Application of a New Family of Organosilicon Quadripolymer as a Fluid Loss Additive for Drilling Fluid at High Temperature

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ABSTRACT: An organosilicon quadripolymer of acrylamide (AM), 2-acrylamido-2-methyl-1-propane sulfonic acid (AMPS), N-vinyl-pyrrolidone (NVP) and a kind of organosilicon monomer was synthesized by solution free radical polymerization. The chemical structure of organosilicon quadripolymer was characterized by Fourier transform infrared (FTIR) spectroscopy, and molecular weight distribution was determinate by gel permeation chromatography (GPC) under the best optimum synthesis conditions, which were identified by orthogonal test according to filtrate volume of fresh water-based drilling fluid. The colloidal properties of the organosilicon quadripolymer drilling fluid were investigated in various media such as fresh-water, 4.0% salt-water, and saturated brine based fluid. The results showed that the filtrate volume decreased with the increase of the organosilicon quadripolymer concentration before and after the thermal aging test at 180°C for 16 h, and the filtrate volume after the thermal aging test was larger than that before the thermal aging test, but was smaller than the base fluid. The colloidal properties and the filtrate volume could be controlled effectively at aging temperatures not exceeding 200°C. The organosilicon quadripolymer drilling fluid performance was better than corresponding terpolymer without organosilicon group and shows favorable inhibitive property and was an excellent fluid loss additive for drilling fluid resisting high temperature in deep wells. A possible mechanism is proposed to explain the improvement according to the comparative adsorption experiment. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

Drilling fluids are primarily water-bentonite suspensions. They are important for the oil, gas, and geothermal drilling industry because they perform many functions like transporting rock cuttings to surface, lubricating the drill bit, applying hydrostatic pressure in the well bore to ensure well safety, and minimizing fluid loss across permeable formations by forming a filter cake on the walls of the well bore.[1,2]

In recent years, there have been a number of challenges for drilling fluids to keep pace with the advancing operational drilling technologies. One of these challenges is high temperature (and by extension, high pressure).[3–5] When drilling in deep wells for oil, gas, and geothermal energy resources in deep environments, high temperatures are usually encountered, which adversely affect the performance of drilling fluids. In particular, bentonite

gels develop that result in loss of filtration control causing formation damage, which can be detrimental not only to the drilling activity but also to later production and cause deterioration of the rheological properties of drilling fluids.[6–11] At extreme temperatures, special formulations and systems must be used.[12–14] Since the 1980s, environmental legislation has increased restrictions on the use of oil-based fluids, which possess high thermal stability, and progressively new water based formulations presenting improved properties for specific applications at high temperature are required.[15–18] To avoid such problems, effective additives (especially fluid loss additives) are used to stabilize water-bentonite suspensions at high temperature.[19–24]

Recently, tendency of fluid loss additives is that simple nature products are improved into modified products and nature products, such as modified cellulose, modified humic acid, and

modified lignite, which are almost used under 180°C barely are replaced by synthetic products gradually.[25–32] However, most fluid loss additives, which can operate in water-bentonite suspension systems more efficiently need chromium salt as additional help at high temperature. Dissociate chromium ions (Cr^{6+} and Cr^{3+}) react with polymeric fluid loss additives, which have more functional groups to produce metallic complexes.[21,28,33,34] Electrostatic adsorption is formed between metallic complexes and clay particles. Because of electrostatic adsorption that is quite insensitive to temperature, clay particles can absorb with additives' chain more steadily at high temperature. It benefits to maintain content of finer clay particles in water-bentonite suspension systems. Compacted and permeable filter cake will be formed on the walls of the bore.[35,36] However, complexes with chromium salt have serious environmental implications, because Cr^{3+} and Cr^{6+} are carcinogenic.[37]

The development of novel synthetic fluid-loss reducers has helped make water-based fluid systems stable for high temperature and high pressure drillings, and the binary copolymer or terpolymer containing N-vinylpyrrolidone (NVP) or 2-acrylamido-2-methyl-1-propane sulfonic acid (AMPS) plays an important role in these synthetic polymers.[38,39] All the former literature indicates that pyrrolidone and sulfonated segments may be resistant to high temperatures and tolerant to the action of salt, and the fluids with these copolymers containing pyrrolidone and sulfonated groups can be used in some hostile environments.[40] Till now, no research has been reported on the organosilicon sulfonated-copolymer, which used in water-bentonite suspension systems as fluid loss additive. The aim of this article is to synthesize by solution free radical polymerization environmental quadripolymer of AM, AMPS, NVP, and a kind of organosilicon monomer and to study the colloid behavior, such as fluid loss and rheological properties of water-based drilling fluids with the organosilicon quadripolymer before and after thermal aging tests at fresh-water base, 4.0% salt-water and saturated brine based systems at 180°C for 16 h. The thermal properties of the organosilicon quadripolymer in different systems were also investigated.

EXPERIMENTAL

Materials

The 2-acrylamido-methylpropane sulfonic acids (AMPS) and acrylamide (AM) were commercial products from Chengdu Shundali Polymer Chemical Reagent and Chengdu Kelong Chemical Reagent, China, respectively. The AMPS was used as received without any purification. The AM was purified by recrystallization. The N-vinyl pyrrolidone (NVP) was commercial products from Shanghai Annaiji Chemical Reagent, China.

The organosilicon monomer was synthesized by coupling the acrylyl chloride (Shanghai Annaiji Chemical Reagent, China) and γ-aminopropyl triethoxysilane (AMEO, Chengdu Chenguang Chemical Reagent, China; Figure 1). The tetrahydrofuran (THF, Chengdu Kelong Chemical Reagent, China) solution of AMEO (18.7 mL) and triethylamine (TEA, Chengdu Chenguang Chemical Reagent, China) (11.6 mL) were mixed well in a reaction flask and then sparged with nitrogen at 0°C while stirring. A volume of 6.5 mL of acrylyl chloride was added to the flask
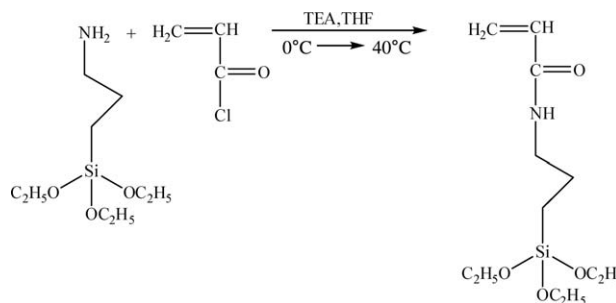

Figure 1. Synthesis of organosilicon monomer.

gradually. After the addition, the reaction mixture was kept at 0°C for 20 min and then heated it to 40°C. The reaction mixture was heated to reflux for 2 h. The reaction primary product was cooled down to room temperature. After filtering reaction primary product through funnel, the ultimate product was separated from THF by distillation at reduced pressure in reaction mixed liquor finally. Its reaction is as follows:

N,N-Dimethylformamide (DMF, Chengdu Kelong Chemical Reagent, China) was distilled under vacuum after drying with $CuSO_4$. The initiator was benzoyl peroxide (BPO, Chengdu Kelong Chemical Reagent, China) purified by recrystallization in methanol at 0°C.

