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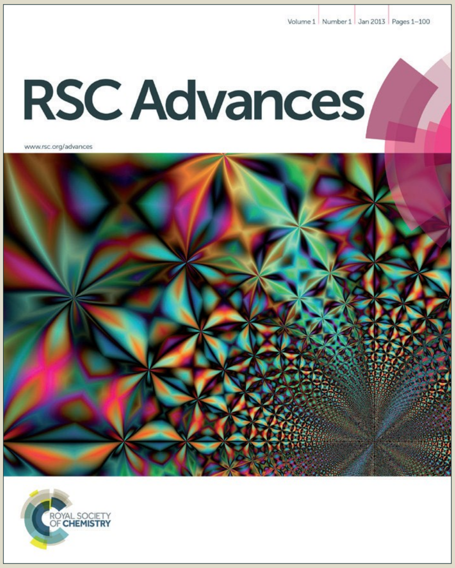

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Nano-fluid loss agent based on Acryl amide based copolymer "grafted" on modified Silica surface

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Abstract:

In this paper, the nano copolymer of acrylamide (AM), 2-acrylamido-2-methyl -1-propane sulfonic acid (AMPS), and modified nano-silica (M-SiO_2) was synthesized by free radical polymerization in water solution. The addition of ethanol was used to control molecular weight of copolymer. The characterization of copolymer was measured by Fourier Transform Infrared Spectroscopy, Particle Size Analyzer, Transmission Electron Microscopy, Atomic Force Microscope and Nuclear Magnetic Resonance. AM and AMPS were grafted on the surface of M-SiO_2 successfully. The grafted copolymer was in nm size not only in water solution but also in drilling fluid. Filtration properties and interaction mechanism of copolymer with montrillonite (MMT) were studied in fresh water drilling fluid system and different kinds of salt water drilling fluid systems. The copolymer as fluid loss agent was equal to commonly used fluid loss agent in fresh water drilling fluid system. The resistance properties to salinity, calcium and high temperature were tested. The copolymer was resistance temperature of 150□. And was saturated brine resistance. The resistance property to calcium was up to 1wt%. The interaction mechanism between montrillonite and copolymer was evaluated by Particle Size Analyzer, Transmission Electron Microscopy, Scanning Electron Microscopy and Surface Area Analyzer. The copolymer was adsorbed in the surface of MMT. Compared to pristine MMT, the addition of copolymer resulted in the new peaks in particle size analyzer image. The filter liquor of drilling fluid with copolymer showed two peaks in nm scale, nerveless the filter liquor of drilling fluid without copolymer showed that no peak appeared under 1000nm. The results presented that copolymer as fluid loss agent was nano material in drilling fluid. Surface area analyzer (BET) results showed that the surface area of natural rock reduced after treated with copolymer, indicating copolymer entered into nanopores of shale because of the adsorption in the surface of shale.

1. Introduction

Increasing demand for energy and depletion of many conventional oil and gas reserves has increased the importance of shale and techniques to drill shale formation [1]. Wellbore stability is a critical issue on drilling progress and troubles the drilling fluid engineers and experts all the time [2]. Shale is a sedimentary rock that mineralogical consists of clays and contains pores with a range of pore throats size from 5nm to 50nm [3]. The permeability of shale is so low that its value is up to nD, leading to filter cake unformed [4]. As showed in Fig.1a. Filter cake was formed in wellbore on drilling operation for conventional drilling fluid, which prevents further invasion of water from shale formation. Conventional fluid loss agents are modified cellulose, modified humic acid, modified lignite and synthetic products [8-9], which are micro polymer. These commonly used conventional fluid loss agents are too large to enter into nanopores of shale formation (Fig.1b). Followed the invasion of water through nanopores throat into shale formation weakens wellbore and leads to problems such as stuck pipe and hole collapse [5-7]. The solution to this problem is to engineer a nano fluid loss agent in the drilling fluid to plug nanopores of shale and shut off the loss of water. As showed in Fig. 1c. Nano fluid loss agent can enter into nanopores of shale formation and adsorbed in the surface of wellbore. Nanomaterial and nanotechnology has attracted a widely research in the past decade with numerous applications in a variety of industries [10-14]. And nanomaterial and nanotechnology has been applied in water based drilling fluid in recently years [15-17]. But their works cannot solve the problem of wellbore instability completely due to seriously aggregation and vast addition of nanomaterial. It is a novel work to synthesis a kind of inexpensive nano fluid loss agent without seriously aggregation for water based drilling fluid to drill shale formation.

Polyacrylamide(PAM) and derivatives were widely applied in oil field [18-21]. Their products were used as flocculating agent, fluid loss agent, viscositier, viscosity reducer, solid coat stabilizer, oil displacement agent, gel plugging agent and drag reducer. The products were a kind of widely applied materials and were fine compatibility with other agents. Polyacrylamide and derivatives used to synthesize nanomaterial by grafting on the surface of nanosilica has attracted much attention in recently decade [22-25]. Generally, there were two main approaches to chemically attaching polymer chains on the surface of nano silica: covalent attachment of end-functionalized polymers to the surface ("grafting to" method) and in situ monomer polymerization with monomer growth of polymers chains from immobilized initiators ("grafting from" method). Therefore, the development of grafting strategies so as to tailor the surface properties of mineral substrates is of great current interest [26-27]. The "grafting-from" technique, also called surface –initiated polymerization appears to be a very promising and versatile method.

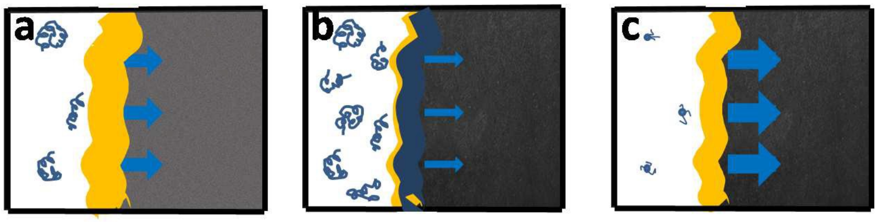

Figure. 1. The thickness of a filter cake is dependent on the fluid loss or leak off into the formation. (a) the conventional fluid loss agent in sand formation; (b) the conventional fluid loss agent in low permeability shale formation; and (c) nano-fluid loss agent in low permeability shale formation .

