Experimental research on anti-ageing property of temperature-resistant polymer solution

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Abstract. In order to research the anti-ageing property of temperature-resistant polymer solution at high temperature, the temperature-resistant polymer solution viscoelastic modulus are measured by type RS6000 rheometer with the temperature of 50℃, 95℃ and the concentration of 1000mg/L, 1500mg/L, 2000mg/L. Then the viscoelastic modulus are measured after ageing 0~90 days at 50℃ and 95℃. The elastic modulus, viscous modulus, composite viscosity and first normal stress difference of temperature-resistant polymer solution improve with the rise of concentration, and decline with rise of temperature. After ageing 90 days at 50℃, viscoelastic modulus retention rate ranges from 85%~93%. After ageing 90 days at 95℃, viscoelastic modulus retention rate ranges from 62%~85%. The result shows that the temperature-resistant polymer is of good anti-ageing property and temperature-resistant property.

1. Preface
It is very early to study the fluidic characteristic of polymer solution in the pore of reservoir, and notice the viscoelastic property of polymer solution in porous media ⁴⁻¹⁻². In recent years, with the further research of polymer flooding mechanism, the effect of viscoelasticity on oil displacement efficiency has aroused people’s concern ⁵⁻¹⁻⁶. The main factors for improving the efficiency of the microcosmic displacement of the core are the elasticity of the fluid ⁴⁻¹⁻⁶, which is pointed out by Wang Demin. Guo Shangping thinks that polymer solution rise oil displacement efficiency due to the viscoelasticity of polymer solution ⁶⁻¹⁻⁶. Han Xianqing believes that the viscoelasticity of polymer solution is beneficial to displace the residual oil in the pore throat ⁷⁻¹⁻⁷. These results show that the viscoelasticity of polymer solution has significant influence on efficiency of oil displacement. However, with the rise of temperature and ageing time, the viscosity and elasticity of conventional polymer solution are decreased by thermal degradation and oxidative degradation, which limits its application of high temperature reservoir.

In this paper, the temperature-resistant (TR) polymer solution is aged 90 days at 50 ℃ and 95 ℃.Then the retention rates of the viscoelastic parameters are measured by rheometer. The anti-ageing property and high temperature-resistant property of TR polymer are evaluated to guide the polymer flooding technology in high temperature reservoir.

2. Experimental method
2.1. Experimental preparation

(1) The polymer mother liquor is produced with polymer molecule and oilfield sewage, which concentration is 5000 mg/L. In order to guarantee the polymer molecular chains are fully hydrated and stretched, the polymer mother liquor is stirred for 3 hours. Then the concentration of polymer mother liquor is diluted into 1000mg/L, 1500mg/L, 2000mg/L.

(2) Put the polymer solution into container by using filter membrane. Then the polymer solution is filtrated into a container.

(3) The filtrated polymer solution is vacuumed by vacuum pump for 6 hours.

(4) The deoxidated polymer solution is placed in incubator ageing for 10 days ~ 90 days at 50℃ and 95℃ respectively.

2.2. Experimental condition

The viscoelastic modulus of polymer solution is measured by type RS6000 rheometer while the angular frequency ranges from 0.01~100 1/s. And viscoelastic modulus of polymer solution is measured at temperature of 50℃ and 95℃ respectively.

3. The change law of polymer solution viscoelastic modulus

3.1. The relation of viscoelastic modulus with concentration and temperature

The change curves of elastic modulus $G'$ and viscous modulus $G''$ with angular frequency are shown in figure 1 and figure 2. With the rise of concentration and angular frequency, the corresponding elastic modulus $G'$ and viscous modulus $G''$ rise respectively. Because with the concentration getting higher, the voluble acting force between polymer molecule and molecular chains gets stronger, what leads to better viscoelasticity. The TR polymer solution of 50℃ shows better viscoelasticity compared with that of 95℃.Because with the temperature getting higher, the hydrolysis degree of polymer molecule and molecular chains gets more intense in order to maintain minimum energy state. The elastic modulus and viscous modulus of TR polymer solution decrease slowly with the increasing temperature. This change is similar to viscosity-temperature curve of polymer solution.

