Development and Evaluation of a novel High-temperature resistant coating flocculant

Fan Zhang¹, Jinsheng Sun, Kaihe Lv, Xiaofeng Chang

¹ School of Petroleum Engineering, China University of Petroleum (East China), Qingdao, Shandong, People’s Republic of China
E-mail: zhangfan51@qq.com

Abstract. In the laboratory experiment, 2-Acrylamido-2-methyl-1-propanesulfonic acid (AMPS), N, N-Dimethylacetoacetamide (DMAA), (Z)-Butenedioic anhydrides (MA) and 3-Methacryloxypropyltrimethoxysilane (KH-570) copolymers were used as reaction monomers, potassium persulfate was used as initiator, and a new type of temperature and salt resistant coating flocculant DMA-57 for water-based drilling fluid was synthesized by free radical copolymerization. The synthesis conditions were optimized by orthogonal experiment, and its performance was evaluated. The experimental results show that DMA-57 has good thermal stability, thermal decomposition temperature up to 339 ℃. Under the condition of 150 ℃, 3.0 MPa and 0.1% dosage, the linear expansion rate of calcium soil can be reduced by 83.83%, and the inhibition rate of calcium soil can be reduced by 67.5%, which has a good effect of flocculation inhibition.

1. Introduction
With the development of drilling technology, various difficult drilling operations such as large angle, horizontal well and directional deviated well are increasing[1, 2]. Therefore, there is a higher standard in the aspects of stabilizing the well wall, preventing the collapse, controlling the hydration and dispersion of drilling cuttings and improving the drilling speed [3-7]. In drilling fluid system, coating agent is an important additive. In the drilling fluid system, coating agent is an important additive, which is used to prevent drilling cuttings and shale from hydration and dispersion, to keep the wellbore stable and prevent collapse. The function of coating agent is to form a protective film through macromolecular polymer on the surface of drilling cuttings and shale, to prevent the cuttings from sticking to each other and increase the screening resistance, so as to form an effective coating on drilling cuttings. The existing flocculants are unstable, easy to deteriorate, large dosage, which cannot meet the needs of drilling construction. Therefore, it is urgent to develop a new strong inhibition flocculant which can meet the needs of high-temperature [8-10].
In this study, a novel inhibiting flocculant (DMA-57) was developed, which has good thermal stability, temperature resistance, good lubrication ability and certain filtration reduction effect, and the effect of inhibiting hydration and dispersion was achieved by adsorption and film formation on clay surface through coating.

2. Materials and methods

2.1. Materials
AMPS (AR), DMAA (AR), and MA (AR) were purchased from Macklin Biochemical Co., Ltd (Shanghai, China). KH-570 (GC), Potassium persulfate (AR), and NaOH (97%) were supplied by Shanghai Wokai Chemical Reagent Co., Ltd. The sodium bentonite used for the drilling fluid cement slurry was purchased from Huawei Bentonite Group Co., Ltd., China. The calcium bentonite used for linear expansion experiment and the drilling cuttings used for rolling recovery experiment were purchased from Bohai Drilling Co., Ltd., China.

2.2 Preparation of polymer
The three monomers of MA, AMPS and DMAA with a certain molar ratio were added into a certain amount of distilled water for complete dissolution (the total monomer concentration of the synthesis reaction was 20 wt-%), and the pH value of the mixture was adjusted to 8.0 with 50 wt-% sodium hydroxide solution. Subsequently, the mixture was placed in a three port flask, heated to 40.0 °C in a constant temperature water bath, and then 0.5 wt-% KH-570 of monomer mass was added. Then, the initiator (potassium persulfate) was added at the rate of 1 drop per 2 seconds. The polymerization reaction should be kept in N2 throughout the whole process. The synthesized product was washed with acetone and dried in a vacuum oven at 60 °C, after grinding, the product of white solid powder is named DMA-57.