Preparation and Characterization of the Organosilicon Quadripolymer

The quadripolymer of AM, AMPS, NVP, and organosilicon monomer was synthesized by solution free radical polymerization. The orthogonal test design was used to arrange experiment to test the effect of the four main factors, that is, molar ratio of AM, AMPS, and NVP, dosage of organosilicon monomer, the amount of initiator, and reaction temperature to establish the best reaction condition and formula according to fluid loss properties of fresh water-based drilling fluids with organosilicon quadripolymer (0.5%) after aging tests at 180°C for 16 h.

A DMF solution of organosilicon monomer was mixed well in a reaction flask and deoxygenated with nitrogen. Then, the solution was heated to reaction temperature and added AM, AMPS, NVP, and BPO to reaction flask in 10 min gradually. After the addition, the reaction was kept 12 h at reaction temperature. While cooled to room temperature, the reaction mixture was filtrated to remove solvent. Then, reaction mixture was washed by 200 mL ethanol three times. After the washing, the reaction mixture was poured into 200 mL acetone and kept 24 h, and the precipitated polymer was isolated and dried under vacuum at 40°C. Finally, a white copolymer product was obtained. The chemical structure of organosilicon quadripolymer is shown in Figure 2.

Before Fourier transform infrared (FTIR) spectra measurements, samples were dried under vacuum and stored in a glove box. The FTIR spectra (4000–400 cm^{-1}) were measured with TENSOR27-type Fourier Transform-Infrared Spectroscopy (Brucker Manufacturing, Germany). Determination of molecular weight distribution of organosilicon quadripolymer by hy-1100-type GPC (Agilent Technologies, American).
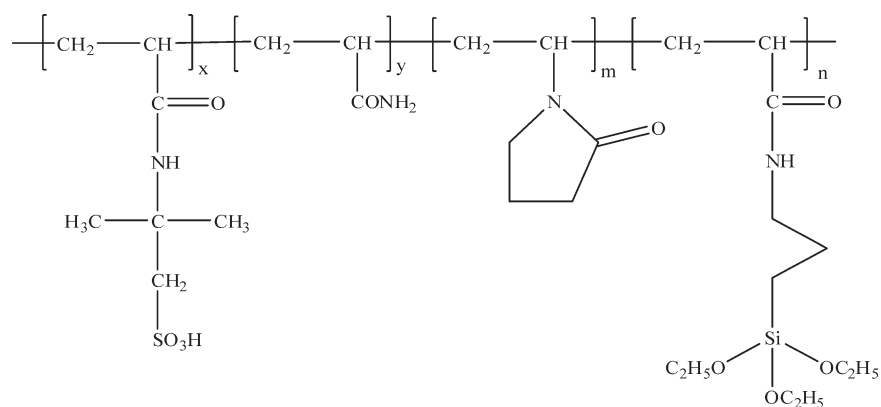
Figure 2. Chemical structure of organosilicon quadripolymer.

Fluid Preparation and Aging Tests

The fresh-water based fluid was made of deionized water and sodium bentonite (Xinjiang Xiazijie Bentonite, China) at a concentration of 8.0%. Na_2CO_3 was added at concentration of 0.2% to the suspension and stirring for 20 min at high speed of 10,000 rmp and aging for 24 h at room temperature. Two types of salt-water based fluids were made of 8.0% of sodium bentonite, 4.0% of NaCl or saturated brine, 0.2%of Na_2CO_3 was prepared by the similar procedure to that of the fresh-water based fluid preparation. Quadripolymer added at concentration of 4.0% to the denionized water. Quadripolymer solution was poured into bentonite suspensions quickly. The quadripolymer fluids were stirred for 20 min at 10,000 rmp and aging for 24 h at room temperature.

Aging experiments of bentonite-quadripolymer fluids were carried out in a GW300-type frequency conversion rolling oven (Qingdao Jiaonan Tongchun Machinery Plant, China) through hot rolling at appointed temperature (150, 180, 200, and 220°C) for 16 h. Fluids property tests were performed before and after the thermal aging experiments.

Fluid Property Tests

Fluid property tests were measured according to American Petroleum Institute (API) specifications and Chinese SY/T5621-93. The API filtrate volume (FL_{API}) of the mud was determined with a ZNZ-D3-type medium-pressure filtration apparatus (Qingdao Bairuida Machinery Corporation, China). The high-temperature and high-pressure filtrate volume (HTHP filtrate volume or FL_{HTHP}) was determined with a GGS42-type high-temperature and high-pressure filtration apparatus (Qingdao Jiaonan Tongchun Machinery Petroleum instrument, China). A volume of water-bentonite suspension was loaded on the filter press equipped with a filter paper and a differential pressure was applied. Over time, allow permeability filter cake is formed on the filter paper resembling the filter cake created during drilling. This reduces the amount of filtrate exiting the press. For a stabilized drilling fluid, FL_{API} and FL_{HTHP} collected over 30 min (fluid loss) should not exceed 15 and 30 mL, respectively.

The rheological parameters, such as the apparent viscosity (AV), the plastic viscosity (PV), and the yield point (YP), were determined through measurements of the viscosities at two rotation rates of 600 and 300 rpm using a ZNN-D6-type rotating viscometer (Qingdao Jiaonan Tongchun Machinery Petroleum instrument, China) at room temperature as follows:

$$AV = \Phi_{600}/2 \ (mPa\,s)$$

$$PV = \Phi_{600} - \Phi_{300} \ (mPa\,s)$$

$$YP = 0.511(\Phi_{300} - PV) \ (Pa)$$

Shale Hot-Rolling Recovery Tests

The weathered shale was ground and sieved to retain a suitable mesh fraction, which belongs to the range from 6 to 10 yard. A 50 g portion of the shale was added to the fresh water based fluid in a stainless steel aging jar and the system was rolled at 120°C for 16 h. The retained shale was washed with clear water and dried to constant weight at 105°C on a vacuum drying oven. When the temperature dropped to room temperature, the weight of the shale was recorded. Recovered shale was added to the fresh water in a stainless steel aging jar and the system was rolled at 120°C for 2 h then. Second, the retained shale was washed with clear water and dried to constant weight at 105°C on a vacuum drying oven. When the temperature dropped to room temperature, the weight of the shale was recorded again. The first shale recovery rate (%R_1), the second shale recovery rate (%R_2), and relative shale recovery rate (%R') were calculated for each sieve on a dry-mass basis as follows:

$$\%R_1 = W_1/W_0 \times 100\%$$

$$\%R_2 = W_2/W_0 \times 100\%$$

$$\%R' = R_1/R_2 \times 100\%$$

where W_1, W_2, and W_0 denote the weight after hot-rolling twice and the weight before hot-rolling, respectively. According to these tests, the effects of concentration of AM-AMPS-NVP-APTS on the shale recovery were investigated.

