Research Article

Preparation and evaluation of amine terminated polyether shale inhibitor for water-based drilling fluid

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Abstract

Facing the problems of shale hydration, swelling and borehole wall instability in shale gas drilling, a new type of amine terminated polyether (ATPE) shale inhibitor used in water-based drilling fluid is successfully synthesized through the method of leaving group. Using the yield of ATPE as index, orthogonal experiments are designed to determine the optimal reaction conditions. When the mole ratio of polyethylene glycol tosylate (PEG-OTs)/ethylenediamine is 1/3.6, mole ratio of PEG-OTs/triethylamine (acid binding agent) is 1/4, reaction time is 3.5 h and reaction temperature is 60 °C, the yield of ATPE is 91.12%. The structure and molecular weight of polyethylene glycol (PEG-400, a kind of oligomer), PEG-OTs and ATPE are characterized by Fourier transform infrared spectroscopy, nuclear magnetic resonance hydrogen spectroscopy (H^1-NMR) and time of flight mass spectrometer. The characterization results show that the ATPE has a reasonable molecular weight, and the both hydroxyls of PEG-400 have been replaced by ethylenediamine. The inhibition property of ATPE, potassium chloride (KCl), potassium formate (KCOOH), methane-siliconic acid (FMS-1) and polymeric alcohol (JLX-B) are comparatively evaluated through shale rolling dispersion experiment, linear expansion experiment and laser particle size test. The results show that the ATPE has a better shale inhibition property than traditional inhibitors. The drilling fluid system performance evaluation results show that the system has good engineering application value with excellent rheological property, low fluid loss and good shale inhibition property, which guarantee the well-bore stability in shale gas drilling.

Keywords Amine terminated polyether inhibitor · Shale inhibition property · Shale recovery · Structural characterization · Well-bore stability

1 Introduction

As a type of clean energy, the shale gas can relieve the problem of energy stress, and it is significant for the stability of energy supply [1]. But in shale gas drilling, the stability of borehole is greatly influenced by the shale hydration, swelling and dispersion [2]. In order to solve these problems, it is imperative to develop a high efficiency shale inhibitor and a kind of water based drilling fluid system with high performance [3–5]. A series of amine type shale inhibitor using in water based drilling fluid system has been developed. In the design of the inhibitor molecular, the reasonable molecular weight, good water solubility and amine groups should be considered, which can inhibit the shale hydration [6]. The main synthetic methods of ATPE are catalytic reductive amination method and leaving group method [7, 8]. Compared to catalytic reductive amination method, leaving group method has benefits from its mild reaction condition and simple synthesis equipment. The synthesis process does not require high temperature and pressure. So, the leaving group method is used to synthesize a new type of amine

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terminated polyether shale inhibitor with reasonable molecular weight. It is based on the molecule of PEG-400, and the two ends of the molecule are modified through two steps. Because of the amino structure at both ends of the molecular chain, the inhibitor can easily adsorb on the clay surface and enter the crystal layer. And then, the shale hydration and swelling are effectively inhibited [9–11]. The chemical reagents with low toxicity, low boiling point are used to improve the efficiency of purification and reduce environmental pollution. The structure and molecular weight of ATPE are characterized, and the shale inhibition property is evaluated.

