energies

Article

Synthesis and Plugging Performance of Poly (MMA-BA-ST) as a Plugging Agent in Oil-Based Drilling Fluid

Jian Yang [1], Zhen Lei [2], Bo Dong [3], Zhongqiang Ai [4], Lin Peng [5] and Gang Xie [2,*]

1 Engineering Technology Management Department, Sinopec Southwest Oil and Gas Branch, Chengdu 610500, China
2 State Key Laboratory of Oil & Gas Reservoir Geology and Exploitation, Southwest Petroleum University, Chengdu 610500, China
3 Pengzhou Gas Field Development Project Department, Sinopec Southwest Oil and Gas Branch, Chengdu 610500, China
4 Engineering Technology Management Department, Sinopec Southwest Oil and Gas Branch, Deyang 618014, China
5 Petroleum Engineering Supervision Center, Sinopec Southwest Oil and Gas Branch, Deyang 618014, China
* Correspondence: 201899010129@swpu.edu.cn

Abstract: Nanopolymer was developed in order to solve the problem that the micron-scale plugging agent cannot effectively plug nanopores, which leads to instability of the wellbore. The oil-based nano plugging agent poly (MMA-BA-ST) was synthesized by Michael addition reaction using styrene, methyl methacrylate and butyl acrylate compounds as raw materials. Poly (MMA-BA-ST) has a particle size distribution of 43.98–248.80 nm, with an average particle size of 108.70 nm, and can resist high temperatures of up to 364 °C. Poly (MMA-BA-ST) has little effect on the rheological performance parameters of drilling fluids, no significant change in the emulsion breaking voltage, significant improvement in the yield point of drilling fluids and good stability of drilling fluids. The mud cake experiment, and artificial rock properties of poly (MMA-BA-ST), showed that the best-plugging effect was achieved at 0.5% addition, with a mud cake permeability of 6.3×10^{-5} mD, a plugging rate of 72.12%, an artificial core permeability of 4.1×10^{-4} mD and a plugging rate of 88.41%. The nano plugging agent poly (MMA-BA-ST) can enter the nanopore joints under the action of formation pressure to form an effective seal, thus reducing the effect of filtrate intrusion on well wall stability.

Keywords: wellbore stabilization; nano plugging agent; oil-based drilling fluids; permeability; plugging rate

check for updates

Citation: Yang, J.; Lei, Z.; Dong, B.; Ai, Z.; Peng, L.; Xie, G. Synthesis and Plugging Performance of Poly (MMA-BA-ST) as a Plugging Agent in Oil-Based Drilling Fluid. *Energies* **2022**, *15*, 7626. https://doi.org/10.3390/en15207626

Academic Editors: Shifeng Zhang, Liangbin Dou, Wenmin Guo, Guoqiang Xing and Yan Zhuang

Received: 3 September 2022
Accepted: 2 October 2022
Published: 15 October 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/licenses/by/4.0/).

1. Introduction

Shale formations account for about 75% of the world's drilled formations, and the development of shale gas resources is necessary for the global energy market and sustainable economic development [1,2]. Shale gas resources in the Sichuan Basin are abundant and have great potential for exploration and development in China [3,4]. Horizontal wells have become the primary drilling method to increase shale gas production, which increases the risk of well wall instability compared to straight wells. Using water-based drilling fluids to drill horizontal shale gas wells can cause hydration and swelling of clay minerals, which can lead to complex downhole accidents, such as stuck drilling and block dropping [5,6]. Oil-based drilling fluids are natural inhibitors that have proven to be excellent in solving drilling problems due to wellbore instability caused by shale hydration. Oil-based drilling fluids to drill shale gas horizontal wells have become a hot topic [7]. Microporous seams in shale formations are extremely developed, and micrometer and nanopore seams coexist, with nanoscale seams occupying most of the proportions [8–10]. However, the commonly used plugging materials in drilling fluids are generally in the micron-scale range in size, which cannot effectively seal nanopores. Drilling fluids will invade nano-fractures, leading to fracture expansion and poor formation stability, resulting in wellbore instability [11,12].

Developing efficient plugging agents is one of the critical aspects of solving well-wall destabilization. Li et al. [13] developed a new oil-based drilling fluids composite-plugging agent, CPA, which can make the mud cake thinner and denser and significantly reduce shale permeability. However, the size of the plugging agent is too large to plug the nano-porosity. Li et al. [14] synthesized a styrene-butadiene resin/nano-SiO_2 (SBR/SiO_2) composite, which can be used in both oil-based and water-based drilling fluids with good temperature resistance and plugging effect. Still, the plugging agent is more likely to agglomerate in oil, the particle size increases significantly, and it cannot plug pores within 200 nm. Geng et al. [15] used oleic acid as a surface modifier to improve the dispersion stability of polystyrene in mineral oil. The plugging agent was resistant to high temperatures of 252 °C and effectively mitigated the decrease in the mechanical stability of the rock. However, the plugging agent did not significantly reduce the high-temperature and high-pressure filter loss, and the reduction rate of 3% was only 21%. Liu et al. [16] investigated an organic–inorganic nanocomposite (NS-D) as a plugging agent. After being added to the drilling fluids, the filtrate volume was reduced by 90.5%. Still, more of this plugging agent was added, which significantly impacted the drilling fluid's performance and was suitable for water-based drilling fluids. Ma et al. [17] used multi-walled carbon nanotubes (MWCNTs) as the main raw material and modified them using the SI-ATRP method. The modified multi-walled carbon nanotubes have good dispersion stability and a good plugging effect with a small addition, but again, they have only been used in water-based drilling fluids. Li et al. [18] synthesized a novel temperature- and salt-tolerant micro-crosslinked polyampholyte gel. The gel can resist the high temperature of 200 °C, effectively reducing the filtration loss of drilling fluids. Unlike the direct plugging of conventional polymer plugging agents, the gel reduces fluid loss by improving the stability of the base fluid suspension. Through research, it has been found that gel polymers are generally used as water plugging agents, plugging malignant leakage, and so on. For example, Tong et al. [19] conducted experimental studies on organochromium gels as water blocking agents, and Yang et al. [20] developed and comprehensively evaluated a polyampholyte (P(MPTC) based on sulfonated and quaternary ammonium functional groups) -co-Nass)) injectable self-healing hydrogels to prevent severe fluid loss into the formation.