3.2. The relation of viscoelastic modulus with ageing time and temperature

The elastic modulus and viscous modulus are measured by rheometer after ageing 15 days, 30 days, 60 days and 90 days respectively. The change curves of elastic modulus $G'$ and viscous modulus $G''$ with the ageing time at 50℃ and 95℃ are shown in figure 3 and figure 4. With the rise of ageing time, elastic modulus and viscous modulus of polymer solution go through three processes. The $G'$ and $G''$
retention rates of TR polymer solution decline firstly, then rise rapidly and finally decline slowly. The \( G' \) and \( G'' \) retention rates of TR polymer solution still remain high degree after ageing 90 days. The retention rate of elastic modulus ranges from 70%~90%, the retention rate of viscous modulus ranges from 82%~88%. The viscoelastic modulus retention rate of high concentration polymer is greater than that of low concentration polymer. The result shows that with the rise of polymer concentration, the anti-ageing property and temperature-resistant property of polymer solution get better.

Figure 3. \( G' \) retention rate with ageing time

Figure 4. \( G'' \) retention rate with ageing time

4. The change law of polymer solution composite viscosity

4.1. The relation of composite viscosity with concentration and temperature

The change curve of composite viscosity \( \eta^* \) with angular frequency at 50°C and 95°C is shown in figure 5. The composite viscosity of polymer solution approximates a linear change with increasing angular frequency in coordinate. With the rise of concentration, the corresponding composite viscosity \( \eta^* \) improves gradually. In other words, with the rise of concentration, the viscosity of polymer solution gets stronger. The composite viscosity \( \eta^* \) of high concentration polymer solution reduces not obviously at 95°C compared with that of 50°C. But the composite viscosity \( \eta^* \) of low concentration polymer solution reduces markedly at 95°C compared with that of 50°C. The result shows that with the rise of polymer concentration, the temperature-resistant property of polymer solution gets better.

4.2. The relation of composite viscosity with ageing time and temperature

The composite viscosity \( \eta^* \) is measured by rheometer after ageing 15 days, 30 days, 60 days and 90 days respectively. The change curve of composite viscosity \( \eta^* \) with the ageing time at 50°C and 95°C is shown in figure 6. With the rise of ageing time, composite viscosity \( \eta^* \) go through three processes. The \( \eta^* \) retention rate of TR polymer solution declines firstly, then rises rapidly and finally declines slowly. The viscosity drops in first 10 days. It is because the solution contains micro oxygen, which can degrade with the TR polymer. During 10~30 days, after oxygen depletion, the degree of hydrolysis rises, viscosity improves, because the formation of TR polymer intramolecular hydrogen bond is the main reason for viscosity change. The intramolecular hydrogen bond is determined by the arrangement of amide group and carboxyl group in the molecular chains. When the intramolecular amide group and carboxyl group are arranged in a nested form, the intermolecular hydrogen bond is difficult to form. And the electrostatic repulsion between carboxyl groups of molecular chains is the main cause of the molecular chains expansion. With the increasing number of carboxyl groups, the electrostatic repulsion is enhanced, the polymer molecular chains tend to extend, and the viscosity of the solution rises. During 30~90 days, the degree of hydrolysis rises slowly. The degradation of the
polymer solution influenced by temperature is still existent, which decreases the viscosity of solution slowly. After 90 days ageing, there is still a high retention rate of composite viscosity. The composite viscosity $\eta^*$ retention rate is between 74% and 89%. The viscosity retention rate of 2000mg/L is better than that of 1500mg/L. It shows that TR polymer solution has good anti-ageing property at high temperature. And with the polymer concentration getting higher, the retention rate gets better.