A large variety of initiating mechanisms, including free radical polymerizations have been applied [28-29]. The preparation of organic/inorganic nanocomposites vis surface-initiated polymerizations has been reviewed by several groups [30-31].

Our group synthesized nano copolymer based on AM/AMPS/ M-SiO_2 grafted polymer and controlled molecular weight by polymerization condition. The size of most of copolymer was from 0 to 50nm, and it was matching with nanopores of shale formation. What is more important, it was inexpensive and not seriously aggregation not only in water but also in drilling fluid. The copolymer exhibited high performance as fluid loss agent in various media.

2. Materials and methods

2.1 Materials

The AM (98%) and AMPS (98%) were commercial products from Beijing Chemical reagent company and AM was purified by recrystallization with acetone. Modified nano- silica (20nm, 99%) which modified by methacryloxy propyl trimethoxyl silane (KH570) was purchased from Xianfeng Chemical Reagent Company. Sodium hydrogen sulfite (99%) and ammonium peroxydisulfate (99%) were purchased from Alfa. Sodium hydroxide and other reagents were purchased from domestic reagent company. All the reagents were not purification further.

2.2 Methods

2.2.1 Synthesized of AM/AMPS/ M-SiO_2 grafted copolymer

The nano grafted copolymer of AM/AMPS/M-SiO_2 was synthesized by free radical polymerization in water solution. The chemistry structure of modified AM/AMPS/ M-SiO_2 grafted copolymer was showed in Fig.2. AM (18g), AMPS (2g) were mixed in 100ml water. Then the water solution was poured into flask. Sodium hydroxide was added into solution and stirred to adjust PH in 7-8. M-SiO_2 (0.5g) was poured into Ethanol (10ml) and stirred until M-SiO_2 was completely solved in ethanol. And then the two solutions were mixed. Heated and kept in 60℃ for 1h, then Sodium hydrogen sulfite (0.20g) and ammonium peroxydisulfate (0.60g) were added into solution and the reaction was kept for 6h. The product was cooled at room temperature. The solution was got and used to property evaluation. The further treatment was carried out for H-NMR and IR-FT test. The product was precipitated by acetone and dried at 70℃ for 24h. Dried product was grinded into powder, and then the powder was purified by soxhlet extraction with acetone. The powder was dried at 70℃ for 24h.

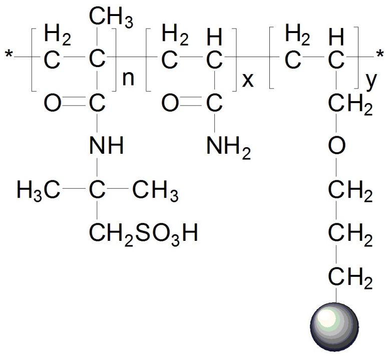

Figure. 2. Chemical structure of AM/AMPS / M-SiO_2grafted copolymer

2.2.2 Fluid preparation

The fresh-water based fluid was made of deionized water and sodium montrillonite (Huawei,China) at a concentration of 4wt%. Na_2CO_3 was added at concentration of 0.25wt% to the suspension and stirring for 20 min at high speed of 10000 rpm and aging for 24h at room temperature. Nano copolymer was poured into montrillonite suspensions slowly with stirred. The nano copolymer fluids were stirred for 20min at 10000 rpm.

The salt-water based fluid was made of fresh-water based fluid (1000ml) and sodium chloride (40g).The suspension was stirred for 20 min at high speed of 10000 rpm and aging for 24h at room temperature.

The saturated salt-water based fluid was made of fresh-water based fluid (1000ml) and sodium chloride (360g).The suspension was stirred for 20 min at high speed of 10000 rpm and aging for 24h at room temperature.

The complex salt-water based fluid was made of fresh-water based fluid (1000ml), sodium chloride (45g), calcium chloride (5g) and magnesium chloride (13g). The suspension was stirred for 20 min at high speed of 10000 rpm and aging for 24h at room temperature.

2.2.3 Fluid property tests.

Fluid property tests were measured according to American Petroleum Institute (API) specifications and Chinese SY/T5621-93.The API filtrate volume of the mud was determined with a ZNZ-D3-type medium-pressure filtration apparatus (Qingdao Bairuida Machinery Corporation, China). A volume of water-montrillonite suspension was loaded on the filter press equipped with a filter paper and fixed pressure in 0.7 MPa. Over time, low permeability filter cake was formed on the filter paper, which resembled the filter cake created during drilling. The filtrate volume was recorded in 30min, which was accustomed to be denoted by API in engineering. In other view, API was defined as the 30min filtrate volume based API specifications. The rheological parameters, such as the apparent viscosity(AV), the plastic viscosity (PV) and yield point (YP) of the nano copolymer suspension were determined through measurements of the viscosities at two rotation rate of 600 rpm and 300 rpm using ZNN-D6L rotational viscometer (Qingdao, China) at room temperature. Calculated from the value of Ø600 (Reading of viscosity at 600 rpm) and Ø300(Reading of viscosity at 300 rpm) by the following formulas:

$$\text{Apparent viscosity (AV)} = 0.5\, Ø600 \text{ (mPa.s)}$$

$$\text{Plastic viscosity (PV)} = Ø600 - Ø300 \text{ (mPa.s)}$$

$$\text{Yield point (YP)} = 0.5(2Ø300 - Ø600) \text{(Pa)}$$

Aging experiments of montrillonite with nano copolymer fluids were carried out in a GW300-type frequency conversion rolling oven (Qingdao Jiaonan Tongchun Machinery Plant, China) through hot rolling at appointed temperature (80℃，100℃，120℃，140℃，150℃). A series of 400ml fresh water drilling fluid were prepared.

A certain concentration of copolymer was added into fluid with stirred at 8000rpm for 20min. The mixture fluid was put into digestion tank and then was taken to roller oven. The rolling time was fixed 16h. The temperature was installed as requirement.

Fluid property tests were performed before and after the thermal aging experiments.

2.3. Structure characterization techniques

2.3.1. *Nuclear magnetic resonance (^{1}H-NMR) measurements.* ^{1}H-NMR spectral analyse of AM/AMPS/M-SiO_2 grafted copolymer was recorded by JNM-ECA 600. 2mg sample was solved in 1ml D_2O. The solution was poured into NMR tube.