There is currently less research on oil-based drilling-fluid plugging agents. The commonly used plugging agents have the disadvantages of considerable size, poor dispersion, insufficient temperature resistance, high addition and high impact on drilling fluid performance. Studying a nano plugging material suitable for oil-based drilling fluids can further improve the plugging performance of oil-based drilling fluids and thus enhance the stability of well walls. In this paper, the oil-based nano plugging material poly (MMA-BA-ST) was synthesized from compounds such as styrene, methyl methacrylate and butyl acrylate by Michael addition reaction under certain conditions. Poly (MMA-BA-ST) is a nanomaterial, and single nanoparticles can seal shale pores, similar to nanoparticles, by plugging. Multiple nanoparticle stacks can plug shale pores larger in diameter than nanoparticle size [21]. The hydrophobic group in the structure of poly (MMA-BA-ST) enables it to be uniformly dispersed in oil-based drilling fluids; it contains a benzene ring with strong temperature resistance, which gives it good temperature resistance. Poly (MMA-BA-ST) can play an excellent plugging effect with a small addition and has little effect on the rheological parameters of the drilling fluids.

2. Materials and Methods

2.1. Materials

Sodium dodecyl sulfate, sodium vinyl sulfonate, styrene (St), methyl methacrylate (MMA), butyl acrylate (BA), divinylbenzene (DVB) and ammonium persulfate (APS) are from Chengdu Kelong Chemical Reagent Factory; 3# white oil, $CaCl_2$, main emulsifier, auxiliary emulsifier, wetting agent, filter loss reduction agent, organic clay, quicklime and barite are all industrial products.

2.2. Instruments

The particle size distribution of the nanomaterials was measured by a laser scattering system (BI-200SM) of Brookhaven Instruments (USA). The characteristic functional groups of the nanomaterials were tested by Fourier transform infrared spectrometer (Nicolet 6700) of Thermoelectric (USA). The pyrolysis property of the material was tested by the Corporation simultaneous thermal analyzer (TGA/DSC1) of METTLER, Switzerland. The plugging performance of nanomaterials was tested by the high-temperature and high-pressure fluid loss instrument (GGS42-2A) of Shandong Meike Instrument Co., Ltd., China. The rheological properties of the drilling fluids were tested by the six-speed rotational viscometer (1103) of Shandong Meike Instrument Co., Ltd., China. The microscopic morphology of the mud cake was observed by scanning electron microscope (Quanta450) of FEI Company (USA). The permeability was tested by the SCMS-C4 high-temperature and high-pressure tight core infiltration device (20172034-1) of Chengdu Haohan Completion Rock Power Co., Ltd., China.

2.3. Preparation of Poly (MMA-BA-ST)

A small amount of sodium dodecyl sulfate and sodium vinyl sulfonate was weighed into a three-port vial, ultra-pure water was added to dissolve it, and appropriate amounts of styrene, methyl methacrylate, butyl acrylate, and divinylbenzene were added in turn, the three-port vial was transferred to a water bath, stirred at 300 rpm for 30 min at room temperature, nitrogen passed, heated to the reaction temperature, ammonium persulfate was added after 20 min and reacted for 8 h to obtain the oil-based nano plugging agent poly (MMA-BA-ST).

2.4. Preparation of Basic Drilling Fluids

We call the oil-based drilling fluids without poly (MMA-BA-ST) added base drilling fluids. The basic drilling fluids are used to evaluate the plugging performance of poly (MMA-BA-ST), and its formula is not fixed.

The basic drilling fluid formula used was: 80% 3# white oil + 20% $CaCl_2$ brine with 25% concentration + 0.6% primary emulsifier + 1.5% secondary emulsifier + 0.8% wetting agent + 3% organic soil + 3% quicklime + 8% filter loss reduction agent + some barite.

The basic drilling fluid preparation process was: First, weigh the main emulsifier, auxiliary emulsifier and wetting agent in a high, stirring cup, pour 3# white oil, and stir for 30 min with a high, stirring machine. Then, organic soil, 20% $CaCl_2$ brine with 25% concentration, quicklime, filter loss reduction agent and barite were added in sequence. Stir for 30 min for each ingredient added.

2.5. Drilling Fluids Rheological Properties Test

Drilling fluid rheology refers to the characteristics of drilling fluid flow and deformation. Testing the rheological properties of drilling fluids was performed using the six-speed rotational viscometer. The six-speed rotational viscometer has six speed variations of 3, 6, 100, 200, 300 and 600 rpm, corresponding to six different shear rates of 5, 10, 170, 340, 511 and 1022 s^{-1}, respectively. The test device of the six-speed rotational viscometer consists of an inner cylinder and an outer cylinder. The drilling fluids can enter the annular space between the inner and outer barrels. When the outer cylinder rotates at a constant speed, the drilling fluids generate torque on the inner cylinder, thereby driving the inner cylinder to rotate at a certain angle. According to Newton's law, the angle is proportional to the viscosity of the liquid. Thus, the measurement of liquid viscosity becomes a measurement of angle, and the angle is reflected in the dial reading. The rheological parameters of the drilling fluids, such as apparent viscosity (AV), plastic viscosity (PV) and yield point (YP), are calculated using standard procedures recommended by the American Petroleum Institute (API) at 600 to 3 rpm readings.

2.6. HTHP Experiment

Next, we added poly (MMA-BA-ST) to the base drilling fluids. In order to simulate the formation temperature, it was aged at 150 °C for 16 h. The aged drilling fluids were stirred evenly, and the filtrate volume was recorded for 30 min using the HTHP fluid loss meter. The experimental temperature was 150 °C. The thickness of the mud cake obtained after the experiment was measured. We calculated the permeability of the mud cake according to Formula (1) and then calculated the plugging rate according to Formula (2).

$$K = 100 \times \frac{Q\mu L}{A\Delta P} \quad (1)$$

In the formula:

K—Permeability of the "artificial mud cake", mD;
Q—Average volume of water loss per second, cm^3/s;
μ—Viscosity of the filtrate, mPa·s;
L—Thickness (or length) of the mud cake, cm;
A—Area of the filter cake, cm^2;
ΔP—Filter loss differential pressure, MPa;

where the area of the filter cake = 23.8 cm^2 and the filter loss pressure difference = 3.5 MPa.

$$K_r = \frac{K - K'}{K} \times 100\% \quad (2)$$

In the formula:

K_r is the plugging rate, %;
K is the permeability before plugging, mD;
K' is the permeability after plugging, mD.

2.7. Core Permeability Experiment

Through the mud cake experiment, we obtain the amount of poly (MMA-BA-ST) addition when the permeability is the lowest. Poly (MMA-BA-ST) was added to 3# white oil to prepare 250 mL of mixed solution, and the added amount was the corresponding amount when the permeability was the lowest in the mud cake experiment. The mixture was stirred uniformly for 30 min and ultrasonically dispersed for 30 min at 50 °C. The 3# white oil and 3# white oil + poly (MMA-BA-ST) mixed solutions were added to the high-temperature and high-pressure tight core permeability testing device to measure their permeability. The experimental temperature was 110 °C, and the pressure difference was 3.5 MPa.

