Preparation and application of a novel high temperature resistant filtration reducer in water-based drilling fluids

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Abstract. 4-vinylpyridine (VP), N, N-dimethylacrylamide (DMAA), 2-Acrylamido-2-methylpropane sulfonic acid (AMPS) and sodium styrene sulfonate (SSS) were synthesized to a novel filtrate reducer in aqueous solution by free radical copolymerization using ammonium persulfate and sodium bisulfite as redox systems. The structure of copolymer was characterized by Fourier transform infrared spectroscopy (FT-IR). Thermogravimetric analysis (TGA) showed that the thermal decomposition temperature of the copolymer was higher than 310°C, which indicated that the copolymer had excellent high temperature resistance. At the same time, the rheological and filtration properties of water-based drilling fluids (WBDFs) were further evaluated by adding copolymer as a filtrate reducer. The results showed that the fluid loss (FL₂₅) of WBDFs was only 5.0 mL when the copolymer content is 2.0 wt%, Even after hot rolling at 260°C for 16 hours, the FL₂₅ of WBDFs was 8.2 mL. The FL₂₅ of fresh water mud was 25.2 mL, and that of aged fresh water mud was 48 mL. In addition, WBDFs with copolymer effectively resists salt and calcium intrusion before and after hot rolling at high temperature for 16 hours, which indicates that the copolymer can be used as an efficient filtration reducer in ultra-deep well drilling operations.

1. Introduction
In recent years, with the exploration and development of oil and gas resources to deep strata, drilling formation is more complex, and the requirement of temperature and salt resistance of drilling fluid is higher [1-3]. Filtration reducer is one of the key types of drilling fluid additives. The main direction is to develop filtrate reducer with high temperature, salt and calcium resistance [4,5]. In particular, the polymer filtrate reducer synthesized with AMPS as the main monomer is the most widely studied and the number of products is increasing year by year [6,7]. At present, the methods to improve the temperature resistance of such filtrate reducers are mainly focused on introducing strong adsorption groups (such as amino group, silicon hydroxyl group) into the molecular chain to improve the adsorption capacity at high temperature [8,9]. However, the structure of the main chain of C-C bond of these filtrate reducers has not changed greatly, but a new type of adsorption group has been introduced into the side chain. The effect of molecular rigidity on the temperature resistance of filtrate reducers has not been taken into account in terms of molecular flexibility, which limits the renewal speed of these products to a certain extent [10,11]. Increasing the rigidity of polymer molecular chains can reduce the thermal movement at high temperatures and slow down the desorption process of molecules at high temperatures [12-14]. DMAA, AMPS, SSS and VP were used for free radical copolymerization to synthesize a kind of Quaternary copolymer filtrate reducer with high temperature and salt-calcium corrosion resistance under redox system initiator, and added to water-based drilling fluid to further
evaluate its rheological properties and filtration properties of water-based drilling fluid. It is expected to change a series of problems such as wellbore instability and collapse.

2. Materials and methods

2.1. Materials

Ammonium persulfate, (AR) sodium bisulfite (AR), DMAA (AR), AMPS, SSS and VP were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China)

Bentonite-based mud was obtained by mixing 40 g bentonite in 1000 mL distilled water at high speed for 20 minutes, then keeping it in airtight condition at room temperature for 24 hours.

2.2. Synthesis of copolymer

AMPS was dissolved in 80 g distilled water, and then the pH was adjusted to a neutral environment with sodium hydroxide solution. DMAA, VP, SSS with molar ratio of 5:3:1:1 were added to the mixed solution under stirring conditions, protected by nitrogen for 30 minutes, and 0.5 wt% ammonium persulfate and sodium bisulfite were added as initiators to react at 60°C for 2 hours, then filtered in MD44 dialysis bag for 24 hours, dried and crushed to obtain the target product.

2.3. Characterization of copolymer

Fourier transform infrared spectroscopy (FTIR) of copolymer was carried out by spectrometer (IR Tracer-100 Shimadzu Corporation). Thermal degradation of copolymer was measured by thermal analyser (TGA, Mettler Toledo Co., Switzerland).