Adsorption Measurements

The adsorbed amount of admixture was determined from the filtrate collected in the fluid loss test at high temperature. Achievement of adsorption equilibrium was checked by comparing different copolymer adsorption in fresh water bentonite suspension. First, mixed copolymer solution (2.0%) and 8.0%
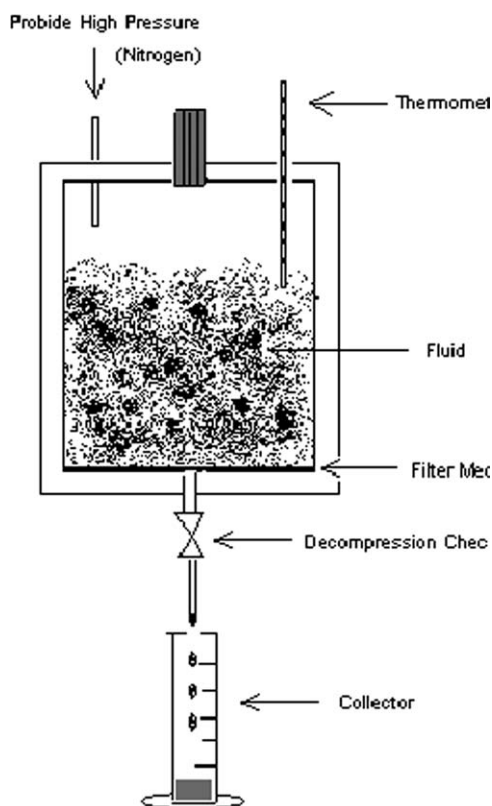
Figure 3. Structural model of metal container.

fresh-water based fluid. Then, put the bentonite-copolymer fluid into metal container after stirring for 20 min. The structural model of metal container, which resembles in shape of metal container on high-temperature and high pressure filtration apparatus, is shown in Figure 3. The filter medium of metal container is special wire netting, which allows only the smallest molecules (water, polymer, and extremely small amount of clay particles) to pass through, whereas filtration limits solid particles to pass through smoothly. The copolymer fluid would be aged at high temperature and pressure for 16 h. Filtrate could be collected via decompression check valve. The adsorbed amount was calculated from the difference in the equilibrium concentrations of copolymer in the liquid phase before and after adsorption. The concentration of copolymer in the filtrate was determined with TNB-type TOC analyzer (Element Analysis System, Germany) after determining adsorption equilibrium time. By subtracting, the mass of copolymer in the filtrate from initial mass of copolymer, the adsorbed amount of organosilicon quadripolymer or AM/AMPS/NVP terpolymer is calculated under the same experimental conditions. The adsorption equilibrium time was determined by dynamic adsorption experiment at 150°C.

RESULTS AND DISCUSSION

Optimum Synthesis Conditions of Organosilicon Quadripolymer

Molecular weight and matching of functional group play a significant part in physical and chemical properties of copolymer, especially in rheological and fluid loss properties. Monomer ra-

tio, initiator amount, reaction temperature, and time are influences on molecular weight and matching of functional group of copolymer. Being the molar ratio of AM, AMPS, and NVP, the percentage of organosilicon monomer in total monomers, initiator amount and reaction temperature, adopting the orthogonal method and the error analysis method, studying the factors affecting these indexes. All of the stoichiometric numbers are shown in Table I. The best optimum synthesis condition identified according to filtrate volume of fresh water-based drilling fluids with quadripolymer (0.5%) after aging tests at 180°C for 16 h. The total weight percentage of all monomers in the solution is 10.0%, and the reaction time is 10 h. The orthogonal design test result is shown in Table II [when the corresponding factor at i level, ki is represents the average of FL_{API}, and Ki is represents the average of FL_{HTHP}. The maximum FL_{API} (or FL_{HTHP}) minus the minimum FL_{API} (or FL_{HTHP}) makes variance].

A technical condition for the reaction by orthogonal test was investigated. By experiment and calculation, the best optimum synthesis conditions for the reaction, for FL_{API} of copolymer fluid, were as follows: n (AM) : n (AMPS) : n (NVP) = 3 : 1 : 1, and percentage of organosilicon monomer in total monomers 1.0%, initiator amount 0.6 wt %, reaction temperature 80°C. Percentage of organosilicon monomer in total monomers had great influence on FL_{API} of quadripolymer fluid. The FL_{API} of quadripolymer fluid was 6.8 mL under the best optimum synthesis conditions.

According to the experimental result and calculation, the best optimum synthesis conditions for the reaction, for FL_{API} of quadripolymer fluid, were as follows: n (AM) : n (AMPS) : n (NVP) = 3 : 1 : 1, and percentage of organosilicon monomer in total monomers 2.0%, initiator amount 0.4%, reaction temperature 80°C. Percentage of organosilicon monomer in total monomers had great influence on FL_{HTHP} of copolymer fluid, too. The FL_{HTHP} of copolymer fluid was 15.4 mL under the best optimum synthesis conditions. Organosilicon quadripolymer was synthesized under this optimum synthesis conditions and should mean the same hereafter.

FTIR and Molecular Weight Distribution Analysis of the Organosilicon Quadripolymer

Figure 4 shows the FTIR spectra of organosilicon quadripolymer, which was synthesized under the best optimum synthesis condition.

Table I. Level of Factor

Level	A n (AM) : n (AMPS) : n (NVP)	B Percentage of organosilicon monomer in total monomers	C Initiator amount (%)	D Reaction temperature (°C)
1	2 : 1 : 1	0.5	0.2	70
2	3 : 1 : 1	1.0	0.4	75
3	2 : 1 : 2	2.0	0.6	80

Table II. $L_9(3^4)$ Orthogonal Design Test Result

Sample	A	B	C	D	FL_{API} (mL)	FL_{HTHP} (mL)
1	1	1	1	1	14.5	34.4
2	1	2	2	2	13.0	27.2
3	1	3	3	3	9.8	20.0
4	2	1	2	3	11.2	30.0
5	2	2	3	1	8.5	25.6
6	2	3	1	2	8.0	17.4
7	3	1	3	2	17.0	38.5
8	3	2	1	3	14.2	32.0
9	3	3	2	1	12.5	24.5
K_1	12.433	14.233	12.233	11.833		
K_2	9.233	11.900	12.233	12.667		
K_3	14.567	10.100	11.767	11.733		
Variance	5.334	4.133	0.466	0.934		
K_1	27.200	34.300	27.933	28.167		
K_2	24.333	28.267	27.233	27.700		
K_3	31.667	20.633	28.033	27.333		
Variance	7.334	13.667	0.800	0.834		

Determination condition of FL_{HTHP}: 180°C, 3.5 MPa, similarly hereinafter.

The spectrum shows a broad band in the range of 2900–3700 cm^{-1}, which is attributed to the typical absorption band of the organosilicon copolymer, including the following characterization: 3423 cm^{-1} (N—H stretching band, primary acylamino), 3201 cm^{-1} (N—H stretching band, secondary acylamino). Others most characteristic absorption bands present in all copolymer are the follows: 1740 cm^{-1} (C=O stretching band, lactam group), 1656 cm^{-1} (C=O stretching band, primary and secondary acylamino), 1617 cm^{-1} (N—H bending oscillation band, primary acylamino), 1554 cm^{-1} (C—N stretching band, primary acylamino), 1250 cm^{-1} (C—N stretching band, secondary acylamino), 785.13 cm^{-1} (C—N bending oscillation band, lactam group and primary and secondary acylamino), 1345, 1185, and 1041 cm^{-1} (stretching SO$_3$, S=O from sulfonic acid group), 1069 cm^{-1} (Si—O—C stretching band). There is no C=C band at 1645–1620 cm^{-1} and no Si—O—Si band at 1020 cm^{-1} nearby.