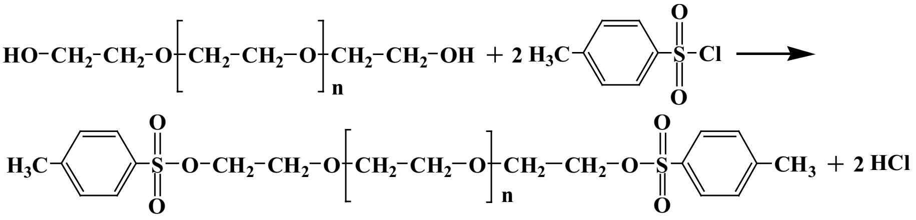
2 Experimental

2.1 Materials and equipments

PEG-400, P-toluenesulfonyl chloride (TsCl), ethylenediamine, triethylamine, potassium chloride and potassium formate were analytical reagents, which were provided by Chengdu Kelong Chemical Reagent Co. (China). Methane-siliconic acid (FMS-1), polymeric alcohol (JLX-B), coating agent (FA367), fluid loss additive (SMP-1), viscosifier (XC-HV) and lubricant (RH-220) were commercial products, which were purchased from Shandong Ziboruihou Commercial and Trade Co. (China). Nuclear magnetic resonance hydrogen spectroscopy (Bruker AVANCE III HD 400) was produced by Bruker Co. (Switzerland). Time of flight mass spectrometer (Agilent 6224) was obtained from Agilent Co. (America). Laser particle size analysis analyzer (MS 2000) was produced by Malvern Co. (England). Scanning electron microscope (ZEISS EV0 MA15) was produced by Carl Zeiss Microscopic Image Co. Ltd (Germany). Shale expansion instrument (type: CPZ-2), mud medium pressure filtration apparatus (type: SD3), frequency conversion rolling oven (type: GW300), and six-speed rotational viscometer (type: ZNN-D6B) were produced by Qingdao Tongchun Petroleum Instrument Co. (China).

2.2 Synthesis of ATPE

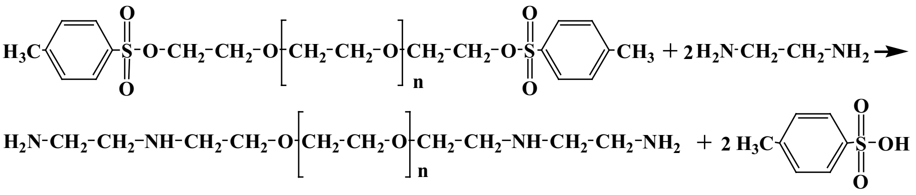
Under the condition of ice bath, PEG-400 and triethylamine were mixed together in a certain proportion, and then, TsCl was slowly dropped into the reaction flask at room temperature. The reaction process was tracked by thin-layer chromatography (TLC). The silica gel prefabricated board acted as TLC board. The developing agent was the mixture of dichloromethane and methanol with a mass ratio of 6:1. The reaction equation was as follows:



(1)

The precipitation in the liquid system was separated through vacuum filtration, and then, the distilled water and ethyle acetate were added to the liquid product. After standing and layering, the upper layer liquid was took out and added with sodium sulfate. The light yellow liquid was obtained after standing, filtration and vacuum distillation. Ethylether was added into the liquid, and then, the whole system was stratified after stirring and standing. The lower liquid was further purified through vacuum filtration. The intermediate product (PEG-OTs) was obtained.

Ethylenediamine and triethylamine were blended in certain proportion. PEG-OTs was previously dissolved in acetonitrile, and then, the PEG-OTs solution was dropped into the mixture of ethylenediamine and triethylamine at a certain temperature. The reaction process was tracked by thin-layer chromatography (TLC). The silica gel prefabricated board acted as TLC board. The developing agent was the mixture of dichloromethane and methanol with a mass ratio of 4:1. The reaction equation was as follows:



(2)

The organic solvent was removed from the primary product through vacuum filtration. Saturated sodium hydroxide solution and ethyl acetate were added in the system one after another. After layering, the upper layer liquid was took out to and added with sodium sulfate. The final light yellow liquid was ATPE, which was obtained after standing, filtration and vacuum distillation.

2.3 Characterization of ATPE

Fourier transform infrared spectrometer (NICOLET 6700) was used to characterize the molecular structures and the chemical compositions of PEG-400, PEG-OTs and ATPE respectively through the infrared absorption peaks of the functional groups. Before the test, potassium bromide was grinded and transferred into the mold to form a circular sheet. The samples were coated evenly on the potassium bromide sheet and tested with Fourier transform infrared spectrometer.

Nuclear magnetic resonance (H^1-NMR) was used to analyze the chemical structure. 10 mg pure sample was dissolved in 0.65 mL chloroform-d ($CDCl_3$), and then, the solution was transferred to the nuclear magnetic sample tube. Nuclear magnetic resonance (Bruker AVANCE III HD 400) was used to record the proton absorption peaks of PEG-400, PEG-OTs and ATPE respectively.

Time of Flight Mass Sepectrometer (Agilent 6224) was used to detect the molecular weight distribution of PEG-400, PEG-OTs and ATPE. The deionized water acted as solvent. The mobile phase included 30 wt% acetonitrile and 70 wt% deionized water. After injection, the PEG-400, PEG-OTs and ATPE were ionized through soft ionization technique, which was called electrospray ionization. The samples were scanned in positive mode respectively.

