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EFFECT OF FLOW CONDITIONS IN THE MECHANICAL DEGRADATION OF POLYMER SOLUTIONS FOR EOR IN A MICROFLUIDIC POROUS MEDIA

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Abstract. *Of the various EOR methods, polymer solution flooding is the most straightforward to apply, as it is one of the simplest and cheapest. It is known that polymer breakup occurs in porous media, so that the efficiency of EOR decreases as the viscosity of the solution. This present work investigates some effects in shear and extensional viscosity of Flopaams and evaluate their pressure behavior in microfluidic a porous media. Shear viscosity was measured using a Discovery Hybrid Rheometer (HR-3) using a cone-and-plate geometry, extensional viscosity was measured using a Haake Caber Extensional Rheometer and flow experience was conducted using a syringe pump (Harvard Apparatus) to inject the polymer solutions in a porous media micromodel (Dolomite) while a pressure transducer (Validyne) was monitoring the injection pressure. Four solutions were prepared with two different concentrations each (FPAAM 3130 2 & 4 g/l and FPAAM 3630 2 & 4 g/l), and then TiO_2 nanoparticles 0.5%wt were added on FPAAMs 3130 & 3630 4 g/l. As expected viscosity increases with molecular weight and polymer concentration, and different flow scenarios shown the degradation of the polymers in terms of shear and extensional viscosity, with higher degradation for higher flow rates imposed. Lastly, nanoparticles shown its potential to damp shear and extensional viscosity reduction of mechanically degraded solutions, being more evident in the extensional viscosity.*

Keywords: *EOR, Polymer solution, Flopaam, Polymer rheology, Nanoparticles*

1. INTRODUCTION

Enhanced oil recovery (EOR) techniques are developed to increase the oil recovery by improving the mobility ratio, for example increasing the displacing fluid viscosity. Researchers found that between different materials used in EOR processes, polymers solutions are a simple but powerful tool to improve oil recovery. Due to high shear and strain rates in a porous media (Barnes *et al.*, 1993), polymer solution viscosity decreases as well as the mobility ratio (Sobie, 1991). So, investigations of how viscosity varies in a porous media becomes necessary in order to choose the best polymeric solution. Some experiences at microscale (Wang *et al.*, 2010) suggest that there is a viscoelastic effect in the polymer flooding, so it becomes important understand how is affected not only the shear viscosity but also the extensional viscosity of a polymer after suffering degradation trough passage in a porous media. We propose a well-controlled experiment at microscale to evaluate the polymer solution degradation measured in both shear and extensional viscosity.

2. MATERIALS AND EXPERIMENTAL PROCEDURES

2.1 Samples preparation and information

Samples were prepared according to (Rezaei *et al.*, 2016) and (Yousefvanda and Jafari, 2015), 200 ml of destilated water and 0.4/0.8 g of FPAAMs 3130S and 3630S (samples from Statoil, molecular weight of 3.6MDa and 18MDa respectively with the same hydrolysis grade of 30%) were stirred about 100-150 rpm for 48 hours.

For the second part of this study, TiO_2 nanoparticles (EVONIK Industries) were added on FPAAM 3130 & 3630 4 g/l following the procedure below:

- 1) FPAAM was added to a fraction of the water and sample was slowly stirred for 48 hours.
- 2) Add TiO_2 nanoparticles (to a total of 0.5% wt.) on the other fraction of distilled water and stir for 30 min.
- 3) Add to item 2) sodium dodecyl sulfate C12H25NaO4S (Vetec Química Fina) solution (to a total of 0.12% wt.) in order to control suspension stability.

- 4) Put item 3) solution in an ultrasonic bath for 30 min.
- 5) Add item 4) solution on item 1) solution and stir for 48 h.

2.2 Experimental procedure

Classical studies have mostly been done via flooding real rock material retrieved from the well or synthetic porous media made of sand or similar materials. These porous media are difficult to make, difficult to characterize and difficult to maintain due to absorption of the polymers. We propose using a microfluidic device as a porous media micromodel particularly for the possibility to carry out experiments with minimum chemicals quantity and also because is a system easy to control and follow.

2.2.1 Shear viscosity - Hybrid Rheometer

In order to measure solutions viscosity, the experiment was performed on Discovery Hybrid Rheometer (HR-3) from TA Instruments and a cone-and-plate geometry was chosen.

