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Preparation and Properties of Temperature Resistant and Salt Resistant Lotion Fracturing Fluid Thickener

Rongsheng Gao[1], Yiping Cao[1], Chen Yu[2], Xianghui Zhang[1], Qi Liu[3] and Lanbing Wu[4]

[1] Shanxi Yanchang Petroleum Fracturing Material Co., Ltd, Weinan 715500, China
[2] Production Plant 12 of Changqing Oilfield, PetroChina Oilfield Company, Xi'an 710000, China
[3] Xi'an Alberta Resources & Environment Analysis and Testing Technology Co., Ltd., Xi'an 710000, China
[4] Engineering Research Center of Oil and Gas Field Chemistry, Universities of Shaanxi Provence, Xi'an Shiyou University, Xi'an, 710065, China

Abstract: In order to prepare fracturing fluid with excellent solubility, temperature resistance, salt resistance and shear resistance, acrylamide (AM), 2-acrylamide-2-methylpropanesulfonic acid (AMPS) and acryloylmorpholine (ACMO) were copolymerized, and anionic cellulose was introduced to synthesize a new type of polyacrylamide copolymer p (AM/AMPS/ACMO) through inverse emulsion polymerization. The structure and morphology were characterized by infrared spectroscopy and scanning electron microscope. The results showed that in 0, 5, 10, 20, 50, 100, 150 and 200 g/L NaCl, $CaCl_2$, and $MgCl_2$ solutions, the viscosity of p (AM/AMPS/ACMO) solution modified by PVA fiber was always higher than that of conventional PAM solution, and the polymer modified by PVA fiber had better salt resistance. The anionic cellulose modified thickener was sheared at 120 ℃ and 150 ℃ for 1 h at 170 s^{-1}, and the viscosity after shearing is 89.92 mPa·s and 80.10 mPa·s, respectively, which is much higher than the viscosity required by the general technical conditions of fracturing fluid more than 50 mPa·s, indicating that anionic cellulose modified p (AM/AMPS/ACMO) has good temperature and shear resistance.

Keywords: Inverted emulsion polymerization; cellulose modification; thickener.

1. Introduction

With the relentless vertical advancement and exploitation of oil and gas fields, the demands for high-temperature resistance in fracturing fluids for deep-well reservoirs have escalated significantly [1-2]. Polyacrylamide (PAM), renowned for its exceptional thickening and rheological properties, has been extensively utilized as a fracturing fluid [3-6]. However, the current approach to formulating high-temperature fracturing fluids primarily relies on powder-type thickeners and cross-linking agents [7-9]. This method is constrained by the limited solubility of powder-type thickeners, the prerequisite for pre-preparing the fluid for construction, and the substantial cost of cross-linking agents. In contrast, lotion thickeners offer a more viable solution due to their swift dissolution rate, simplicity in preparing construction solutions, and adaptability to large-scale continuous mixing on-site [10-12]. This article presents a novel approach to formulate a high-temperature-resistant fracturing fluid by utilizing water-soluble anionic cellulose as a base material. The anionic cellulose is then modified with main chain monomer AM, as well as temperature-resistant and salt-resistant monomers AMPS and ACMO, through inverse emulsion polymerization. The choice of anionic cellulose as the starting material is driven by its inherent solubility and ability to enhance the overall viscosity of the fracturing fluid. The addition of AM as the primary monomer ensures robust thickening capabilities, while AMPS and ACMO are incorporated to impart temperature and salt resistance, crucial for fracturing operations in harsh subterranean environments. The inverse emulsion polymerization technique selected for this study offers several advantages, including improved control over the polymerization process, enhanced homogeneity of the resulting polymer, and the potential for scale-up production. This method involves emulsifying the monomer mixture in a non-aqueous solvent, creating a stable emulsion system that facilitates polymerization. In summary, the development of an anionic cellulose-based modified p (AM/AMPS/ACMO) fracturing fluid represents a significant stride forward in meeting the challenging demands of high-temperature and salt-tolerant fracturing operations. This approach leverages the inherent advantages of lotion thickeners while introducing tailored modifications to enhance the performance of the fracturing fluid.