2.4 Shale rolling dispersion experiment

Several kinds of ATPE solution (350 mL) were prepared. 40.0 g Karamay Oilfield cuttings (6–10 mesh) were added into the solutions respectively. The suspension system was sealed in the aging cups and hot rolled at different temperatures (80 °C, 90 °C, 100 °C, 110 °C and 120 °C) for 16 h in the frequency conversion rolling oven (type: GW300). After hot rolling, the cuttings were sieved by 40-mesh sieve after cooling, and the remaining cuttings were dried for 4 h at 105 ± 3 °C. After weighting, the recovery rate was calculated as follows:

$$\text{Recovery rate} = \frac{M}{40} \times 100\,(\%) \tag{3}$$

M (g) represents the weight of the remaining cuttings.

2.5 Linear expansion experiment

The bentonite (10.0 g) was dried for 4 h at 105 ± 3 °C before it was put into the test tube, which was filled with filter paper. The bentonite was compressed under the pressure of 10 MPa for 5 min, and then, a certain concentration of inhibitor solution was added into the test tube. The expansion rates of bentonite in each solution were tested and calculated:

$$\text{Expansion rate} = \frac{H_{8h}}{H_0} \times 100\,(\%) \tag{4}$$

H_{8h} (mm) represents the expansion height of the bentonite core after 8 h; H_0 (mm) represents the original height of the bentonite core.

2.6 Laser particle size test

The certain mass fraction of ATPE, potassium chloride (KCl), potassium formate (KCOOH), methane-siliconic acid(FMS-1), and polymeric alcohol(JLX-B) were added to the pre-hydrated bentonite suspension (4.0 wt%) respectively, and then, the suspensions were mixed under high speed stirring for 30 min. The suspensions were for 24 h at room temperature, and then stirred for 10–15 min under high speed before they were added into the sample injector of the laser particle size analyzer (MS2000). When the particle concentration met the test requirements and the sufficient strength of the columnar data distribution of the shading degree was displayed, the small angle laser light scattering method was used to test the particle size distribution of the bentonite suspension.

2.7 Microscopic morphology test

Two bentonite solutions (4.0 wt%) were prepared, one of which was added with ATPE (3 wt%), the other one acted as blank sample. Dissolved and held for a period of time, took part of the solution and placed it in a steel sample box for freeze-drying, and then transferred the steel sample box to the testing room of ZEISS EV0 MA15 electron microscope. At last, the micromorphology and shape of bentonite at different regions were respectively observed. The magnifications were 200 times.

2.8 Performance evaluation of the ATPE drilling fluid

The coating agent (FA367), fluid loss additive (SMP-1), viscosifier (XC-HV) and lubricant (RH-220) were optimized on the basis of ATPE. The water-based ATPE drilling fluid was composed of pre-hydrated bentonite suspension (4.0 wt%), ATPE (4.0 wt%), FA367 (0.3 wt%), SMP-1 (1 wt%), XC-HV (1 wt%), RH-220 (0.2 wt%) and barite. The performance of ATPE drilling fluid was evaluated according to American Petroleum Institute (API) test programs. At first, the API filtration loss (FL_{API}) of the mud was evaluated through the mud medium pressure filtration apparatus (SD3). Then, the aging tests was carried out by the frequency conversion rolling oven (type: GW300) through hot rolling at 120 °C for 16 h. During the filtration loss test, filter cake was formed on the filter paper, which can contribute to reduce the filtration loss. Apparently, if the filtration loss is small, the drilling fluid would have better performance. Finally, the rheological parameters of the drilling fluid were measured with the six-speed rotational viscometer (ZNN-D6B) at room temperature. Apparent viscosity (AV), plastic viscosity (PV), and yield point (YP) were evaluated through the numerical values when the rotational speed was 600 rpm and 300 rpm. Φ600 represents the numerical value shown on the indicator dial of the six-speed rotational viscometer when it was rotated with 600 rpm. Φ300 represents the numerical value shown on the indicator dial of the six-speed rotational viscometer when it was rotated with 300 rpm. The computation formulas were as follows [12, 13]:

$$AV = {}^{1}\!/_{2}\Phi600\,(\mathrm{mPa\ s}) \tag{5}$$

$$PV = \Phi600 - \Phi300\,(\mathrm{mPa\ s}) \tag{6}$$

$$YP = {}^{1}\!/_{2}(\Phi300 - PV)\ (\mathrm{Pa}) \tag{7}$$

3 Results and discussion

3.1 Orthogonal experiment results and analysis

The orthogonal L_{16} (4^4) experiments are designed to optimize the synthesis conditions of amination reaction. The four main factors, including mole ratio of PEG-OTs/