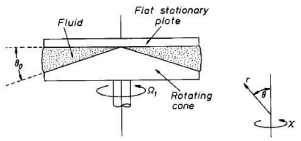


Figure 1. Cone-and-plate viscometer geometry with polar coordinates. Available from (Sobie, 1991)

With this geometry, about 0.6 ml of sample and a gap of 57 μm is needed, a flow sweep was performed with 2 min per point of equilibration time and 3% tolerance to secure sample equlibration, shear rate range used was $0.01s^{-1}$ to $300s^{-1}$ and temperature control of 22°C was set. The authors recommend, in this kind of experiment, execute at least one round trip measure ($0.01s^{-1}$ to $300s^{-1}$ to $0.01s^{-1}$), in order to evaluate if the solution experiences any mechanical degradation or thixotropic effect, since flow history must be taken into account. It's important to mention that we observed environmentally degradation on solutions, and their original characteristics are maintained for at least 2 months.

2.2.2 Extensional viscosity - CaBER

The Capillary Breakup Extensional Rheometer quickly pulls a small volume of a liquid apart to form a liquid filament. It measures the thickness of this filament (Fig. 2) or, more precisely, how quickly this filament collapses. The thickness of the collapsing filament is measured at the mid-point between the two plates. It allows for a systematic characterization exposing polymer solutions to an extensional field directly.

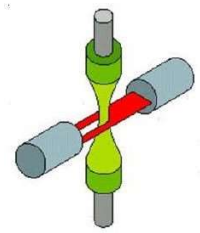


Figure 2. Simplified principle of the HAAKE CaBER 1. The liquid sample is pulled upwards to form a filament (light green).

In order to measure extensional viscosity, two other properties are needed: density and surface tension. Density was measured on Density Meter DMA 4200 M (Anton Paar), 5 ml of sample is necessary and the experiment lasted about 30 min, all samples have densities very close to 1 g/ml. Surface tension was measured on DCAT 25 (DataPhysics), using PT9 Wilhelmy Plate and 40 ml of sample, experiment lasted about 2 hours, until curve stabilization. FPAAM 3130 2 & 4 g/l and FPAAM 3630 2 & 4 g/l presented 38, 53, 48, 64 mN/m respectively. With then on hands, a small quantity of sample is placed between two 6 mm diameter of circular plates.

The principal experimental results obtained from the CaBER are the evolution of the midpoint diameter of fluid samples with time. This evolution is driven by the capillary pressure and resisted by the extensional stress in the fluid. Preliminary experiments were performed in order to choose the most suitable parameters. Firstly, final aspect ra- tio(FAR) was chose to be 5.8 and strike times varied from 25-75 ms, but in order to get a smooth curve, FAR was halfed and strike time setted up to 75 ms. It's important to mention that variations on strike time does not significantly change extensional viscosity behavior. Final parameters are highlighted on Table 1.

Table 1. Extensional viscosity measurement parameters

Parameters	Values
Temperature	Room Temperature
Initial Gap	3 mm
Final Aspect Ratio	2.9
Strike Time	75 ms

The strike time quantifies the separation velocity of top plate until final gap, while laser micrometer monitors the midpoint diameter of the thinning fluid filament as a function of time.

2.2.3 Mechanical Degradation - Syringe pump and microchip setup

Setting an arrange of syringe pump, pressure transducer and a microchip is a simple way to experimentally simulate porous media flow (Fig. 3). The microfluidic porous media (Fig. 4a) comprises a network of almost circular channels (diameter of 110 μm) arranged in a regular square lattice of 10 x 60 mm^2 area. Three different types of channels are randomly distributed in a unit square of 2 x 2 mm^2 (Fig. 4b): straight, with constrictions of 83 μm and 67 μm (Fig. 4c). The pattern of this unit square is periodically repeated throughout the device.