3. Results and Discussion

3.1. Infrared Spectrum

The infrared spectral analysis allows the determination of whether the final synthesized substance contains characteristic functional groups. The infrared spectrum of the oil-based nanoplugger poly (MMA-BA-ST) is shown in Figure 1. In Figure 1, the -OH stretching vibration peak of liquid water appears at 3355 cm^{-1}, which is because the solvent of the synthesized poly (MMA-BA-ST) is ultrapure water. The stretching vibration peak of the benzene ring skeleton appears at 1639 cm^{-1}, and the external deformation vibrational peak of C-H on the benzene ring appears at 690 cm^{-1}, proving the presence of the benzene ring in the structure, which is mainly provided by styrene. The structure contains ester group C=O, its stretching vibration peak is near 1720 cm^{-1}, covered by the peak at 1639 cm^{-1}, and the ester group is mainly provided by methyl methacrylate and butyl acrylate. The characteristic functional groups of poly (MMA-BA-ST) can be tentatively determined by IR spectroscopy. The benzene ring enhances the temperature resistance of poly (MMA-BA-ST), and the ester group enhances lipophilicity.

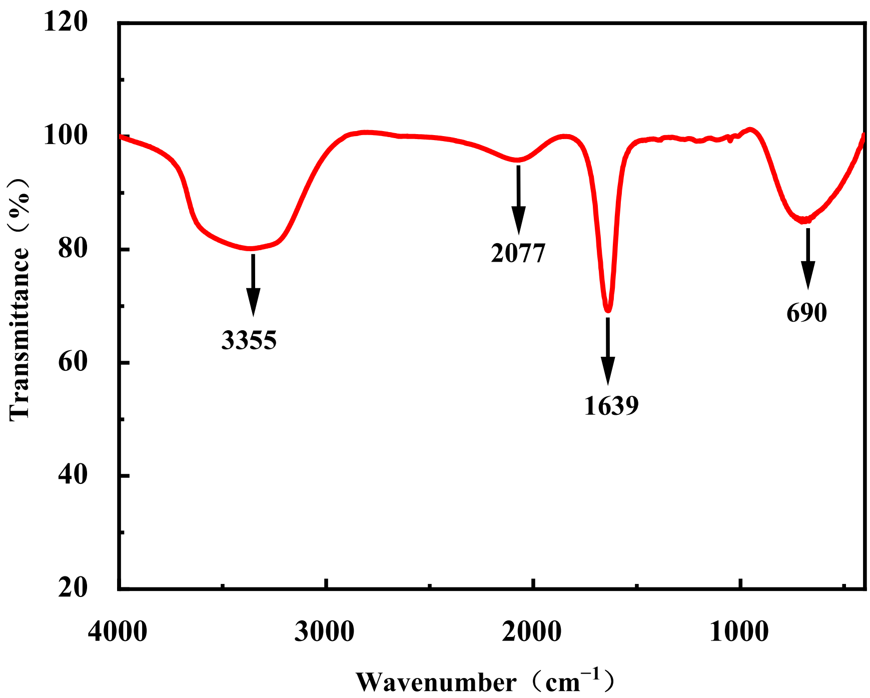

Figure 1. Infrared spectra of poly (MMA-BA-ST).

3.2. Particle Size Distribution of Poly (MMA-BA-ST)

The particle size distribution of poly (MMA-BA-ST) is measured by a laser scattering system shown in Figure 2. The particle size distribution of poly (MMA-BA-ST) is 43.98–248.80 nm. When the cumulative content accounts for 50% of the total, the corresponding particle size is 92.41 nm; therefore, poly (MMA-BA-ST) can be identified as a nanomaterial. Poly (MMA-BA-ST) can be used as a nano-plugging agent for plugging nanopores and seams in formations.

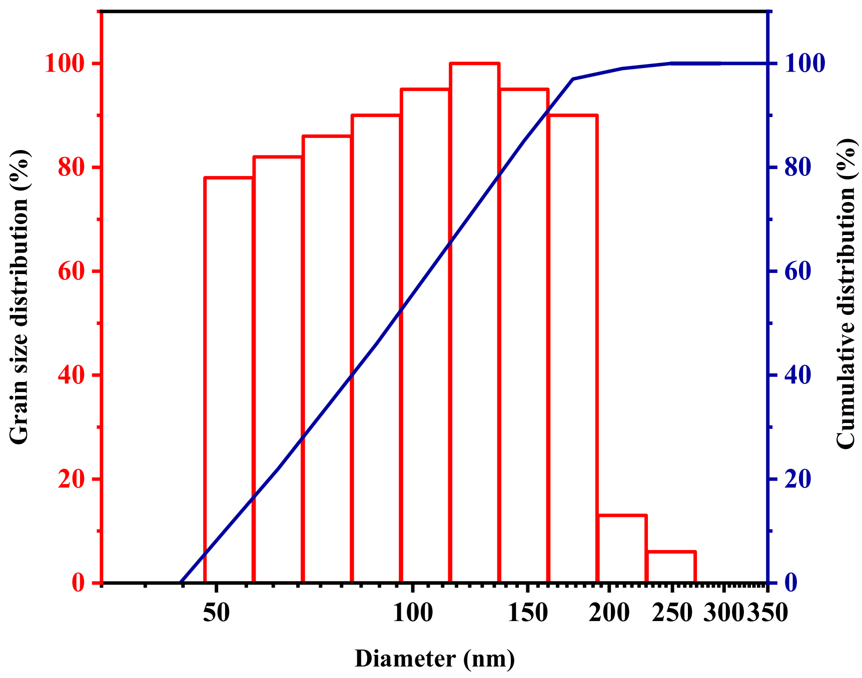

Figure 2. Particle size distribution of poly (MMA-BA-ST).

3.3. Thermogravimetric Analysis

Thermogravimetric experiments can detect the temperature resistance of poly (MMA-BA-ST). Figure 3 shows the TG-DTG curve of the nano plugging agent poly (MMA-BA-ST). It can be seen from Figure 3 that the mass of poly (MMA-BA-ST) gradually decreases with the increase in temperature. The decrease in poly (MMA-BA-ST) before 300 °C is small, indicating that the main structure is not damaged by high temperature, which is mainly manifested by the evaporation of bound water and free water, and a small number of compounds are decomposed. We take the intersection of TG curves with different trends and determine the initial decomposition temperature of poly (MMA-BA-ST) to be 364 °C. At this time, the molecular chain of poly (MMA-BA-ST) begins to break down and decompose at this high temperature. The final decomposition temperature of poly (MMA-BA-ST) is 417 °C, and it can be seen from the DTG curve that the decomposition rate is the fastest at around 399 °C. The mass loss from 364 to 417 °C is 77.66%, which basically completes the thermal decomposition of poly (MMA-BA-ST) [22,23]. The results of thermogravimetric experiments show that poly (MMA-BA-ST) can withstand high temperatures above 300 °C because the polymer contains benzene rings with strong temperature resistance, which makes poly (MMA-BA-ST) have good temperature resistance.

