

Rheological properties of polymer micro-gel dispersions

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Abstract: The influence of swelling time, temperature, NaCl concentration and polymer micro-gel concentration on rheological properties of polymer micro-gel dispersions was studied by using a HAAKE rheometer. The results showed that with increasing swelling time and NaCl concentration, the polymer micro-gel dispersions changed from a shear-thickening fluid to a Newtonian fluid. The polymer micro-gel dispersion show shear-thinning in non-saline water. At higher swelling temperature, the time of the polymer micro-gel dispersion showing shear-thickening was shorter. With increasing polymer micro-gel concentration, the dispersion changed from shear-thickening to shear-thinning.

Key words: Polymer micro-gel, rheological property, shear-thickening, shear-thinning

1 Introduction

In our previous work we have developed a linked polymer solution (LPS), which is used for in-depth profile control of oil-bearing reservoirs with water flooding (Dong et al, 2004; Li et al, 2000; 2004; Lin et al, 2004; 2007; 2008; Luo et al, 2006; Sun et al, 2005). Based on the research of LPS, polymer micro-gel dispersion has been developed in recent years in our laboratory for in-depth profile control of oil-bearing reservoirs with high salinity formation water and high temperature (Han et al, 2006; 2008; Ma et al, 2006; Wang and xiao, 2008; Zong et al, 2007). The size of the polymer micro-gel is about 50-300 nm and the polymer micro-gel particles are hydrated and swollen in water during injection of the dispersions. As the polymer micro-gel dispersion is injected into oil-bearing reservoirs the rheological properties and the flow property of the dispersions affect the profile control and the enhanced oil recovery (EOR) significantly. In this paper we studied the influence of polymer micro-gel concentration, salinity of water, reservoir temperature and swelling time on rheological property of the polymer micro-gel dispersions.

2 Experimental

2.1 Materials and preparation of samples

The polymer micro-gel is a water/oil (W/O) micro-emulsion produced by Shengli-fanghua Company Ltd., China, with a content of the polymer micro-gel in the micro-emulsion of 20%. The water used in the experiments was deionized water passed through a 0.22 μm filter before use. The NaCl (GC >99.5%) used was produced by Beijing Shuanghuan Chemical Factory, China. The polymer micro-

gel dispersions were prepared by mixing the polymer micro-gel micro-emulsion with different concentrations of NaCl solution. Swelling of the polymer micro-gel particles was carried out at 40 °C and 90 °C, respectively.

2.2 Measurement of rheological parameters

The rheological parameters of the polymer micro-gel dispersion were measured by using HAAKE RS 600 rheometer made by HAAKE company (German) at 30 °C after the samples were placed in the rheometer for 20 minutes.

For pseudoplastic (shear-thinning) and dilatant (shear-thickening) fluids, the relationship between shear stress (σ_s) and shear rate ($\dot{\gamma}$) is expressed by a power law relation as follows:

$$\sigma_s = K (\dot{\gamma})^n \quad (1)$$

where K is the consistency coefficient, and n is the non-Newtonian index. The larger the K , the more viscous the fluid is. For the pseudoplastic fluid, $n < 1$, for the dilatant fluid, $n > 1$, and for the Newtonian fluid, $n = 1$. Taking logarithms of equation (1) gives:

$$\lg \sigma_s = \lg K + n \lg (\dot{\gamma}) \quad (2)$$

The curve of the logarithms of the shear stress (σ_s) versus the logarithms of the shear rates is linear with a slope of n and an intercept of K . The rheological property of the polymer solutions fits the power law model (Lei et al, 1994).

3 Results and discussion

3.1 Swelling time

Fig. 1 shows the viscosity vs. the shear rate of the polymer micro-gel dispersion with 100 mg·kg⁻¹ polymer micro-gel and

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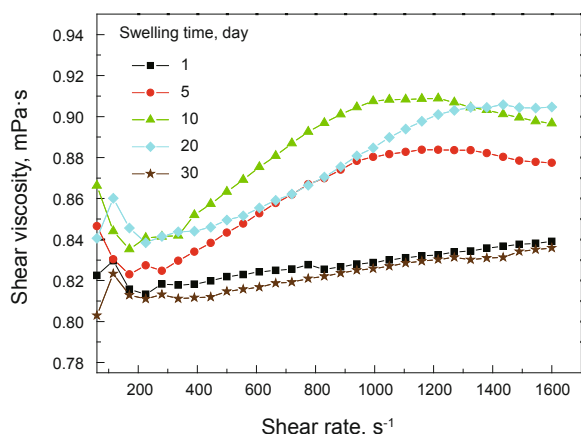


Fig. 1 Viscosity vs. shear rate of the polymer micro-gel dispersion with different swelling times

2,000 mg·kg⁻¹ NaCl, for different swelling times at 40 °C. The results showed that in the shear rates range of 225-1,215 s⁻¹, with the increase of the swelling time, the dispersion changed from shear-thickening to Newtonian fluid.