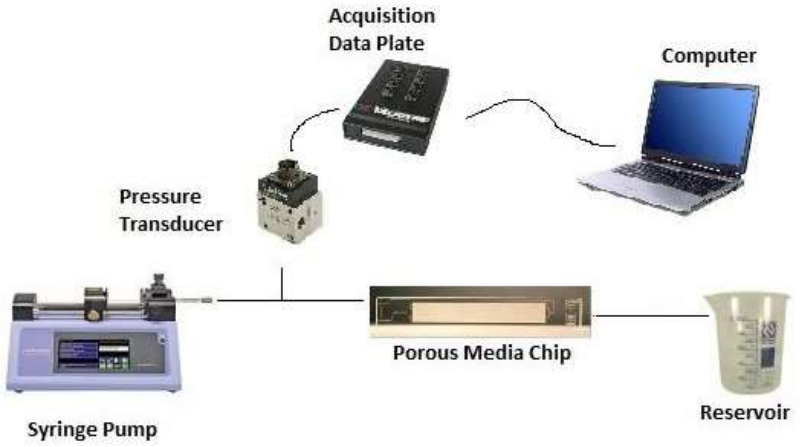
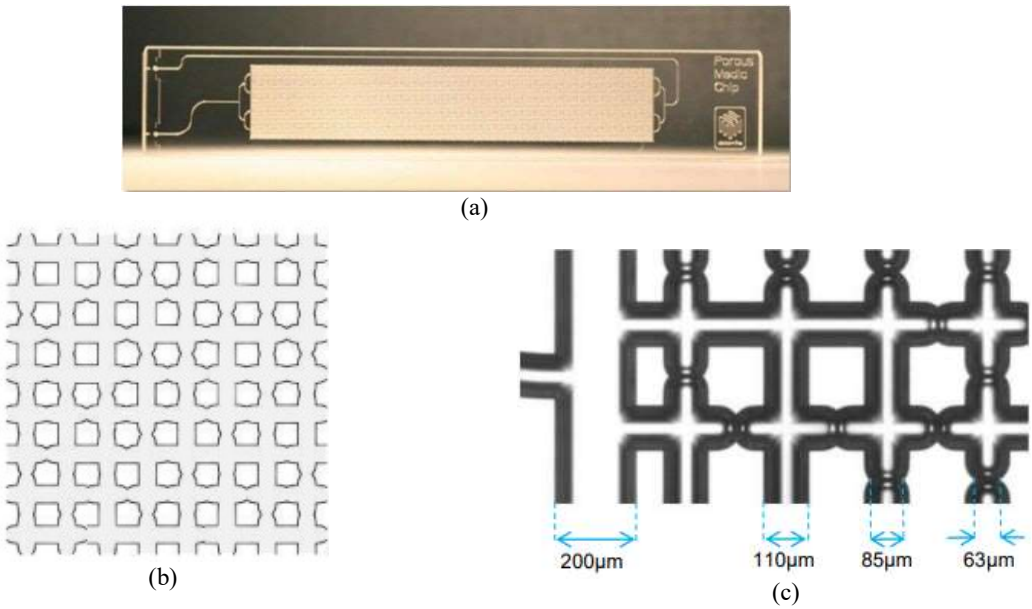


Figure 3. Typical setup for porous media flow simulation



(a) (b) (c)

Figure 4. Microfluidic model pore network used in the experiments

Other relevant information of porous media micromodel is shown in Table 2.

Table 2. Porous media chip information

Chip size [mm]	Permeability [D]	Channel Volume [µl]
90 x 15	12	38

The syringe pump controls the flow rate (Q) while transducer (Validyne) analyze pressure values (ΔP), in this work, a plate of 80 psi (maximum pressure) was established as the syringe pump stalls for higher values. The syringe model used was BD 10 ml (Becton Dickinson) and before starting to inject any solution in the microchip, a simple cleaning process was performed : (1) inject filtered ethanol until fulfilling the porous media, (2) put the microchip in the oven at 100°C for about 60min. With the porous media cleaned, the polymer solution started being injected at 0.5 ml/hr until steady state and flow rate was then increased by 0.5 ml/hr per steady state.

2.3 Results

At first, we show in Fig. 5 the shear rheology behavior of HPAM solutions that would be used in this study. As expected, higher molecular weight and higher concentration of the polymer results in higher viscosity. All the solutions show a shear thinning behavior.

