.2, 0.4, 0.6, 0.8, 1wt%)were dispersed in distilled water to form stable dispersion byultrasonication via an ultrasonic bath (FB15057, Fisher Scientific) for 20 minutes. Then HPAM powderswere introduced intoaqueous SiO_2 suspensions at designed concentrations from 0.01 wt% to 1 wt%.In order to allow enough time for silica NPs contactingwith graft polymer, the inorganic/organic mixtures were gently stirred using a magnetic stirrer (SB 162-3, Stuart) at room temperature for one day. FinallyNaClwas added to the hybrid solution at different concentrations up to 8 wt%, followed by one- day stirring before rheological tests.

2.3 Characterization

Rheology measurement

The viscosities of these samples were measured by a Physica MCR 301 rheometer(Anton Paar, Austria)equipped with a convection oven and a 'TC30' temperature controller unit, which can stabilize the sample temperature from 0 to +1000 °C with an accuracy of 0.1 °C. A cone-and-plate geometry was selected for the rheological measurement, because the shear rate is uniform across the radius, and the gap is pre-set to the standard (0.098 mm) determined by the manufacture. The system only requires a small amount of sample (0.7 ml) for each test and is easy to clean. Prior to any measurement, the rheometer was tested with a standard oil and pure water at different temperatures to ensure that both the instrument and this particular setup were calibrated, yielding reliable data.

The rheological behaviour of samples was determined under both steady and oscillatory shearing conditions to obtain steady and dynamic viscoelastic properties. Dynamic frequency spectra were conducted in the linear viscoelastic regimes, as determined from dynamic stress-sweep measurements. All experiments were conducted under a shear rate controlled mode.

Infrared spectroscopy

Infrared spectroscopy (FTIR spectrometer 100, Perkin-Elmer) was used to measure the FTIR spectra of vacuum-dried HPAM and HPAM/silica hybrid samples. The data was collected at a spectral resolution of 4 cm^{-1} within the scanning range of 4000-400 cm^{-1}.

Long-term thermal stability

The sample of 0.5 wt% HPAM cross-linked by 0.8 wt% SiO_2NP was selected for the long-term thermal stability test, while a particle-free sample with the same polymer concentration was selected as the reference. The samples were stored in glass bottles covered by screw-caps with promoted sealing by a sealing tape, and were placed into an oven at 80 °C. The viscosities of those samples were measured at 85 °C atdifferent sampling timesspanning 12 days.

3.Results and discussion

3.1 Nanoparticle and hybrids characterisation

The real size and morphology was detected by transmission electron microscope (TEM, FEI Tecnai TF20) as shown in Figure 1 错误！未找到引用源。. The hydrodynamic particle size distribution in distilled water was measured using a Malvern Nanosizer based on the dynamic light scatting (DLS) method, which shows anaverage size of 187.5 ±2.9 nm,peaking at 200.8 ±64.9 nm (Figure 1b). The zeta potential of the dispersion was measured as -32.0±1.0 mV.

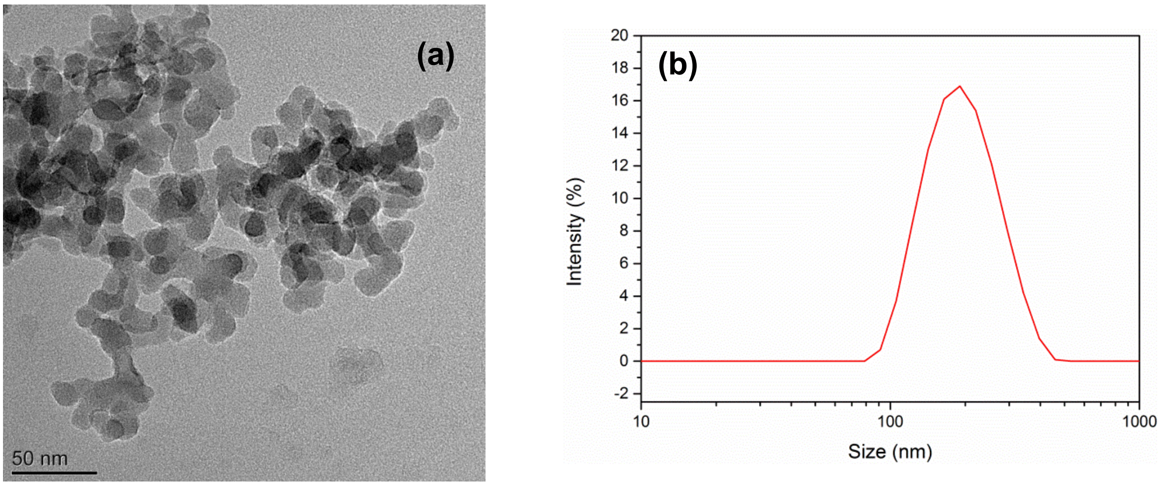

Figure 1. (a) TEM image of SiO_2 nanoparticles, and (b) particle size distribution of SiO_2 in distilled water measured by the dynamic light scattering (DLS) method.