According to the order-disorder transition theory (Hoffman, 1972; 1982) and the clustering theory (Brady and Bossis, 1985) (shown in Fig. 2), when the dispersion flows at very low shear rates, the polymer micro-gel particles have to move around each other or “bounce off” each other for overall flow to occur. On the other hand, the distribution of the particles remains essentially undisturbed because the Brownian motion dominates the shear motion and restores the randomness of the rest-state distribution. At high shear

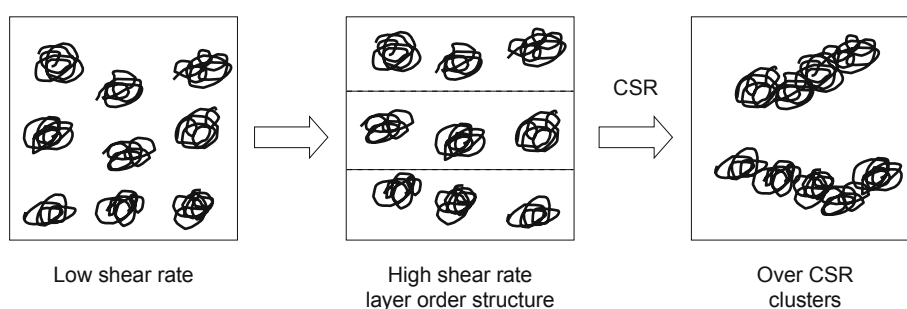


Fig. 2 Shear-thickening process of polymer micro-gel dispersion

The process of the polymer dissolving in water includes two stages. The first stage is that water molecules diffuse into the polymer particles and the particles swell. The second stage is that the swollen particles dissolve in water and become macromolecular coils. Like the polymer particles, when the time of the polymer micro-gel particles swelling in water is long enough, the particles can dissolve and form macromolecular coils in water. In this case, the volume fraction of the polymer coils is great and the polymer micro-gel particles or polymer coils can deform easily. On the other hand, part of the polymer segments of the polymer coils and the cross-linking points of the polymer micro-gel could be broken due to oxygen degradation of the polymer. Therefore,

rates, the imposed velocity gradient induces an orientation of the polymer micro-gel particles, which could not be restored by the Brownian motion, and the particles form layer-ordered structures. The particles are oriented and move in their own layers independently (Barnes et al, 1989), so the dispersion is shear-thinning. At even higher shear rates, the shear stress makes the dispersion change from a layer-ordered structure to a disordered structure (of clusters) and the dispersion is shear-thickening. The shear rate that makes the dispersion change from shear-thinning to shear-thickening is defined as the critical shear rate (CSR) (Sun et al, 2004).

When the swelling time was 1 day, the polymer micro-gel particles were rigid and could not deform easily. At this case, if shear rate was higher than the CSR, the clusters of the particles could not be formed easily, and the dispersion was just slight shear-thickening. With the increase of the swelling time (5-20 days), more water entered the polymer micro-gel particles, the hydration degree and apparent size of the particles increased. As a result, the volume fraction of the particles increased and the particles deformed more easily. In this case, if the shear rate was higher than the CSR, the polymer micro-gel dispersion changed from a layer-ordered structure to a disordered structure, and at the same time, the intermolecular forces or hydrogen bonds which exist between carbonamide groups of the polymer and water molecules made the particles form clusters. Therefore, the dispersions are shear-thickening. With the shear rate increasing (>1,215 s⁻¹), the shear stress not only caused the micro-gels to form new clusters but also broke the formed clusters. At this time, the dispersions showed different shear-thinning properties at different swelling times.

the dispersion that had swollen for 30 days is close to a Newtonian fluid, neither shear-thickening nor shear-thinning.

3.2 NaCl concentration

Fig. 3 shows the viscosity vs. the shear rate of the polymer micro-gel dispersion swollen 10 days at 40 °C, with a polymer micro-gel concentration of 100 mg·kg⁻¹, at different NaCl concentrations.