2. Experimental Part

2.1. Materials and instruments

Acrylamide (AM), 2-acrylamide-2-methylpropanesulfonic acid (AMPS), acryloyl morpholine (ACMO), water-soluble anionic cellulose (specification 1.25dtex length 4 mm), span-80, tween-60, white oil medicine, etc. are all industrial grade; Ammonium persulfate, sodiumbisulfite, sodium hydroxide, ethyl alcohol absolute, etc. are all analytical reagent. VERTEX-80 fourier transform infrared spectrometer; FEIVerios 460 high resolution field emission scanning electron microscope; Haake mars40 rotational rheometer; ZNN-D6B button type six-speed viscometer; 1835 capillary viscometer; BDL-3000L nitrogen analyzer; WZ-50C6 micro-injection pump.

2.2. Synthesis of anionic cellulose modified copolymer p (AM/AMPS/ACMO)

Weigh 10 g of Span-80 and 5 g of Tween-60 into a beaker, add 300 g of white oil and mix to get the oil phase. Weigh 220 g of AM, 50 g of AMPS, 20 g of ACMO, 20 g of anionic cellulose and 2 g of 2% of ammonium persulfate into 300 g of distilled water, stir and fully dissolve them, and then use 50 mL of sodium hydroxide solution of certain concentration to adjust the pH to 6.9~7.1 to obtain the aqueous phase. When the temperature of the water phase drops to room temperature, the water phase is injected into the oil phase under the condition of high-speed stirring and fully stirred to obtain a stable water in oil lotion. Pour the lotion into a three necked flask, mix with nitrogen for 45 min, and then start the reaction. Add 2 g of 1% sodiumbisulfite to the three-necked flask in batches according to a certain proportion. Under the protection of nitrogen, the required copolymer can be prepared by controlling the temperature to 40 °C and reacting for 4-5 h, and then adding a certain amount of phase conversion agent to obtain the copolymer p (AM/AMPS/ACMO) for fracturing fluid.

2.3. Infrared Spectroscopy (FTIR) characterization

The prepared polymer was repeatedly washed with ethyl alcohol absolute to remove impurities, purified, filtered, dried to constant weight, ground and crushed to obtain white powder. The mass ratio of polymer powder and potassium bromide powder was 1:75, and the Infrared spectroscopy of the polymer was determined by KBr compression method and Fourier infrared spectrometer.

2.4. Scanning electron microscope (SEM)

The prepared polymer white powder was prepared into 0.2% water solution, which was frozen in liquid nitrogen and dried in vacuum. After that, the micro-morphology and structural characteristics of the polymer were observed by scanning electron microscope.

2.5. Salt resistance test

1% polymer and 0, 5, 10, 20, 50, 100, 150, 200 g/L NaCl are respectively used to prepare a series of NaCl polymer saline solutions, and the polymer saline solutions of $CaCl_2$ and $MgCl_2$ are prepared in the same way. The apparent viscosity is measured by electronic six-speed viscometer.

2.6. Temperature resistance test

The 1% polymer solution was prepared with clean water, and the shear rate was 170 s^{-1} by using HAAKE Mars 40 rotary rheometer for 1 hour. The temperature and shear resistance curves of the polymer solution were obtained at 120 °C and 150 °C respectively.

2.7. Gel breaking performance test

Prepare 1% polymer solution with clear water and add 0.01%, 0.02%, 0.03%, 0.04% and 0.05% ammonium persulfate respectively. After mixing evenly, put it in a 90 °C thermostatic water bath for gel breaking, and test the apparent viscosity of the solution every 30 minutes.