3.2 Concentration dependence of HPAM

There is a critical concentration existing for a polymer solution, often called the critical association concentration (CAC), where intramoleculesstart to self-associate. The CAC values can be obtained by several ways such aslight scattering determination and the variations of fluorescence properties when micellisation occurs.[35] In this work, the rheological properties at 25 °C and 85 °C for HPAM solution were studied to determine the CAC at different temperatures. Figure 2 shows the viscosity of HPAM at 85^{o}C under different shear rates. It reveals that when the HPAM concentration was lower than 0.1 wt%, the viscosities were almost independent of the shear rate, behaving like Newtonian fluids. While when the concentration was over 0.1 wt%, the viscosities were gradually reduced with the increase of shear rate,indicating shear-thinning properties.

Figure 3 shows the average viscosity at shear rates from 600 S^{-1} to 1000 S^{-1}as a function of HPAM concentration at 25 and 85 °C. The high temperaturecurve is divided into two partsat a HPAM concentration of 0.45 wt%. Below that, the viscosity increased slowly with the increase of polymerconcentration, but rapid increase was observed at concentrations of over 0.5 wt%. This trend suggested that 0.5 wt% is the CAC for HPAMat 85°C. Similarly, a lower CAC value was observed at 25°C, i.e., ~0.2wt %.

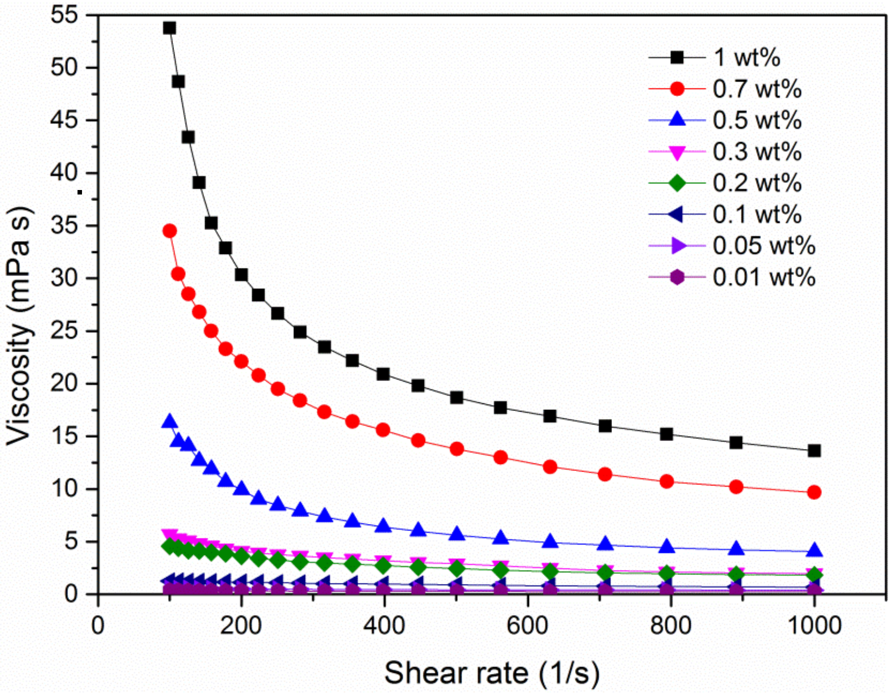

Figure 2. The dependence of viscosity for HPAM on shear rate (T= 85 °C, no electrolytes).

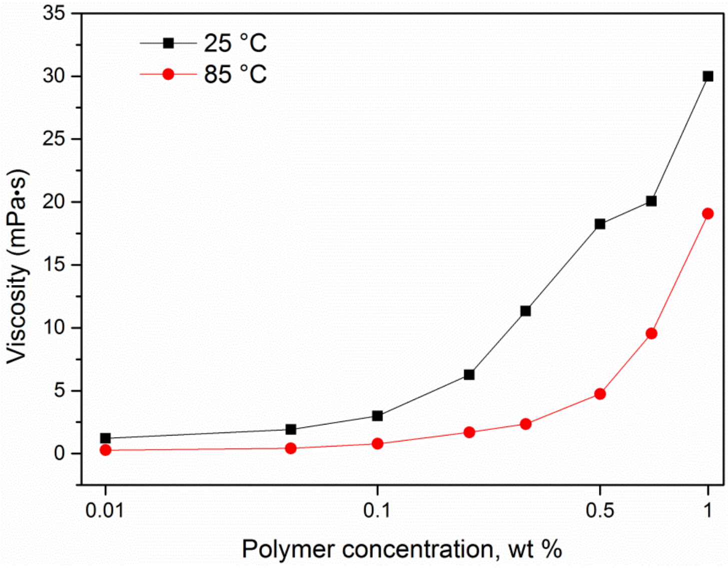

Figure 3 Average viscosity for various concentrations of HPAM at 25 and 85 °C (no electrolytes, shear rate from 500 s^{-1} to 1000 s^{-1})