2.3.2. *Fourier transform infrared spectroscopy (FT-IR) measurements.* FT-IR spectral analyse of SiO_2, M-SiO_2 and AM/AMPS/M-SiO_2grafted copolymer were recorded by Magna-IR 560 spectrometer. 2mg samples and 200mg KBr be fully blend. The mixture be put into the mold and be kept in 50MPa pressure by hydraulic press.

2.3.3. *Scanning electron microscopy (SEM).* SEM analyses were performed by a Quanta 200F scanning electron microscope. 800ml fresh-water based fluid was prepared. 8g copolymer was added into 400ml fresh-water based fluid. The solution and another 400ml fresh-water based fluid were loaded on the filter press equipped with a filter paper and fixed pressure in 0.7 MPa. Two parts of filter liquor and filter paper were got. The filter liquor was used for TEM test and particle size analysis. The filter papers were dried at 60℃ for 24h. The dried samples were adhered to adhesive tapes, and then metal sprayed for 2 min.

2.3.4. *Transmission electron microscopy (TEM).* TEM analyses were performed by a F20 transmission electron microscope. One sample was prepared as followed: a 20ml 0.010wt% MMT solution was prepared. The solution was divided into two. 10mg copolymer was poured into one solution. The solutions were dispersed by ultrasonicator at room temperature for 2min. Another sample was the filter liquor gained from filter press. 1 drop of solutions was added to carbon membrane. The carbon membranes were dried at infrared light for 20 min

2.3.5. *Atomic force microscopy (AFM).* AFM analyses were performed using a SPM-9600 instrument. 50ml 0.01wt% concentration of copolymer solution was prepared. The solutions were dispersed by ultrasonicator at room temperature for 2min, and then the solutions were diluted 5times and put for 24h. 10μL solutions were added to mica sheet. The samples were dried at room temperature for 6h.

2.3.6. *Particle size analysis.* The suspensions were performed by Zetasizer Nano ZS instrument. 20ml 0.1wt% MMT suspensions were prepared and dispersed by ultrasonicator at room temperature for 20min. 10mg copolymer was added in 10ml MMT aqueous suspension to make MMT/copolymer suspension.

3. Results and Discussions

3.1 AM/AMPS / M-SiO_2 grafted copolymer characterization

The nano-fluid loss agent was synthesized based on AM/AMPS/M-SiO_2 grafted copolymer. ^{1}H-NMR spectral of copolymer was showed in Fig.3. The structure formula of copolymer and the corresponding peaks were labeled by a-f. All the peaks

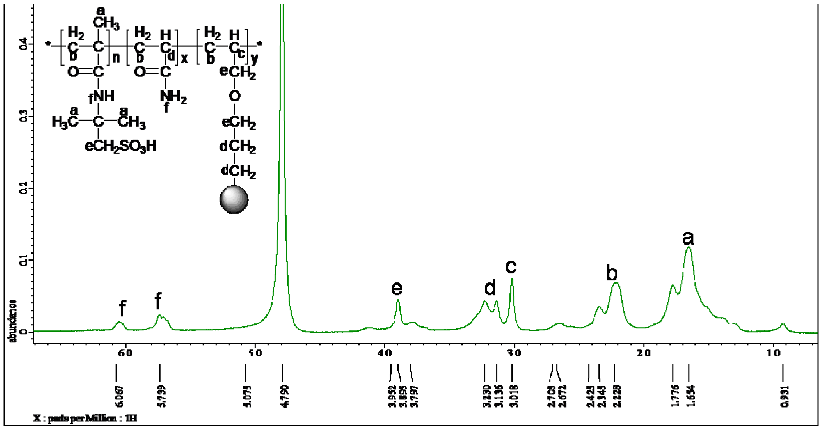

Figure 3. ^{1}H-NMR spectral of AM/AMPS/ M-SiO$_2$ grafted copolymer. The peaks in spectral and the corresponding structure were labeled a-f.

were assigned to the formula. The results exhibited that AM and AMPS were grafted on the surface of M-SiO2 successfully. FT-IR spectra of SiO$_2$ and M-SiO$_2$ were exhibited in Fig.4a. In pristine spectra of SiO$_2$, 3420cm^{-1} was O-H stretching band and

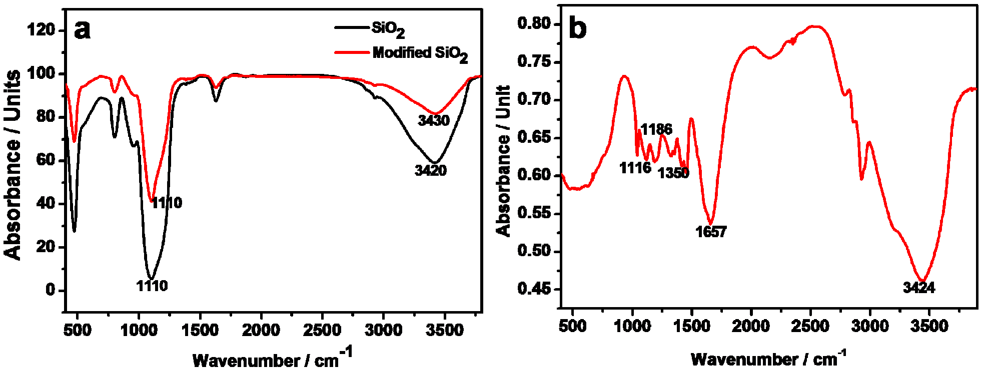

Figure 4. FT-IR spectra of SiO$_2$, modified SiO$_2$ and AM/AMPS/ M-SiO$_2$ grafted copolymer. (a) SiO$_2$, modified SiO$_2$;(b) AM/AMPS / M-SiO$_2$grafted copolymer

1110 cm^{-1} were Si-O stretching band. Compared to pristine spectra of SiO$_2$, stretching band of O-H (3430 cm^{-1}) in M-SiO$_2$ showed red shift 10 cm^{-1} due to the interaction between O-H in the surface of SiO$_2$ and KH570. The FT-IR spectrum of copolymer was showed in Fig. 4b. The major characteristic peaks were showed as follow. 3424cm^{-1} was N-H stretching band. 1657cm^{-1} was C=O stretching band. 1350 cm^{-1} and 1186 cm^{-1} were S=O stretching band. 1116 cm^{-1} were Si-O stretching band and red shifted 6 cm^{-1}, compared to pristine of SiO$_2$. O-H stretching band (3420 cm^{-1}) was coincided by N-H stretching band (3424 cm^{-1}).There was no C=C band at 1645 cm^{-1}-1620 cm^{-1}. The results exhibited the copolymer was AM/AMPS/M-SiO$_2$ grafted copolymer.