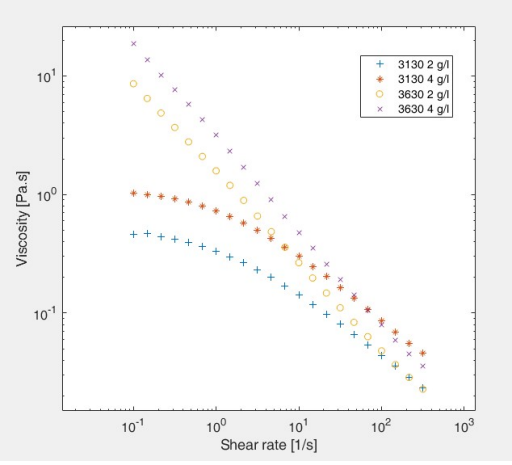


Figure 5. Shear viscosity for FPAAM 3130S and 3630S

Mechanical degradation on the microfluidic porous media was performed for 2 g/l and 4g/l of both polymer solutions, pressure behavior varying flow rate is shown in Figure 6 and an example of steady state pressure drop is summarized in Table 3. For every experiment steady state step, we collected a sample to perform shear and extensional rheology characterization of the degraded polymer.

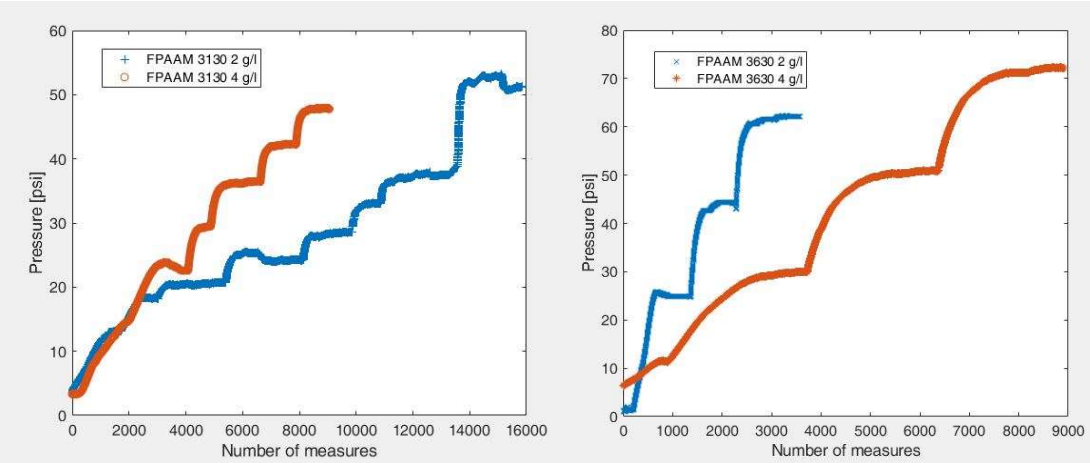


Figure 6. Pressure gradient vs. Number of measures for FPAAM 3130 2 g/l & 4 g/l (a) and FPAAM 3630 2 g/l & 4 g/l (b)

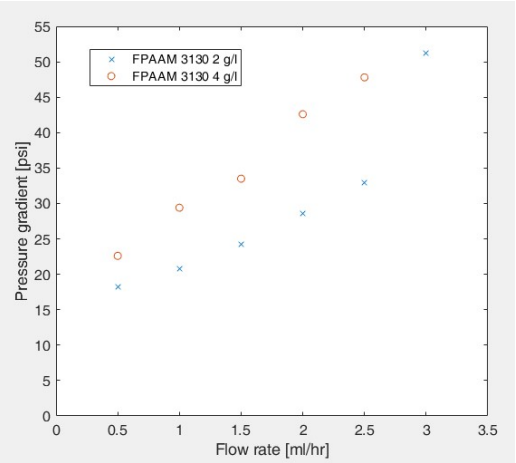
Table 3. Input flow rate and stabilized pressure

Flow Rate [ml/hr]	FPAAM 3130 2 g/l	FPAAM 3130 4 g/l	FPAAM 3630 2 g/l	FPAAM 3630 4 g/l
	Pressure [psi]			
0.5	18.2	22.6	25.3	30
1	20.8	29.4	44.3	50.8
1.5	24.2	33.5	61.5	72.3
2	28.6	42.6		
2.5	33	47.8		
3	51.2			

A preliminary analyses of Table 3, shows conformity to Darcy´s Law (Equation 1), pressure gradient shows a linear behavior against flow rate except for the highest flow rate for the FPAAM 3130 2 g/l where a jump in the pressure drop is noticed (Fig. 7).