3.3 Effect of nanoparticle loading on the viscosity of HPAM/silica hybrids

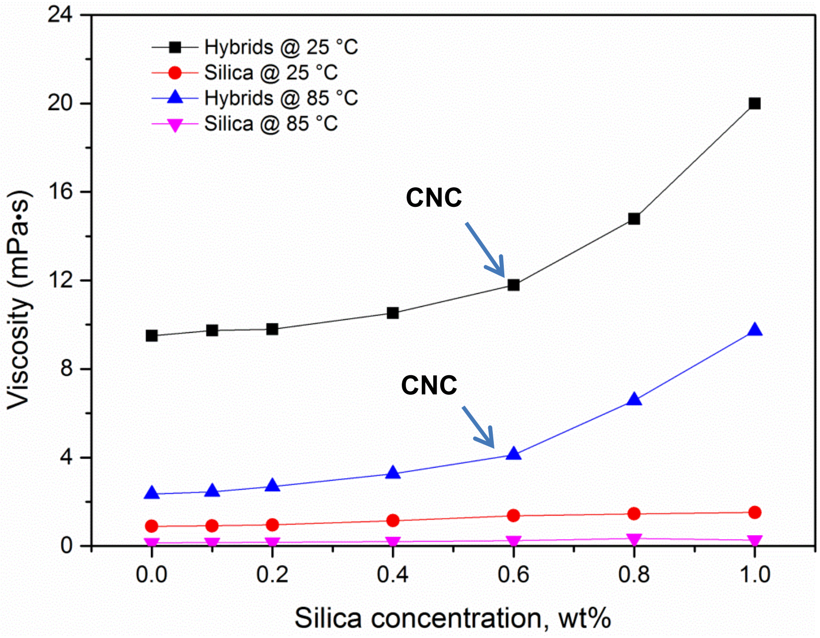

Figure4.Viscosities of 0.5 wt% HPAM with different SiO_2NP loadings (T= 25 and 85 °C, 8 wt% NaCl andshear rate from 500 s^{-1} to 1000 s^{-1}). Under the same condition, the viscosity for sole 0.5 wt% HPAM was measured as 2.9mPa·sfor 85°C, and 9.1mPa·s at 25 °C.

In addition to the CAC of HPAM, it is also worthy to examine the effect of NP on the viscosity of hybrids.To do this, 0.5 wt% HPAM solution was chosen as the reference solution in which a series of SiO_2 NPs at different concentrations were added. The same concentrations of SiO_2NP dispersed in distilled water were also included for comparison. It is clearly from Figure 4that the viscosities of the hybrids were increased with increasingNP concentrations.Similar to the pure HPAM case, a rapid increase in viscosity was observed beyond a certain particle loading, i.e., defined as critical nanoparticle concentration (CNC) here. For 0.5w% HPAM solution, the CNC values were found to be around 0.6 wt%in spite of the temperature at25 °C or 85 °C.

