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EFFECTS OF SIO$_2$ NANOPARTICLES ON THE SHEAR AND EXTENSIONAL RHEOLOGY OF MECHANICALLY DEGRADED PARTIALLY HYDROLYZED POLYACRYLAMIDE SOLUTIONS

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Abstract. *Partially hydrolyzed polyacrylamide (HPAM) is the most commonly used synthetic polymer in enhanced oil recovery (EOR) activities. However, polymer molecules break down as they flow through porous media, which reduces the average molecular weight and, consequently, the viscosity of the solution and its effectiveness in displacing a high-viscosity oil phase. It has been demonstrated that incorporating silicon dioxide (SiO_2) nanoparticles (NPs) into HPAM solutions can inhibit the degradation of polymer solutions and protect the molecule backbone to prevent the breakdown of the polymer molecule during polymer flooding. This research evaluated the effect on the rheological properties of combining various concentrations of SiO_2 nanoparticles into HPAM polymer solutions of different molecular weights. The polymer solution degradation was caused by the flow through a valve at varying constriction and flow rates. Using rotational rheometry, we evaluated the changes in shear viscosity of the non-degraded and degraded solutions. In addition, we determined the viscoelastic properties using a capillary elongational breakdown rheometer (CaBER). The results showed that, at the concentrations used, the addition of nanoparticles had a negligible effect on the non-degraded solutions' extensional and shear viscosity but increased the values of extensional viscosity as a function of Hencky strain on the degraded solutions, which is an indication of reduced polymer mechanical degradation.*

Keywords: *Enhanced Oil Recovery (EOR), Nanoparticles, Polymers, Mechanical degradation, Capillary breakup elongational rheometry (CaBER), Viscoelasticity*

1. INTRODUCTION

One of the biggest challenges of the oil industry is to increase the rate of oil recovery because crude oil that has formed underground is trapped in the porous rock (Hinch, 1987) In the first phase of production, also called primary recovery, the crude oil is recovered thanks to the natural forces present in the reservoir. The pressure difference between the reservoir and the surface allows natural drainage from the crude to the surface. However, the natural forces decrease during production and become insufficient to continue extracting the crude oil. At the end of this phase, the recovery rate is, on average, around 15%. External energy must therefore be injected into the reservoir to maintain the crude oil production, this is the secondary recovery. This technique consists in injecting a fluid, generally water (water flooding) or gas (CO_2, for example), to maintain or restore the reservoir pressure and promote the flow of crude oil to the producing well. The global average rate of this recovery phase is about 35 %, then 2/3 of the oil remains trapped in the reservoir. Indeed, the characteristics of the reservoir and the fluids in place (heterogeneity of the rock, high viscosity of the crude, etc.) make the sweep of some reservoir regions impossible. In addition, the small pores of the rock trap the crude oil because of the capillary forces that dominate. Therefore, different methods have been developed to improve the recovery, all these techniques are part of what is called tertiary oil recovery or Enhanced Oil Recovery (EOR) (Figure 1).

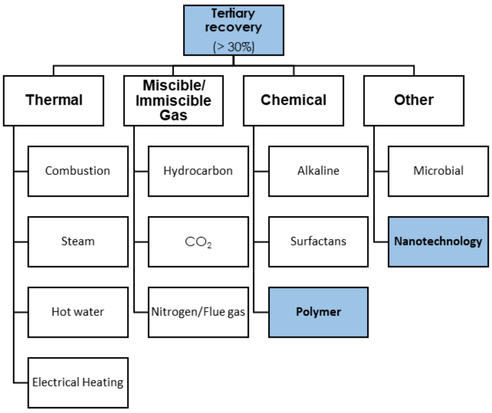


Figure 1: Flow sheet of tertiary oil recovery methods

One chemical method (Fig. 1) involves injecting polymers to increase the viscosity of the displacement fluid to better control mobility and sweep efficiency. One of the most commonly used polymers to reduce the mobility radius is partially hydrolyzed polyacrylamide (HPAM) (Scott et al., 2020).

The main challenge of using HPAM for EOR is to avoid their tendency to mechanical degradation which is an irreversible effect in the presence of high shear forces, i.e., at high pumping rates. The consequences of mechanical degradation on HPAM chains are their breakage into smaller fragments, modifying the molecular weight distribution(Zhu et al., 2014), which significantly reduces the viscosity of HPAM solutions(Dupas et al., 2012), and altering the mobility of the polymer flooding in porous media (Xiong et al., 2020) thus deteriorating the oil sweep. Polymers have been found to experience a loss of more than 65% of their initial viscosity as they flow from injector to producer wells in some field applications (Wang et al., 2006).