2.4. Performance of copolymer in water-based drilling fluids

Thirty minutes of fluid loss (FL_API) was tested by medium pressure filter (SD3, Qingdao Haixin Optical Co., China) according to API standard which is as follows:

- Measure and record the initial temperature of the drilling fluid to the nearest degree Celsius (degree Fahrenheit).
- Inspect the cell and all components, and especially the screen, to ensure that all parts are clean and dry, and the gaskets are not cracked, distorted, or worn. Assemble the cell by placing a gasket in the base cap, place the screen on top of the gasket, place the filter paper on top of the screen, place the sealing gasket on top of the paper, then assemble the cell. Pour the drilling fluid sample into the cell to within 12 mm (0.5 in.) of the top and complete the assembly.
- Place a clean dry graduated cylinder under the drain tube to collect the filtrate. Close the relief valve and adjust the regulator so that a pressure of 690 kPa ±35 kPa (100 psi ±5 psi) is applied within 30 s or less. Start the 30 min-timer immediately at the time of pressure application.
- At the end of the 30 min-test period, measure and record the filtrate volume. Shut off the flow through the pressure regulator and open the relief valve carefully. The time interval, if other than 30 min, shall be reported.

The rheological properties of bentonite-based mud are measured using a flow rate rotating viscometer. The apparent and plastic viscosities are calculated by reading 300 and 600 rotating speeds of the viscometer.

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\text{Apparent Viscosity (AV)} = \frac{\theta_{600}}{2} (\text{mPa} \cdot \text{s})
\]

\[
\text{Plastic Viscosity (PV)} = \theta_{600} - \theta_{300} (\text{mPa} \cdot \text{s})
\]

\[
\text{Yield Point (YP)} = \frac{(\theta_{300} - \text{PV})}{2} (\text{Pa})
\]

3. Results and discussion

3.1. Characterization of copolymer
Figure 1 shows that the peak at 2944 cm$^{-1}$ is attributed to the stretching vibration of the product methylene. The peak at 1633 cm$^{-1}$ is attributed to the C=O bond ν stretching vibration of tertiary amines in DMAA. The vibration absorption peaks at wavelength 1552 cm$^{-1}$ and 775 cm$^{-1}$ are caused by the vibration of pyridine group in VP molecular chain. The peak at 1490 cm$^{-1}$ is attributed to the stretching vibration of C-N bond in DMAA. The peak absorption vibration at 1188 cm$^{-1}$ and 1037 cm$^{-1}$ is attributed to the stretching vibration of sulfonic groups on AMPS. The peak at 605 cm$^{-1}$ is attributed to the stretching vibration of C-S bond. The peak at 680 cm$^{-1}$ is the absorption peak of benzene ring. It can be seen from the infrared spectrum that the synthesized PDANS is the target product.

![Figure 1. FT-IR of copolymer.](image1)

3.2. Thermal stability of copolymer

As shown in figure 2, the temperature of the copolymer decreases as the high temperature. The mass loss rate of the copolymer was 7.49% in the temperature range of 40 to 130°C. It is because the copolymer molecule contains adsorption groups, which can absorb moisture in the air. The temperature rise leads to the evaporation of free water, which leads to the mass loss of the copolymer in the temperature range. The mass loss rate of the copolymer was 54.34% in the temperature range of 310 to 430°C. It is because the side chains of amide and sulfonic acid groups in the copolymer...
molecular chains are thermally degraded and separated from the main chains with the further increase of temperature, which results in the mass loss of the copolymer at this stage. The mass loss of the copolymer was 38.17% after 430℃. In this stage of mass loss, the main chain of the copolymer is basically broken and decomposed at high temperature. Generally speaking, copolymers have excellent thermal stability.

3.3. Performance evaluation of copolymer in WBDFs
Figure 3 shows that the increase in viscosity of bentonite base mud is attributed to the addition of a large number of copolymers. When the concentration of copolymer is 2%, AV is 34 mPa·s, and it still reaches 27 mPa·s after high temperature aging, the FL API was 5.0 mL and 8.2 mL after high temperature aging. It is due to the high molecular weight of copolymer, when it is added as drilling fluid additive, it will increase the viscosity of WBDFs. At the same time, due to the extension of copolymer macromolecular chains in water-based drilling fluids, the adsorbing groups on the side chains of molecular chains can effectively adsorb clay particles and prevent clay particles from coalescing, thus reducing the amount of fluid loss [15,16].

Figure 3. Effect of PDANS concentration on WBDFs before (BHR) and after hot rolling (AHR) at 260℃ for 16 h.