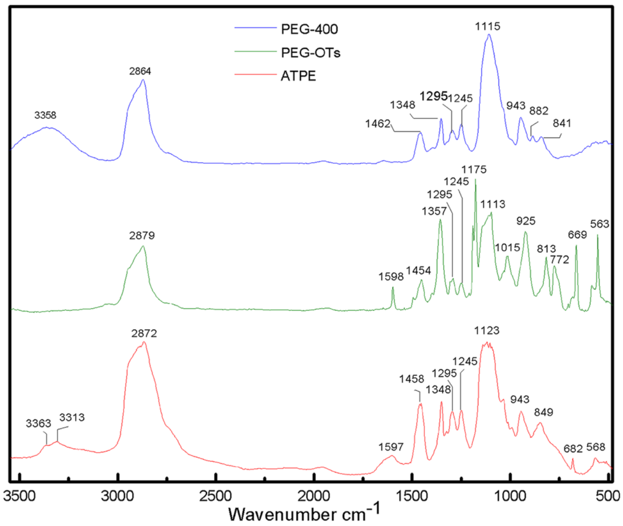


Fig. 1 FTIR of ATPE, PEG-OTs and PEG-400

Table 1 Orthogonal experimental results of amination reaction

Sample	n(PEG-OTs): n(ethylenediamine) [A]	n(PEG-OTs): n(triethylamine) [B]	Reaction temperature/°C [C]	Reaction time/h [D]	Yield/%
1	1:2.4	1:2.5	50	2.0	73.65
2	1:2.4	1:3.0	60	2.5	82.33
3	1:2.4	1:3.5	70	3.0	84.64
4	1:2.4	1:4.0	80	3.5	84.57
5	1:2.8	1:2.5	60	3.0	87.76
6	1:2.8	1:3.0	50	3.5	85.42
7	1:2.8	1:3.5	80	2.0	79.78
8	1:2.8	1:4.0	70	2.5	88.54
9	1:3.2	1:2.5	70	3.5	86.67
10	1:3.2	1:3.0	80	3.0	86.31
11	1:3.2	1:3.5	50	2.5	88.69
12	1:3.2	1:4.0	60	2.0	87.33
13	1:3.6	1:2.5	80	2.5	85.03
14	1:3.6	1:3.0	70	2.0	86.79
15	1:3.6	1:3.5	60	3.5	91.04
16	1:3.6	1:4.0	50	3.0	87.07
Kj1	81.297	83.278	83.707	81.888	
Kj2	85.375	85.213	87.115	86.148	
Kj3	87.250	86.038	86.660	86.445	
Kj4	87.483	86.877	83.922	86.925	
Rj	6.186	3.599	3.408	5.037	

ethylenediamine, mole ratio of PET-OTs/triethylamine, reaction temperature and reaction time are selected to research the synthesis conditions as listed in Table 1.

Setting the yield of ATPE as index, the order of the influence on the yield is n(PEG-OTs): n(ethylenediamine) > reaction time > n (PEG-OTs): n(triethylamine) > temperature. According to the orthogonal experiment results, the order of main factors is ADBC. The optimal level is A4D4B4C2. The optimized synthesis conditions are as follows: mole ratio of PEG-OTs/ethylenediamine is 1/3.6, the reaction time is 3.5 h, the mole ratio of PEG-OTs/triethylamine is 1/4 and reaction temperature is 60 °C.

3.2 FTIR analysis of ATPE

The spectrum shows the infrared characteristic absorption peaks of PEG-400, PEG-OTs and ATPE, which are shown in Fig. 1.

In the spectrum of PEG-400, the absorption peaks at 3358 cm^{-1} and 2864 cm^{-1} respectively correspond to the stretching vibration of –OH and -CH_2-. The absorption peak at 1115 cm^{-1} corresponds to the anti-symmetric stretching vibration of C–O–C. The Infrared characterization of the middle production PEG- OTs shows that the main chain structure of PEG-400 is unchanged. The disappeared absorption peak at 3358 cm^{-1} indicates that the terminal hydroxyl of PEG-400 has been replaced. The absorption peaks at 1357 cm^{-1} and 1175 cm^{-1} respectively correspond to the anti-symmetric stretching vibration and symmetric stretching vibration of O=S=O. The Infrared characterization of ATPE indicates that 3363 cm^{-1}, 3313 cm^{-1} and 1597 cm^{-1} respectively correspond to the anti-symmetric stretching, symmetric stretching and variable angle stretching vibration peaks of –NH_2. The symmetric stretching vibration peak of O=S=O at 1175 cm^{-1} disappears.