To address the issues affecting the potential application of HPAM in EOR, the oil and gas industry is applying nanotechnology to help improve the efficiency of polymers during flooding operations and, therefore, the overall EOR process with polymers (Hendraningrat et al., 2013). The presence of nanoparticles (NPs) in polymer solutions strengthens the intermolecular hydrophobic bonds and improves the rheological properties of the polymer. In addition, NPs have the potential to enhance the network structure of HPAM, which can improve the thermal stability of the solution (Ruiz et al., 2020) and reduce mechanical degradation (Carvalho et al., 2019).

The main objective of this study is to experimentally investigate the influence of various concentrations of SiO_2 nanoparticles in HPAM polymer solutions on the rheological properties of the fluid after mechanical degradation.

2. EXPERIMENTAL SECTION

Preparation of polymer and nanopolymer solutions

Polymer solutions

Flopaam 3130s (HPAM) a well-known oilfield commercial viscosifier with a molecular weight of 3×10^6 g/mol and a 30 % hydrolysis degree, was purchased from SNF. A stock solution of 12 g/L is prepared by adding the polymer to filtered deionized water. The water is placed on a magnetic stirrer with the vortex set at 700 rpm, and then the polymer powder is added on the side of the vortex to avoid poor dispersion during the mixing process. The mixing speed is then reduced to 125 rpm, and the polymer solution is left in agitation for 12 hours. The other polymer solutions are obtained from the dilution of the stock solution.

Nanopolymer solutions

Nanopolymer solutions are made in two steps. First, the hydrophilic fumed silica SiO_2 nanoparticles (AEROSIL® 200, Evonik) (Tab. 1) with an average primary particle size of 12 nm are dispersed in Milli-Q® water under ultrasonication (Q700, Qsonica) for 40 min at 30 % of amplitude with the following characteristics: output frequency 20 kHz, maximum power 700 W (Hutin & Carvalho, 2022). The intensity-weighted mean hydrodynamic size (Z_{av}) of the dispersion, measured by the dynamic light scattering (DLS) method, is approximately 150±50 nm. In a second step, the polymer is added to the nanofluid previously obtained by following the same protocol mentioned above for polymer solutions.

Table 1: Properties of AEROSIL® 200.

Specific surface area	175–225 m^2/g
Specific weight	2.2 g/cm^3
Heat capacity *Cp* at 50 °C	0.85 $J\cdot g^{-1}\cdot K^{-1}$
Heat of wetting of water	$-150\cdot 10^7$ $J\cdot m^{-2}$
pH value in 4% dispersion	3.7–4.5

Fluid characterization

All the rheological tests were conducted at 23 °C.

Shear Viscosity

The rheological properties of HPAM and NPs-HPAM solutions were characterized with a Discovery hybrid rheometer (DHR-3) from TA Instrument, using the cone-plate geometry (diameter 40 mm, angle 2°). The gap is preset to the standard 0.057 mm. In order to obtain steady state shear viscosity values, we used the following protocol: between 0.1 and 10 s^{-1}, 3 measurements with a ramp time of 30 s are carried out and compared, if the error between the values is greater than 3%, then up to 3 new measurements of 30 s are performed. For higher shear rates, a ramp of 120 s is performed for each measurement. The percentage of degradation was analyzed by calculating the solutions' zero viscosity (η_0) from the Williamson model (Nehdi & Rahman, 2004) directly with the TRIOS Rheological software (v5.1.1). The percentage of degradation is calculated by comparing η_0 of the degraded solutions to η_0 of the non-degraded solution.

Extensional Viscosity

A Capillary Break-up Extensional Rheometer (CaBER) manufactured by Thermo Haake was used to characterize extensional viscosity. The rheometer works by forming an unstable fluid filament, which can expand and break due to its own dynamics. A liquid bridge is formed between two cylindrical plates of a predetermined diameter in the capillary rupture test. The plates are rapidly split over a predetermined distance, thus applying uniaxial tensile stress to the sample. A strike time is given for the separation of plates. The result is a decrease in filament midpoint diameter, called D_{mid}, which is monitored over time using a sensitive laser micrometer. The apparent extensional viscosity is calculated with the following relationship:

$$\eta_E = \frac{-\sigma}{\left(\frac{dD_{mid}}{dt}\right)} \qquad (1)$$

with σ the surface tension, measured from Tracker Standard Drop Tensiometer (Teclis Scientific).