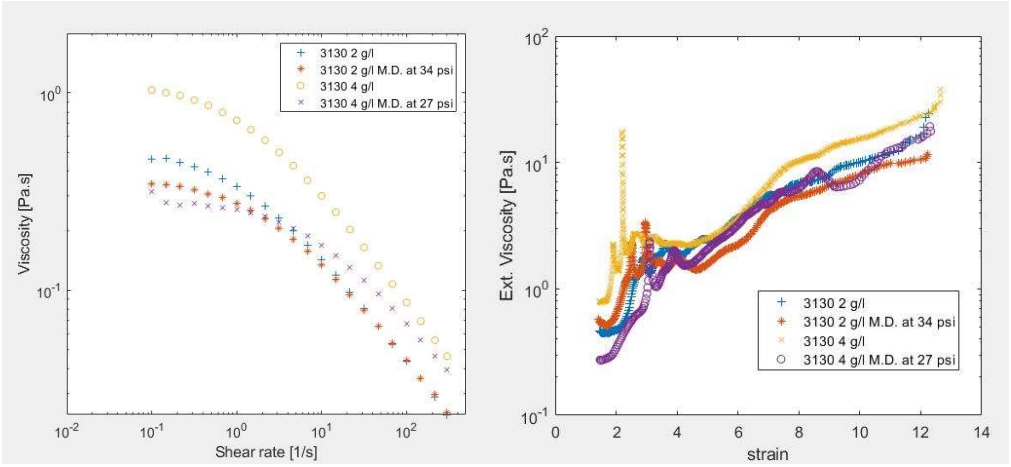
$$\Delta P = \frac{\eta Q L}{kA} \tag{1}$$

In all cases the most viscous solution (varying concentration or molecular weight of the polymer) exhibits higher pressure gradient at the same flow rate. With these results we demonstrate that this experimental setup, besides being practical because the pressure is easily controlled and acquired, is a good approximation to evaluate flow in porous media. With mechanically degraded samples in hands, we were able to compare those new values with the ones measured with the original solutions and evaluate if the imposed pressure is high enough to cause considerable changes in the polymer solution.



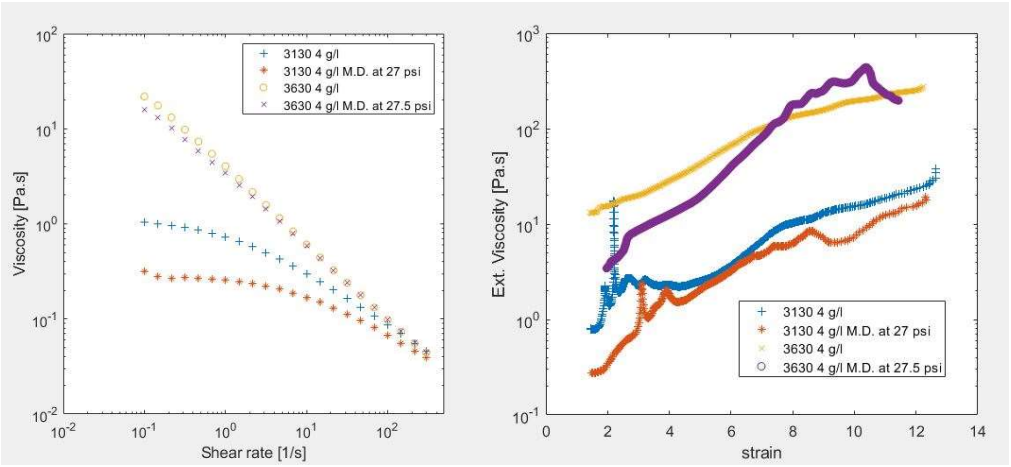
F igure 7. Presure gradient vs. Flow rate for FPAAM 3130 2 g/l (a) and FPAAM 3130 4 g/l (b)

A closer look in the polymer solutions rheology after the mechanical degradation for some examples (even at low pressure gradients) confirms, without any doubt, the several effect of the passage through the porous media on the solutions characteristics. Figure 8a shows that the viscosity reduction was much higher for concentrated solutions of low molecular weight polymers if we compare it under the same pressure gradient. Additionally, Fig. 9a shows that using the same concentration of polymer, viscosity reduction is also higher for the lower molecular weight polymer. In conclusion, more concentrated solutions of low weight polymers had a higher shear viscosity reduction.



