

Preparation and performance of AMPS/AA/DMAA/SA copolymer as a filtrate reducer for oil well cementing

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ABSTRACT: A new water-soluble polymer was prepared and evaluated as a filtrate reducer for oil well cementing. The filtrate reducer (WSP) was synthesized from 2-acrylamido-2-methylpropane sulfonic acid (AMPS), acrylic acid (AA), dimethyl acrylamide (DMAA), and sodium allylsulfonate (SA) by aqueous free radical polymerization. The synthesis conditions were optimized by orthogonal experiment. The molecule structure of the synthesized copolymer (WSP) was verified by Fourier transformer infrared spectrum (FTIR) and nuclear magnetic resonance hydrogen spectroscopy (¹H-NMR). The molecule weight of the synthesized copolymer was determined by gel permeation chromatography (GPC). The thermal stability of the synthesized copolymer was tested by thermogravimetry and differential thermogravimetry (TG and DTG). When the dosage of WSP is up to 3% in fresh water cement slurry, the FL_{API} can be controlled within 58 mL. In 37% salt water cement slurry, the FL_{API} can be controlled within 90 mL when the dosage of WSP is 5%. The thermal degradation of WSP is not obvious before 289 °C. Compared with a commercial filtrate reducer BS-100L and a reported copolymer HTF200C, the WSP has better performance. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43824.

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INTRODUCTION

In cementing an oil or gas well, the cement slurry is pumped down into the casing string to the bottom of the well and then flows up through the annular space between the casing and the borehole wall. The oil well cementing is considered a critical and challenging operation, not only during drilling, but also for all remaining period of production.^{1,2} Oil well cementing requires more careful plan than conventional cementing works.³ The placement process requires the use of suitable cement slurry to ensure secure and effective operation. It is well known that the filtration characteristics of cement slurry play a key role in ensuring the safety of oil well cementing operation and improving the cementing quality.^{4–6} When the cement slurry is pumped along porous formations in the bore hole, the loss of water from it can result in excessive density increase or form annulus bridging blockage, which effect cementing operation safety. In oil and gas producing zones, the filtrate invasion will decrease the relative permeability of the fluids in the reservoir, which can cause a significant decrease in the well's productivity.^{5–7} So, for the different cementing jobs, the filtration has different scopes. For example, the fluid loss of the casing cementing is from 100 to 200 mL/30 min, the fluid loss of squeeze cementing or liner cementing is 50–150 mL/30 min.

However, the fluid loss of the anti-gas channeling cementing job is 20–40 mL/30 min.⁸

To reduce fluid loss, the cement slurry must be able to produce thin membrane with low permeability in well walls called filter cake.⁹ The filtrate and the thickness of cake are two main parameters routinely measured to evaluate cement slurries in terms of filtrate loss control. In such case, the filtrate reducer is added to cement slurry to perform this function. In the past, bentonite, natural gum, starch derivatives, cellulose derivatives, deformable particles, and other organic materials have been used as filtrate reducer.^{5,8,10–12} Generally speaking, these additives can mainly be classified into two categories. The one is insoluble fine particles which may fill up the pores of the filter cake, such as bentonite, latex, etc. The other is water-soluble polymers which may form films on the well wall, such as gum, starch derivatives, and so on. Sometimes these additives have some additional influences on cement slurry such as accelerating or retarding cement hydration, increasing mixing viscosities and polluting the environment during the actual field using process because cement slurries are multiphase complicated systems, composed of a mixture of water, cement, insoluble solid particles, organic materials, dissolved salts, and even gases, in different proportions. The fluid loss additive used in oil well

cementing is different from these used in drilling fluid. So, some additives are limited in the use of field due to all kinds of reasons. This fact combined with the variety of well cementing conditions, such as temperature, pressure, and formation characteristics, requires the development of specific additives for filtrate loss control to meet the needs of well cementing. Nowadays the most of fluid loss additives (filtrate reducer) are water-soluble synthetic polymers products.⁴ Some novel water-soluble polymers have reported. For example, Plank *et al.* prepared a copolymer of N, N-dimethylacrylamide and Calcium 2-acrylamido-2-methylpropanesulfonate which effectively reduces filter cake permeability of oil well cement slurry.¹³ Tiemeyer *et al.* reported a synthetic polymer based on allyloxy-2-hydroxy propane sulfonic acid which exhibits excellent fluid loss performance.¹⁴ Salami *et al.* described a graft copolymer which comprised side chains connected to the backbone by aqueous free radical copolymerization. The backbone was humic acid, and the lateral terpolymer chains contained the monomers of sodium 2-acrylamido-2-methylpropane sulfonate, N,N-dimethyl acrylamide, and acrylic acid.¹⁵ A new spherical microparticles of poly(methyl methacrylate-co-vinyl acetate) was synthesized by Nunes *et al.*¹⁶ It was observed that the performance of the material is related to the rubbery characteristic which forms the desirable filter cake to block the entrance of fluid into the formation.