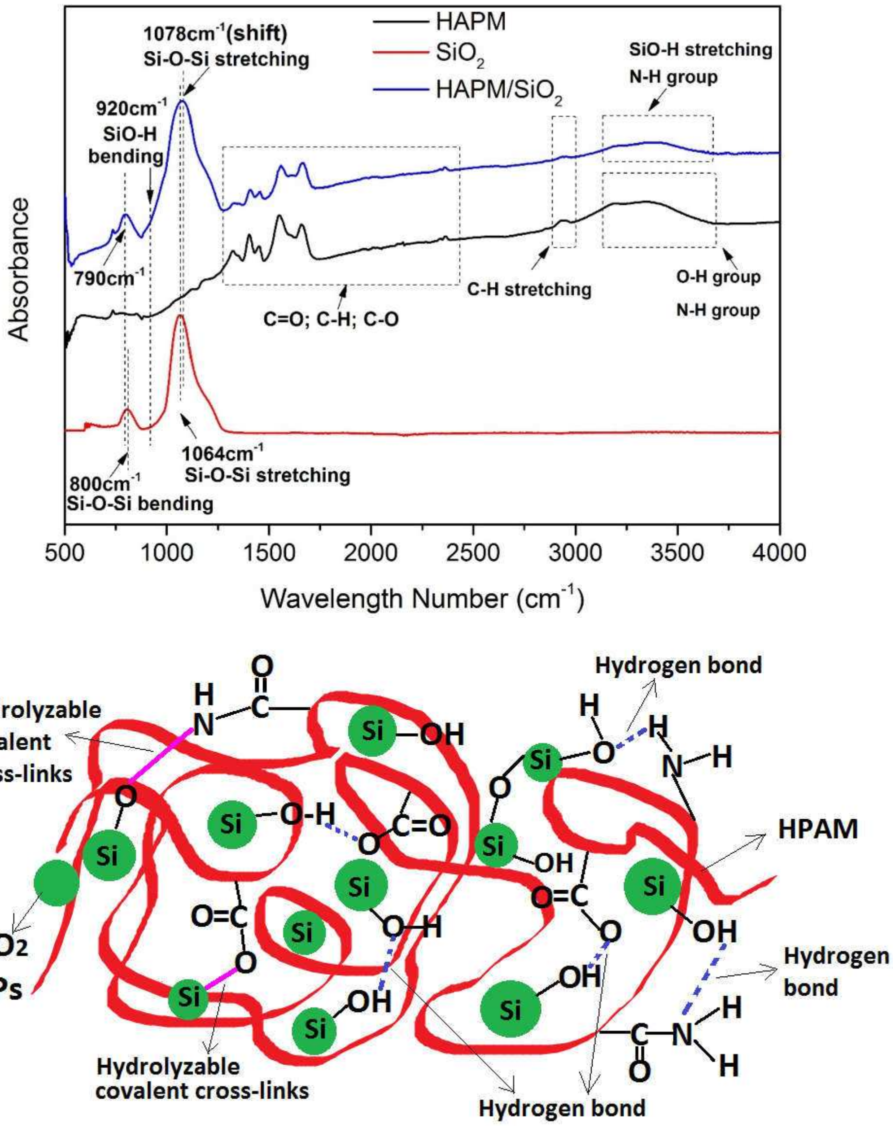

Figure 5. (a) FTIR spectra for 0.5 wt% HPAM, 0.5 wt% HPAM/ 0.8 wt% SiO_2NP hybrid, and SiO_2 NP; (b) Potential interactions between SiO_2 NP and HPAM.

In order to find out the reason why adding SiO_2NP could increase the viscosity of hybrids, FT-IR spectroscopy was employed to check if there were some potential bonding effects formed between silica and HPAM. For pure SiO_2sample, only two major peaks at 1064 cm^{-1} and 800 cm^{-1} are found as shown in Figure 5a, which corresponds tothe Si-O-Si asymmetric stretching vibration and Si-O-Si bending vibration, respectively. Figure 5a also showstwopeaks at 1078 cm^{-1} and 790 $cm^{-1}$for HPAM/SiO_2 hybrid sample, where pure HAPM sample does not show these two peaks. These are also due to the Si-O-Si asymmetric stretching vibration and Si-O-Si bending vibration, respectively.However, compare with the spectra for SiO_2, these two peaks all show notable shift. Such results might originate from some combination effects between the SiO_2 NPs and HAPM. For instance, hydrolysable covalent cross-links between SiO_2 and HAPM (Figure 5b) might exist in the system.[36]In addition, another peak at 920 $cm^{-1}$was found, which correspond to Si-O-H bending vibration, introduced bythe hydroxyl on silica surfaces. Such –OH groups can react with the amide groups, forming hydrogen bonding between the hydrogen from the SiO2 surface and the oxygen or nitrogen from HPAM (SiO-H·····N-H or SiO-H·····O-CNH2), or between the oxygen from SiO_2 surface and the hydrogen from HPAM (SiO·····HNH-CO-C, as shown in Figure 5b. After blended with SiO_2 NPs,the peak area ranging from3100 to 3800 $cm^{-1}$for HPAM became broader, which indicates the vibration of –OH, SiO-H and N-H groups. The formed hydrogen bonding might be overlapped in this range. However, no peak appeared in this range for pure SiO_2 sample. In addition, the possible formation of hydrolysable covalent cross-links between the SiO_2 NPs and HPAM also strengthened their connection and enhanced the viscosity of the hybrids.

As mentioned above, the viscosity for the hybrids would increase more quickly when the particle loading is beyond a certain concentration, i.e., defined as critical nanoparticle concentration (CNC). Here it is assumed that the CNC is related to the adsorption status of SiO_2 NPs onto HPAM, as illustrated in Figure 6. When the NP concentration is lower than the CNCvalue, particles are absorbed onto hydrophobic chain due to the formation of hydrogen bonds between the carbonyl groups of HPAM and sialons functions of silica.[37] Consequently there is nofree silica NP in the bulk solution at low particle concentrations. But when the particle concentration is increased beyond the CNC value, free silica NPs become available, which can bridge between different polymer chains, preventing them from moving or rotating. This would result in a rapid increase in the viscosity. In addition, free particles may also agglomerate and attach together via Si-O-Si bindings, which further increase the viscosity.

