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A novel film-forming silicone polymer as shale inhibitor for water-based drilling fluids

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Abstract: A novel shale inhibitor was synthesized by free radical copolymerization in aqueous solution, using acrylic acid (AA), acrylamide (AM), maleic anhydride (MA) KH-570 as reaction monomers and potassium persulfate as initiator. The structure of the 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 226°C, which indicated that the copolymer had good high temperature resistance. At the same time, the inhibition performance of the copolymer was further evaluated by linear expansion, immersion test and rolling recovery. The experimental results show that the inhibition performance of organosilicon polymer is obviously better than that of potassium chloride (KCl) and potassium polyacrylate (KPAM), and it can be used as an inhibitor in shale gas drilling.

Keywords: film-forming; shale inhibitor; water-based drilling fluid; organic silicate; polymer

1 Introduction

Global shale gas resources are unconventional oil and gas resources with huge potential, which is equivalent to the sum of coalbed methane and tight sandstone gas resources. In recent years, more and more shale gas has been exploited. In shale gas drilling operations, borehole wall instability is the main problem. This is due to the water sensitivity of shale. When water-based drilling fluid contacts with formation shale, water will form cracks and extended cracks along the interface of highly active clay minerals (1). Shale is easy to soften and expand, which will cause wellbore instability. Therefore, restraining clay hydration is the key to solve wellbore instability. Potassium chloride is a common inhibitor in industry. The hydration expansion of clay is inhibited by substituting K^+ for Ca^{2+} and Na^+ (2). The performance of organic ammonium inhibitors is excellent, but their disadvantages are high toxicity, incompatibility with anionic drilling fluid additives, flocculation and so on (3). Polyether amine inhibitors have low molecular weight and are easy to enter the intergranular compression and diffusion double layers of clay to inhibit them. However, they cannot form effective coating on clay surface, and the inhibition is limited (4). Researchers have been trying to find high-performance copolymer inhibitors, but the performance of the inhibitors is still insufficient (5). One reason is that the bonding strength between these copolymers and clay particles is not enough, and they cannot be firmly adsorbed on the clay surface at high temperature, resulting in a sharp decline in inhibition (6-8). Therefore, it is necessary to introduce new monomers to improve the performance of the inhibitors. By introducing side chains with Si-O bonds into the CC main chain, the inhibitors can form Si-O-Si chain compounds with Si in clay particles. Because of the strong bonding energy of Si-O, the polymer can be adsorbed with clay on the wellbore to form a "hydrophobic membrane" with a certain strength, which can prevent water and drilling fluid from entering the formation, effectively prevent formation hydration expansion, plug formation fractures, prevent clay particles from migrating in the formation and protect the wellbore (9-11). Compared with previous literatures, in this study, a novel organosilicate polymer has been prepared in aqueous solution, which is conducive to cost reduction and environmental protection. The novel organosilicate polymer inhibitor shows better adsorption and inhibition properties.

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2 Materials and methods

2.1 Materials

AM (AR), AA (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 fresh water cement slurry was purchased from Huai'an Bentonite Group Co., Ltd., China.

2.2 Preparation of copolymer

AA, AM, KH570 and MA were dissolved in distilled water at a certain molar ratio (3:5:0.25:3) in a water bath at 40°C, stirred for 30 min, and then NaOH (52 wt%) was used to adjust the solution pH = 7. Then, the mixed solution prepared according to the above order and proportion was added to the three-neck flask. Potassium persulfate of 0.5 wt% of the total mass of dissolved monomer was used as initiator in 20 mL distilled water. It was stirred and heated in a magnetic stirred water bath. The reaction temperature was 40°C and the reaction time was 4 h. A powdered organosilicate polymer called KMAA was prepared by vacuum drying at 40°C and then purifying and crushing with acetone (12-16).

2.3 Structure characterization techniques

The polymer KMAA 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 40-700°C, and the protective gas was nitrogen.

2.4 Inhibitive properties

2.4.1 Immersion test

The mud ball was prepared with a certain proportion of the ingredients and then immersed in the experimental solution. After 20 h, the solution was removed, the mud balls were photographed and weighed (17-19).

2.4.2 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 h. Then, 50 g samples and experimental solution were put into the aging tank and rolled for 16 h at 150°C. The remaining shales were washed with 40 mesh sieve, dried at 103°C for 4 h and weighted (20-22).

2.4.3 Scanning electron microscopy (SEM) observations

Scanning electron microscopy (Zeiss Evo MA 15/LS) was used to study the micro-morphology of the original shale surface and the shale surface modified by polymer KMAA solution. The shale samples were polished by sub-ion polishing. The modified shale samples were immersed in 4.0 wt% KMAA solution for 20 h after polishing and dried in a vacuum drying chamber at 60°C.