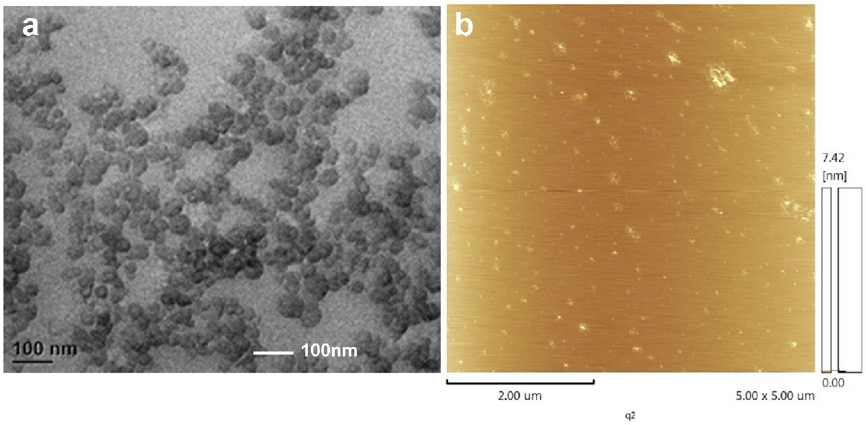

Figure 5. TEM and AFM images of AM/AMPS/ M-SiO_2 grafted copolymer. (a) TEM; (b) AFM.

There were an amount of microspheres in TEM image of copolymer (Fig. 5a). The size of microsphere was about 20nm, indicating the nano copolymer was synthesized successfully. The accordant observation of AFM image was showed in Fig.5b. The copolymer was dispersed in nm scale. The thickness of microsphere was labeled in the right. The average thickness was 7.42nm, indicating the diameter of microsphere was about 7.42nm. In spite of the calculation was not precise duo to the sample was dried in the process of preparation, but the size of microsphere under 50nm was accurate. As showed in Fig. 6. There were three peaks in nm scale in particle size analysis. One of peaks was from 0nm to 50nm, and the intensity of this peak was up to 6%. The intensity of the 100nm Microsphere was 10 times than 10nm microsphere. The 6% intensity of peak under 50nm exhibited the large amount of number. The analysis showed that there was the large amount of copolymer under 50nm in the copolymer.

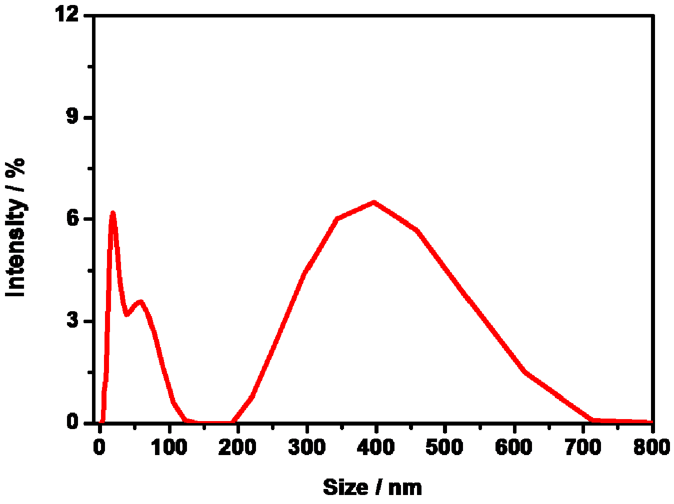

Figure 6. Particle size analysis of AM/AMPS/ M-SiO_2 grafted copolymer.

3.2 Property evaluations

Based on evaluation procedure of fluid loss agent in drilling fluid, the most frequently methods to evaluate fluid loss agent property according to American Petroleum Institute (API) specifications and Chinese SY/T5621-93.The API filtrate volume of the mud was determined with a ZNZ-D3-type medium-pressure before and after rolled at fixed temperature. The value of API filtrate volume was under 12ml for commonly used fluid loss agent at room temperature in fresh water drilling fluid. 15ml was rational after rolled at fixed temperature. The fixed temperature was considered as bear temperature. The rheological parameters, such as the apparent viscosity (AV), the plastic viscosity (PV) and yield point (YP) was used to exhibit rheological properties of drilling fluid. The larger AV showed the worse rheological properties. And the larger YP indicated the better cuttings carried ability. The ratio of YP/PV represented suspension capability of drilling fluid. The larger ratio showed the better suspension capability. The value of AV over 80 was not rational in fresh water drilling fluid system. The rheological properties were basement of drilling fluid. The worse rheological properties were considered as the major factor of wellbore problems. The rheological properties and API filtrate volume were used to evaluate fluid loss agent in drilling fluid. The API filtrate volume after rolled at fixed temperature was used to evaluate heat resistance. The addition of salt was used to evaluate salt resistance. Copolymer was synthesized at fixed reaction condition based on previous work. Fig. 7 showed that the change of rheological properties and filtrate volume of copolymer with the addition of copolymer before rolled and after rolled. The apparent viscosity increased with the addition of copolymer before rolled and after rolled (Fig. 7a). When the concentration of copolymer was up to 1.5wt% the apparent viscosity was about 30.0mPa.s which less than commonly-used fluid loss agent. The apparent viscosity was kept on 17.5mPa.s after rolled at 150 ℃for 16h. The plastic viscosity and the yield point curve showed the similar trend. What was more important, the value of the plastic viscosity was lower than 15mPa.s when the concentration of copolymer was up to 1.5wt%, meanwhile yield point was about 15Pa. The ratio of YP/PV was up to 1.0. Even if after rolled at 150 ℃for 16h, the ratio of YP/PV still kept on 0.59. In addition of 0.5wt% copolymer, the filtration volume was sharp declined, and the filtration volume was 12.4ml which was equal to the commonly-used fluid loss agent. With the increase of copolymer the filtration volume reduced. In the addition of 1.5wt% copolymer, the filtration volume was 8.4ml. The filtration volume was sharp declined after rolled 150 ℃for 16h, comparing to fresh water fluid. The filtration volume was up to 12.4ml in 1.0% addition of copolymer. The results showed the copolymer as fluid loss agent exhibited high-performance rheological and fluid loss properties. Heat temperature was up to 150℃.