As the filament diameter decreases, the numerical differentiation of the experimental data for diameter, D, becomes increasingly noisy. To overcome this problem, the diameter data were fitted with the following empirical equation (Romero et al., 2004):

$$D(t) = \left(D_1 + \frac{k_1}{t+t_1}\right) e^{\left(-\frac{t}{3\lambda}\right)} - V_2(t-t_2) \qquad (2)$$

with D_1, t_1, k_1, V_2, and t_2 as fitting parameters.

Mechanical degradation

The experimental setup of degradation is shown in Fig 2. The polymeric solution was injected from the stainless-steel piston cylinder (~100 mL) with a high-precision HPLC pump at different flow rates (2, 5, 7, and 10 mL/min) through the constriction (micrometer valve), causing shear stress, which generated the mechanical degradation of the solution. The valve constrictions used were 0.15 and 0.25 mm. All the effluents are characterized one day after the mechanical degradation step to avoid any problem related to the flow memory of the polymer chains due to the stresses applied by the flow through the constriction (Al Hashmi et al., 2013).

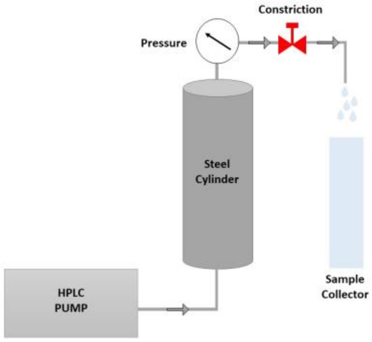


Figure 2: Experimental setup for mechanical degradation

3. RESULTS AND DISCUSSION

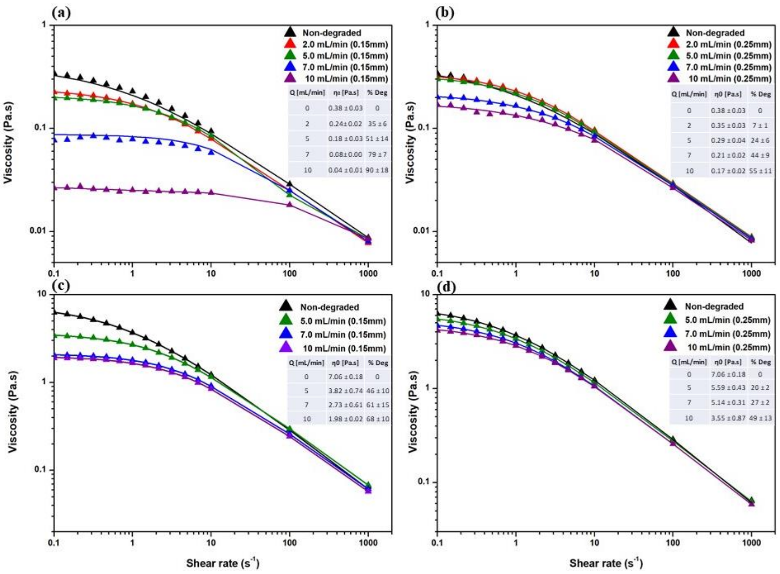
Before studying the effect of nanoparticles, it is first important to characterize the effect of the different parameters of our degradation system on the rheological behavior of polymer solutions.

Degradation of polymer solutions

In Fig. 3, it can be seen that the viscosity of polymer solutions measured at low shear rates decreases as the volume flow rate of injection through the valve increases. For example, for a polymer concentration of 1 g/L and a constriction of 0.15 mm (Fig. 3a), the degradation obtained is about 35 % for a flow rate of 2 mL/min while it is about to 90 % for a flow rate of 10 mL/min. Moreover, if the valve opening is increased to 0.25 mm (Fig. 3b), it is observed that the degradation obtained at a given volume flow rate is lower. Indeed, 55 % degradation is achieved at 10 mL/min instead of 90 % with an opening of 0.15 mm. This result confirms the observations made by Herrera (2020), who reported that the smallest diameters generate the highest percentage of degradation. This phenomenon is closely related to the high shear stresses to which the polymer is subjected. Therefore, it can be concluded that the degradation rate increases with increasing volume flow rate and decreasing valve opening.

The effect of volume flow rate and valve opening on HPAM degradation is also confirmed at higher polymer concentration. For a concentration of 12 g/L (Fig. 3c and 3d), the degradation rate (68 %) is maximum for a flow rate of 10 mL/min and a constriction of 0.15 mm. Although the viscosity at 12 g/L without degradation is 20 times that of the low concentration without degradation, the polymer is also highly degraded. The usual solution considered to counter the effect of mechanical degradation on viscosity loss is to inject higher concentrations of polymer to keep the value high enough after degradation.