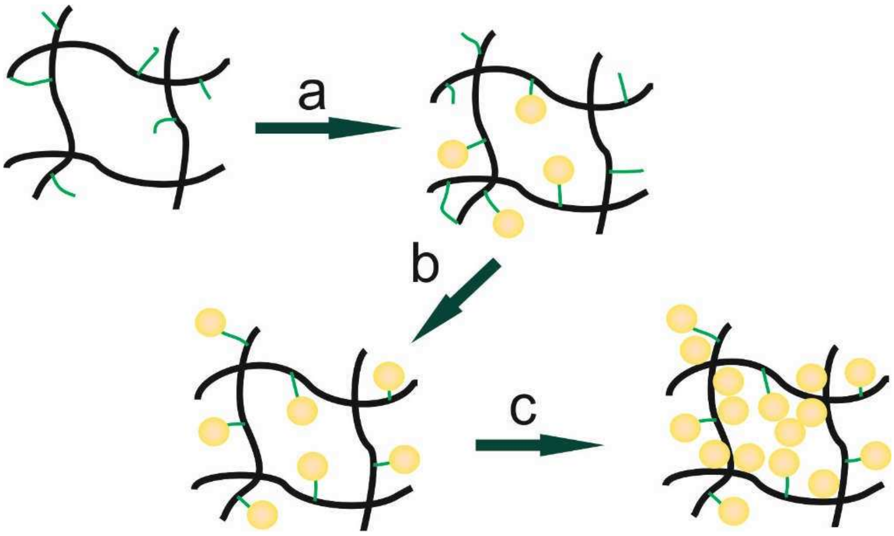

Figure 6.Cartoons illustrate the adsorption of SiO_2NPonto polymer chains for a given polymer concentration:a): particle increasingly adsorb onto polymer chains viahydrogen bonds; b) saturation is reached(i.e. CNC value) with all the carbonyl groups were attached by SiO_2 nanoparticle; and c) particles accumulate and bridge in the network.

3.4 Effect of temperature on viscosity of HPAM/Silica hybrids

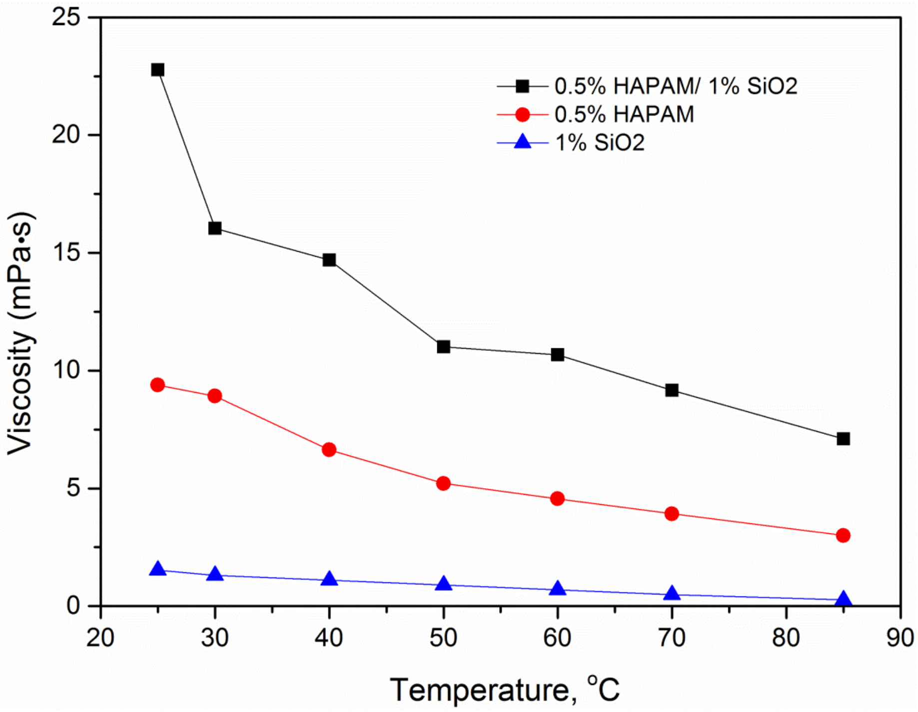

Figure7. Comparison of the temperature effect on effective viscosities at different temperature (8 wt% NaCl and shear rate 500 s^{-1} to 1000 s^{-1})

To investigate the temperature effect, a hybrid sample, i.e., 0.5 wt% HPAM mixed with 0.8 wt% SiO_2,and the corresponding pure polymer and SiO_2 solution were examined (Figure 7). It is found that the effective viscosities for all tested samples underwent significant decrease at elevated temperatures. Compared with the pure HPAM solution, the HPAM/SiO_2 hybrids still maintained ~ threefold higher in the effective viscosity in the whole temperature range studied, albeit with a larger dependence on the temperature. Similar to the analysis above, the presence of silica NPs would crosslink individual polymer molecules to form a solid hybrid network via hydrogen bonding.Howeveras the hydrogen bond is sensitive to temperature, a large viscosity reduction was observed for HPAM/SiO_2 hybrid, probably due to thedisassociation of the network junctions and the bindings of NPs to HPAM. For pure HPAM,the increase of temperature would still break down intermolecular hydrophobic associationsunavoidably, and hydrolyse the acrylamide group in HPAM into acrylate groups. Both factors would cause the viscosity reduction for HPAM solutions.