Figure 5 shows the molecular weight distribution of organosilicon quadripolymer, which was synthesized under the best optimum synthesis condition. The measuring conditions are listed below: standard sample is glucan, eluent is mixed by NaH$_2$PO$_4$/Na$_2$PO$_4$·12H$_2$O (4 : 6, quality ratio), the concentration is 8.0 g L^{-1}, the flow rate 1.0 mLmin^{-1}. The result showed that the weight average molecular weight is 1.4769×10^5, and the number average molecular is 1.3772×10^5. Thus, the molecular weight distribution coefficient is 1.0724.
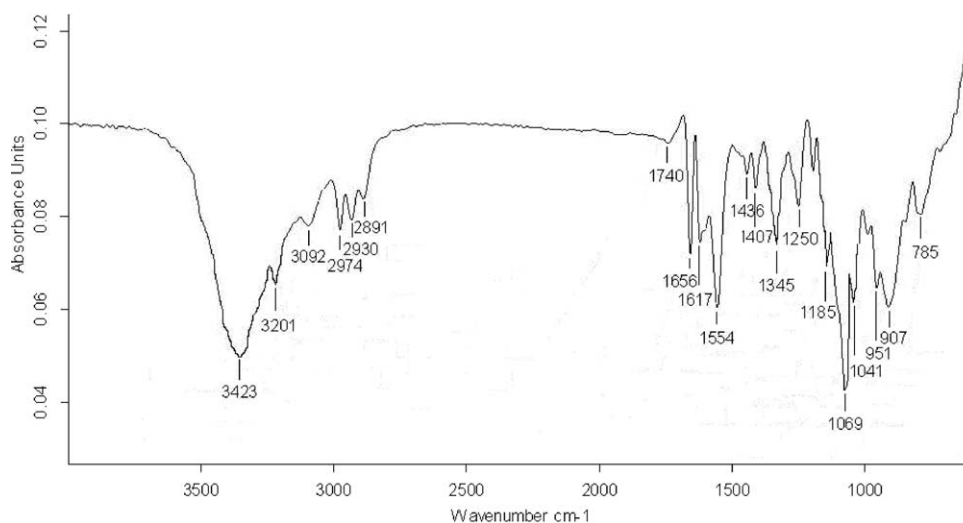

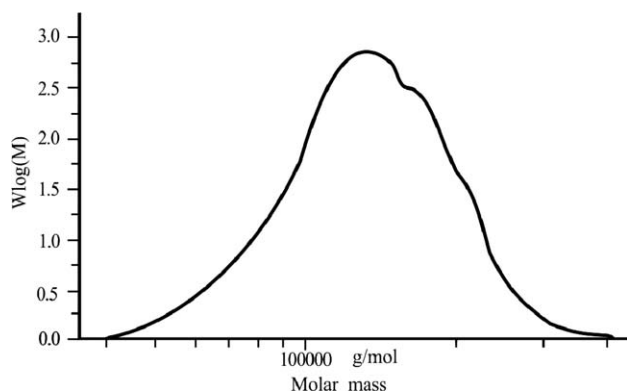**Figure 4.** FTIR of organosilicon quadripolymer.

Figure 5. Molecular weight distribution of organosilicon quadripolymer.

Rheological Properties of the Organosilicon Quadripolymer Fluid

A series of fresh-water, 4.0% salt-water and saturated brine based fluid formations with different quadripolymer concentrations were prepared, and the fluid properties (such as AV, PV, and YP) were measured before and after thermal aging tests at 180°C for 16 h. The clay samples used in the measurements of the rheological properties were investigated, in other words the colloidal properties of the organosilicon quadripolymer bentonite system could be disclosed.

The effects of organosilicon quadripolymer concentration on rheological parameters of the fresh-water, 4.0% salt-water, and saturated brine based fluid are listed in Tables III–V, respectively.

Before thermal aging test, with the addition of the organosilicon quadripolymer into the corresponding base fluid, all the rheological parameters, including AV, PV, and YP are greatly increased and increase further with increments in the quadripolymer concentration. This increasing tendencies of AV and PV still persisted in the quadripolymer concentration after thermal aging tests. These results showed that the quadripolymer contributes to the building up the network structure, thereby resulting in a viscosity-building ability. However, after thermal aging at 180°C for 16 h, most fluids increase a large amount of AV and PV, but YP of all fluids was reduced at the same fluid formulation. In the water-based suspension, competition existed between the aggregation and dispersion of the clay particles.[41]

Clay particles in water are attracted to each other and build up network structure with viscosity and strength.[42] Like ordinary polymeric fluid loss additives, organosilicon quadripolymer was degradated at high temperature partly, which can lead to breaking up the network structure to a certain extent. Meanwhile, organosilicon quadripolymer with Si—OC$_2$H$_5$ group can react polycondensation between molecules in the water-based suspension. High temperature advantageously improves strength of network structure, and this capability is more obvious than breaking up the network structure.[43] So, the AV and PV was increased after thermal aging tests.

As organosilicon polymer brushes with Si—OH group can adsorbed on the surface of silicon wafer, organosilicon quadripolymers adsorbed on clay particles by chemical adsorption, which is not affected by temperature.[44] It may reduce or inhibit the attraction between particles by electrostatic repulsion. Therefore, the YP of fluid was reduced after aging tests.

Filtrate Properties of the Organosilicon Quadripolymer Fluid

The effects of the organosilicon quadripolymer concentrations on the filtrate volumes of fresh-water, 4.0% salt-water, and saturated brine based fluid formations before and after thermal aging tests at 180°C for 16 h are shown in Figures 6–8, respectively.

It could be seen that FL$_{API}$ decreased with the increase of the organosilicon quadripolymer concentration before the thermal aging test. Similar variations in FL$_{API}$ and FL$_{HTHP}$ after thermal aging test were also recorded, respectively. With an addition of the organosilicon quadripolymer into the corresponding base fluid, the FL$_{API}$ and FL$_{HTHP}$ were decreased and changed very slowly as quadripolymer concentration were further increased, thereby indicating that the organosilicon quadripolymer was a very efficient fluid loss additive (i.e., that a small dosage of quadripolymer can attain excellent filtration control). According to the view of Wu[45] adsorption between polymers and clay particles was prerequisite to exerting function of polymeric fluid loss additive. Only when enough polymeric additives adsorbed on the clay surface, the filtrate volume can be controlled efficiently. The reasons about organosilicon quadripolymer to reduce FL$_{API}$ and FL$_{HTHP}$ after thermal tests is that the organosilicon auqdripolymer can be degraded without completely, and residual organosilicon quadripolymers continue to play a certain

Table III. Rheological Behaviors of 4.0% Salt-Water Based Fluid Under Different Organosilicon Quadripolymer Concentrations (Before and After the Thermal Aging Tests)

Fluid formulation	AV (mPa s)		PV (mPa s)		YP (Pa)	
	Before	After	Before	After	Before	After
Fresh-water based fluid (I)	8.0	29.5	6.0	17.0	2.0	12.5
(I) + 0.2% organosilicon quadripolymer	11.0	30.5	8.0	25.0	3.0	5.5
(I) + 0.4% organosilicon quadripolymer	17.5	35.0	11.0	31.0	6.5	4.0
(I) + 0.6% organosilicon quadripolymer	29.0	39.0	19.0	32.5	10.0	6.5
(I) + 0.8% organosilicon quadripolymer	40.5	41.0	25.0	33.0	15.5	8.0
(I) + 1.0% organosilicon quadripolymer	51.0	43.5	32.0	35.0	19.0	8.5

All rheological data were measured at 25 ± 0.5°C.