3.3 H^1-NMR analysis of ATPE

The nuclear magnetic resonance hydrogen spectrum (H^1-NMR) of PEG-400, PEG-OTs and ATPE are shown in Fig. 2.

In the H^1-NMR spectrum of PEG-400, the absorption peaks at 3.662 ppm and 3.092 ppm respectively correspond to the proton peak of -O-CH_2-CH_2-O- and -OH. The peak area ratio is 12:1. In the H^1-NMR spectrum of PEG-OTs, the absorption peak at 2.448 ppm corresponds to the proton peak of –CH_3 on the benzene ring. The absorption peak at 4.156 ppm corresponds to the proton peak of –CH_2– which links with sulfonic acid ester. The absorption peak at 7.787 ppm corresponds to the proton peak of C which is on the benzene ring at 3-positon. The absorption peak at 7.354 ppm corresponds to the proton peak of C which is on the benzene ring at 4-positon. The peak area ratio of 2.448 ppm and 4.156 ppm is 2:3, which indicates that the intermediate product is double substituted sulfonic acid ester. In the H^1-NMR spectrum of ATPE, the absorption peak at 3.654 ppm corresponds to the proton peak of –O–CH_2–CH_2–O–. The absorption peaks at 2.742 ppm and 2.435 ppm respectively correspond to the proton peak of –NH–CH_2–CH_2–NH_2 and –NH–CH_2–CH_2–O–. The absorption peak at 1.983 ppm corresponds to the proton peak of –NH–. The absorption peak at 1.236 ppm corresponds to the proton peak of –NH_2. The integral area ration of –NH– and –NH_2 is 1:2.

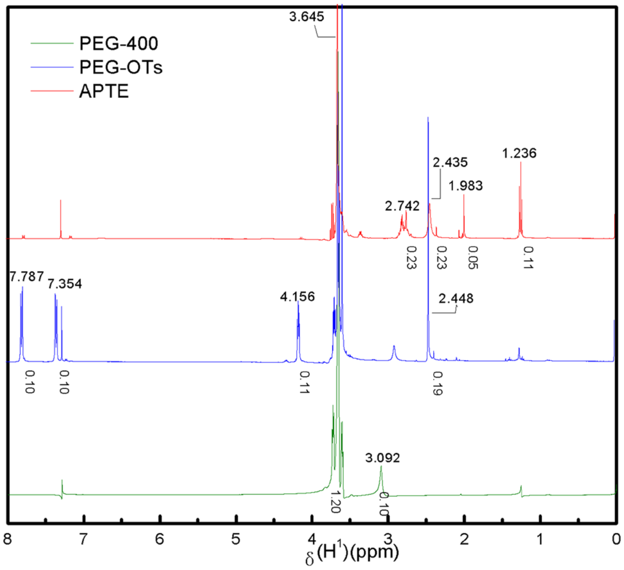


Fig. 2 H^1-NMR of ATPE, PEG-OTs and PEG-400

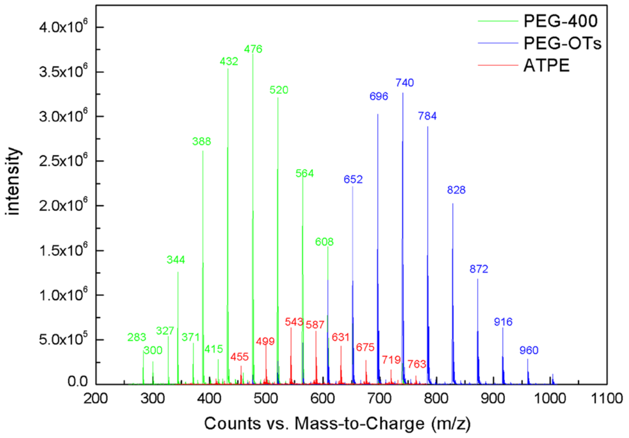


Fig. 3 Mass spectrogram of PEG-400, PEG-OTs and ATPE

Table 2 Mass spectrometry analysis results of PEG-400, PEG-OTs and ATPE

Numbers of repeating structure unit/n	Theoretical molecular weight			Mass-to-charge ratio (m/z)			The measured molecular weight/u		
	M(PEG-400)	M(PEG-OTs)	M(ATPE)	PEG-400/ $(M+NH_4)^+$	PEG-OTs/ $(M+NH_4)^+$	ATPE/ $(M+NH_4)^+$	M(PEG-400)	M(PEG-OTs)	M(ATPE)
7	370	678	454	388	696	455	370	678	454
8	414	722	498	432	740	499	414	722	498
9	458	766	542	476	784	543	458	766	542
10	502	810	586	520	828	587	502	810	586
11	546	854	630	564	872	631	546	854	630
12	590	898	674	608	916	675	590	898	674
13	634	942	718	652	960	719	634	942	718