3.5 Long-term thermal stability of HPAM/silica hybrid

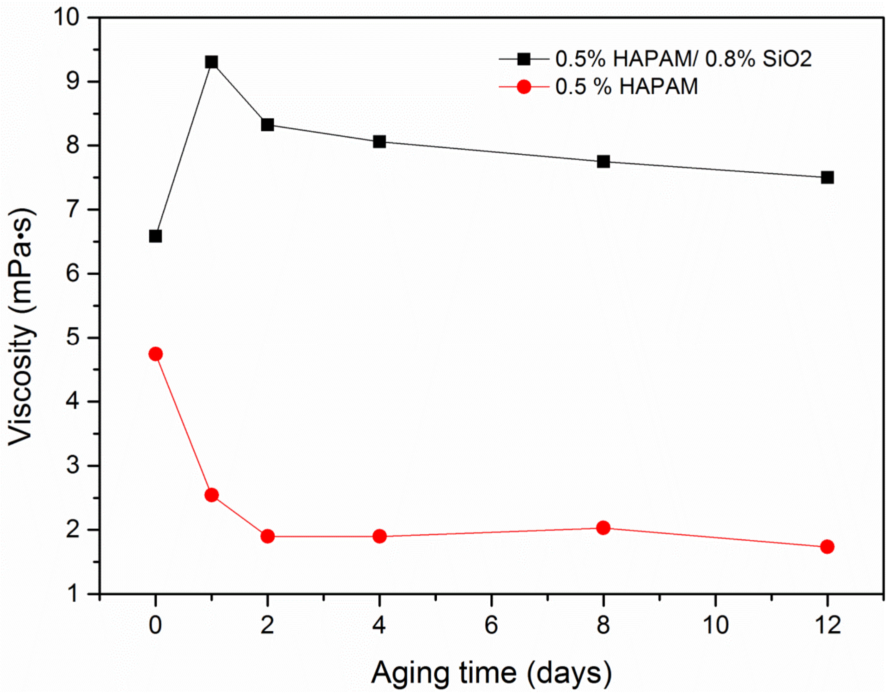

Figure8.Example viscosity changing with the aging time (aging at 80 °C and 8 wt% NaCl)

In a typical polymer flooding process, polymers have to stay for a long time inside reservoirs, and continuous aging of the polymers would result in a decrease in the effective viscosity and hence a detrimental effect in oil recovery.[38]The remaining viscosity representsa basic benchmark for any polymer to be used in hostile environment. To examine the aging effect, 0.5 wt% HPAM and 0.5 wt% HPAM/0.8 wt% silica NP hybrid ina brine (8w% NaCl) were tested at 80 ^{0}C, as shown in Figure 8. The result clearly shows that the NP /HPAM hybrid had a much better thermal stability. The viscosity impairment was much lower for the hybrid. For example, the HPAM solution viscosity was dropped sharply from 4.8 cP to ~1.5cPafter 12 days' aging, whereas a slight increase in the effective viscosity was observed for the HPAM/silica hybrid. The increase was peaked after one-day's aging, and started to slightly decline over the following days, yet still with a value higher than the original sample. The effective viscosity was about 5 times higher than the pure HPAM after 12 day's aging.Such a result isquite different to what reported in theliterature.[39]The exact mechanism on the aging effect is still unclear but it appears that a gentle heating could promote the formation of bindings between silica nanoparticles and polymer chain and an optimum heating duration exists to reach the maximum viscosity. For the sample investigated, one day's aging produced the highest viscosity forHPAM/silica hybrid. Such an aging effect shows an encouraging application prospect for such NP /HPAM hybridsin EOR process.

3.6 Effect of electrolyte on viscosity of HPAM/silica NP hybrid

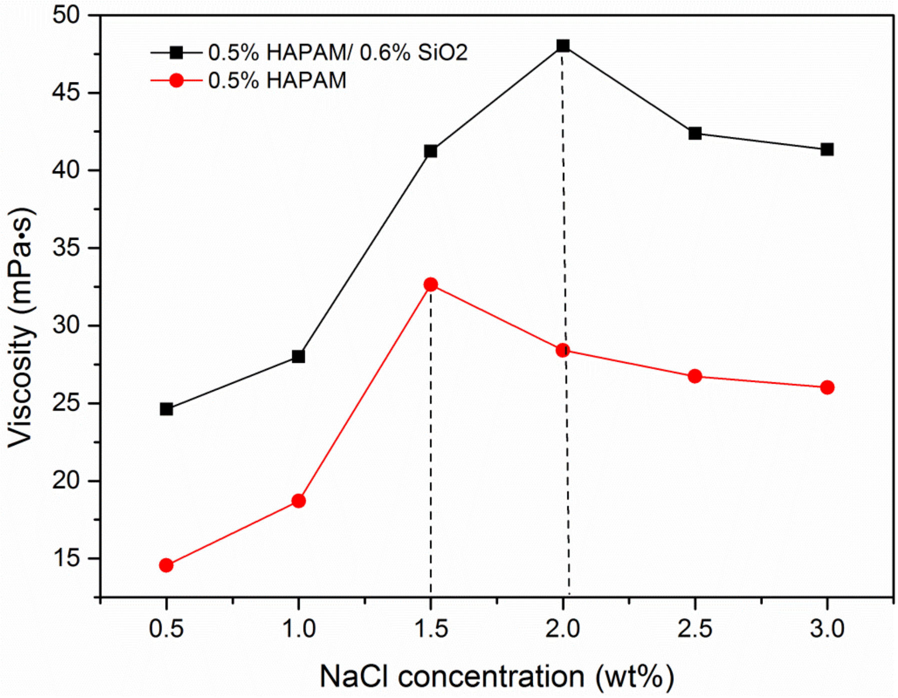

Figure 9.Example influence of ionic strength on average viscosity (T= 25 ^{0}C and shear rate from 500 S^{-1} to 1000 S^{-1})