The results showed that the rheological properties of the polymer micro-gel dispersion were significantly influenced by the salinity. In the shear rate range of 5 s⁻¹ to 1,600 s⁻¹, when the NaCl concentration was 0-5,000 mg·kg⁻¹, the apparent viscosity of the dispersions decreased with an increase of

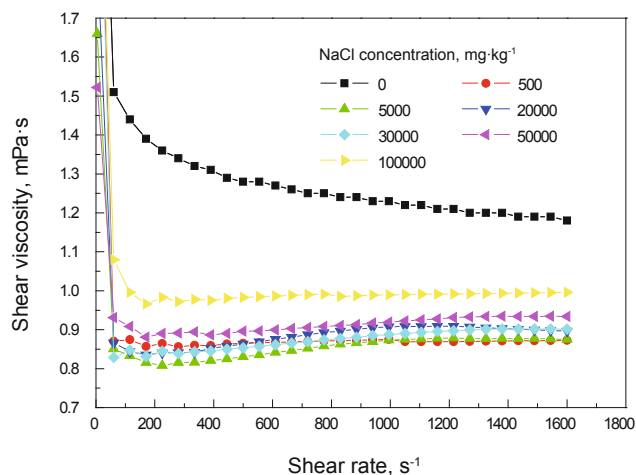


Fig. 3 Viscosity curves of polymer micro-gel dispersion at different NaCl concentrations

NaCl concentration. When the NaCl concentration was greater than $20,000 \text{ mg}\cdot\text{kg}^{-1}$, the apparent viscosity of the dispersions increased with an increase of NaCl concentration.

The polymer micro-gel dispersion in non-saline water was shear-thinning and its apparent viscosity was the largest in comparison with the other dispersions with the same micro-gel concentration. In the shear rate range of 60 s^{-1} to $1,600 \text{ s}^{-1}$, n was 0.93. In the same shear rate range, the dispersion with low NaCl concentration of $500 \text{ mg}\cdot\text{kg}^{-1}$ was close to a Newtonian fluid, that is, its apparent viscosity almost remains constant with n being 1.01. In the NaCl concentration range of $5,000$ to $20,000 \text{ mg}\cdot\text{kg}^{-1}$, the dispersion showed different rheological properties: In the low shear rate range (60 - 170 s^{-1}), the dispersion was shear-thinning; In the high shear rate range (390 - $1,215 \text{ s}^{-1}$), the dispersion was shear-thickening. For the dispersion with $5,000 \text{ mg}\cdot\text{kg}^{-1}$ NaCl, n was 1.07; for the dispersion with $20,000 \text{ mg}\cdot\text{kg}^{-1}$ NaCl, n was 1.06; and for the dispersion with $100,000 \text{ mg}\cdot\text{kg}^{-1}$ NaCl, n was 1.01. These results showed that, in the NaCl concentration range of $5,000$ - $100,000 \text{ mg}\cdot\text{kg}^{-1}$, with the increase of NaCl concentration, the shear-thickening degree of the dispersion decreased.

In the low NaCl concentration range of 0 - $500 \text{ mg}\cdot\text{kg}^{-1}$, the ionic strength was small, and the apparent size of the hydrated micro-gels was large, hence the hydrated micro-gels were stretched and oriented more easily by shear stress (Lei et al, 1994). Meanwhile, the thick electrical double layer and hydration layer of the micro-gels protected the micro-gels against aggregating under the shear stress. Therefore, the dispersion was shear-thinning.

In the NaCl concentration range of $5,000 \text{ mg}\cdot\text{kg}^{-1}$ to $20,000 \text{ mg}\cdot\text{kg}^{-1}$, the ionic strength became large in comparison with that in the NaCl concentration of 0 - $500 \text{ mg}\cdot\text{kg}^{-1}$, and the electrical double layer and hydration layer of the micro-gels became thin. The apparent size of the hydrated micro-gel was small and the micro-gels were firm, hence it was more difficult for the micro-gels to deform. The volume fraction of the micro-gels in the dispersion decreased, as a result, the micro-gels aggregated to form temporary clusters under the action of shear stress, and the dispersions are shear-thickening.

In NaCl concentrations above $20,000 \text{ mg}\cdot\text{kg}^{-1}$ and up to $100,000 \text{ mg}\cdot\text{kg}^{-1}$, the ionic strength was much larger, and the electrical double layer and hydration layer of the micro-gels became thinner. At this case, the micro-gels cannot be dispersed very well and were aggregated easily. The apparent size of the aggregated micro-gels (clusters), and the apparent viscosity of the dispersions, was greater.