2.3 Orthogonal experiment
According to the synthesis principle of polymer fluid loss agent, the main factors that affect the performance of polymer are monomer molar ratio, reaction temperature and initiator dosage. The reaction conditions of synthesis experiment are further optimized by orthogonal experiment. The rolling recovery rate of rock cuttings is taken as the evaluation index of orthogonal experiment. The experimental condition of rolling recovery rate is 150 °C/16h. The orthogonal test of three levels and three factors design is shown in Table 1.

| Factor level | A | B | C |
|-------------|---|---|---|
| Mole ratio  | Reaction temperature (°C) | Initiator ratio (%) |
| 1           | 6:2:2 | 30 | 0.3 |
| 2           | 5:3:2 | 40 | 0.5 |
| 3           | 4:4:2 | 50 | 0.7 |

2.4 Structure characterisation techniques
The polymer DMA-57 was characterized by IRTRACER-100 FTIR (Shimadzu Switzerland). The spectral range of infrared scanning is 4000-500 cm⁻¹, and the scanning resolution is 4 cm⁻¹. Thermal
stability of polymers was measured by Mettler-Toledo thermal analyzer. The heating rate was 10 k/min, the heating temperature was 40-1000 °C, and the protective gas was nitrogen.

2.5 Inhibitive properties
2.5.1 Linear expansion test
In this experiment, using calcium bentonite, 10g calcium bentonite was accurately weighed and placed in a standard mold, and pressurized 10MPa with a manual hydraulic pump for 10min, which is recommended according to the shale expansion test standard. Then, the linear expansion test is carried out with shale dilatometer to measure the expansion amount for 24 hours, the experimental temperature is 150 °C, and the pressure is 3.0 MPa so as to evaluate the inhibition and anti-expansion ability of coating agent on shale [11-13].

2.5.2 Rolling recovery test
Shale samples were crushed on steel plates and core particles were collected between 6 meshes and 10 meshes. The samples were placed in a constant temperature oven and dried at 90 °C for 10 hours. Then, 50 g samples and experimental solution were put into the aging tank and rolled for 16 hours at 150 °C. The remaining shale cuttings were washed with 40 mesh sieve, dried at 103 °C for 4 hours and weighted [14-16].

3. Results and discussion

3.1 Orthogonal Test of DMA-57
It can be seen from the range analysis results of orthogonal experiment that the influence of various factors on the properties of the synthesized products is A > C > B, that is, the mole ratio of monomer is the main factor, followed by the amount of initiator, and then the reaction temperature. It can be seen from the results of orthogonal experiment that the optimal reaction conditions are: mole ratio of DMAA: amps: Ma = 5:3:2, reaction temperature is 40 °C, initiator amount is 0.5% of the total monomer. The results are shown in Table 2.

| Sample | A       | B     | C       | Rolling recovery |
|--------|---------|-------|---------|------------------|
|        | Mole ratio of DMAA:AMPS:MA | Reaction temperature/°C | Initiator amount/% |                      |
| 1      | 6:2:2   | 30    | 0.3     | 45               |
| 2      | 6:2:2   | 40    | 0.5     | 55               |
| 3      | 6:2:2   | 50    | 0.7     | 40               |
| 4      | 5:3:2   | 40    | 0.7     | 80               |
| 5      | 5:3:2   | 50    | 0.3     | 75               |
| 6      | 5:3:2   | 30    | 0.5     | 78               |
| 7      | 4:4:2   | 50    | 0.5     | 58               |
3.2 DMA-57 characterization

3.2.1 Structural characterisation of DMA-57

Fig.1 shows the FTIR spectra of DMA-57. The characteristic peaks around 3447 cm\(^{-1}\) at DMA-57 were identified as the stretching vibration absorption peaks of \(-\text{OH}\) in MA. The characteristic peaks around 2983 cm\(^{-1}\) at DMA-57 were assigned to the stretching vibration peaks of DMAA. The characteristic peaks around 1292 cm\(^{-1}\) were identified as the vibration absorption peaks of the ester group in KH-570. The absorption peaks around 1035 cm\(^{-1}\) were identified as the vibration absorption peaks of Si–O in KH-570. The characteristic peaks around 1021 cm\(^{-1}\), which indicated the polymer is partially hydrolyzed to form Si–O–Si. The absorption peak of CO in AMPS was observed at 559 cm\(^{-1}\). The results of FTIR showed that the synthesised product had a target functional group unique to the monomer, all the monomers were fully reacted, and the desired target product was obtained through synthesis \(^{[17-20]}\).