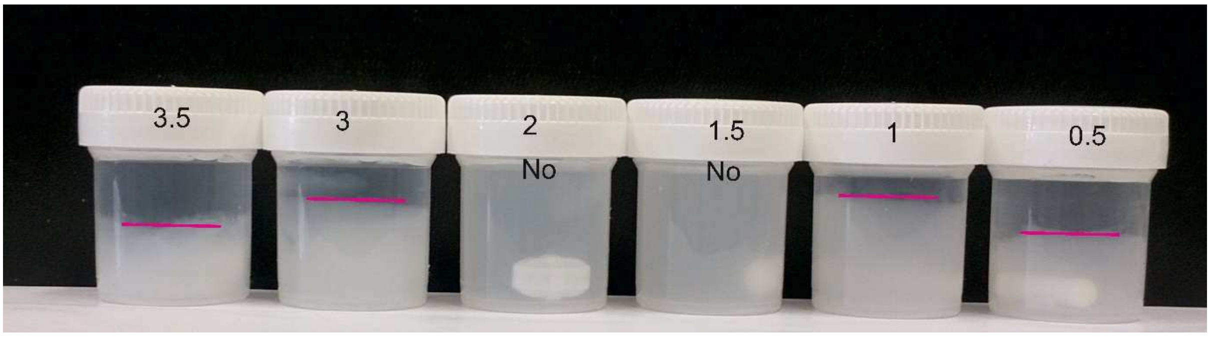

Figure 10.Phase separation after storing in the room temperature for 2 months for sample prepared with salinity ranging from 0.5 wt% to 3.5 wt%.

Salt tolerance is another consideration for the application of this kind of hybrids. Since HPAM is a polyelectrolyte, the hydrodynamic size and consequently its viscosity are sensitive to electrolyte concentration.The influences of NaCl on the effective viscosity of silica NPs, HPAM and HPAM/SiO_2hybrids were examined at 25 ^{0}C and one example is shown in Figure 9.Unlike previous results presented,[7,39] which reported that the effective viscosity of HPAM was either increased or decreased by the addition of NaCl, our work showed a non-monotonic trend. The viscosity was found to significantly increase at low salt concentrations, reaching a peak value, and then start to decline. It is also notethat adding SiO_2 nanoparticle increased the value of peak salt concentration, i.e., it increased from 1.5wt% to 2wt% in the presence of nanoparticles. Corresponding to the viscosity data, Figure 10 shows that samples with 1.5 wt% and 2 wt%NaCl also have the best stability. It is believed that the initial increase in viscosity was associated with increased inter-molecular interactions. With the increase of NaCl concentration, the polarity of the solvent increased correspondingly, which contributed to reinforced intermolecular associations of the hydrophobic groups, leading to higher viscosities. As the intermolecular associations prevail over the electrostatic screening, the viscosity of aqueousHPAM solutions increased, as also observed by.[40, 41]However the addition of Na^+ also screened the negative charges (Carboxyl groups), and resulted in a reduction in the electrostatic repulsion within polymer chains. Consequently the conformational transition of the polymer from a stretched state to a shrinkable state would decrease the hydraulic radius of the chain and the degree of polymer chain entanglement, responsible for the reduction of viscosity of polymer solution. Clearly the salt concentration affects the viscosity significantly, hence the EOR effect.Careful selection of materials that could push the peak viscosity values towards high salt concentration will be of high value, which is currently under investigation.

3.7 Viscoelastic propertiesat differentnanoparticle loadings

The viscoelastic properties for polymer solutionsare used broadly to gain understanding into the molecular structure and deformation of polymers, and itplayed a crucial role in the oil recovery process.[42-45]Theoscillatory test were performed for both HPAM/silica hybrid and pure HPAM solutions, and the storage modulus (G'), loss modulus (G''), damping factor (tan δ) and complex viscosity (η^*) are plotted as a function of angular frequency (ω) in a high salinity solution (8 wt% NaCl) at 85^{o}C. The results showed that the solutions of both pure HPAM and HPAM/silica hybrids were elastically dominated (tan δ <1) over the investigated frequency range, and became more elastic as the NP concentration increased (Figure 11b). When the particle loading was increased from 0 wt% to 0.8 wt%, G' and G'' both increased (Figure 11a). From the shapeof G' and η^*, it can be concluded that pure polymer (i.e., 0 wt% SiO_2)had a long-term relaxation timedue to none or insufficient network structure and links between macromolecules. However the ones with silica NPs showed almost no relaxation time due to the formation of stable 3D-network structure cross-linked by SiO_2NPs.Although the salinity and temperature were very high, the HPAM/silica hybrid still provided strong interactions between the cyclic components of HPAM andNP surfaces, as such the HPAM structure was strengthened, yielding large hybrid elasticities.