3.3 Swelling temperature

Table 1 shows the non-Newtonian index n of the polymer micro-gel dispersion, with a NaCl concentration of $2,000 \text{ mg}\cdot\text{kg}^{-1}$ and a polymer micro-gel concentration of $100 \text{ mg}\cdot\text{kg}^{-1}$, at different swelling times at $40 \text{ }^{\circ}\text{C}$ and $90 \text{ }^{\circ}\text{C}$. The shear rates in the experiments were measured in the range of 500 s^{-1} to $1,995 \text{ s}^{-1}$.

The results showed that at the beginning of the swelling, the dispersion which was swelled at $40 \text{ }^{\circ}\text{C}$ is slightly shear-thickening. The n of the dispersion that had swollen 1 day was 1.02. With increasing swelling time, the degree of the shear-thickening of the dispersion increased firstly and then decreased. The n of the dispersion that had swollen 10 days was 1.06, and then decreased to 1.02 after the dispersion had swollen 20 days.

Table 1 The n of the polymer micro-gel dispersion at different swelling times

Swelling temperature $^{\circ}\text{C}$	n at different swelling times					
	1d	5d	10d	15d	20d	30d
40	1.02	1.04	1.06	1.05	1.02	1.02
90	1.02	1.09	1.01	1.02	1.02	1.01

At the beginning of the swelling, the $90 \text{ }^{\circ}\text{C}$ polymer micro-gel dispersion was slightly shear-thickening too. The n of the dispersion that had swollen for 1 day was 1.02. With increasing swelling time, the rapidity of the shear-thickening of the dispersion was much greater at $90 \text{ }^{\circ}\text{C}$ than at $40 \text{ }^{\circ}\text{C}$. The n of the dispersion that had swollen 5 days increased up to the maximum 1.09 and then decreased rapidly. After the dispersion had swollen 10 days, the dispersion was close to a Newton fluid.

The experimental results showed that the rheological property of the dispersions that swelled at different temperatures was different. The rapidity of the shear-thickening of the dispersion swelled at $90 \text{ }^{\circ}\text{C}$ was faster than that at $40 \text{ }^{\circ}\text{C}$, and the time achieving the equilibrium swelling is shorter at $90 \text{ }^{\circ}\text{C}$ than at $40 \text{ }^{\circ}\text{C}$. The time when the dispersion showed the highest shear-thickening was 5 days at $90 \text{ }^{\circ}\text{C}$, and 10 days at $40 \text{ }^{\circ}\text{C}$.

3.4 Micro-gel concentration

Fig. 4 shows the viscosity vs. the shear rate of the polymer micro-gel dispersions swollen 10 days at $40 \text{ }^{\circ}\text{C}$, with $2,000 \text{ mg}\cdot\text{kg}^{-1}$ NaCl, at different micro-gel concentrations. The n of the dispersions are shown in Table 2.

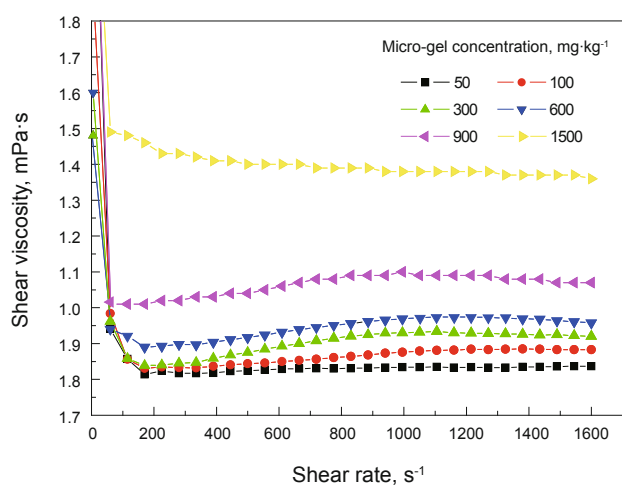
The results showed that with the increase of the polymer micro-gel concentration, the apparent viscosity of the

Table 2 The n of polymer micro-gel dispersions with different micro-gel concentration at different shear rate ranges

Micro-gel concentration $\text{mg}\cdot\text{kg}^{-1}$	n at different shear rate ranges			
	60-170 s^{-1}	335-1160 s^{-1}	1380-1600 s^{-1}	CSR, s^{-1}
50	0.86	1.01	1.01	170
100	0.88	1.06	0.99	335
300	0.94	1.08	0.94	170
600	0.97	1.08	0.93	170
900	1.02	1.05	0.94	995
1500	0.95	0.97	0.97	335

dispersions increased.

