Synthesis and evaluation of new slickwater fracturing fluid for drag reduction

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Abstract. Currently, slip water fracturing fluid is widely used as a fracturing fluid for shale reservoirs. Non-ionic hydrophobic modified polyacrylamide (HM-PAM), partially hydrolyzed water-soluble hydrophobic associating polyacrylamide (HMWSP) and partially hydrolyzed anionic polyacrylamide (HPAM) solutions were modeled by molecular simulation software Materials Studio. The radius of gyration (Rg) and mean square displacement (MSD) of HPAM and HMWSP at different NaCl concentrations were calculated. From the simulation results, compared with HPAM and HM-PAM, HMWSP had a larger radius of gyration, a larger intrinsic viscosity number, and a larger hydrodynamic size, which would produce better drag reduction effects. Using acrylamide (AM), acrylic acid, 2-acrylamido-2-methylpropanesulfonic acid (AMPS) as basic raw materials, a hydrophobic associative drag reducer (HMWSP) was prepared by an inverse emulsion method. Infrared spectroscopy (FIIR) was used to characterize the synthesized products, and fluorescence chromatography was used to test the association of polymer solutions. Using a friction tester to test the drag reduction performance of the drag reducer, HMWSP has good resistance to salt reduction. HMWSP had good resistance reducing salt performance.

Key words: slippery water fracturing fluid; hydrophobic association; molecular dynamics simulation; drag reduction rate.

1. Introduction
In recent years, with the development of tight reservoirs, volume fracturing has gradually become an important means of unconventional oil and gas resources development. Slick water volume fracturing has attracted much attention due to its low cost and little damage to formation[1-2]. The system improves the fracture volume by injecting large displacement fracturing fluid into the bottom of the well. The higher the friction resistance in the shaft, the greater the construction pressure, so reducing the friction becomes an urgent problem to be solved in the construction process [3-4]. Drag reducer can inhibit turbulent fluctuations and vortices through molecular chains, thereby reducing flow resistance. The addition of drag reducer can significantly improve the construction effect [5-7].

Hydrophobically associating water-soluble polymer is a new kind of polymer [8-10] which can be dissolved in water by introducing a small amount of hydrophobic groups (mole fraction < 4%) into the main chain of water-soluble polymer[11-12]. The hydrophobic effect produced by hydrophobic groups
on hydrophobic associations exhibits different rheological properties from conventional water-soluble polymers [13-15]. When the solution concentration is higher than CAC (critical Association concentration), the hydrophobic groups aggregate to form a reversible three-dimensional network structure through association[16-18]. The shear dilution and viscoelasticity can play a greater drag reduction effect [19-20]. In recent years, computer simulation has become an important means to guide polymer synthesis and modification. Comparing with traditional experiments, computer simulation can give more explanations at the micro and molecular scale[21-23]. It can not only make up for the shortcomings of traditional experimental methods, but also improve the research efficiency and shorten the research cycle[24].

2. Molecule simulation

2.1. Model Construction

Three polymer chains, HM-PAM, HPAM and HMWSP, were constructed by Visualizer module in the R2 package of Materials Studio 2017. Three polymer chains, HM-PAM, HPAM and HMWSP, were constructed by Visualizer module in the R2 package of Materials Studio 2017. HM-PAM was a random polymer chain with a degree of polymerization of 100, in which the molar ratio of hydrophobic monomer to acrylamide was 3:97 (as shown in Fig 1 (a)). HPAM was a random polymer chain with a polymerization degree of 100 and a hydrolysis degree of 20% (as shown in Fig 1 (b)). HMWSP was a random polymer chain with 100 degree of polymerization and 20% degree of hydrolysis. The molar ratio of hydrophobic monomer, -COONa group and acrylamide was 3:20:77 (as shown in Fig. 1 (c)). The polymer chains were added to the water molecules containing different Na+, Cl- contents (the number of water molecules was 1000), and the polymer models with different NaCl concentrations were obtained as shown in Fig 2.

![Fig. 1 Molecular structure of different polymer chains](image-url)
The Geometry Optimization tool in Forcite module was used to optimize the structure of the model to achieve the optimal configuration of energy. The Atom based method and Ewald method were used to calculate van der Waals force and static power respectively. Smart Optimization method was used in the Optimization process. Using the Dynamics tool in Forcite module, the optimized layer in Fig 2 was calculated. Ensemble was selected as NVT (canonical ensemble), Temperature: 303K, Time step: 1fs, Total simulation time: 500ps, Number of: 500000. The molecular dynamics simulation was carried out under the Compass force field. The computations were repeated for each model several times. The deviation of each group of data was within 5%, and the final dynamic trajectory was analyzed.