Figure 4 shows that Viscosity of bentonite-based mud containing copolymer decreases at high temperature, while FL API and FL HTHP increase gradually. The FL API is 8.2 mL when the temperature is 260℃. In high temperature environment, the degradation and hydrolysis of copolymers are the main reasons for the chemical degradation of copolymers [17-19]. This chemical degradation will result in the change of functional groups of side chains, the decrease of molecular weight and intrinsic viscosity of copolymers, and eventually lead to the failure of copolymers, resulting in the increase of fluid loss in WBDFs [20,21]. Compared with other products, the new product PDANV has the most obvious
effect in reducing drilling fluid filtration.

![Figure 4](image)

**Figure 4.** Effect (a) of temperature on performance of water-based drilling fluids with PDANS and comparisons with other products (b).

Table 1 shows that when a large number of salt ions are added, the viscosity of water-based drilling fluid decreases gradually before and after hot rolling at high temperature. When the salt content is 35%, the apparent viscosity is 28.5 mPa·s, and the AV can still reach 15 mPa·s after hot rolling at high temperature. At the same time, the FL
_{API}
 is 11.2 mL and 14.5 mL after hot rolling, which shows that the product is insensitive and can effectively protect the stability of drilling fluid in salt-gypsum formation.

| NaCl/% | AV/mPa·s | PV/mPa·s | FL
_{API}/mL | YP/Pa |
|--------|----------|----------|-------------|--------|
|        | BHR      | AHR      | BHR         | AHR    | BHR  | AHR |
| 0      | 34.0 27  | 30 19    | 5.0 8.2     | 4.0 8  |
| 5      | 33.0 20  | 21 18    | 6.6 7.4     | 12.0 2 |
| 10     | 32.0 18  | 21 17    | 6.8 8.9     | 11.0 1 |
| 20     | 30.0 17  | 20 16    | 8.5 9.6     | 10.0 1 |
| 35     | 28.5 15  | 19 14    | 11.2 14.5   | 9.5 1  |

Table 2 shows that with the increase of calcium content, the viscosity of water-based drilling fluid decreases gradually before and after hot rolling at high temperature. When the salt content is 2%, the AV is 27 mPa·s, and the AV can still reach 20 mPa·s after hot rolling at high temperature. At the same time, the FL
_{API}
 is 9.7 mL and 16.4 mL after hot rolling, which indicates that the copolymer is insensitive to calcium intrusion.

| CaCl₂%/ | AV/mPa·s | PV/mPa·s | FL
_{API}/mL | YP/Pa |
|---------|----------|----------|-------------|--------|
|         | BHR      | AHR      | BHR         | AHR    | BHR  | AHR |
| 0       | 34.0 27  | 25 19    | 5.0 8.2     | 4.0 8  |
| 0.5     | 32.5 25  | 26 20    | 5.8 10.5    | 7.5 5  |
| 1.0     | 30.0 22  | 24 18    | 7.6 14.0    | 4.0 4  |
| 2.0     | 27.0 20  | 14 14    | 9.7 16.4    | 3.0 3  |

Table 2 shows that with the increase of calcium content, the viscosity of water-based drilling fluid decreases gradually before and after hot rolling at high temperature. When the salt content is 2%, the AV is 27 mPa·s, and the AV can still reach 20 mPa·s after hot rolling at high temperature. At the same time, the FL
_{API}
 is 9.7 mL and 16.4 mL after hot rolling, which indicates that the copolymer is insensitive to calcium intrusion.

The toxicity and biodegradability of PDAVS were determined by modern water Delta tox II, BOD
rapid determinator and COD determinator (LEICI-571) respectively. It can be seen from table 3 that PDAVS is an environmentally friendly filter loss reducer.

| Table 3. Environmental friendly evaluation of PDAVS. |
|-------------|--------|---------|----------------|-----------------|
| sample      | EC(50)(mg/L) | toxicity | BOD5/COD (%)  | Biodegradability |
| PDAVS       | 30500       | Non-toxic | 26.4          | Easily degraded  |

4. Conclusions

4-vinylpyridine (VP), N, N-dimethylacrylamide (DMAA), 2-Acrylamido-2-methylpropane sulfonic acid (AMPS) and sodium styrene sulfonate (SSS) were successfully synthesized to a novel filtrate reducer in aqueous solution by free radical copolymerization using ammonium persulfate and sodium bisulfite as redox systems. FT-IR spectra showed that the target product has been successfully synthesized and had excellent thermal stability. Meanwhile, the properties of WBDFs were further revealed by adding copolymer as a filtrate reducer. The results revealed that the $FL_{API}$ of WBDFs was only 5.0 mL when the copolymer content is 2.0 wt%. Even after hot rolling at 260°C for 16 h, the $FL_{API}$ of water-based drilling fluids was 8.2 mL. In addition, water-based drilling fluid containing copolymer effectively resists salt and calcium intrusion. Therefore, copolymers are recommended as effective filtrate reducers for ultra-deep well drilling operations with high salinity.