Table IV. Rheological Behaviors of Saturated Brine Based Fluid Under Different Organosilicon Quadripolymer Concentrations (Before and After the Thermal Aging Tests)

Fluid formulation	AV (mPa s)		PV (mPa s)		YP (Pa)	
	Before	After	Before	After	Before	After
4.0% Salt-water based fluid (II)	5.5	6.0	4.0	4.0	1.5	2.0
(II) + 0.2% Organosilicon quadripolymer	9.0	11.5	5.0	8.0	4.0	3.5
(II) + 0.4% Organosilicon quadripolymer	15.0	17.0	9.0	10.0	6.0	7.0
(II) + 0.6% Organosilicon quadripolymer	23.5	19.5	14.0	12.0	9.5	7.5
(II) + 0.8% Organosilicon quadripolymer	29.0	24.0	20.0	17.0	9.0	7.0
(II) + 1.0% Organosilicon quadripolymer	36.5	30.0	21.0	21.0	15.5	9.0

All rheological data were measured at 25 ± 0.5°C.

role in drilling fluid. The FL_{API} and FL_{HTHP} can reach requirement with 0.4% of organosilicon quadripolymer in fresh-water based fluid. For 4.0% salt-water based fluid, the suitable organosilicon quadripolymer of copolymer is 0.8%. When the concentration of organosilicon quadripolymer is above 1.0% in saturated brine-based fluid, FL_{API} and FL_{HTHP} can be controlled effectively.

Apparently, at the same concentration of organosilicon quadripolymer, the FL_{API} after and before thermal aging test and FL_{HTHP} after thermal aging test were larger in 4.0% salt-water and saturated brine based fluid formation than that in fresh-water based fluid. In accordance the view of Wu,[40] the negative charge density on the molecular chain was reduced in salt-water based fluid. The molecular chain contracted and the zeta potential on the clay surface decreased owing to the salt screening effect of NaCl on the electric double layer of the clay particles, especially in saturated brine based fluid. Hence, the greater the NaCl concentration, the larger the filtrate volumes.

Obviously, the FL_{API} after the thermal aging test was lager than that before the aging test (comparing Figures 6 and 7), and the FL_{HTHP} was larger than that the FL_{API} after thermal aging test (comparing Figures 7 and 8), meaning that the elevated temperature could raise the permeability of the filter cake and spoil a part of clay gel structure. Despite of that, not all organosilicon quadripolymers were degraded at high temperature condition. After thermal aging test, the residual polymers could still adsorb on the clay surface and build up network structure in drilling

fluid system.[46] The FL_{API} and FL_{HTHP} after thermal aging test showed capability against high temperature of the organosilicon quadripolymer as fluid loss additive directly. Thus, it was found in the experiment results that the organosilicon quadripolymer had good filtration properties.

Temperature Resistant Capacity

With the increase in well depth, the impact of the temperature on the operation of drilling fluid is beginning to appear. The condition of high temperature is very detrimental to the flow properties and filtration control of the fluid, owing to hydrolysis, depolymerization, or other chemical degradation of the polymeric additives and to flocculation or irreversible transformations of the clay inevitably. So, rheological and filtrate properties should be determined after different thermal aging temperature for 16 h necessarily. The results of the studies are listed in Table VI and Figures 9 and 10, respectively.

The results show that when the aging temperature is not higher than 200°C. AV, PV, and YP reduced and FL_{API} and FL_{HTHP} increased gradually with the ascension of aging temperature. Rheological properties and filtrate volumes (FL_{API} and FL_{HTHP}) of three drilling fluid systems were controlled effectively from 150 to 200°C. It is well-known that elevated aging temperature can degrade polymeric additives and decrease the hydration abilities of clay particles and hence, all the fluid systems lose amount of viscosity and YP.[47,48] But these negative influence held within limits and control. However, on exceeding 220°C, performance of rheological behavior, FL_{API} and FL_{HTHP} got

Table V. Rheological Behaviors of Fresh-Water Based Fluid Under Different Organosilicon Quadripolymer Concentrations (Before and After the Thermal Aging Tests)

| Fluid formulation	AV (mPa s)		PV (mPa s)		YP (Pa)	
	Before	After	Before	After	Before	After
Saturated brine-water based fluid (III)	5.0	7.5	3.0	6.0	2.0	1.5
(III) + 0.2% Organosilicon quadripolymer	7.5	10.5	5.0	4.0	2.5	5.5
(III) + 0.4% Organosilicon quadripolymer	11.5	15.0	8.0	7.0	3.5	8.0
(III) + 0.6% Organosilicon quadripolymer	20.0	19.0	11.0	12.0	9.0	7.0
(III) + 0.8% Organosilicon quadripolymer	23.5	24.0	12.0	18.0	11.5	6.0
(III) + 1.0% organosilicon quadripolymer	28.0	29.5	14.0	21.0	14.0	8.5

All rheological data were measured at 25 ± 0.5°C.
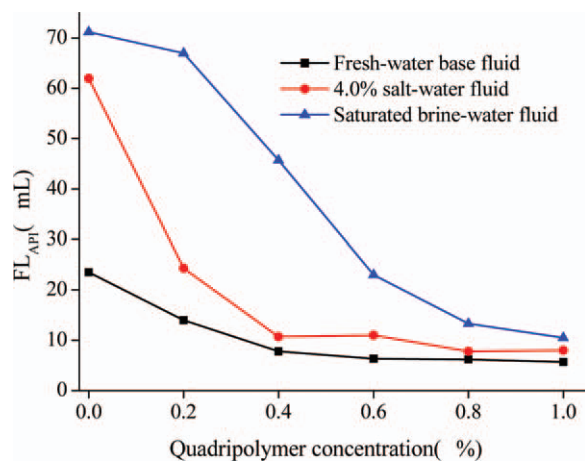
Figure 6. The effect of the organosilicon quadripolymer concentration on the FL_{API} of the fresh-water, 4.0% salt-water, and saturated brine based fluid formations before thermal aging tests. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

degradation or instable, meaning that the organosilicon quadripolymer lost its potence by to a certain extent, especially in saturated brine fluid. This is due to the thermal degradation and dissociative adsorption of organosilicon quadripolymer under 220°C possibly.