3 Results and discussion

3.1 KMAA characterization

3.1.1 Structural characterization of KMAA

Figure 1 shows the FTIR spectrum of KMAA. The characteristic peak of KMAA is about 3363 cm^{-1}, which is assigned to be the characteristic peak of OH in KH-570. Characteristic peaks of about 1516 cm^{-1} and 1421 cm^{-1} were identified as CH_3 asymmetric tensile absorption peaks in KH-570. The characteristic peak is about 1213 cm^{-1}, which is identified as the vibration absorption peak of ester group in KH-570. The absorption peak is about 1076 cm^{-1}, which is assigned as the vibration absorption peak of Si–O in KH-570. The characteristic peak of $(CH_2)_3$ oscillation was observed at 862 cm^{-1}. The characteristic absorption peaks of C=C were not observed at 1625 cm^{-1}, indicating the absence of unreacted monomers in the samples. In addition, no double absorption peaks of the same strength were observed at 1020 cm^{-1}, which indicated that there was no Si–O–Si in the copolymer. Therefore, the hydrolysis and self-condensation of siloxane groups did not occur in KMAA.

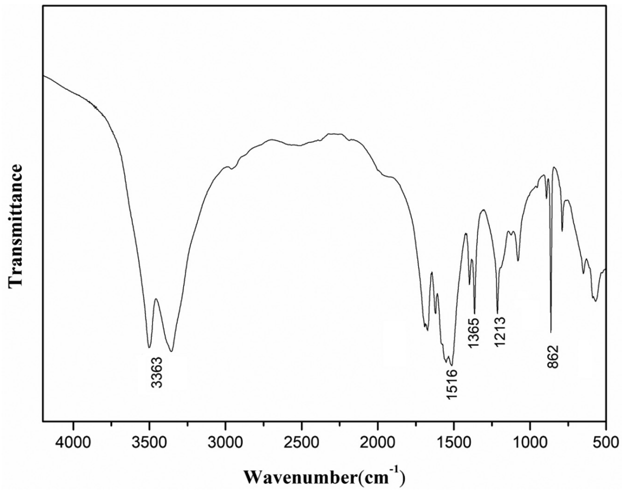

Figure 1: FTIR spectrum of KMAA.

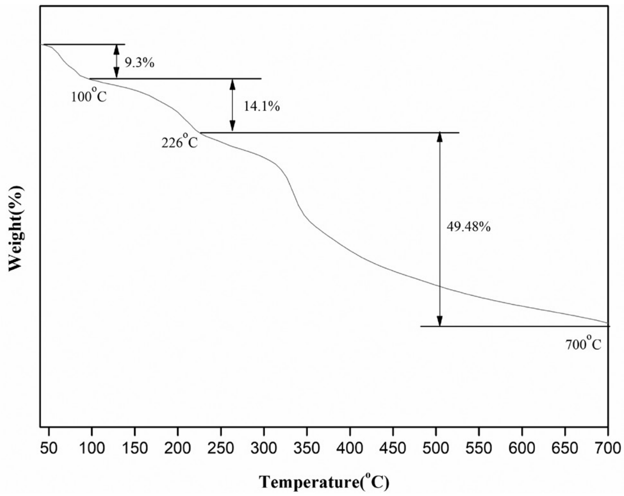

Figure 2: TGA curve of KMAA.

3.1.2 Thermal stability of KMAA

The TGA curve of KMAA is shown in Figure 2. Weightlessness occurring before 100°C is mainly due to the volatilization of water in the sample. The bound water adsorbed by strong hydrophilic groups such as amide group began to volatilize at 107-226°C, the mass of the sample is reduced by 14.1%. The thermogravimetric curve of KMAA decreases dramatically from 226 to 700°C. The weight loss is attributed to the breakage of the main chain and the side chain. The weight loss of the sample has been less up to 226°C, which proved that KMAA had good thermal stability.

3.2 Inhibition evaluation

3.2.1 Immersion test

The results of immersion experiments are shown in Figure 3. The pictures show that the control state of the mud ball immersed in different solutions for 16 h. The experimental solutions in Figure 3a is tap water, and the solution in Figures 3b-d is 0.5 wt%, 1.0 wt% and 2.0 wt% KMAA, respectively. The results show that KMAA solution inhibits the hydration expansion of clay balls to a certain extent. The weight of each clay ball before immersion is 10 g, and the weight after immersion is 35.52 g, 20.13 g, 17.45 g and 15.03 g, respectively. This indicates that the Si–O bond formed by KMAA hydrolysis is adsorbed by clay, which covers the surface of clay sphere and forms a hydrophobic membrane, which prevents water from entering the clay sphere, thus inhibiting the hydration expansion of clay.

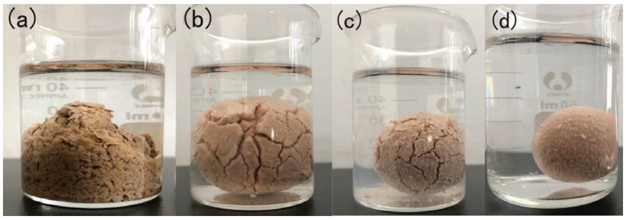

Figure 3: Images of the mud balls after immersion.