Since the viscosity losses of the polymers in field conditions are greater than 30 % (al Hashmi et al., 2013), we have chosen to work with a system above this range of percentage degradation to analyze the effects of the addition of nanoparticles. The system chosen for the analysis has the following characteristics: a flow rate of 5 mL/min through a valve with a constriction of 0.25 mm.



(a)

Q [mL/min]	η0 [Pa.s]	% Deg
0	0.38 ± 0.03	0
2	0.24 ± 0.02	35 ± 6
5	0.18 ± 0.03	51 ± 14
7	0.08 ± 0.00	79 ± 7
10	0.04 ± 0.01	90 ± 18

(b)

Q [mL/min]	η0 [Pa.s]	% Deg
0	0.38 ± 0.03	0
2	0.35 ± 0.03	7 ± 1
5	0.29 ± 0.04	24 ± 6
7	0.21 ± 0.02	44 ± 9
10	0.17 ± 0.02	55 ± 11

(c)

Q [mL/min]	η0 [Pa.s]	% Deg
0	7.06 ± 0.18	0
5	3.82 ± 0.74	46 ± 10
7	2.73 ± 0.61	61 ± 15
10	1.98 ± 0.02	68 ± 10

(d)

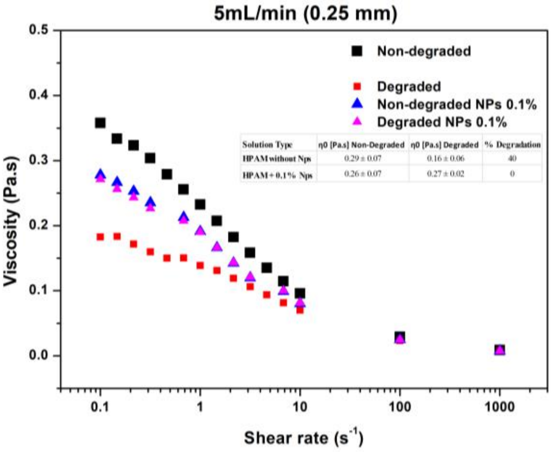
Q [mL/min]	η0 [Pa.s]	% Deg
0	7.06 ± 0.18	0
5	5.59 ± 0.43	20 ± 2
7	5.14 ± 0.31	27 ± 2
10	3.55 ± 0.87	49 ± 13

Figure 3: Shear Viscosity of non-degraded and degraded polymer solutions

Effect of nanoparticle addition on the degradation of polymer solutions

Shear Viscosity

The solutions studied were 1 g/L HPAM without and with 0.1 wt.% of silica nanoparticles. Fig.4 shows the viscosity as a function of the shear rate for the polymeric sample and the polymer-nanoparticle system. The polymer sample without nanoparticles (red) reached 40 % degradation, the drop-in viscosity occurs mainly in the region of low shear rate. The addition of 0.1 wt% of NPs prevents the viscosity drop observed for the polymer solution. Indeed, there is no difference in viscosity between the nanopolymer solution before (blue) and after degradation (pink). We can therefore conclude that the presence of nanoparticles strengthened the structure of the polymers, and thus the shear stress applied during the passage through the constriction did not mechanically degrade the polymers. These results are in agreement with the literature (Shahram Khalilinezhad et al., 2016) where it was found that dispersed silica nanoparticles improve the viscosity of the degraded solution due to the ion-dipole interaction between the nanoparticles and the cations.



Solution Type	η0 [Pa.s] Non-Degraded	η0 [Pa.s] Degraded	% Degradation
HPAM without Nps	0.29 ± 0.07	0.16 ± 0.06	40
HPAM + 0.1% Nps	0.26 ± 0.07	0.27 ± 0.02	0

Figure 4: Shear viscosity (η) plotted as a function of shear rate (γ) for the 1g/L HPAM solutions and HPAM-NPs systems

Extensional Viscosity

Shear viscosity showed interesting results with the addition of nanoparticles to the polymer solution. We now wish to confirm this by studying the extensional behavior of polymers subjected to degradation without or with nanoparticles.