3. Results and Discussion

3.1. Infrared spectroscopy characterization

Figure 1 shows the infrared spectroscopy of PAM modified by ACMO, AMPS and anionic cellulose, in Accordance with to p (AM/AMPS/ACMO) infrared spectroscopy, 3383 cm^{-1} is the stretching vibration absorption peak of N-H in - NH_2, and 2931 cm^{-1} is the stretching vibration absorption peak of C-H in - CH_3 and - CH_2 -, 1675 cm^{-1} is the stretching vibration absorption peak of C=O, 1408 cm^{-1} is the bending vibration absorption peak in - CH_3 and - CH_2 -, and 1121 cm^{-1} is the C-O bond absorption peak in the morpholine ring in ACMO, 1188, 1043 cm^{-1} is the stretching vibration absorption peak of O-S of - HSO_3 in AMPS [8], and the stretching vibration absorption peak of carbon-carbon double bond near 1642 cm^{-1} is weak, indicating that most monomers are fully polymerized.

3.2. Stability of lotion

The anionic cellulose aqueous solution is easy to form a film at the oil-water interface due to its hydrophilic and lipophilic structure, which can improve the stability of the lotion system together with emulsifiers. No. 1 in Figure 3 is PAM water in oil lotion modified by anionic cellulose, No. 2 is the water in oil lotion of conventional PAM.

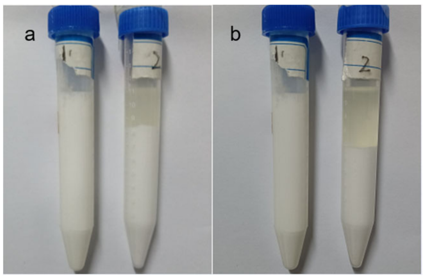

Figure 3. Emulsion stability test((a)Lotion after standing for 2 months; (b) Lotion after 4 months)

Figure 3 (a) shows the state of lotion after standing for 2 months, and Figure 3 (b) shows the state of lotion after standing for 4 months. The experimental results showed that the water in oil lotion of conventional PAM appeared delamination after static, and the delamination became more obvious with the increase of static time. The emulsification state of the water in oil lotion of anionic cellulose modified PAM was very stable and did not delaminate after static. It shows that anionic cellulose has a certain effect on the stability of lotion.

3.3. Salt resistance

Add 1% anionic cellulose modified p (AM/AMPS/ACMO) to NaCl, $CaCl_2$ and $MgCl_2$ solutions with concentrations of 0, 5, 10, 20, 50, 100, 150, 200 g/L respectively, and test the apparent viscosity change of the solution. The introduction of anionic cellulose into the polymer will make the molecular space structure of polyacrylamide more complex and support the molecular chain of polyacrylamide as a large framework, so that it can better maintain the molecular chain structure, and the sulfonic group of p (AM/AMPS/ACMO) containing the salt-resistant monomer AMPS has strong electrostatic repulsion, it is not easy to be electrostatic shielded by bivalent calcium and magnesium ions, making it more salt-resistant; The cyclic group of ACMO has a large steric hindrance, which can better keep the molecular chain intact in salt water, which is conducive to improving the salt resistance of polyacrylamide. It can be seen from Fig.4, Fig.5 and Fig.6 that in different concentrations of NaCl, $CaCl_2$ and $MgCl_2$, the viscosity of PAM solution modified by anionic cellulose is always higher than that of conventional PAM solution, indicating that the polymer modified by anionic cellulose has better salt resistance.