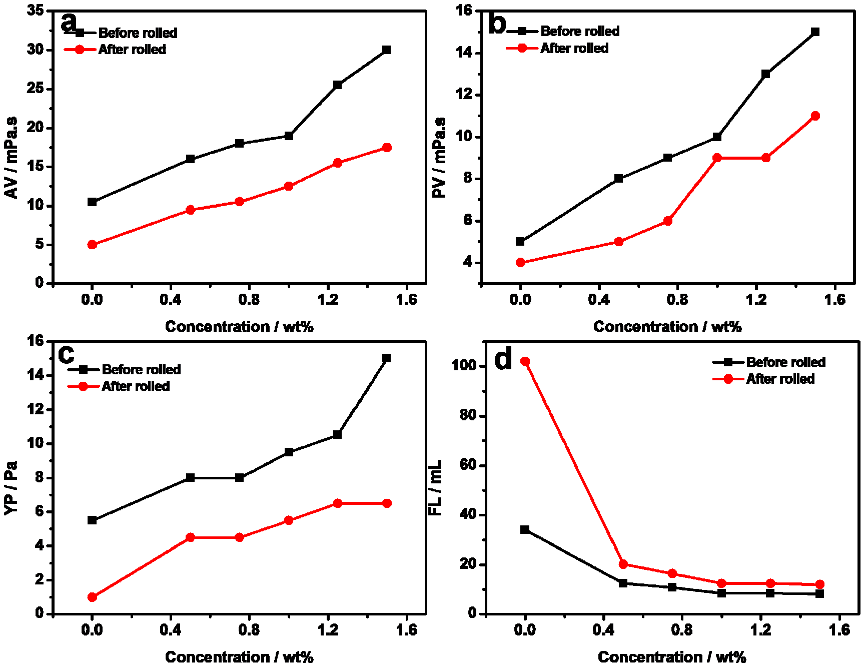

Figure 7. Change of rheology parameters and filtration volume of AM/AMPS/ M-SiO_2 grafted copolymer with concentration of copolymer after rolled and before rolled (rolled at 150℃). (a) Apparent viscosity; (b) Plastic viscosity; (c) Yield point; (d) Filtration volume.

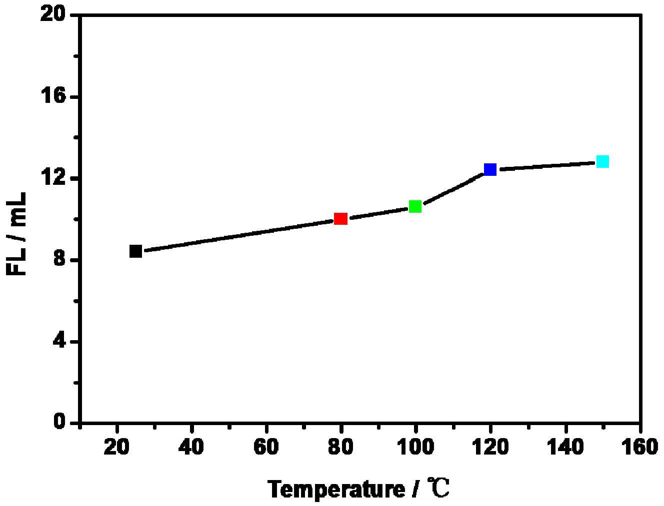

Figure 8. Change of filtration volume with temperature. The concentration of copolymer was 1wt%.

The high-temperature resistance was evaluated by heat rolled at different temperature (Fig.8). The filtration volume increased with temperature. The filtration volume was 8.6ml without rolled and the volume still kept on 12.4ml after rolled at 150℃. The filter papers with copolymer

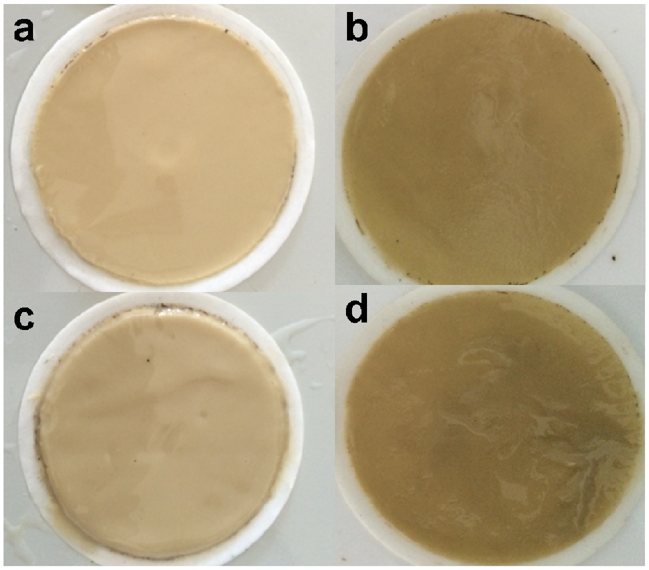

Figure 9. Images of filter paper with copolymer and without copolymer after rolled (at 150℃ for 24h) and before rolled. (a) With copolymer before rolled; (b) with copolymer after rolled; (c) without copolymer before rolled; (b) without copolymer after rolled.