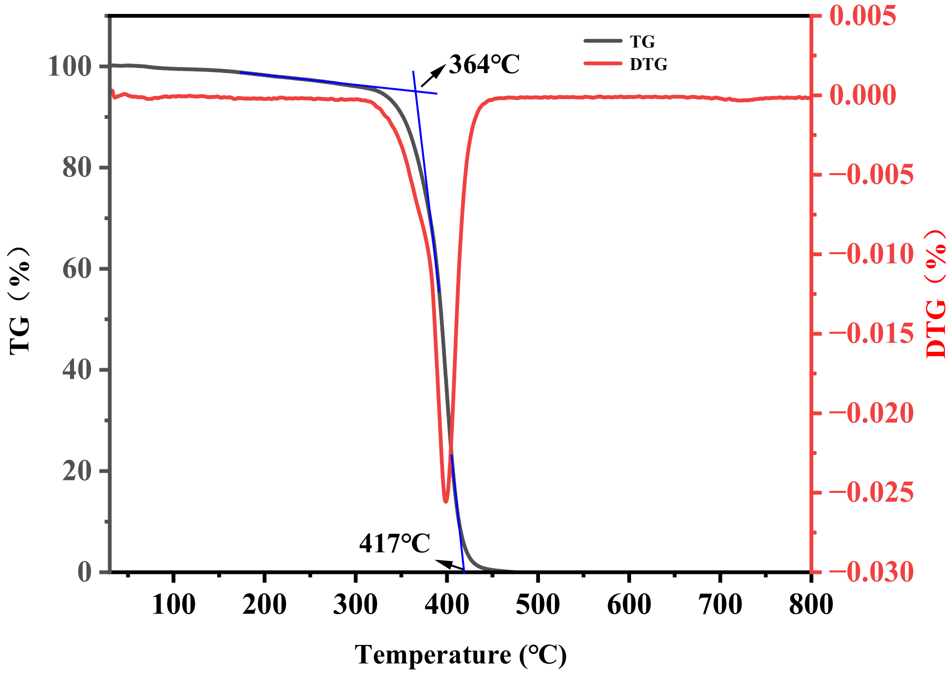

Figure 3. Poly (MMA-BA-ST) thermogravimetric analysis chart.

3.4. Effect of Poly (MMA-BA-ST) on Drilling Fluids Properties

Through characterization experiments, poly (MMA-BA-ST) was proven to be a nanomaterial with good temperature resistance, which can be used to plug nanopores and seams in formations. However, the plugging agent will have an impact on the rheological properties and electrical stability of the drilling fluids, and the more that is added, the greater the impact. This characteristic is detrimental to drilling fluids. Therefore, it is necessary to study the effect of poly (MMA-BA-ST) on the performance of drilling fluids, which is the premise of judging whether poly (MMA-BA-ST) can be used as a nano plugging agent in drilling fluids.

We added 0.00%, 0.25%, 0.50%, 0.75% and 1.00% poly (MMA-BA-ST) to the base drilling fluids in sequence. The rheological properties (AV, PV, YP) and emulsion breaking voltage of drilling fluids were tested at 50 °C. The changes in drilling fluids performance parameters with different poly (MMA-BA-ST) addition amounts are shown in Figures 4–7.

3.4.1. Effect of Poly (MMA-BA-ST) on AV

Figure 4 shows the change curve of AV of drilling fluids after poly (MMA-BA-ST) was added. As can be seen from Figure 4, the AV of the basic drilling fluids is 62.0 mPa·s. With the increase in the poly (MMA-BA-ST) addition amount, the AV of the drilling fluids also increases. When the addition amount is 1.0%, the AV of the drilling fluids increases to 70.5 mPa·s, which is 13.71% higher than that of the basic drilling fluids. This variation has little effect on the drilling fluids.

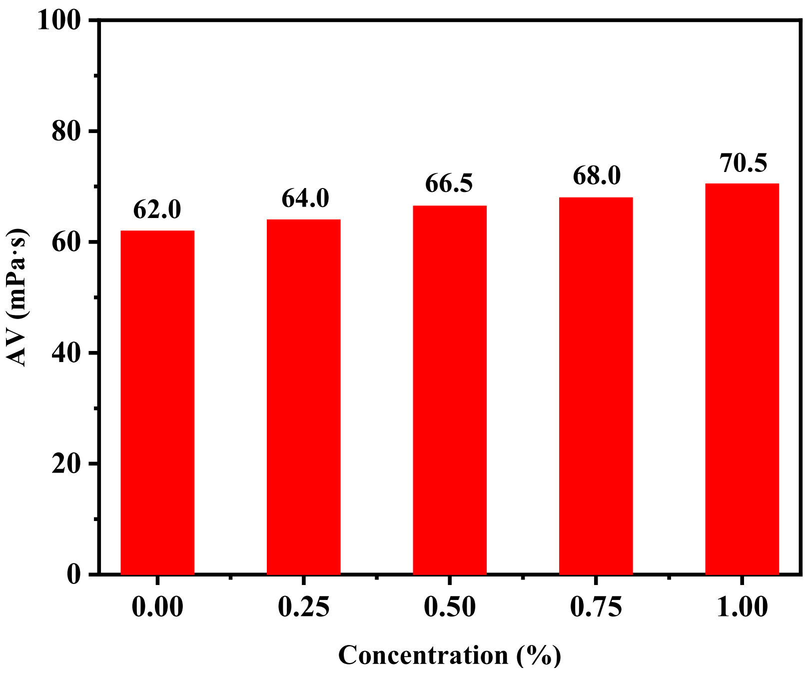

Figure 4. AV change curve after aging of oil-based drilling fluids with the addition of poly (MMA-BA-ST).

3.4.2. Effect of Poly (MMA-BA-ST) on PV

Figure 5 shows the variation curve of PV of drilling fluids after poly (MMA-BA-ST) was added. As can be seen from Figure 5, the variation trend of PV is similar to the AV, and the plastic viscosity of the basic drilling fluids is 51.0 mPa·s. When the addition amount is 1.0%, the PV of the drilling fluids is 57.0 mPa·s, which increases by 11.76% compared with the basic drilling fluids, with small variation. It indicates that poly (MMA-BA-ST) has little effect on the PV of drilling fluids.

3.4.3. Effect of Poly (MMA-BA-ST) on YP

Figure 6 shows the YP change curve of oil-based drilling fluids with poly (MMA-BA-ST) added. As can be seen from Figure 6, the YP of the oil-based drilling fluids base slurry is 11.0 and 13.5 Pa when the poly (MMA-BA-ST) addition amount is 0.50%. The addition of poly (MMA-BA-ST) significantly increases the YP of the drilling fluids, which is beneficial for the ability of the drilling fluids to carry bottom-hole cuttings and clean the wellbore.