Comparative Test Between Organosilicon Quadripolymer and AM-AMPS-NVP Terpolymer

To investigate the effect of organosilicon group in quadripolymer, especially in high temperature, comparative experiment between organosilicon quadripolymer and terpolymer AM-AMPS-NVP, which were used in fresh-water based fluid with the concentration 1.0% after thermal aging tests for 16 h was fulfilled. The fluid property comparison of the organosilicon quadripolymer with the AM-AMPS-NVP terpolymer is shown in Table VII, Figures 11 and 12, respectively.
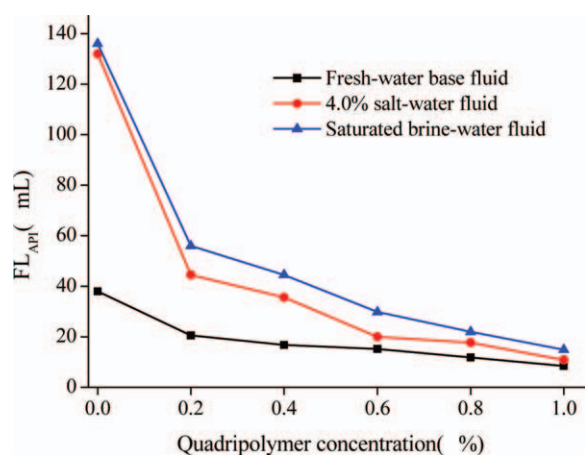

Figure 7. The effect of the organosilicon quadripolymer concentration on the FL_{API} of the fresh-water, 4.0% salt-water, and saturated brine based fluid formations after thermal aging tests at 180°C for 16 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
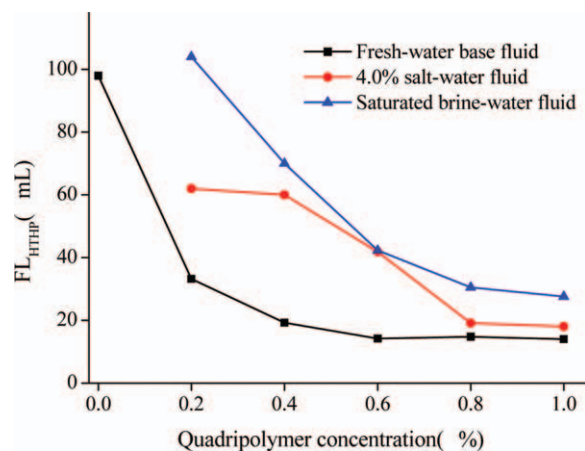

Figure 8. The effect of the organosilicon quadripolymer concentration on the FL_{HTHP} of the fresh-water, 4.0% salt-water, and saturated brine based fluid formations after aging tests at 180°C for 16 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The AM-AMPS-NVP terpolymer was synthesized by free radical polymerization under the same synthesis condition of organosilicon quadripolymer. This terpolymer belongs to ordinary polymeric fluid loss additive, which can adsorb on the surface of clay by hydrogen. It contributes to raising the quality of clay particles and reduces the coefficient of penetration and filtration.

It can be seen that, AV and PV of AM-AMPS-NVP terpolymer fluid and organosilicon quadripolymer fluid reduced with aging

Table VI. Rheological Behaviors of Fresh-Water, 4.0% Salt-Water, and Saturated Brine Based Fluid Formations Under Different Thermal Aging Temperatures After the Thermal Aging Tests

Fluid formulation	Aging temperature (°C)	AV (mPa s)	PV (mPa s)	YP (Pa)
(I) + 1.0% Organosilicon Quadripolymer	150	45.0	37.0	8.0
	180	43.5	35.0	8.5
	200	39.0	27.0	11.0
	220	14.0	10.0	4.0
(II) + 1.0% Organosilicon Quadripolymer	150	34.5	27.0	7.5
	180	30.0	21.0	9.0
	200	22.0	16.0	6.0
	220	15.0	13.0	2.0
(III) + 1.0% Organosilicon Quadripolymer	150	32.0	25.0	7.0
	180	29.5	21.0	8.5
	200	21.5	17.0	4.5
	220	13.5	13.0	0.5

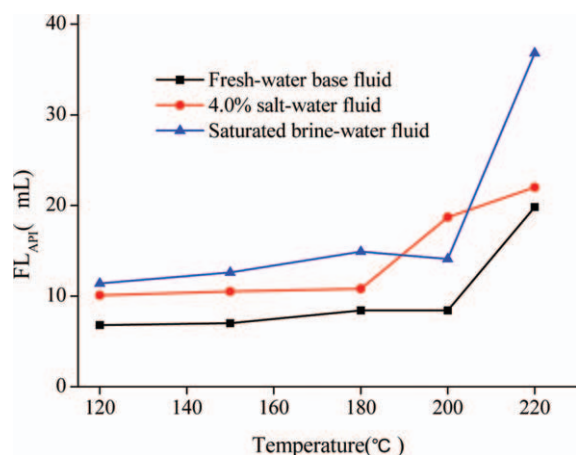All rheological data were measured at 25 ± 0.5°C.

Figure 9. The effect of the FL_{API} of the fresh-water, 4.0% salt-water and saturated brine based fluid formations after different aging temperatures for 16 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

temperature increasing. The downward tendency was becoming more and more obvious, mainly because of the thermal degradation of copolymer, and especially for the AM-AMPS-NVP terpolymer fluid. The filtrate volume increased correspondingly with raising aging temperature. Under the same aging temperature, the FL_{API} and FL_{HTHP} of organosilicon quadripolymer fluid was smaller than that of AM-AMPS-NVP terpolymer fluid. AM-AMPS-NVP terpolymer as fluid loss additive in fresh-water based fluid had not already controlled fluid loss exceeding aging temperature 200°C. However, organosilicon quadripolymer still worked well under the same condition. Hence, there is ample reason to believe that the organosilicon monomer in quadripolymer, which used in drilling fluid as fluid loss additive plays a positive role.

Shale Hot-Rolling Recovery Rate

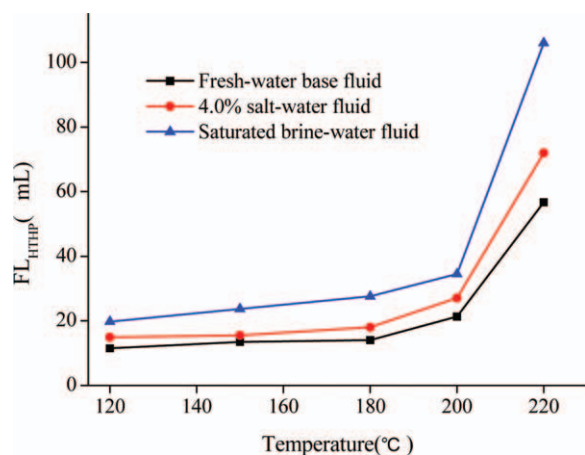The values of shale recovery rate in aqueous solutions containing different concentrations of AM-AMPS-NVP-APTS are

Table VII. The Rheological Behaviors of the Organosilicon Quadripolymer Compared with the AM-AMPS-NVP Terpolymer After Different Aging Temperatures for 16 h

Fluid formulation	Aging temperature (°C)	AV (mPa s)	PV (mPa s)	YP (Pa)
Organosilicon quadripolymer fluid	120	47.0	38.0	9.0
	150	45.0	37.0	8.0
	180	43.5	35.0	8.5
	200	39.0	27.0	11.0
	220	14.0	10.0	4.0
AM-AMPS-NVP terpolymer fluid	120	42.0	33.0	9.0
	150	34.0	27.0	7.0
	180	23.5	15.0	8.5
	200	20.0	11.0	9.0
	220	6.0	5.0	1.0

showed in Table VIII. The $\%R_1$ in the fresh water based fluid with AM-AMPS-NVP-APTS are greater than the $\%R_1$ in fresh water based fluid without AM-AMPS-NVP-APTS. With an addition of AM-AMPS-NVP-APTS into the fresh water based fluid, $\%R_1$, $\%R_2$, and $\%R'$ were increased and changed very slowly as the concentrations, and indicating that AM-AMPS-NVP-APTS played an important role in the disintegration or dispersion of the shale. Perhaps because, AM-AMPS-NVP-APTS can be adsorbed on the surface of the shale and form a film, thus hindering water from entering the shale.