References
[1] Xu C C, Zou W H, Yang Y M et al 2017 Status and prospects of exploration and exploitation of the deep oil & gas resources onshore China Nat. Gas Geosci 28 1139-53
[2] Zhao Z, Shujuan Xu, Jiang X et al 2016 Deep strata geologic structure and tight sandy conglomerate gas exploration in Songliao Basin, East China Pet. Explor. Dev 43 13-25
[3] Dong D, Wang Y, Li X et al 2016 Breakthrough and prospect of shale gas exploration and development in China Nat. Gas Ind B 3 12-26
[4] Mao H, Qiu Z, Shen Z et al 2014 Synthesis and mechanism of hydrophobic associated polymer based nano-silica filtrate reducer Acta Pet. Sin 35 771-8
[5] Cheng M A, Zhen J, Wang Z et al 2014 Synthesis and evaluation of filtrate reducer SPH-F for calcium chloride clay-free drilling fluids Drill. Fluid Completion Fluid 2014 95-102
[6] Tang X, Yuan B, Yang Y et al 2016 Preparation and performance of AMPS/AA/DMAA/SA copolymer as a filtrate reducer for oil well cementing J. Appl. Polym. Sci 133 43824 (1-9)
[7] Zhang Y M, Zhu H, Wang F H et al 2008 Preparation and characterization of CTAB/polymer composite modification of montmorillonite as filtrate reducer J. Funct. mater 12 2028-2031
[8] Zhao X, Xie J and Zhang L 2012 Synthesis and properties of high temperature-resistant phenyl cationic starch filtrate reducer Petrochem. Technol 41 801-805
[9] Yu W U, Sun D, Tao W U et al 2001 Study on mud properties of AMPS/AM/IA terpolymer as temperature resistant and salt tolerant filtrate reducer Oilfield Chem 18 101-104
[10] Sun J, Ning F, Wu N et al 2015 The effect of drilling mud properties on shallow lateral resistivity logging of gas hydrate bearing sediments J. Pet. Sci. Eng 127 259-69
[11] Xin J, Xi F, Lv D et al 2011 The effect of the chitosan membrane properties on the enzyme adsorption and performance for the construction of horseradish peroxidase biosensors Carbohydr. Polym 85 786-91
[12] Palmeri J, Manghi M and Destainville N 2008 Thermal denaturation of fluctuating finite DNA chains: the role of bending rigidity in bubble nucleation Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys 77 011913
[13] Tendero R, Miguel P, Jimenez et al 2006 Viscoelastic and thermal characterization of crosslinked PVC Eur Polym J 42 961-9
[14] Fenouillot F, Cassagnau P and Majesté J C 2009 Uneven distribution of nanoparticles in immiscible fluids: Morphology development in polymer blends Polym 50 1333-50
[15] Mao H, Qiu Z, Shen Z, et al 2015 Hydrophobic associated polymer based silica nanoparticles
composite with core–shell structure as a filtrate reducer for drilling fluid at ultra-high temperature. J. Pet. Sci. Eng. 129 1-14

[16] Ritter H and Spee A G V 1994 Bacterial production of polyesters bearing phenoxy groups in the side chains, 1. Poly (3-hydroxy-5-phenoxypentanoate-co-3-hydroxy-9-phenoxynonanoate) from Pseudomonas oleovorans Macromol. Chem. Phys 195 1665-72

[17] Zaikov G E and Livshitz V S 1987 The mechanism of chemical degradation of polymers: Part III—The anomaly in the hydrolysis of glycolide copolymers Polym. Degrad. Stab 17 65-9

[18] Siracusa V, Rocculi P, Romani S, et al 2008 Biodegradable polymers for food packaging: a review Trends Food Sci. Technol 19 634-643

[19] Middleton J C, Tipton A J 2000 Synthetic biodegradable polymers as orthopedic devices Biomater 21(23) 2335-2346

[20] Peron J, Shi Z and Holdcroft S 2011 Hydrocarbon proton conducting polymers for fuel cell catalyst layers Energy Environ. Sci 4 1575-91

[21] Chang X F et al 2019 Synthesis of a novel environment-friendly filtration reducer and its application in water-based drilling fluids Colloids Surf., A 568 284-93