Table 3 Shale rolling dispersion experiment results

T (°C)	Recovery rate (16 h)/%							
	Distilled water	1 wt% ATPE	2 wt% ATPE	3 wt% ATPE	7 wt% KCl	7 wt% KCOOH	3 wt% FMS-1	3 wt% JLX-B
80	12.9	61.35	65.13	71.33	36.48	38.93	41.6	35.23
90	12.8	61.05	64.92	71.2	36.26	38.74	41.42	35.07
100	12.65	60.73	64.69	70.5	36.13	38.66	41.29	34.93
110	12.4	60.51	64.3	70.36	36.02	38.52	41.07	34.81
120	12.1	60.05	64.24	70.19	35.91	38.40	40.89	34.68

3.4 Time of flight mass spectrometer analysis

The mass distribution of the molecular ion of test samples is shown in Fig. 3. The analysis of the results is shown in Table 2.

As the results shown from Fig. 3, the difference between the signals of mass-to-charge ratio in each group of peaks is 44, which corresponds to the molecular repetitive structure unit of –CH_2–CH_2–O–. In Fig. 3, the m/z signals 283, 327, 371, 415, 459 are the $(M+H)^+$ ion signals of PEG-400 when n is 5–9, which supports the accuracy of the molecular weight of PEG-400. As shown in Table 2, the characterization testing values of PEG-400, PEG-OTS and ATPE match with the theoretical calculations, which further prove that the intermediate product and the target product are synthesized successfully. The molecular weight distribution of ATPE is mainly from 454 to 718. The molecular weight is reasonable and met with the design requirements. Studies have shown that low molecular weight amines can be inserted into the clay crystal layer [14, 15]. ATPE has reasonable molecular weight, which makes it can enter the clay mineral crystal layer. And then, the adjacent crystal layer spacing is compressed and the water molecules are pushed out. As a result, the clay is not easy to hydrate and disperse.

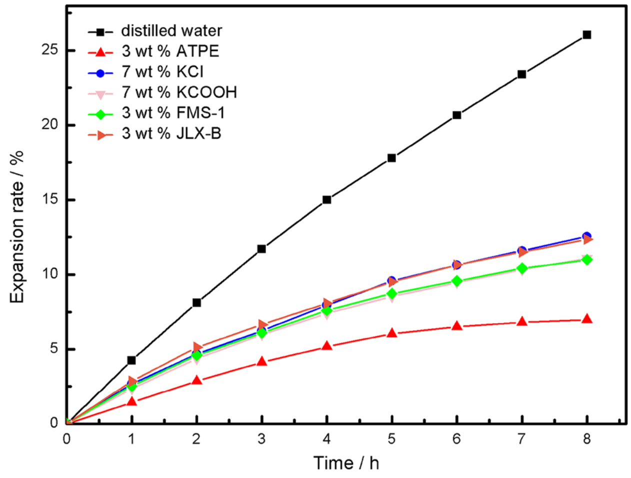


Fig. 4 Linear expansion experiment results

3.5 Analysis of shale rolling dispersion

Shale rolling dispersion experiment is used to evaluate the shale inhibitive effect of ATPE under high temperature for a long aging time. The experimental results are shown in Table 3.

As is shown in Table 3, the shale recovery rate in the 3 wt% ATPE solution is the highest under different temperature. With the increasing of temperature, the recovery rate of shale gradually decreases. The main reason is that the increasing of temperature promotes the hydration and dispersion of shale. On the other hand, the shale inhibitive effect is better than other traditional inhibitors such as KCl, KCOOH, FMS-1 and JLX-B. The experiments indicate that ATPE has a strong ability to inhibit the dispersion and hydration of shale under high temperature for a long aging time. Because ATPE is a kind of nonionic shale inhibitor, the mutual repulsion of the negative charges on the shale surface is weakened by the adsorption of ATPE. As a result, the clay is not easy to hydrate and disperse.

3.6 Linear expansion experiment analysis

Linear expansion experiment is used to evaluate the shale inhibitive effect of ATPE under normal pressure and temperature. The results are shown in Fig. 4.