2.2. The mean square displacement of different polymer chains in solution

The mean square displacement is an important parameter to characterize the dynamic properties of a particle, which is the average of the square of the particle displacement.

$$\text{MSD} = \langle |r_i(t) - r_i(0)|^2 \rangle$$

In the formula, brackets denote the average, $r_i(t)$ denotes the position of the first molecule at time $t$, and $r_i(0)$ denotes the position of the first molecule at the initial time.

According to the Einstein formula, the slope of the MSD curve can be used to calculate the diffusion coefficient of molecules.

$$D = \lim_{t \to \infty} \frac{\langle |r_i(t) - r_i(0)|^2 \rangle}{6t}$$
Fig. 3 Diffusion coefficient of water molecules in different polymer solution systems at different NaCl concentrations

The diffusion coefficient of water molecules could reflect the migration ability of effluent molecules in the system. The smaller the diffusion coefficient, the more severe the water molecules were bound. It could be seen from Fig 3 that the diffusion coefficient of water molecules in the modified polymer was smaller than the HPAM. With the increase of NaCl concentration, the diffusion coefficient of modified polymer HMWSP and HM-PAM first decreased and then increased. At the same NaCl concentration, the order of the diffusion coefficient of water molecules in polymer solution was HPAM > HM-PAM > HMWSP, which was consistent with the trend of its gyration radius.

2.3. Effect of salt concentration on the radius of gyration of HMWSP, HPAM and HM-PAM

Due to the flexibility of the polymer molecular chain, its conformation can be constantly changes, the conformation changes, and the molecular size changes. The conformational size of a molecular chain is generally described by the radius of gyration. The radius of gyration is the mean square value of the distance between each link in the molecular chain and the centroid of the molecular chain.

\[ R_g^2 = \frac{1}{N} \sum_{i=1}^{N} s_i^2 \]

N is the number of links, and Si is the distance from the i atom to the centroid.

Fig. 4 The Rg of HMWSP, HM-PAM and HPAM at different NaCl concentrations

It could be seen from Fig 4, the modified polymer had a larger radius of gyration at different NaCl concentrations than HPAM. The modified polymer did not cause a sharp drop in the radius of gyration with the increase of NaCl concentration. The salt tolerance after modification was improved. With the increase of NaCl concentration, the gyration radius of HMWSP and HM-PAM firstly increased and then decreased. When the external electrolyte was added to the initial stage of the solution, counterion (Na+) would produce shielding effect. At this time, the polarity of the solution increased, which made the main chain form from curl to stretch. The shielding effect of Na+ decreased with increasing NaCl concentration. High concentration of Na+ would destroy the hydration layer, released free water, and began to inhibit the repulsion of -COO- groups. The shape of the main chain was changed from stretching to curling, shown the reduction of the radius of gyration. When the concentration of HMWSP...
was higher than the critical association concentration (CAC), the intermolecular association was dominated in the polymer chain solution. The three-dimensional network structure made the hydrodynamic volume increased sharply, so the radius of gyration of HMWSP was larger at different NaCl concentrations.

3. Results and analysis

3.1. Infrared spectrum test

During the experiment, a certain amount of AMPS was weighed and dissolved in deionized water, the solution was adjusted to neutral with NaOH aqueous solution. C16-DMAAC and AM were added, and the aqueous phase was fully dissolved under magnetic stirring. A certain amount of Span80 and Tween80 were weighed and adjusted to the appropriate HLB value to fully mix with kerosene. The emulsion of AM / C16-DMAAC / AMPS could be obtained by adding an appropriate amount of initiator and controlling the reaction temperature at 50 °C.

The purified white powder and potassium bromide powder were mixed and compressed into tablets, and the FTIR spectrum of the sample was measured by an infrared spectrometer. It could be seen from Fig5 that 3405cm⁻¹ was the stretching vibration of -NH bond; 1674cm⁻¹ was the stretching vibration of -C=O bond; 3202cm⁻¹ was the symmetric stretching vibration of -CN- bond, and 2924cm⁻¹ and 2854cm⁻¹ were the stretching vibration of the-CH bond.1458cm⁻¹ was the bending vibration of the -CH2-group; 1324cm⁻¹ and 1190cm⁻¹ were the infrared characteristic absorption peaks of the sulfonate. IR results indicated that the substance contains amide group and sulfonic acid group, which was consistent with the target product.