Mechanism of Organosilicon Copolymer

Several studies exist reporting the combined use of bentonites with polymer to extend water based fluid suspension stability at higher temperatures. Polymeric additives may be adsorbed on
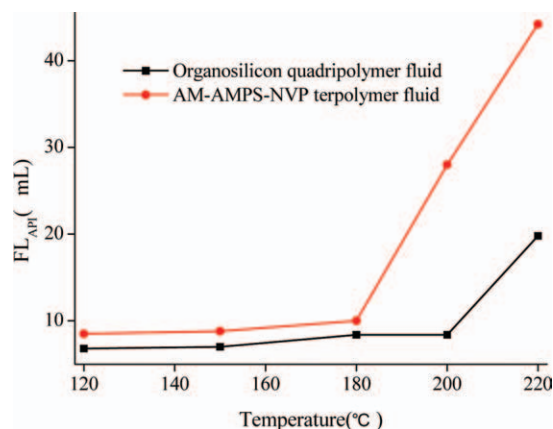

Figure 10. The effect of the FL_{HTHP} of the fresh-water, 4.0% salt-water and saturated brine based fluid formations after different aging temperatures for 16 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 11. The FL_{API} of the organosilicon quadripolymer compared with the AM-AMPS-NVP terpolymer after different aging temperatures for 16 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
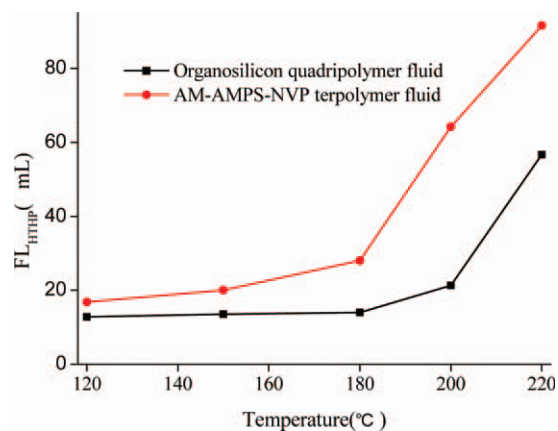
Figure 12. The FL_{HTHP} of the organosilicon quadripolymer compared with the AM-AMPS-NVP terpolymer after different aging temperatures for 16 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 13. Representation of (a) montmorillonite multiscale organization and (b) bentonite interaction.

the clay surface by hydrogen and coordination bonding to raise the zeta potential and hydrated shell thickness of the clay particles by electrostatic stabilization, strengthen clay gel structure, plug the filter cake holes, keep clay particles multiple dispersion, improve the quality of the filter cake, and reduce the coefficient of penetration and filtration. Therefore, the fluid filtrate volume gets reduced.[49] The polymeric additives used could be anionic, cationic, or nonionic and various modes of interaction have been proposed, as depicted in Figures 13[50] and 14.

However, the attraction between polymeric additives and clay particles belongs to weak adsorption. The temperature, especially high temperature, can destroy the adsorption equilibrium. In other words, polymeric additives can desorbed from the surface of clay at high temperature. Therefore, the adsorption capacity of polymeric fluid loss additives can be seen as essential element in improving efficiency at high temperature in drilling fluid.

A possible mechanism for the interaction of organosilicon copolymer is described in Figure 15. Siloxane group ($Si-OC_2H_5$) in organosilicon copolymer converts into silanol group ($Si-OH$) by hydrolysis reaction in water. $Si-OH$ of copolymer react with $Si-OH$, which exists in the surface of clay particle extensively; thus generating $Si-O-Si$ by the polycondensation. The chemical bond of $Si-O-Si$ is stable, even in high temperature. Hence, the organosilicon copolymers are adsorbed on the surface of clay particle steadily. Chemical adsorption affinity is

stronger than physical adsorption affinity in high temperature. The adsorbed polymer helps to build up hydrated membrane on the surface of clay particles, and so prevent the occurrence of gathering. Thus, organosilicon copolymer is better for the particle distribution of clay than average polymer. So, the organosilicon copolymer is more effective than average polymeric fluid loss additives in the drilling fluid at high temperature. To verificate this mechanism, we devised a serious of absorption experiments to uncover the mechanism. The results were shown in Figures 16 and 17.

The adsorption reaction reached balance after 40 min. It is also found that the type of copolymer has certain effects on the time of the adsorption equilibrium. The organosilicon group can promote copolymer adsorption on clay particles.

The polymer adsorption onto clay particles to two kinds of copolymer decreased with in crease of temperature. Adsorbed amount of terpolymer AM-AMPS-NVP is 0.126 g g^{-1} clay particle at 150°C. With temperature increasing to 200°C, adsorbed
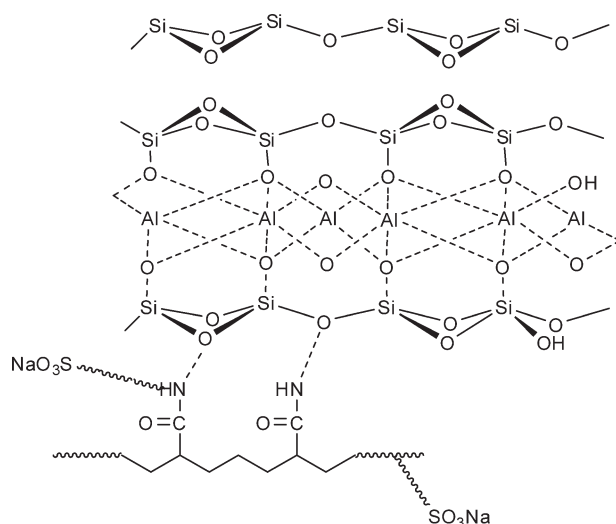
Table VIII. Shale Recovery Performance (%R)

Fluid formulation	$\%R_1$	$\%R_2$	$\%R'$
Fresh-water base fluid (I)	17.5	–	–
(I) + 0.2% AM-AMPS-NVP-APTS	52.4	43.8	83.6
(I) + 0.4% AM-AMPS-NVP-APTS	79.6	71.0	89.2
(I) + 0.6% AM-AMPS-NVP-APTS	83.7	78.2	93.4
(I) + 0.8% AM-AMPS-NVP-APTS	84.9	82.0	96.6
(I) + 1.0% AM-AMPS-NVP-APTS	85.2	83.8	98.4