3.4.4. Effect of Poly (MMA-BA-ST) on Emulsion Breaking Voltage

Figure 7 shows the change curve of the emulsion breaking voltage of oil-based drilling fluids with the addition of poly (MMA-BA-ST). From Figure 7, it can be seen that the emulsion breaking voltage of oil-based drilling fluids gradually decreases with the increase in poly (MMA-BA-ST) addition, but the decrease is small, and the emulsion breaking voltage is always higher than 600 V. At this time, the drilling fluids still has good stability.

From a holistic point of view, poly (MMA-BA-ST) has less influence on the rheology and electrical stability of drilling fluids. The performance of oil-based drilling fluids with the addition of nano plugging agent poly (MMA-BA-ST) is relatively stable, with no significant changes in rheological parameters, indicating that poly (MMA-BA-ST) can be applied in oil-based drilling fluids.

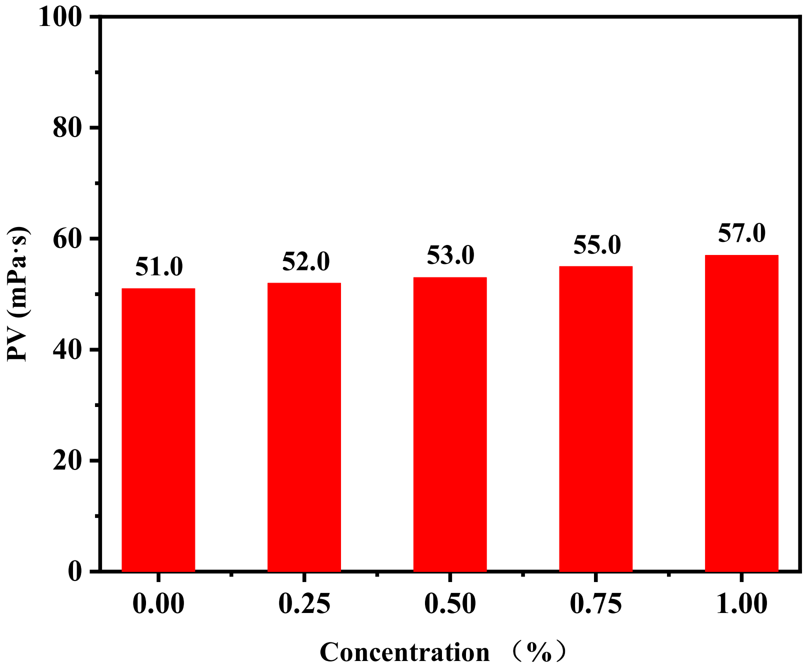

Figure 5. PV change curve after aging of oil-based drilling fluids with the addition of poly (MMA-BA-ST).

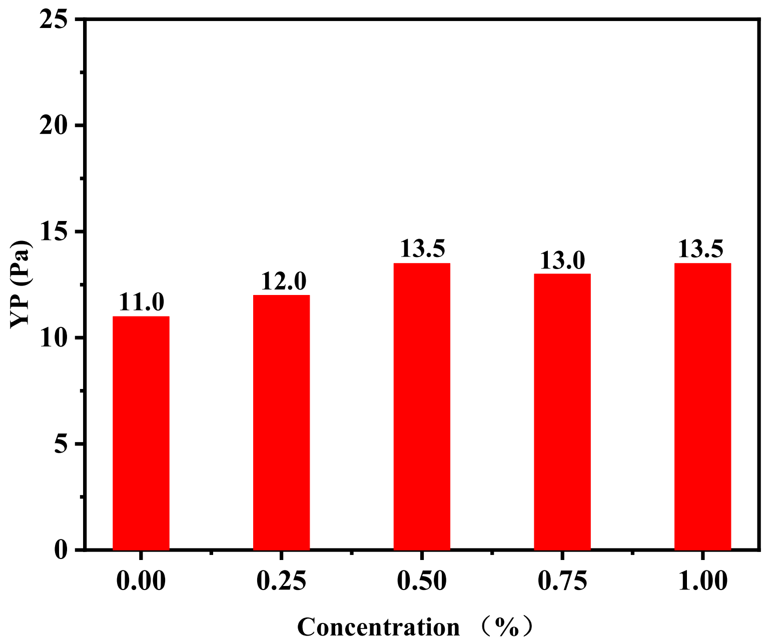

Figure 6. YP change curve after aging of oil-based drilling fluids with the addition of poly (MMA-BA-ST).

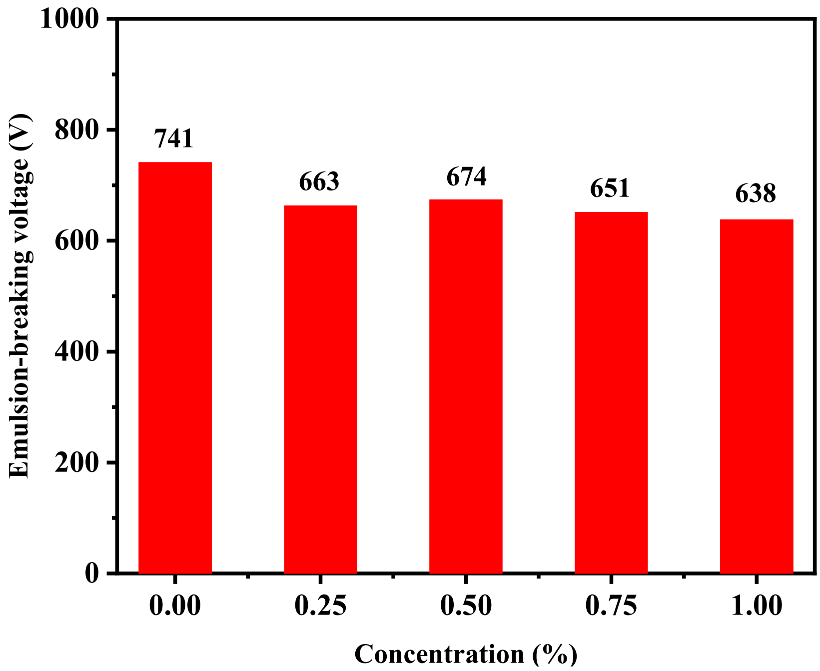

Figure 7. Emulsion-breaking voltage change curve after aging of oil-based drilling fluids with the addition of poly (MMA-BA-ST).