Figure 5. Relation of $\eta^*$ with angular frequency

Figure 6. $\eta^*$ retention rate with ageing time

5. The change law of polymer solution first normal stress difference

5.1. The relation of first normal stress difference with concentration and temperature

The change curve of first normal stress difference $N_1$ with angular frequency at 50℃ and 95℃ is shown in figure 7. The first normal stress difference of polymer solution approximates a linear rise with increasing angular frequency in coordinate. Because with the angular frequency getting greater, the interaction force between polymer molecule and molecular chains gets stronger. The deformation of polymer molecule gets greater, what reflects better elasticity of polymer solution. Therefore, with the angular frequency getting greater, the elasticity of polymer solution rises gradually. The elasticity of polymer solution is direct proportional to the angular frequency. With the rise of concentration, the corresponding first normal stress difference $N_1$ rises gradually. In other words, with the rise of concentration, the elasticity of polymer solution gets stronger. Because with the concentration getting higher, the number of polymer molecules per unit volume gets larger. The ability of polymer molecules to attract and tangle with each other is enhanced, what leads to stronger elasticity. The first normal stress difference $N_1$ of polymer solution decreases slowly with the increasing temperature. It shows that with the rise of temperature, the elasticity of polymer solution gets weaker.

5.2. The relation of first normal stress difference with ageing time and temperature

The first normal stress difference $N_1$ is measured by rheometer after ageing 15 days, 30 days, 60 days and 90 days respectively. The change curve of first normal stress difference $N_1$ with the ageing time at 50℃ and 95℃ is shown in figure 8. With the rise of ageing time, first normal stress difference $N_1$ goes through three processes. The $N_1$ retention rate of TR polymer solution declines firstly, then rises rapidly and finally declines. Because the interaction of chain orientation and chain conformation determines the elasticity of polymer solution, and the initial viscosity drop makes the polymer long chain macromolecules shrink. At this time, the chain conformation is mainly curled, and the elasticity of polymer solution decreases. With the increase of ageing time, the rise of intermolecular repulsion leads to further elongation of polymer coils, and the conformation effect is increasing. The rise of
viscosity in this phase allows the entanglement and cross-linking of macromolecular chains in the solution to rise. The structure of the approximate network is formed in the solution, and the elasticity is improved rapidly, peaking at 30 days. With the rise of ageing time, the effect of temperature on the elasticity of polymer solution is reflected. The flexibility of polymer molecular chains is enhanced, which reduces the elasticity of molecule chains, and decreases the elasticity of polymer solution. After 90 days ageing, there is still a high retention rate of first normal stress difference. The first normal stress difference $N_1$ retention rate is between 62% and 93%. The $N_1$ retention rate of 2000mg/L is better than that of 1500mg/L. It shows that TR polymer solution has good anti-ageing property at high temperature. And with the polymer concentration getting higher, the retention rate gets better.

![Figure 7. Relation of $N_1$ with angular frequency](image1)

![Figure 8. $N_1$ retention rate with ageing time](image2)

6. Conclusion

(1) The elastic modulus, viscous modulus, composite viscosity and first normal stress difference of TR polymer solution improve with the rise of the concentration. It shows that with the rise of polymer concentration, the viscoelasticity of polymer solution gets greater.

(2) The viscoelastic modulus retention rate of high concentration polymer is greater than that of low concentration polymer after ageing 90 days at the same temperature. The result shows that with the rise of polymer concentration, the anti-ageing property of TR polymer solution gets better.

(3) The elastic modulus, viscous modulus, composite viscosity and first normal stress difference of TR polymer solution improve with the rise of the concentration, and decline with the rise of temperature. After ageing 90 days at 50°C, viscoelastic modulus retention rate ranges from 85%~93%. After ageing 90 days at 95°C, viscoelastic modulus retention rate ranges from 62%~85%. The result shows that the TR polymer is of good anti-ageing property and temperature-resistant property.

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