3.4. Temperature resistance

The temperature and shear resistance of polymer solution were tested by rotating rheometer at 120 °C and 150 °C, and the shear rate was 170 s^{-1}. Fig.7 and Fig. 8 show the temperature and shear resistance curves of 1% modified p (AM/AMPS/ACMO) solution at 120 ℃ and 150 ℃ respectively. It can be seen from the figure that the viscosity of polymer solution can still reach 89.92 mPa·s after heating to 120 ℃ for shearing for 1 hour, and 80.10 mPa·s after heating to 150 ℃ for shearing for 1 hour, which is far greater than 50 mPa·s required by the general technical conditions of fracturing fluid. Both curves show a downward trend of viscosity with the increase of temperature. After the temperature rises to the required temperature, the viscosity basically remains unchanged. The introduction of anionic cellulose makes the spatial network structure of polymer solution more complex, and the molecular structure is not easy to deform under high temperature and high shear. The combined effect of the chemical action of p (AM/AMPS/ACMO) molecule and the physical action of anionic cellulose makes its temperature resistance better. The temperature resistance test shows that the PAM solution modified by anionic cellulose has good temperature resistance and shear resistance, which meets the needs of high temperature deep well site construction. At present, in order to improve the temperature resistance of high temperature polymer, cross-linking agent or increasing the dosage of thickener are usually used, which will lead to high fracturing cost and complicated fluid preparation process. However, the solid content of the lotion polymer prepared in this paper is 31.8%. During the temperature resistance experiment, the amount of thickener is only 1%, and no cross-linking agent and other additives are added. The p (AM/AMPS/ACMO) modified by anionic cellulose has good temperature resistance.

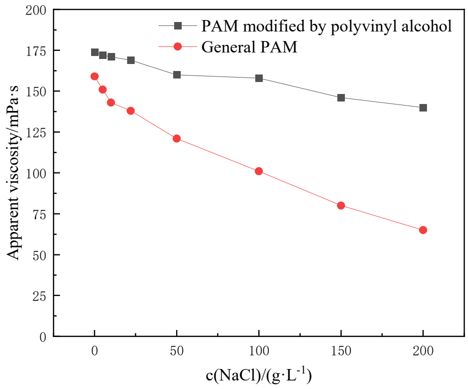

Figure 4. Effect of c(NaCl) on viscosity of polymer solution

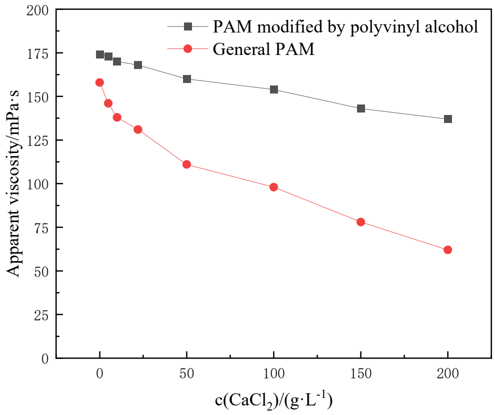

Figure 5. Effect of c($CaCl_2$) on viscosity of polymer solution

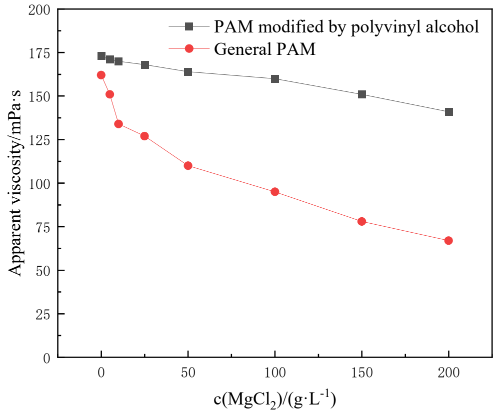

Figure 6. Effect of c($MgCl_2$) on viscosity of polymer solution

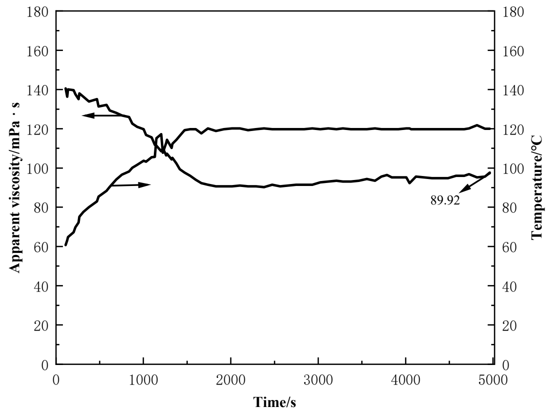

Figure 7. Temperature and shear resistance curve of anionic cellulose modified PAM-120 ℃