In the low shear rate range (60-170 s^{-1}), the polymer micro-gel dispersions with low micro-gel concentration were shear-thinning. With the increase of the polymer micro-gel concentration, the shear-thinning property of the dispersions was weakened. With the polymer micro-gel concentration of 900 $\text{mg}\cdot\text{kg}^{-1}$, the dispersion was shear-thickening. With the polymer micro-gel concentration of 1,500 $\text{mg}\cdot\text{kg}^{-1}$, the dispersion was shear-thinning again.

**Fig. 4** Viscosity curves of polymer micro-gel dispersions with different micro-gel concentrations

In the high shear rate range (335-1,600 s^{-1}), with the increase of the polymer micro-gel concentration the dispersions showed more evident shear-thickening. For the dispersion with 50 $\text{mg}\cdot\text{kg}^{-1}$ micro-gel, the non-Newton index n was 1.01; For the dispersions with 300 $\text{mg}\cdot\text{kg}^{-1}$ and 600 $\text{mg}\cdot\text{kg}^{-1}$ micro-gel, the maximum value of the n was 1.08. With the polymer micro-gel concentration of 900 $\text{mg}\cdot\text{kg}^{-1}$, the shear-thickening property of the dispersion was weakened, and the n of the dispersion was 1.05. When the polymer micro-gel concentration was increased further, the dispersions became shear-thinning. For example, the n of the dispersion with 1,500 $\text{mg}\cdot\text{kg}^{-1}$ micro-gel was 0.97.

In the even higher shear rate range (1,380-1,600 s^{-1}), the apparent viscosity of the polymer micro-gel dispersion with

low micro-gel concentration (50 $\text{mg}\cdot\text{kg}^{-1}$) did not vary with shear rate, and the dispersion was close to Newtonian fluid. The dispersions with higher micro-gel concentration (100-500 $\text{mg}\cdot\text{kg}^{-1}$) were shear-thinning.

The results showed that the rheological property of the dispersions with different micro-gel concentration was different. In the low shear-rate range (60-170 s^{-1}), the low concentration micro-gels dispersed well in the dispersions, and the hydrated micro-gels were stretched and oriented easily by shear stress. In this case, the polymer micro-gel dispersion was shear-thinning. With the increase of the polymer micro-gel concentration, the micro-gels easily overlapped each other, and the shear-thinning property of the dispersion was weakened. With the polymer micro-gel concentration of 900 $\text{mg}\cdot\text{kg}^{-1}$, the dispersion was shear-thickening. When the polymer micro-gel concentration was large enough (1,500 $\text{mg}\cdot\text{kg}^{-1}$), the micro-gels overlapped and aggregated to form network structures. The micro-gels with the network structure can entirely move easily, so the dispersion was shear-thinning again.

In the high shear-rate range (335-1,160 s^{-1}), when shear rate increased above CSR, the micro-gels in the dispersion changed from a layer order structure to a disordered structure and can form clusters easily. With the increase of the polymer micro-gel concentration, the volume fraction of the micro-gels in the dispersion increased too. Therefore, the shear-thickening property of the dispersions was enhanced. When the polymer micro-gel concentration increased up to 900 $\text{mg}\cdot\text{kg}^{-1}$, the micro-gels could overlap each other to form network structures easily and resulting in a flow as a body. So the shear-thickening property of the dispersion weakened. When the polymer micro-gel concentration was 1,500 $\text{mg}\cdot\text{kg}^{-1}$, the dispersion was shear-thinning.

In the even higher shear rate range (1,380-1,600 s^{-1}), the shear stress not only caused the micro-gels to form new clusters but also broke the formed clusters. At the low micro-gel concentration (50 $\text{mg}\cdot\text{kg}^{-1}$), the number of the polymer micro-gel particles was small, and the volume fraction of the micro-gels in the dispersion was not great. Therefore, the high shear rate could not affect the rheological property of the polymer micro-gel dispersion significantly. With the increase of the polymer micro-gel concentration, the volume fraction of the micro-gels in the dispersion increased too,

and the formed network structure of the micro-gels could be broken easily by the high shear rate. So the polymer micro-gel dispersions showed different shear-thinning properties.

4 Conclusions

This research shows that the rheological properties of the polymer micro-gel dispersion is complicated. With the increase of swelling time and NaCl concentration, the polymer micro-gel dispersion changes from shear-thickening to a Newtonian liquid. At high swelling temperature, the time of the dispersion showing shear-thickening is shorter than that at low swelling temperature. With the increase of polymer micro-gel concentration, the polymer micro-gel dispersion changes from shear-thickening to shear-thinning.

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