With the increase of the energy demand and the development of drilling technology in the world, the drilling of deep well and ultra-deep well will become an important aspect of the petroleum industry. Hence, there is a demand for a filtrate reducer which performs well under high temperature conditions, the bottom-hole static temperature of formation may range up to 260 °C.^{14,17,18} In recent studies about the filtrate reducer in oil well cementing, it is clear that recently more and more researchers pay attention to the AMPS-based polymers which show outstanding thermal-resistant and salt-tolerant ability.^{19–21} Plank *et al.* studied the working mechanisms of different kinds of fluid loss control additive.^{22–28}

In order to further improve the resistance to high temperature and the salt, we select the sodium allylsulfonate (SA), which contain sulfonate functionality, as one of the structure monomers. Based on this scenario, the objective of this investigation is to synthesis a novel filtrate reducer using 2-acrylamido-2-methylpropane sulfonic acid (AMPS), sodium allylsulfonate (SA), acrylic acid (AA), and dimethyl acrylamide (DMAA) as monomers, and to characterize and evaluate in terms of their performance to control filtrate loss of cement slurry. The influence of copolymerization reaction parameters such as the reaction time, temperature, the mole ratio of AMPS/SA/AA/DMAA, and the initiator concentration on the additive performance was investigated.

EXPERIMENTAL

Materials

Sodium allylsulfonate (SA) was supplied by Aladdin Industrial Reagent Corporation (Shanghai, China). 2-acrylamido-2-methylpropane sulfonic acid (AMPS), acrylic acid (AA), dimethyl acrylamide (DMAA), ammonium peroxydisulfate [(NH₄)₂S₂O₈]

(AR grade), sodium hydrogen sulfite (NaHSO₃) (AR grade), sodium hydroxide (NaOH) (AR grade), ethyl alcohol absolute (C₂H₆O) (AR grade) and other chemical reagents were purchased from Chengdu Kelong Inc. (Chengdu, China), and were used without further purification. Water used in this study was de-ionized water. A commercial filtrate reducer, that is, BS-100L, obtained from Southwest Petroleum Institute, China, was also used for comparison.

Synthesis of Filtrate Reducer

Copolymers of AMPS, AA, DMAA, and SA were prepared via free radical aqueous solution polymerization technique in the laboratory. The synthesis formula of the WSP is presented in Figure 1.

The orthogonal test was used to optimize the synthesis conditions. The optimized parameters can be obtained according to the minimum value of FL_(API) of the fresh water cement slurry with the same copolymer amount (4% BWOC-By Weight of Cement). The five main factors, including mole ratio of AMPS:DMAA:AA:SA, monomer concentration, reaction temperature, initiator concentration, and the pH value are selected to research the synthesis conditions as listed in Table I.

The filtrate reducer was prepared according to the following steps: first, the initiator (ammonium peroxydisulfate and sodium hydrogen sulfite with mole ratio 1:1 in aqueous solution) was first dissolved in some volume of water, which was labeled as solution A, and then, a certain amount of de-ionized water was fed into a 1-L three-neck round-bottomed flask with a stirrer, a thermometer and an intelligent control temperature device. Second, the monomers (AMPS/AS/DMAA/AA) were added into the flask by stirring it in nitrogen atmosphere. Sodium hydroxide or diluted hydrochloric acid was added to regulate pH value of the reaction mixture with constant stirring thoroughly. To avoid the premature polymerization induced by excessive heat released by the reaction of solution system, this monomer solution has to be kept at a temperature below 40 °C. Third, after bubbling with nitrogen for 30 min, solution A was slowly added to the reaction mixture over 30 min. During the synthesis, the mixtures were constant stirred at about 200–300 rpm and the temperature was kept by a water bath. The viscous filtrate reducer could be synthesized after 4 hours, which was used to evaluate the property of fluid loss control ability. The specimens used for the characterization and measurements were subjected to precipitation with a large amount of ethanol. The precipitation production was converted into the powdery size through drying in vacuum and crushing break in agate mortar.