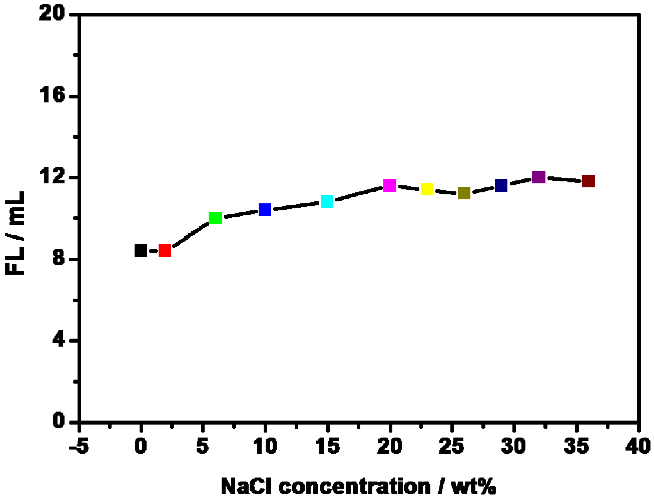

Figure 10. Change of filtration volume with NaCl concentration

and without copolymer after rolled (at 150℃ for 24h) and before rolled were showed in Fig. 9. The filter papers with copolymer both at room temperature and after rolled were obvious thinner than filter papers without copolymer. In the addition of copolymer, the space grid structure was formed between copolymer and MMT, resulting in the lower filtration volume. The salt resistance of copolymer was exhibited in Fig. 10. The suspension of copolymer and fresh water drilling fluid was prepared. NaCl was gradually added into the suspension, the filtration volume was recorded at room temperature. It spite of gradually increase, the value still kept on 12ml with saturation salt, indicating copolymer as fluid loss agent bear salt to saturation. The sulfonic acid group assigned to AMPS resulted in the copolymer resistance salt to saturation. As the evaluation of resistance salt, the same suspension was prepared. The gradually addition of $CaCl_2$ was carried out. Calcium resistance was presented in Fig. 11. The filtration volume without calcium was 8.6ml

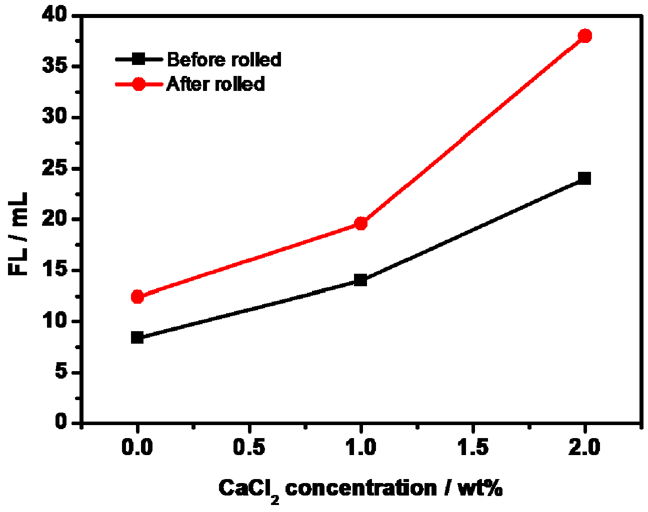

Figure 11. Change of filtration volume with $CaCl_2$ concentration

Table 1. Rheology properties and filtration volume of AM/AMPS/ M-SiO_2 grafted copolymer were evaluated in various media fluids. (a) fresh-water fluid; (b) salt-water fluid; (c) saturated salt-water fluid; (d) complex salt-water fluid.

Sample	600 rpm	300 rpm	200 rpm	100 rpm	6 rpm	3 rpm	**10s**	10min	API(mL)
a	19	16	14	12	9	8	8	9	27
a+1% polymer	35	28	23	20	11	10	9	11	8.8
b	14	11	9	8	6	6	6	11	56.8
b+5% polymer	14	9	8	6	4	4	4	4	12.4
c	27	21	19	16	11	10	10	13	105.6
c+5% polymer	21	12	9	5	3	3	3	3	20
d	13	11	10	8	6	6	6	9	73.6
d+5% polymer	14	9	8	6	4	4	4	6	22.8

and 12.6ml after rolled (at 150℃for 24h). After 1wt% calcium was added into the suspension fluid, the filtration volume was up to 14ml before rolled and 19ml after rolled. Continuing to add calcium, the filtration volume sharp increased both before rolled and after rolled. It was obvious that the copolymer as fluid loss agent was non-resistance to calcium. Calcium was divalent cation has been troubled engineers

and experts in drilling operation all the time. The little amount of commonly used fluid loss agent can bear over 2wt% calcium in fresh water drilling fluid after rolled 150℃. We evaluated the fluid loss property in various media fluids. The data was presented in Table 1. In generally, the rheology property was exhibited by rheology parameters got from 600rpm and 300rpm mentioned in method section. Presenting all the rotate speed was another commonly used method to show rheology property. The value of 10s and 10min was got from 3rpm based API specifications. The value of 10s was defined initial shear and 10min was defined finally shear, which was important parameter to indicate the suspension capability. The fluids were prepared as method section. In fresh water fluid, the filtration volume was 8.8ml. The volume was 20ml in saturated salt water fluid. The data were similar to the result mentioned in Fig. 10. In complex salt water fluid, the filtration volume was up to 22.8ml.The rheological properties in various salt water fluids changed slight before and after added copolymer, but 10s and 10min reduced obviously. The results exhibited the copolymer as fluid loss agent can be used in various salt water fluids.

3.3 Copolymer in drilling fluid

The copolymer in nm scale has been proved in above analysis. Firstly, we should prove the copolymer was in nm scale. What is more important, we should prove the copolymer was in nm scale in MMT solution which was the important additive to prepare drilling fluid. Particle size analysis of MMT solutions with and without copolymer was showed in Fig. 12. The peak from 2000nm to 5000nm was observed in MMT solution and no peak in nm scale appeared. In the MMT solution with copolymer, there was one peak in nm scale was observed. Another peak was in 1000nm scale and the 5 μ m peak appeared. In the addition of copolymer, partly copolymer resulted in aggregation of MMT due to the repulsion of negative charge and the other was dispersed in MMT solution in nm scale. The similar

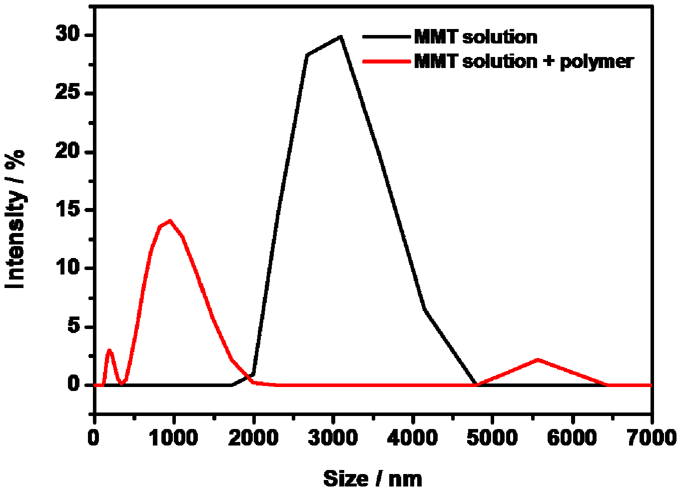

Figure 12. Particle size analysis of MMT solutions with and without copolymer.