3.5. Evaluation of Poly (MMA-BA-ST) for Oil-Based Drilling Fluid Plugging Properties

3.5.1. Mud Cake Experiment

Figure 8 shows the evaluation of the plugging effect of poly (MMA-BA-ST) on the mud cake at 150 °C and a differential pressure of 3.5 MPa. It can be seen from Figure 8 that the permeability of the basic drilling mud cake is 2.26×10^{-4} mD. After adding poly (MMA-BA-ST), the permeability of drilling mud cake decreases, and the lower the permeability, the better the leakage plugging effect. When the amount of poly (MMA-BA-ST) reaches 0.5%, the permeability drops to 0.63×10^{-4} mD, the plugging rate is 72.12%, and the plugging effect on mud cake is the best. When the amount of poly (MMA-BA-ST) continued to increase, the plugging rate did not improve. This shows that 0.5% poly (MMA-BA-ST) is the best addition amount in drilling fluids and has a good plugging effect.

3.5.2. Core Permeability Experiment

From the mud cake experiment, it can be seen that the plugging agent has the best plugging effect at the dosage of 0.5%. To verify the plugging effect of poly (VS-St-BMA-BA) on real cores, the permeability of the sealer at 105 °C was tested using a core permeability experiment, and the results are shown in Table 1. From Table 1, it can be seen that compared with pure white oil, the permeability of white oil after adding 0.50% poly (MMA-BA-ST) is 0.41×10^{-3} mD; compared with pure white oil, its permeability decreased by 88.41%. The permeability results indicate that poly (MMA-BA-ST) has good plugging performance and can be used as a plugging agent for oil-based drilling fluids.

Table 1. Evaluation of plugging effect of poly (MMA-BA-ST) on artificial cores at 105 °C.

Concentration/%	Permeability after Plugging/10^{-3} mD	Plugging Rate/%
0.00	3.54	/
0.50	0.41	88.41

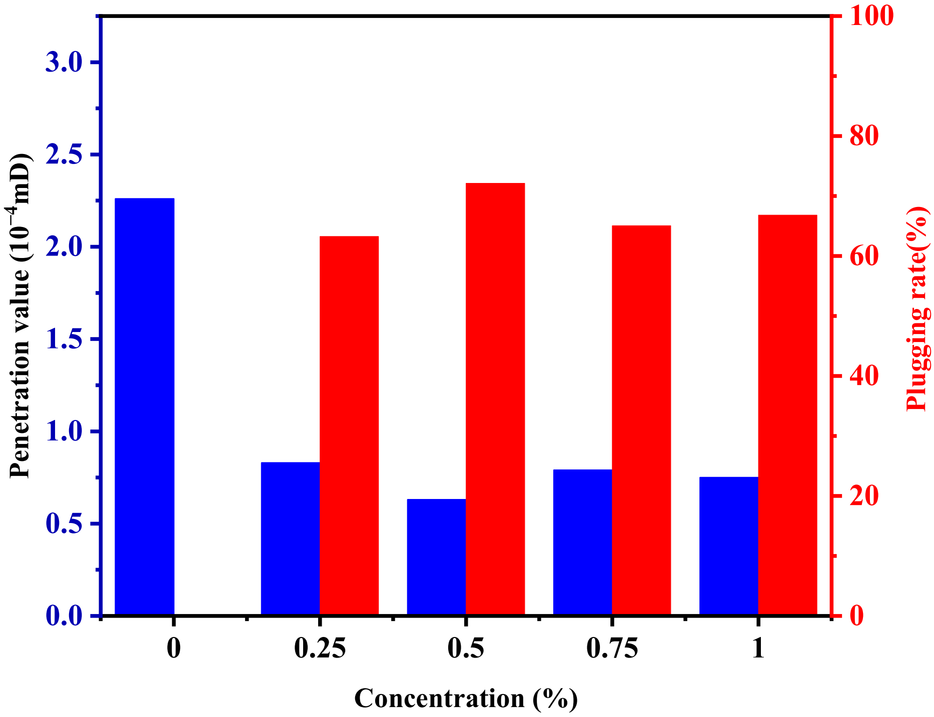

Figure 8. Variation of permeability and plugging rate for different doses of poly (MMA-BA-ST).

3.6. Plugging Mechanism

The microscopic morphology of poly (MMA-BA-ST) was observed by scanning electron microscopy, as shown in Figure 9.

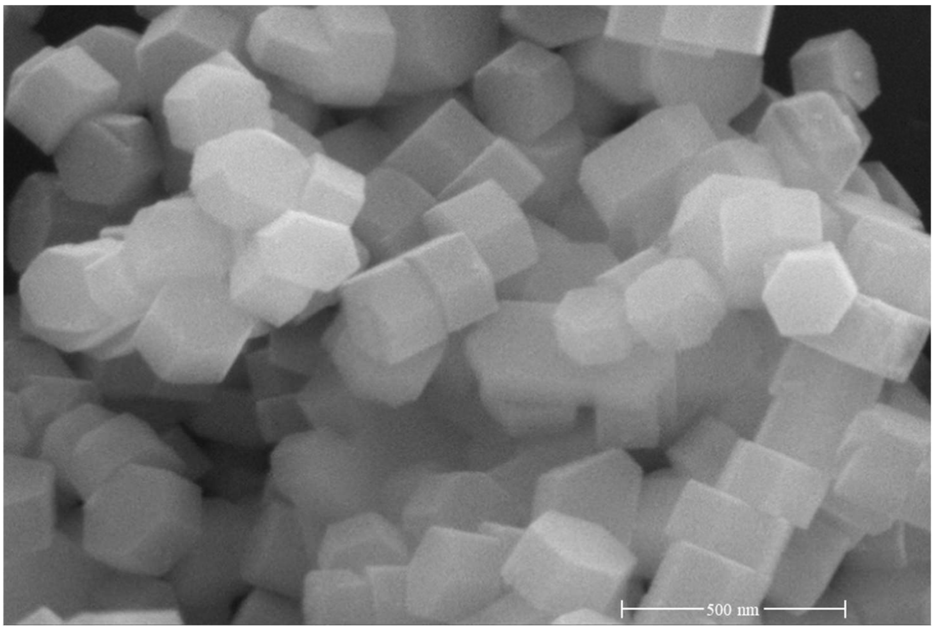

Figure 9. Microscopic morphology of poly (MMA-BA-ST).

Poly (MMA-BA-ST) is a nanoparticle that has a hexagonal prism shape. This means that poly (MMA-BA-ST) can enter the nanopore and the prismatic shape is easier to accumulate into a stable plugging layer. Figure 10 shows the mud cake diagram before and after the addition of poly (MMA-BA-ST).