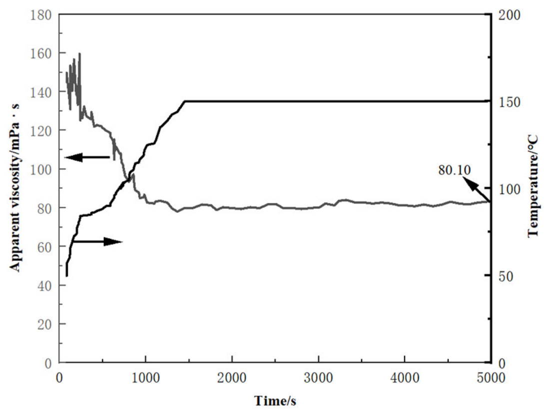

Figure 8. Temperature and shear resistance curve ofanionic cellulose modified PAM-150 ℃

3.5. Gel breaking performance

As a gel breaker, ammonium persulfate is easy to decompose when heated to produce strong oxidizing free radicals, which can destroy the molecular chain structure and make it break into small molecules. Gel breaker (ammonium persulfate) with different dosage was used to break 1% polymer solution at 90 ℃. The results are shown in Fig.9. When the dosage of ammonium persulfate is greater than 0.03%, the viscosity of polymer solution is less than 5 mPa·s within 120 min, According to the shale gas fracturing fluid Part 3: Performance index and evaluation method of continuously mixed fracturing fluid[13-17], it is shown that the polymer solution has been completely broken. With the increase of the amount of gel breaker, the viscosity of gel breaker decreases and the breaking speed is faster. The breaking time of the polymer solution can be adjusted according to the amount of gel breaker.

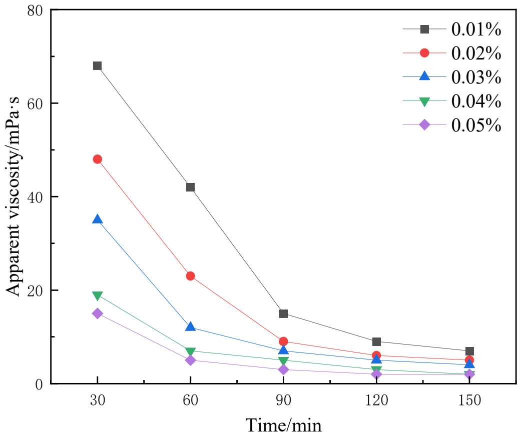

Figure 9. Broken performance of theanionic cellulose modified PAM solution

4. Conclusion

A novel anionic cellulose modified temperature-resistant and salt-resistant polyacrylamide copolymer was synthesized by inverse emulsion polymerization. The synthesis of anionic cellulose modified polymers was confirmed by infrared spectroscopy and scanning electron microscopy .Scanning electron microscope showed that the PAM modified by anionic cellulose had a denser and more complex internal network structure than conventional PAM. The rheological property test shows that the PAM modified by anionic cellulose has good temperature resistance and shear resistance. At 120 ℃ and 150 ℃. After shearing at 170 s^{-1} for 1 hour, the final viscosity was 89.92 mPa·s and 80.10 mPa·s respectively, and the solution was easy to break. According to all the experiments, it can be concluded that a new type of polyacrylamide copolymer p (AM/AMPS/ACMO) has been successfully synthesized, which can prepare fracturing fluid with good solubility, salt resistance, temperature resistance and shear resistance.

Acknowledgment

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