observation was showed in TEM images (Fig. 13). Sheet of MMT was observed in image without copolymer. There was no nano particle appeared (Fig.13a). Two nano particles were observed in MMT sheet and the size of MMT sheet increased due to the interaction between MMT and copolymer. To further prove partly copolymer was still in nm scale in

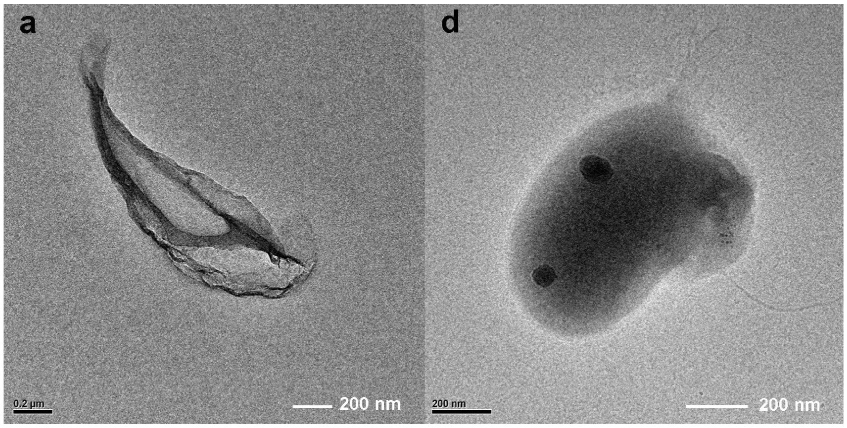

Figure 13. TEM images of MMT solutions with and without copolymer. (a) Without copolymer and (b) with copolymer.

MMT solution and the strong interaction between copolymer and MMT. To further study the size of copolymer in drilling fluid. The filter liquors of MMT solution with and without copolymer were prepared as method section. The particle size analysis of filter liquor was showed in Fig. 14. No peak under 1000nm appeared in the filter liquor without copolymer. One of peak under 100nm and another peak under 1000nm were observed in filter liquor with copolymer. The results showed

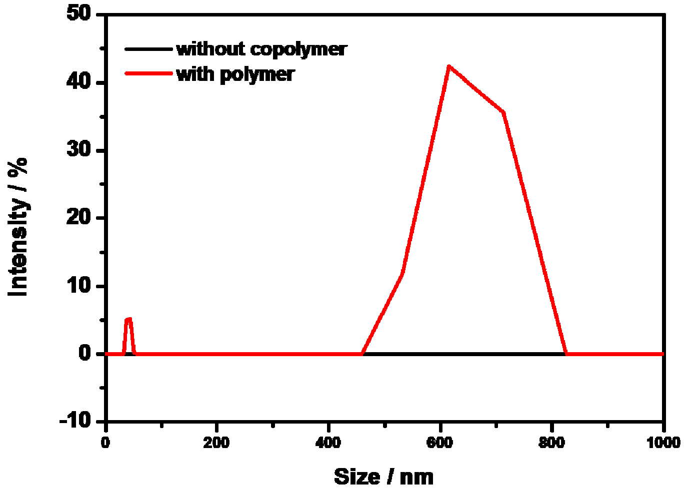

Figure 14. Particle size analysis of filter liquor of based fluid with and without copolymer .

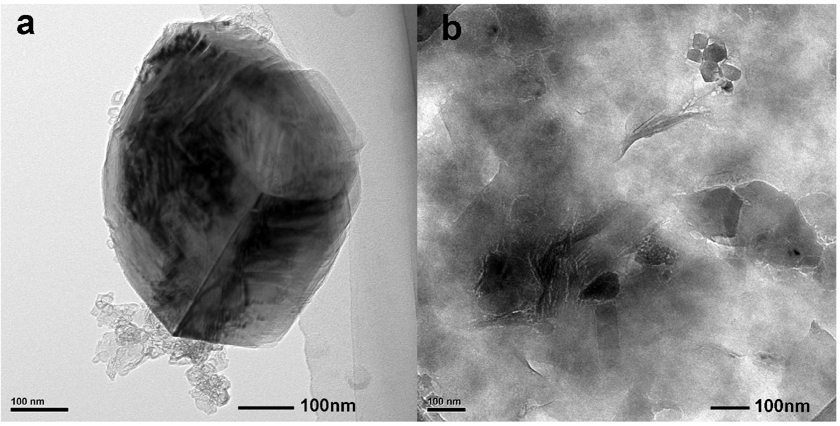

Figure 15. TEM images of filter liquor of based fluid with and without copolymer. (a) Without copolymer and; (b) with copolymer.

that the copolymer as nano fluid loss agent was in nm scale in drilling fluid. The place of peaks were different from the peaks mentioned in Fig.12. The residual MMT in filter liquor was through pores of filter paper. Most of MMT had been blocked by filter paper. The size of composition of MMT in filter liquor was different from pristine MMT solution. Most of copolymer had been interacted with MMT and a small amount of copolymer passed by filter paper and enterred into filter liquor. The different solution lead to the different peak. TEM images of filter liquor were presented in Fig.15. The sheet of MMT was observed in Fig. 15a. The size of sheet was over 100nm. It was typical characterization of MMT sheet. In the addition of copolymer, some small sheets under 100nm appeared. It was in accord with the datas mentioned in Fig.14. Surface area analysises of rock with copolymer and without were measured by surface area analyzer (BET). As showed in Table 2, surface area, pore volume and pore size reduced with copolymer. The results exhibited that pores of shale have been partly plugged by copolymer. Nano silica and modified nano silica were inorganic nano materials. These nano materials aggregated seriously in water solution. They could not enter into nanopores of shale due to aggregation. SEM images of filter cake of based fluid with and without copolymer were showed in Fig. 16. The filter cake of based fluid without copolymer was sag and crest, indicting the filter cake was loosed. The filter cake was smooth after added copolymer. The compact film was made due to interaction between copolymer and MMT particle. This compact film resulted in the high performance of fluid loss property of copolymer.