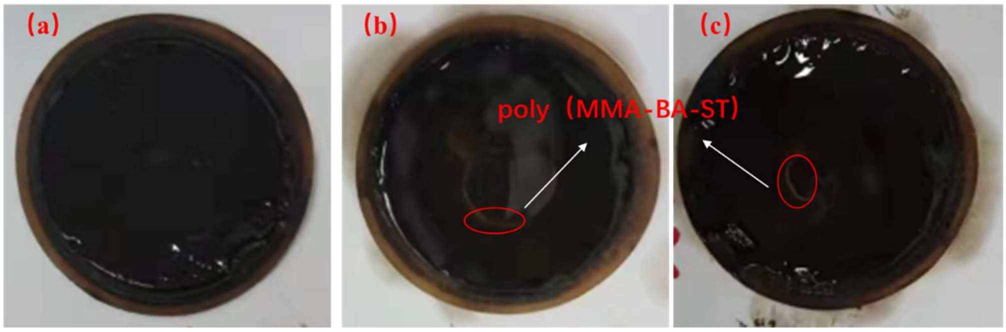

Figure 10. Mud cake samples before and after the addition of poly (MMA-BA-ST), (**a**) no addition, (**b**) 0.5% addition, (**c**) 1.0% addition.

From Figure 10, it can be seen that poly (MMA-BA-ST) formed a plugging layer on the surface part of the mud cake and effectively participated in the formation of the mud cake. Combined with the evaluation of mud cake plugging properties in 3.5., it can be concluded that poly (MMA-BA-ST) enhanced the plugging properties of the mud cake and made the mud cake denser, thus reducing the permeability of the mud cake. Figure 11 shows the plugging mechanism of poly (MMA-BA-ST) on the nanopore seams of shale formations.

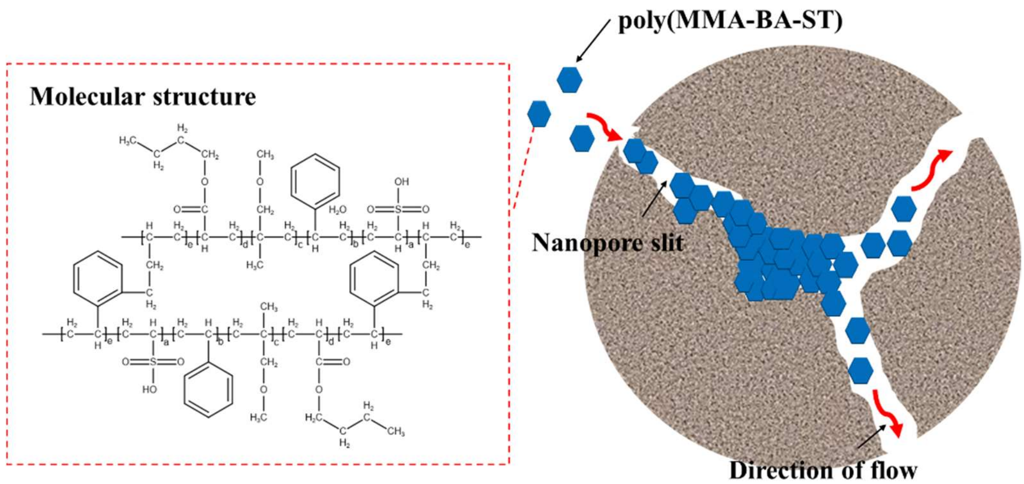

Figure 11. Diagram of poly (VS-St-BMA-BA) plugging mechanism.

It can be seen from Figure 11 that poly (MMA-BA-ST) contains more ester groups and benzene rings, which makes poly (MMA-BA-ST) hydrophobic and temperature resistant [24,25]. In the process of plugging pores and fractures, poly (MMA-BA-ST) effectively participated in the formation of the filter cake. It formed a plugging layer on the surface of the filter cake, preventing oil-based drilling fluids from invading deep shale. Part of the poly (MMA-BA-ST) enters the nanopores and cracks with the intrusion of the filtrate, and the polygonal shape is more favorable for the aggregation of poly (MMA-BA-ST) in the pores and cracks. The pressure action deforms the poly (MMA-BA-ST) and forms a tight plugging layer in the pores and slits, further preventing the filtrate's intrusion.

4. Conclusions

(1) The oil-based nano plugging agent poly (MMA-BA-ST) was synthesized by Michael addition reaction using styrene, methyl methacrylate and butyl acrylate compounds. Poly (MMA-BA-ST) contains hydrophobic groups such as ester groups and can be well dispersed in oil-based drilling fluids with a temperature resistance of up to 364 °C and an average particle size of 108.70 nm. It is capable of plugging nano-sized pore slits.

(2) The oil-based nano plugging agent poly (MMA-BA-ST) has less effect on the performance of oil-based drilling fluids. When the addition amount was 0.50%, the stability and rock-carrying properties of drilling fluids were better; the permeability of the mud cake was 6.3×10^{-5} mD, and the permeability reduction rate was 72.12%; the permeability of the artificial core was 4.1×10^{-4} mD, and the permeability reduction rate was 88.41%. Poly (MMA-BA-ST) had an excellent plugging effect in oil-based drilling fluids.
(3) As a nano plugging material, poly (MMA-BA-ST), an oil-based nano plugging agent, can enter the nanopores and participate in the filling of the nanopores under the action of formation pressure, thus reducing the influence of filtrate on the formation, maintaining the stability of the well wall and reducing the complexity of the well. The cost of poly (MMA-BA-ST) is low and adding less than 1 wt% of poly (MMA-BA-ST) to oil-based drilling fluids has an excellent plugging effect, which significantly reduces the plugging cost of drilling fluids. Therefore, poly (MMA-BA-ST) is expected to be a potential nano plugging agent used in oil-based drilling fluids.

Author Contributions: J.Y., Z.L. and G.X. conceived and designed the experiments; J.Y. and Z.L. performed the experiments; B.D., Z.A. and L.P. analyzed the data; J.Y. and G.X. wrote the paper. All authors have read and agreed to the published version of the manuscript.

Funding: This work is supported by the scientific research project of Southwest Oil&Gas Company of Sinopec, Research on Horizontal Well Drilling Technology in Ultra-deep and Long Horizontal Section of West Sichuan Gas Field (No.:KJ-649-2119) and National Natural Science Foundation. The mechanism and method of reinforcing the reinforced body by plugging in shale water-based drilling fluid (No.:51974270).