As is shown in Fig. 4, the expansion rate of bentonite core has a minimum value in the 3 wt% ATPE solution, which is only 6.99%. Compared with other traditional inhibitors, such as KCl, KCOOH, FMS-1 and JLX-B, The shale inhibitive effect of ATPE is better. The experiments indicate that ATPE has a strong ability to inhibit the dispersion and hydration of shale under normal pressure and temperature. ATPE molecules adsorbed on the clay surface, the hydrophobic chain in ATPE results in the hydrophobic clay surface, while the hydrophilic property of the clay surface is weakened. Water molecules are prevented to enter into the clay crystal layers, as a result, the clay is not easy to hydrate and disperse. Ma [16] synthesized an inhibitor DAM by diallyl dimethyl ammonium chloride (DMDACC), methyl allyl alcohol (MP), 2-acrylamido-2-methyl propane sulfonic acid (AMPS). When the DAM dosage was 3 wt%, the linear expansion rate was 16%. Zhong [17] used 4,4′-methylenebis-cyclohexanamine (MBCA) as shale inhibitor and added to bentonite solution, the linear expansion rate was 10% after 5 h. An [18] added 4 wt% polyethyleneimine (PEI) to montmorillonite solution, and the linear expansion decreases by 73% after 6 h. Comparatively, the linear expansion decreases by 75% after adding 3 wt% APTE for 6 h in this paper.

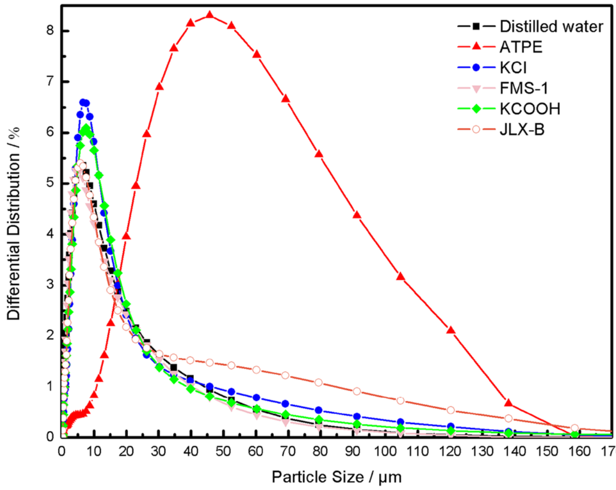


Fig. 5 Particle size distribution of bentonite suspensions with different inhibitors

3.7 Particle size and distribution analysis

The bentonite suspensions with different inhibitors are tested by laser particle size analyzer (MS 2000). The results are shown in Fig. 5 and Table 4.

As the results shown above, the average diameter of the clay particles in 3 wt% ATPE solution increases from 5.479 to 37.533 μm compared with distilled water. The controlling effects of the other traditional inhibitors on the average particle size of bentonite are not obvious. The order of average particle size in different suspensions is ATPE > KCl > KCOOH > JLX-B > distilled water > FMS-1, which proves that ATPE has a strong inhibition ability to clay dispersion.

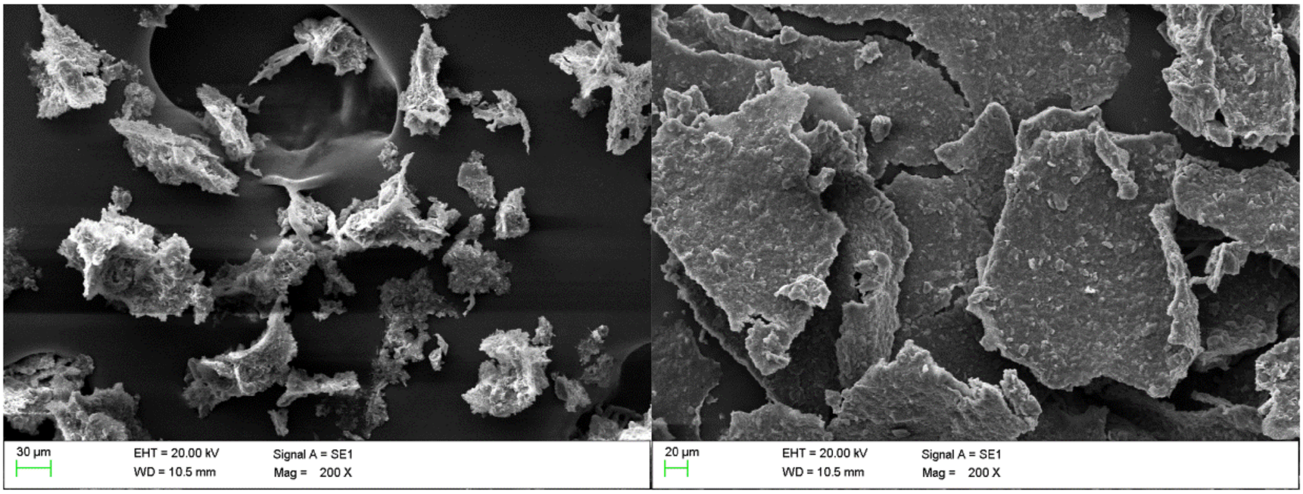
3.8 Micromorphology analysis of bentonite particles