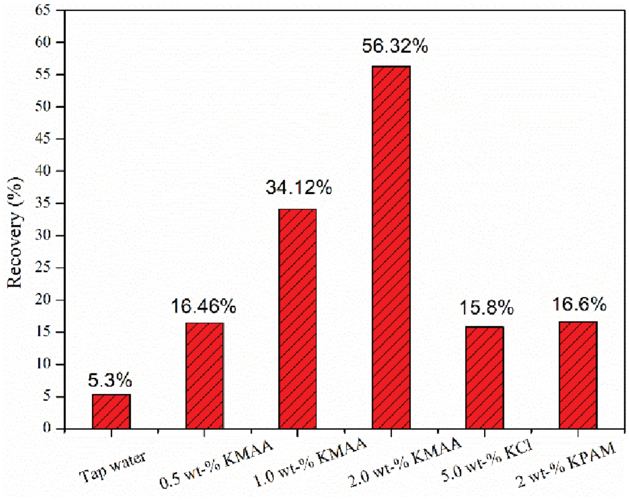

Figure 4: Rolling recovery of inhibitors.

3.2.2 Rolling recovery test

The experimental results (Figure 4) show that the recovery of water is 5.3%, the rolling recovery of 5.0 wt% KCl and 2.0 wt% KPAM is 15.8% and 16.6%, respectively. The

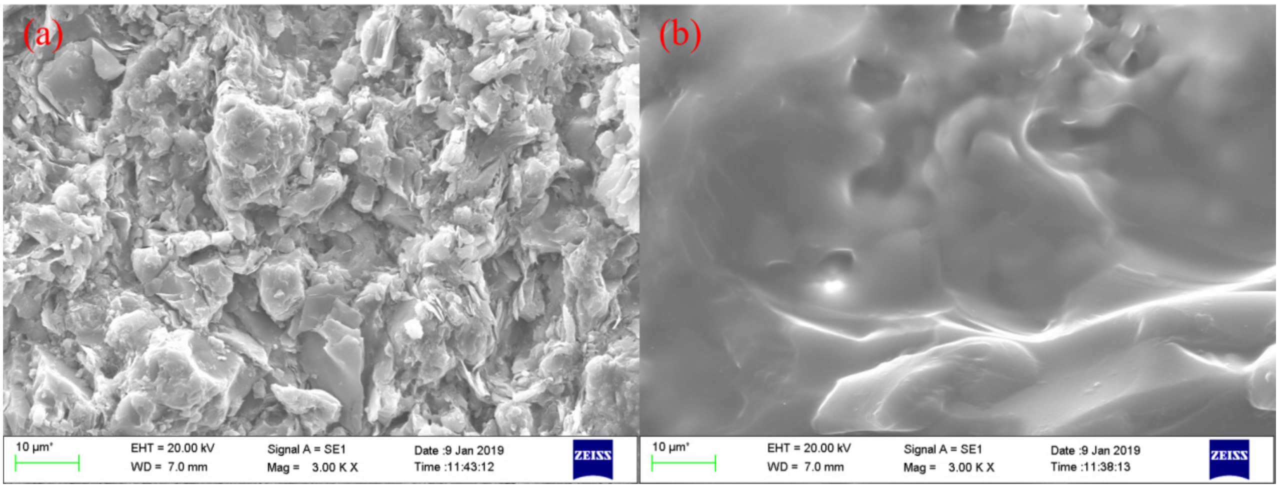

Figure 5: SEM image of the original shale (a) and the modified shale surface immersed in 1.0% KMAA solution (b).

recovery rate of 2.0 wt% KMAA solution is obviously higher than that of other inhibiting solutions (56.32%), which indicates that KMAA has a good ability to inhibit shale hydration.

3.2.3 Scanning electron microscopy (SEM) observations

Figure 5a is a scanning electron microscopic image of the original shale. Figure 5b is a scanning electron microscopic image of the modified shale surface immersed in 1.0% KMAA solution. Under a 3000-fold magnifying, it can be observed that polymer KMAA forms a layer of film on the surface of shale through multi-point adsorption, which effectively prevents water molecules from entering shale. Therefore, the hydration and dispersion of shale have a good inhibition effect.

4 Conclusions

Organosilicon polymer KMAA has good shale inhibition performance, which is obviously superior to the commonly used KCl and KPAM. In this study, infrared spectroscopy showed that a new type of organosilicon polymer shale inhibitor was successfully synthesized by AA, AM, KH-570 and MA in aqueous solution, which is different from the previous studies on modification in organic solvents. The synthetic conditions ensure low cost and environmental protection. Experiments show that KMAA can form Si–O bonds by hydrolysis, thus adsorbing and forming films on clay surface, preventing water molecules from intruding into clay, thus inhibiting the hydration and dispersion of clay. The inhibition of KMAA was also verified by immersion and rolling recovery experiments. The rolling recovery increased from 5.3% to 56.32% in clean water, and the performance of KMAA was obviously better than that of KPAM and KCl. Therefore, KMAA is recommended as an effective inhibitor of shale drilling.

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