Figure 14. Schematic diagram of the interaction of clay and polymeric fluid loss additives.
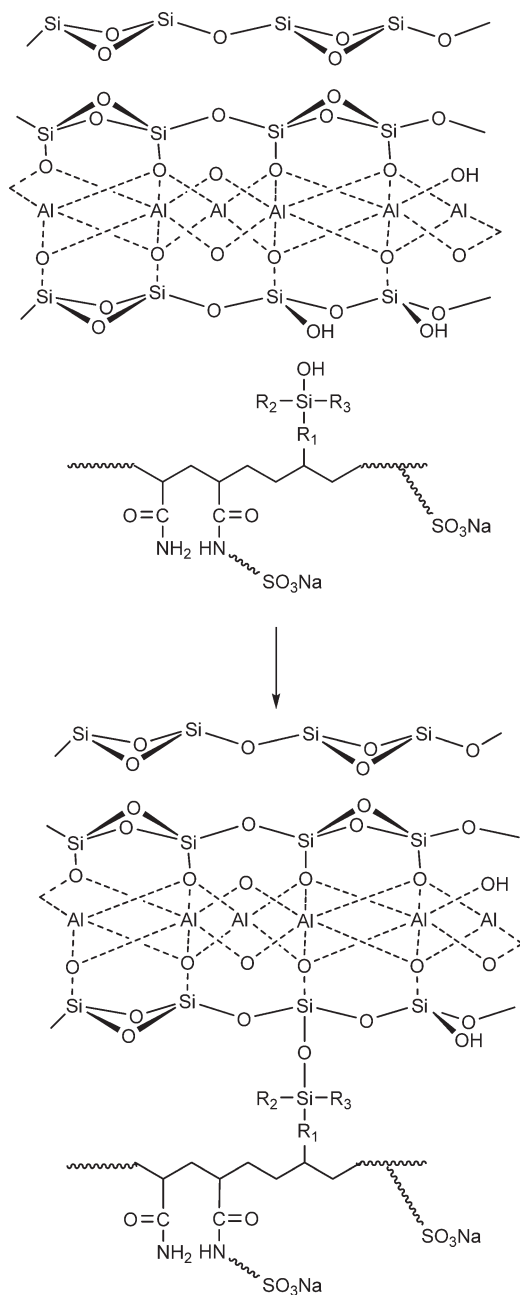
Figure 15. Schematic diagram of the interaction of clay and organosilicon copolymer.
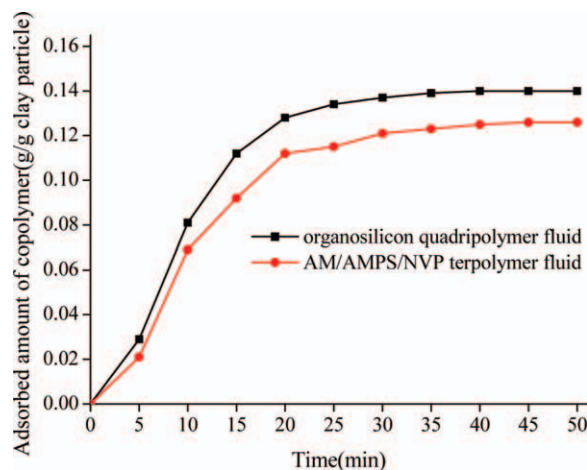

Figure 16. Dynamic adsorption curves of copolymer fluid. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

mer, the smaller of corresponding FL_{HTHP}. The experimental results indicate a synergistic effect between polymer adsorption and FL_{HTHP} markedly. It is only sufficient polymer adsorption of copolymer that has good effectiveness of fluid loss property. The results show that organosilicon quadripolymer has good adsorption effect in drilling fluid system at high temperature, compares with copolymer without organosilicon group, as a polymeric fluid loss additive, and has the broad application prospect.

CONCLUSIONS

The organosilicon quadripolymer was synthesized through free-radical polymerization and characterized using the FTIR spectroscopy method. The best optimum synthesis condition identified according to filtrate volume of fresh water-based drilling fluids. The following conclusions were drawn from this investigation the organosilicon quadripolymer.
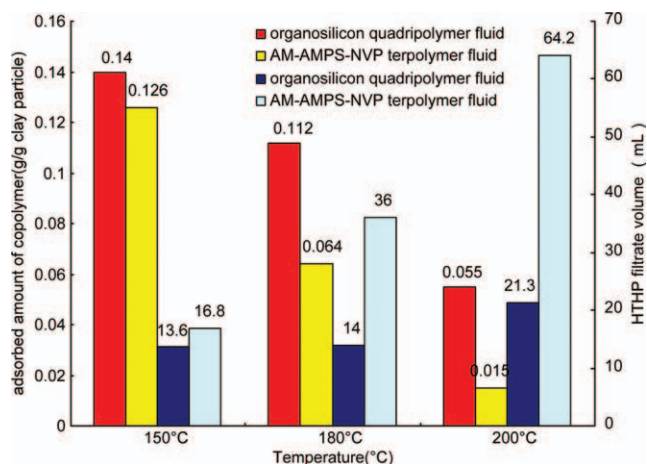

Figure 17. HTHP filtrate volume and adsorbed amount of copolymer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

amount of terpolymer AM-AMPS-NVP has dropped to $0.015 \cdot g \ g^{-1}$ clay particle quickly. Adsorbed amount of organosilicon quadripolymer reduced to 0.14 g g^{-1} clay particle to 0.055 g g^{-1} clay particle when the temperature ranges from 150 to 200°C. Obviously, the adsorbed amount of terpolymer is lower than the adsorbed amount of organosilicon quadripolymer at the same temperature, and descend degree of terpolymer has been speeded up in comparison with descend degree of organosilicon quadripolymer.

The FL_{HTHP} of two kinds of copolymer shows an opposite tendency. The higher of polymer adsorption of two kinds of copoly-

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The polymer with organosilicon group as fluid loss additive is applied to drilling fluid for the first time. The organosilicon quadripolymer have strong effects on the fluid properties. Before thermal aging test, with an addition of the organosilicon quadripolymer into the fresh-water, 4.0% salt-water and saturated brine-based fluid, AV, PV, and YP are greatly increased. After thermal aging test, the increasing tendencies of AV and PV still persisted, but YP is reduced with increment in the organosilicon quadripolymer concentration. The filtrate volume (FL_{API} and FL_{HTHP}) decreased with the increase in the organosilicon quadripolymer concentration. The FL_{API} of organosilicon quadripolymer fluid after aging test is larger than that before the aging test, but it is still smaller than that fluid without organosilicon quadripolymer. Organosilicon quadripolymer can make fluid loss property performance more superior in salt-water based fluid than that in fresh-water based fluid at the same concentration. After aging at 200°C for 16 h, rheological behavior and filtrate volume of various fluids can be controlled effectively. There is the synergetic effect between filtrate volume and adsorption characteristic via adsorption comparative experiment in fresh-water based fluid at high temperature. As a new type of polymeric fluid loss additive, the organosilicon quadripolymer is supposed to replace general polymeric fluid loss additives, which were used with dissociate chromium ions in drilling fluid.

ACKNOWLEDGMENTS

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