Table 2. Surface area analysis of rock with copolymer and without copolymer

Sample	Surface Area(m²/g)	Pore Volume(cm³/g)	Pore Size(nm)
Rock	16.17	0.0186	4.65
Rock+nano-polymer	13.83	0.0165	4.52

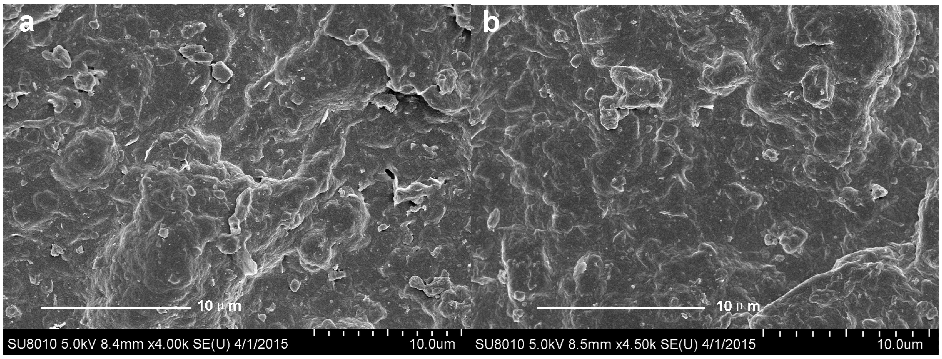

Figure 16. SEM images of filter cake of based fluid with and without copolymer. (a)Without copolymer; (b) with copolymer.

3.4 Probable mechanism

The copolymer was synthesized by free radical polymerization in water solution based on acrylamide (AM), 2-acrylamido-2-methyl -1-propane sulfonic acid (AMPS) and modified nano-silica (M-SiO_2). The polymerization degree was controlled by interaction condition. AM and AMPS was polymerized and grafted on the surface of M-SiO_2, The negative charge of grafted copolymer resulted in the stabilization of nano copolymer based on Cullen theorem. The results mentioned in above proved that the copolymer was still nano scale both in water solution and MMT solution. AM was widely used to product oil chemistry products. Acylamino assigned in AM and AMPS was strong adsorption group, which can be adsorbed in the surface of rock through hydrogen bond. AMPS exhibited high temperature and salt resistance. M-SiO_2 showed high temperature resistance. The addition of AMPS and M-SiO_2 enhanced the temperature resistance. The adsorption groups were adsorbed in the surface of MMT duo to high performance of fluid loss property. Meanwhile the copolymer can enter into the nanopores of shale to plug the nanopores. The cooperative interaction of filtration property and plugging nanopores of shale endowed the copolymer high performance as fluid loss agent in variously drilling fluid systems.

Conclusion

In summary, we synthesized the nano grafted copolymer at fixed reaction conditions based on previous work. The structure was characterized that AM and AMPS were grafted on the surface of M-SiO_2 and the grafted copolymer was in nm scale both in water and MMT solution. The negative charge of grafted copolymer resulted in the stabilization of nano copolymer based on the same charges repel each other. The filtration property of copolymer was studied by drilling fluid filter press in fresh water drilling fluid system and different kinds of salt water drilling fluid systems. The filtration property of copolymer was equal to conventional fluid loss agent in fresh water drilling fluid system. The resistance properties to salinity, calcium and high temperature were studied, and the results showed that copolymer was resistance temperature of 150℃, resistance salt to saturation and calcium to 1wt%. The interaction mechanism between montrillonite (MMT) and copolymer was studied by

Particle Size Analyzer, Transmission Electron Microscopy, Scanning Electron Microscopy and Surface Area Analyzer. The adsorption of copolymer in the surface of MMT was major driving force. Compared to pristine MMT, the addition of copolymer resulted in the new peaks in particle size analyzer image. The filter liquor of drilling fluid with copolymer showed two peaks in nm scale, nerveless the filter liquor of drilling fluid without copolymer showed that no peak appeared under 1000nm. All the results presented that copolymer as fluid loss agent was nano material in drilling fluid. Surface area analyzer (BET) results showed the reduce of surface area of natural rock after treated with copolymer, indicating copolymer entered into nanopores of shale because of the adsorption in the surface of shale. The copolymer exhibited high performance as fluid loss agent. It still exist some problems. The mechanism of copolymer needs further to study and plugging property needs to improve. The compatibility with other agents was not clearly. The next work is in progress.

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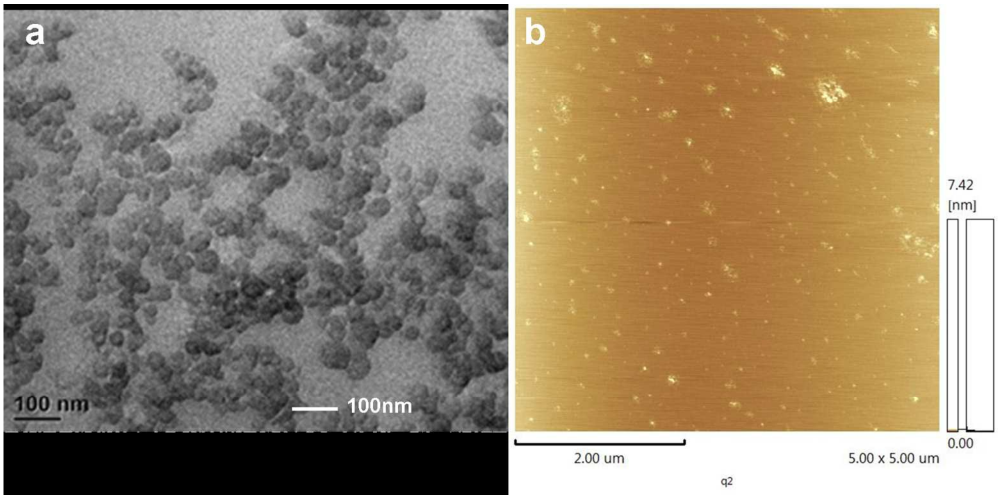

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