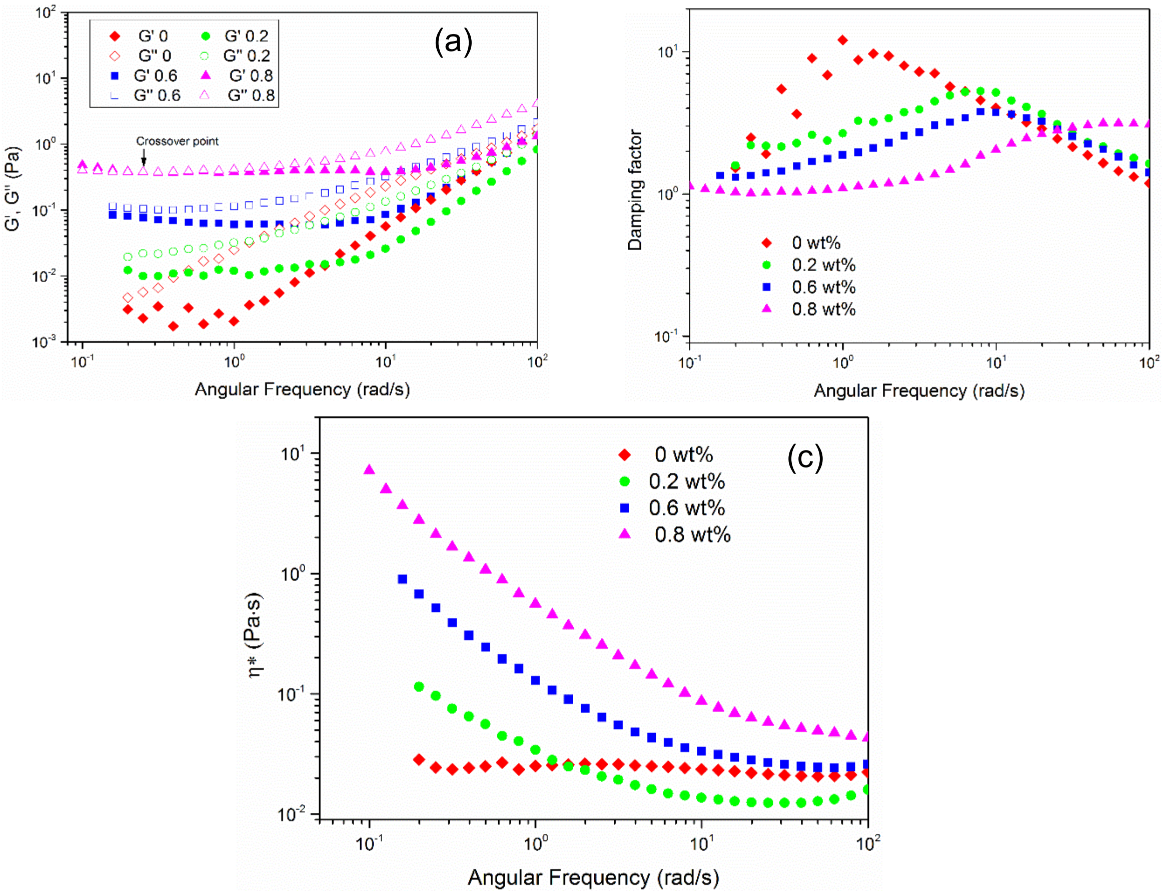

Figure 11. (a) Storage modulus (G') and loss modulus (G''), (b) damping factor (tan δ), (c) complex viscosity (η*) as a function of angular frequency (ω) for HPAM/silica hybrids(8 wt% NaCl, T = 85 °C).

4. Conclusion

This work examined the rheological properties of aqueous HAPM/SiO_2 hybrids under different salinities, temperature and aging time. The hybrid of silica nanoparticles was found to improve significantly the rheological properties of HPAM especially under high temperature and high salinities. More specifically,

- There was a critical SiO_2nanoparticle concentration existing for agiven amount of HPAM. When NP concentration is higher than this critical value, free silica

NPswould bridgeamong different polymer chains, leading to a sharp increase in the effective viscosity.

- The FT-IR spectra data confirmed that the formation of hydrogen bonds between the carbonyl groups in HPAM and the silanol functionalities on the surface of silica nanoparticles, which attributed to the improved rheological performance.
- The use of nanoparticles significantly improved the thermal stability of HPAM over a 12-day test, i.e. the effective viscosity was ~5 times higher at 0.8w% nanoparticle loading.
- The inclusion of silica nanoparticles improved HPAM's salt tolerance, and the viscosity peaked at 1.5 wt% and 2 wt% of salt concentration for HPAM and HPAM/NP hybrids respectively.
- The viscoelastic test verified a high level of cross-linkage formed by SiO_2 nanoparticle and, and the hybrids were elastic dominant at temperature up to 85 °C and salinity up to 8 wt% NaCl.

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Abstract Graphics