3.2. Drag reduction performance test

The drag reduction effect of drag reducing agent were the increase of flow velocity and the decrease of flow resistance. When the pump pressure remained constant, the flow rate increased. When the flow rate remained unchanged, the pressure drop at both ends of the pipeline decreased. Both the rate of increase and the rate of decrease can reflect the drag reduction performance.

The reduction in the flow resistance of the fluid in the pipeline is essentially a reduction in the fluid friction coefficient. Therefore, the drag reduction rate can be expressed as:

\[ DR\% = \frac{\lambda_0 - \lambda_{DR}}{\lambda_0} \times 100\% \]

\[ \lambda = \frac{2d}{\rho \lambda^2 L} \Delta P \]
d: the inner diameter of the pipe, m;
ρ: density of fluid, kg/m³;
u: fluid flow velocity, m/s;
L: length of the pipe, m;
ΔP: frictional pressure drop across the pipe, Pa.

Since d, ρ, and L are both constants, the friction coefficient at the same flow rate is only related to the pressure drop across the pipe. So the formula (1-2) is substituted in the formula (1):

$$ DR\% = \frac{\Delta P_0 - \Delta P_{DR}}{\Delta P_0} \times 100\% $$ (3)

Where: $\Delta P_0$: frictional pressure drop at both ends of the pipe when no drag reducer is added, Pa;
$\Delta P_{DR}$: The frictional pressure drop across the pipe after adding the drag reducer, Pa.

It could be seen from Formulas 1-3 that the drag reduction rate can be calculated as long as the pressure drop across the pipe before and after the addition of the drag reducer can be obtained.

A slick water friction tester was used to test the drag reduction rate of the HMWSP drag reducer at different salinities. Test fluid formula: mass fraction was 0.15% HMWSP aqueous solution, test flow rate: 10m/s, test temperature was 25℃.

![Fig. 6 Relationship between drag reduction rate and salinity](image)

It could be seen from Fig.6 that HMWSP drag reducer had good salt resistance. When the salinity was less than 50000mg/L, the drag reduction rate of slick water decreased slowly, but the drag reduction rate value had remained above 60%. When the salinity was greater than 50000mg/L, excessively high salinity would inhibit the repulsion of the -COO- group and destroy the hydration layer, releasing free water, which would destroy the three-dimensional network structure and cause viscosity. The rapid decline was manifested by the reduction in drag reduction rate.

3.3. Evaluation of temperature and shear resistance of fracturing fluid

During the experiment, the prepared water in fracturing fluid system was put into a closed cylinder, and the cylinder was placed on the rheometer for shear resistance experiment. The rheometer temperature was set at 70 ℃, and the viscosity of fracturing fluid was measured under different shear rates.
From the analysis of Fig 7, in the first 15 minutes of shearing at 170 s⁻¹ shear rate, the viscosity of the emulsion fracturing fluid showed a general downward trend. After 8 minutes, the viscosity tended to be stable, and finally remained at about 228 mPa.s. When the shear rate increased from 170 s⁻¹ to 500 s⁻¹, the viscosity decreased sharply to 150 mPa.s, and then stabilized at about 141 mPa.s; when the shear rate returned to 170 s⁻¹, the viscosity of fracturing fluid fluctuated obviously, but remained at about 200 mPa.s all the time. It can be seen that the viscosity of the fracturing fluid system changed with the change of shear rate. To sum up, the fracturing fluid system had good shear resistance at 70 ℃.

4. Conclusion

Hydrophobically associating drag reducing agent (HMWSP) was prepared by inverse emulsion polymerization. Compared with HPAM, HMWSP has a larger radius of gyration, a larger intrinsic viscosity and a larger hydrodynamic size, which will produce a better drag reduction effect. When the temperature was 70 ℃ and salinity was 50 000mg/L, the drag reduction rate was still more than 60%. The sliding hydraulic fracturing fluid system had good temperature and shear resistance. The viscosity of the fracturing fluid could still be stable above 141 mPa.s, when the shear rate was 170 s⁻¹ for more than 45 min. HMWSP has a good drag reduction effect and can meet the requirements of fracturing operation.

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