The SEM is used to observe the micromorphology of bentonite particles in different solutions, and the images are shown in Fig. 6.

As shown in Fig. 6, the surface hydration of bentonite particles in blank sample is more serious, which can be proved by the porous structure on the bentonite surfaces. The bentonite particles are smaller and more dispersive. When ATPE is added, the surface hydration of bentonite particles is greatly weakened and the particles are more aggregated. The main reason is that ATPE is a kind of nonionic shale inhibitor, which can adsorb on the bentonite surface and shield the original negative charge on the

Table 4 Laser particle size experiment results

Samples	Distilled water	3 wt% ATPE	7 wt% KCl	7 wt% KCOOH	3 wt% FMS-1	3 wt% JLX-B
d (0.5)/μm	5.479	37.533	6.565	6.394	5.024	6.071
Specific surface area/ ($m^2 g^{-1}$)	1.880	0.391	1.460	1.620	1.980	1.700



(a) SEM of bentonite blank sample

(b) SEM of bentonite with 3 wt % ATPE

Fig. 6 SEM of bentonite particles in different solutions

Table 5 Performance evaluation results of ATPE drilling fluid

Sample	Conditions	Sample recovery weight (16 h)/g	Recovery rate (16 h)/ %	AV/mPa s	PV/mPa s	YP/Pa	FL_{API}/mL
Optimizing composition	Before aging	37.00	92.50	58	39.5	18.5	4.3
	After aging			56	38	18	5.1

surface. As a result, the electrostatic repulsion between the bentonite particles is decreased, and the bentonite particles are more easily aggregated. Secondly, as a small molecular polymer, ATPE can insert into the double-layer structure of bentonite and squeeze out the water molecules. At last, the hydration and expansion of bentonite are inhibited.

3.9 Performance of ATPE drilling fluid

The water-based ATPE drilling fluid is composed of prehydrated bentonite suspension (4.0 wt%), ATPE (4.0 wt%), FA367 (0.3 wt%), SMP-1 (1 wt%), XC-HV (1 wt%), RH-220 (0.2 wt%) and barite. The performance of ATPE drilling fluid was evaluated according to American Petroleum Institute (API) test programs. The shale recovery, the rheological parameters and API filtration are tested respectively. The results are shown in Table 5.

As is shown in Table 5, the shale recovery rate reaches 92.5% due to the synergistic effect of the coating agent and the inhibitor, which demonstrates the excellent shale inhibition property of ATPE drilling fluid. In addition, the AV, PV, YP and FL_{API} of ATPE drilling fluid have little change. The FL_{API} is less than 5.1 mL for the ATPE drilling fluid after the thermal aging at 120 °C for 16 h.

4 Conclusions

A new type of amine terminated polyther (ATPE) shale inhibitor used in water-based drilling fluid is synthesized through the method of leaving group, and the optimal polymerization conditions are obtained: the mole ratio of polyethylene glycol tosylate (PEG-OTs)/ethylenediamine is 1/3.6, mole ratio of PEG-OTs/triethylamine (acid binding agent) is 1/4, reaction time is 3.5 h and reaction temperature is 60 °C. The structure of ATPE is characterized by FTIR, H^1-NMR and TOFMS. The results show that ATPE contains all the designed functional groups and reasonable molecular weight. The shale recovery rate of ATPE for 16 h reaches 71.33% and the 8 h linear expansion rate is only 6.99%. ATPE makes the specific surface area of prehydrated bentonite particles reach the relatively minimum value, which is 0.391 m^2/g. The average diameter of the clay particles in 3 wt% ATPE solution increases from 5.479 to 37.533 µm compared with distilled water. All the results prove that the inhibitive effect of ATPE is superior to other traditional inhibitors. ATPE drilling fluid has strong shale inhibition property, good rheological property and filtration property.

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Compliance with ethical standards

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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