(a) (b)

Figure 8. Effect of mechanical degradation on polymer solution rheology varying polymer concentration



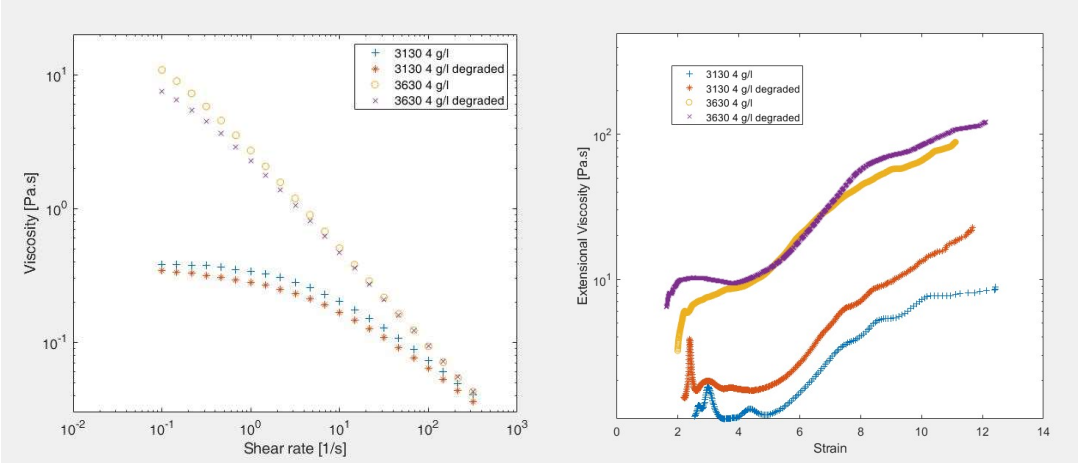
(a) (b)

Figure 9. Effect of mechanical degradation on polymer solution rheology varying polymer molecular weight

In the other hand, if we compare Fig. 8b and Fig. 9b, extensional viscosity of systems showed a more important reduction for the high molecular weight polymer on lower strains. Thus we have a competitive effect between shear viscosity reduction (more important for low molecular weight polymers) and extensional viscosity reduction (more important for high molecular weight polymers).

After this initial conclusions, we passed to the second part of our work, adding TiO_2 nanoparticles to selected polymers solutions and study its influence on the reduction of shear and extensional viscosity. It´s important to mention that (Ehtesabi *et al.*, 2014) did not reveal considerable change neither in shear viscosity of the fluid nor the interfacial tension of the fluid system with the simple addition of small quantities of TiO_2 nanoparticles, this information was confirmed by additional experiments by the authors.

Figure 10a and Fig. 10b shows the results with the addition of nanoparticles, this experiments are still under development but it's clear for the first series of tests (Fig. 10a), that the shear viscosity reduction is drastically reduced, considering that both experiments were conducted with a pressure gradient of 50psi.



(a) (b)

Figure 10. Effect of nanoparticles addition on the mechanical degradation on shear and extensional viscosity of polymer solutions varying polymer molecular weight. Pressure gradient of 50psi

We can also see on Fig. 10b that the behavior of extensional viscosity is qualitatively different from that of the shear viscosity. Often highly elastic polymers solutions that possess a viscosity that decreases monotonically in shear, exhibit an extensional viscosity that increases dramatically with strain (tension-thickening), this was noticed by Khandavalli and Rothsteina (2014). Extensional viscosity of degraded solutions showed to be a bit higher than the original ones, this behavior may be explained by the stiffness of nanoparticles on the reconstructed polymeric chains.

3. CONCLUSIONS

From the first part of the experiment, it can be stated that molecular weight of polymer solutions has a high impact in mechanically degraded shear and extensional viscosity reduction, being more evident the shear viscosity reduction of low molecular weight polymer solutions. Nanoparticles addition demonstrated to be efficient on retaining original properties of most the polymeric solutions, even for considerable pressure gradients, it even reverses the trend in extensional viscosity that increases after passing through the porous medium instead of decreasing. For further studies, the investigation of retention due and adsorption after the addition of nanoparticles should be considered, as well as the effect of nanoparticles concentration on shear and extensional viscosity.

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