In Fig. 5, for the non-degraded solution, we can see that as the Hencky deformation increases, the apparent extensional viscosity of the sample gradually increases until a constant viscosity value. According to the literature, this behavior is known as strain-hardening (Walter et al., 2019), a characteristic widely found in polymeric HPAM solutions. The degraded sample has a global behavior similar to the non-degraded one, however we can observe a drop of the apparent viscosity in extension, which confirms that there is indeed a degradation. This phenomenon is due to the stretching of the chain by the mechanical degradation resulting in its fragmentation and a loss of viscosity (Al-Shakry et al., 2019)

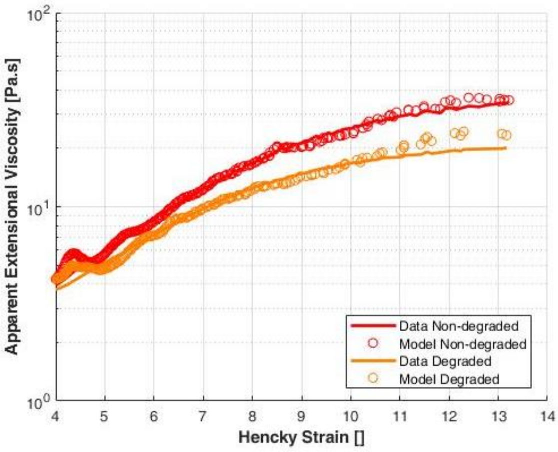


Figure 5: Apparent viscosity as a function of Hencky Strain for non-degraded and degraded polymer solutions

The addition of NPs has an effect on the apparent extensional viscosity of the non-degraded polymer. It can be observed in Fig. 6 that the nanopolymer solution (with NPs) (green) has a higher viscosity than the polymer solution (red) for Hencky strain ranging from 4 to 8. When the Hencky strain is higher than 8 there is no difference between the 2 solutions. Therefore, the presence of nanoparticles in the polymeric solution reinforces the extensional properties of polymers. These results are similar to those reported by Gupta (1999), with a strain hardening increased with the addition of nanoparticles. This behavior could be due to a competition between polymer-polymer and polymer-nanoparticle.

The degraded solution without NPs (orange) shows an important decrease in the extensional viscosity, whereas the extensional viscosity of the degraded solution with NPs (blue) is slightly altered by mechanical degradation. The addition of nanoparticles has the effect of improving the elastic properties of the polymer solution and thus enhancing their resistance to mechanical degradation.

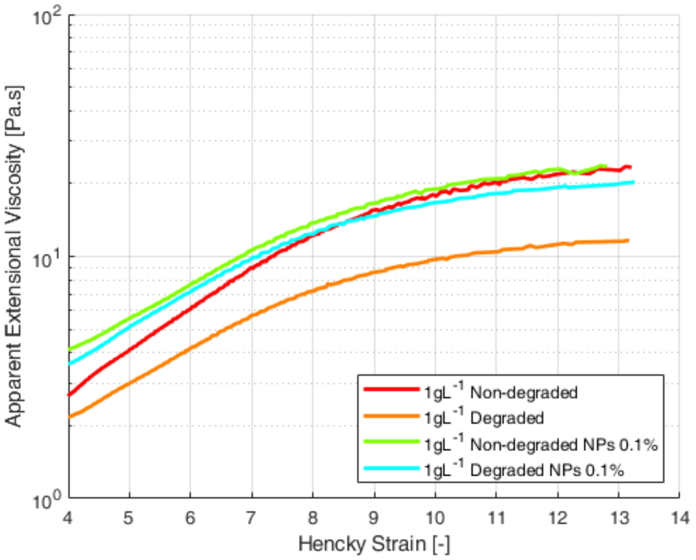


Figure 6: Effect of nanoparticles addition on the mechanical degradation of extensional viscosity of polymer solutions

4. CONCLUSIONS

The experimental results obtained confirmed the effect of mechanical degradation on the properties of HPAM polymer solutions. Significant drops in shear and extensional viscosity were measured as a function of the polymer concentration, the applied volume flow rate, and the constriction opening.

Our objective is to characterize the effect of adding nanoparticles to polymer solutions. Therefore, we have chosen degradation conditions that allow to reach at least 30 % drop in viscosity at low shear.

The characterization of shear viscosity revealed that a low concentration of nanosilica (0.1 wt%) stops the viscosity drop caused by the shear stress induced in the constriction. This effect was also confirmed by measuring the extensional viscosity, even showing an enhancement effect of the elastic properties of the polymer solution in the presence of a low concentration of nanoparticles.

In the future, we plan to study the interactions between nanoparticles and polymers by varying the concentration of each and by subjecting the nanopolymer solutions to stronger mechanical degradation.

5. ACKNOWLEDGEMENTS

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