![FTIR spectrum of DMA-57](image)

3.2.2 Thermal stability of DMA-57

The TGA curve of DMA-57 is shown in Fig 2. Weightlessness occurring before 185\(^\circ\)C is mainly due to the volatilization of water in the sample, the mass of the sample is reduced by 14.1%. The bound water adsorbed by strong hydrophilic groups such as amide group began to volatilize at 185-339\(^\circ\)C, the mass of the sample is reduced by 53.3%. The thermogravimetric curve of DMA-57 decreases from 339 to 658 \(^\circ\)C. The weight loss is attributed to the breakage of the main chain and the side chain. The
thermogravimetric curve of DMA-57 decreases from 658 to 997 ºC, the mass of the sample only reduced 2.4%, which proved that DMA-57 had good thermal stability.

![Fig.2 TGA curve of DMA-57](image)

3.3 Inhibition evaluation

3.3.1 Linear expansion test

The linear expansion rate of the coating agent synthesized in this study was measured by experiments, and compared with the coating agent inhibitors commonly used in water-based drilling fluid, in distilled water, the linear expansion rate of calcium soil is 98%. The results are shown in Table 3.

| Expansion rate/% | DMA-57/0.1% | FA-367/0.1% | Expansio n rate/% | PLUS-L/0.1% | Expansio n rate/% | SDJZ-1/0.1% | Expansio n rate/% |
|------------------|-------------|-------------|-------------------|-------------|-------------------|-------------|-------------------|
| DMA-57           | 0.1         | 0.1         | 35.4              | 0.1         | 33.7              | 0.1         | 34.3              |
|                  | 0.3         | 0.3         | 31.9              | 0.3         | 31.4              | 0.3         | 32.5              |
|                  | 0.5         | 0.5         | 28.4              | 0.5         | 29.2              | 0.5         | 29.2              |
|                  | 0.7         | 0.7         | 28.0              | 0.7         | 28.3              | 0.7         | 27.8              |
|                  | 0.9         | 0.9         | 26.8              | 0.9         | 26.7              | 0.9         | 26.5              |

The results of the high temperature and high pressure expansion rate experiment are shown in Table 3. Considering the use cost and the effect of inhibiting expansion comprehensively, comparing with the three commonly used coating agents on the market, the addition of DMA-57 in the range of 0.3% ~ 0.5% has anti-expansion performance.

3.3.2 Rolling recovery test

The recovery of tap water is 15.3%. The rolling recovery is 4.7% in the based slurry system, the results show that the rolling recovery can be increased to 83.83% by adding 0.1% DMA-57, and DMA-57 has a better coating flocculation effect when adding 0.1~0.5%, the rolling recovery can reach 84.26%, which is better than other similar inhibitors.
Table 4. Effect of coating agent dosage on rolling recovery

| Coating agent/% | 0.1  | 0.3  | 0.5  | 0.7  | 0.9  |
|----------------|------|------|------|------|------|
| DMA-57         | 83.83| 84.26| 85.56| 87.63| 88.62|
| FA-367         | 81.41| 81.23| 82.51| 82.96| 85.94|
| PLUS-L         | 74.51| 73.96| 76.89| 78.19| 81.97|
| SDJZ-1         | 77.87| 75.46| 77.19| 80.26| 82.16|

4. Conclusions

(1) The developed coating flocculant DMA-57 has good coating inhibition, thermal stability. The linear expansion test at 3MPa and 150 °C can verify that the high temperature and high pressure anti-expansion ability of DMA-57 is superior to that of similar products.

(2) The amount of coating flocculant DMA-57 is relatively low. Through the rolling recovery experiment, we can see the formation of rock debris, which can effectively flocculate useless solid phase. In terms of adsorption mode, dma-57 can carry out multiple adsorption, which is a strong adsorption of Si-O-Si formed by cation electrostatic adsorption in DMAA and Si-O bond on KH-570 and inorganic silicon on clay.

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