Data Availability Statement: The data that support the findings of this study are available from the corresponding author.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Melikoglu, M. Shale gas: Analysis of its role in the global energy market. *Renew. Sustain. Energy Rev.* **2014**, *37*, 460–468. [CrossRef]
2. Li, H.; Lv, K.; Huang, X.; Lu, Z.; Dong, X. The Synthesis of Polymeric Nanospheres and the Application as High-Temperature Nano-Plugging Agent in Water Based Drilling Fluid. *IOP Conf. Ser. Front. Chem.* **2020**, *8*, 247. [CrossRef] [PubMed]
3. Nie, H.; Jin, Z.; Sun, C.; He, Z.; Liu, J.; Liu, Q. Organic Matter Types of the Wufeng and Longmaxi Formations in the Sichuan Basin, South China: Implications for the Formation of Organic Matter Pores. *Energy Fuels* **2019**, *33*, 8076–8100. [CrossRef]
4. Zhong, Y.; Kuru, E.; Zhang, H.; Kuang, J.; She, J. Effect of Fracturing Fluid/Shale Rock Interaction on the Rock Physical and Mechanical Properties, the Proppant Embedment Depth and the Fracture Conductivity. *Rock Mech. Rock Eng.* **2019**, *52*, 1011–1022. [CrossRef]
5. Xie, G.; Luo, P.; Deng, M.; Wang, Z.; Gong, R. Hyperbranched Polyamine as Nano-Plugging Agent Used in Water-Based Drilling Fluid. *Nanosci. Nanotechnol. Lett.* **2017**, *9*, 310–315. [CrossRef]
6. Liu, J.; Dai, Z.; Li, C.; Lv, K.; Huang, X.; Sun, J.; Wei, B. Inhibition of the hydration expansion of sichuan gas shale by adsorption of compounded surfactants. *Energy Fuels* **2020**, *33*, 6020–6026. [CrossRef]
7. Ibrahim, M.; Saleh, T. Advances in functionalized Nanoparticles based drilling inhibitors for oil production. *Energy Rep.* **2019**, *5*, 1293–1304. [CrossRef]
8. Alharthy, N.; Teklu, T.; Nguyen, T.; Kazemi, H.; Graves, R. Nanopore Compositional Modeling in Unconventional Shale Reservoirs. *SPE Reserv. Evaluation Eng.* **2016**, *19*, 415–428. [CrossRef]
9. Jin, J.; Wang, Y.; Nguyen, T.; Bai, B.; Ding, W.; Bao, M. The morphology and surface-chemistry of gas-wetting nanoparticles and its effect on the liquid menisci in porous media. *Ind. Eng. Chem. Res.* **2019**, *58*, 6747–6755. [CrossRef]
10. Wu, Y.; Li, J.; Ding, D.; Wang, C.; Di, Y. A Generalized Framework Model for the Simulation of Gas Production in Unconventional Gas Reservoirs. *SPE J.* **2014**, *19*, 845–857. [CrossRef]
11. Sinha, B.; Bratton, T.; Cryer, J.; Nieting, S.; Ugueto, G.; Bakulin, A.; Hauser, M. Estimation of Near-Wellbore Alteration and Formation Stress Parameters Using Borehole Sonic Data. *SPE Reserv. Eval. Eng.* **2009**, *11*, 478–486. [CrossRef]
12. Guo, H.; Voncken, J.; Opstal, T.; Dams, R.; Zitha, P. Investigation of the Mitigation of Lost Circulation in Oil-Based Drilling Fluids by Use of Gilsonite. *SPE J.* **2014**, *19*, 1184–1191. [CrossRef]
13. Li, L.; Ma, C.; Xu, X.; Li, S.; Zhang, J.; Li, Y. Novel plugging agent for oil-based drilling fluids to overcome the borehole instability problem in shale formations. *IOP Conf. Ser. Mater. Sci. Eng.* **2019**, *479*, 012103. [CrossRef]

14. Li, W.; Jiang, G.; Ni, X.; Li, Y.; Wang, X.; Luo, X. Styrene butadiene resin/nano-SiO_2 composite as a water-and-oil-dispersible plugging agent for oil-based drilling fluid. *Colloids Surfaces A Phys. Eng. Asp.* **2020**, *606*, 125245. [CrossRef]
15. Geng, Y.; Sun, J.; Wang, J.; Wang, R.; Yang, J.; Wang, Q.; Ni, X. Modified Nanopolystyrene as a Plugging Agent for Oil-Based Drilling Fluids Applied in Shale Formation. *Energy Fuels* **2021**, *35*, 16543–16552. [CrossRef]
16. Liu, F.; Zheng, Z.; Wang, X.; Li, X.; Zhang, Z.; Wang, X.; Dai, X.; Xin, Y.; Liu, Q.; Yao, H.; et al. Novel modified nano-silica/polymer composite in water-based drilling fluids to plug shale pores. *Energy Sources Part A Recovery Util. Environ. Eff.* **2022**, *44*, 8662–8678. [CrossRef]
17. Ma, L.; Luo, P.; He, Y.; Zhang, L.; Fan, Y.; Jiang, Z. Improving the stability of multi-walled carbon nano-tubes in extremely environments: Applications as nano-plugging additives in drilling fluids. *J. Nat. Gas Sci. Eng.* **2020**, *74*, 103082. [CrossRef]
18. Li, J.; Sun, J.; LV, K.; Ji, Y.; Liu, J.; Huang, X. Temperature- and Salt-Resistant Micro-Crosslinked Polyampholyte Gel as Fluid-Loss Additive for Water-Based Drilling Fluids. *Gels* **2022**, *8*, 289. [CrossRef] [PubMed]
19. Tong, L.; Fan, R.; Yang, S.; Zhang, Q.; Pan, Y. Experimental Study of Oilfield Water Plugging with Organic Chromium Gel. *Chem. Technol. Fuels Oils* **2022**, *57*, 991–999. [CrossRef]
20. Yang, L.; Xie, C.; Ao, T.; Cui, K.; Jiang, G.; Bai, B. Comprehensive evaluation of self-healing polyampholyte gel particles for the severe leakoff control of drilling fluids. *J. Pet. Sci. Eng.* **2022**, *212*, 110249. [CrossRef]
21. Zhang, H.; Zhong, Y.; She, J.; Kuang, J. Experimental study of nano-drilling fluid based on nano temporary plugging technology and its application mechanism in shale drilling. *Appl. Nanosci.* **2019**, *9*, 1637–1648. [CrossRef]
22. Xie, G.; Luo, P.; Deng, M.; Wang, Z. Nanoplugging Performance of Hyperbranched Polyamine as Nanoplugging Agent in Oil-Based Drilling Fluid. *J. Nanomater.* **2015**, *2015*, 821910. [CrossRef]
23. Xie, G.; Xiao, Y.; Deng, M.; Luo, Y.; Luo, P. Low Molecular Weight Branched Polyamine as a Clay Swelling Inhibitor and Its Inhibition Mechanism: Experiment and Density Functional Theory Simulation. *Energy Fuels* **2020**, *34*, 2169–2177. [CrossRef]
24. Huang, K.; Huang, X.; Jia, Y.; Wang, S.; Cao, Z.; Zhong, H. A novel surfactant styryl phosphonate mono-iso-octyl ester with improved adsorption capacity and hydrophobicity for cassiterite flotation. *Miner. Eng.* **2019**, *142*, 105895. [CrossRef]
25. Cao, Z.; Chen, M.; Yu, J.; Han, X. Preparation and characterization of active rejuvenated SBS modified bitumen for the sustainable development of high-grade asphalt pavement. *J. Clean. Prod.* **2020**, *273*, 123012. [CrossRef]