Characterization of the Synthesized Copolymer

In identifying the chemical structure, the dried specimens with a certain mass were mixing with KBr and pressed into a transparent disk using a PerkinElmer table press die set. The FT-IR spectra of the specimen were recorded on FT-IR spectrometer (Equinox 55, Bruker Analytische Messtechnik GmbH). The spectra were collected from 4000 to 400 cm⁻¹, with a 1 cm⁻¹ resolution over 32 scans, measurements were performed in the transmission model.

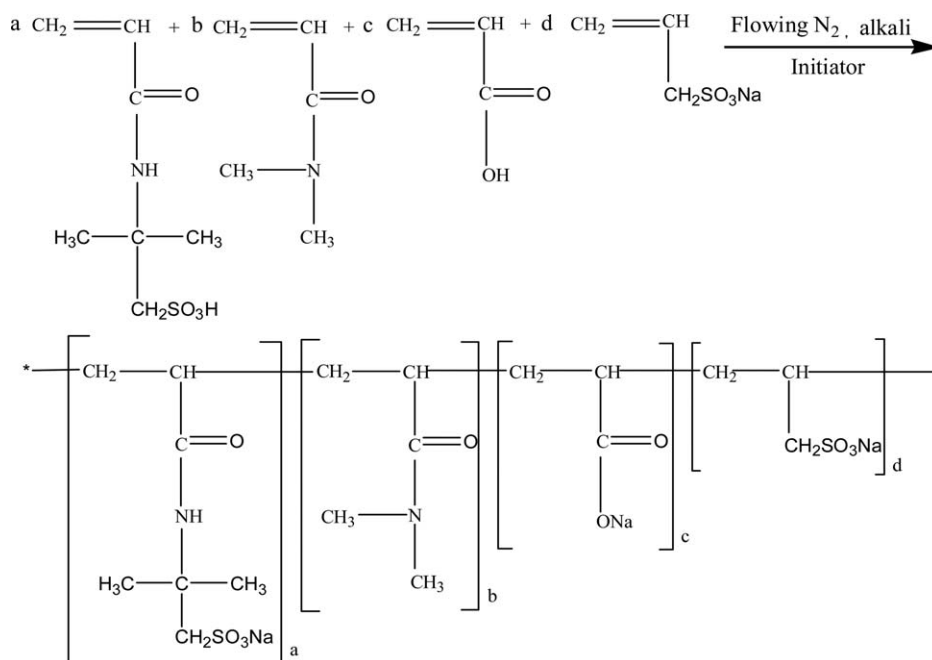


Figure 1. Schematic diagram of the free-radical copolymerization.

Nuclear magnetic resonance was used to analyze the chemical structure. ¹H NMR spectrum was obtained at room temperature (25 °C) with an ARX-400 spectrometer (Bruker Co., Germany) operating at frequencies of 400 MHz, and the chemical shift values were expressed in δ values (ppm) relative to tetramethylsilane (TMS) as internal standard. Measurements were carried out in D₂O at a constant concentration of 1 mg/0.60 mL. All spectra were recorded in 5-mm NMR tubes using an air flow rate of 535 L/h. For each experiment, 32 spectra with 16 K data points were collected using 64 scans. The duration of the magnetic field pulse gradients (δ) was 4.0 ms. The diffusion time (Δ) was 150 ms, and the eddy current delay was set to 4.8 ms. The pulse gradient (g) was incrementally increased from 1 to 98% of the maximum gradient strength via a linear ramp.

The number average molecular weight (M_n), weight average molecular weight (M_w), and polydispersity index (PDI) of sample (specimen) were determined by a gel permeation chromatography (GPC, also known as size exclusion chromatography) Water 1525/2414 instrument (Water, The United States) with a differential refraction detector was used for the measurement of

the molecular weight of sample. The mobile phase consisted of an aqueous solution of 0.5 mol/L sodium nitrate, and its flow rate was 0.6 mL/min, where large molecules pass the column more quickly than small molecules. The measurement was performed at 35 °C, using polyethylene glycol as calibration standards. The characteristic properties of the polymer obtained from GPC analysis are shown in the “Results and Discussion” section.

Perkin-Elmer thermogravimetric analyzer of type PETA7 was used to check the performance under high temperature. The temperature range was from 40 to 650 °C at heating rate of 10 °C/min under the flow of argon gas.

Cement Slurry Preparation

The cement used in this study was class G oil-well cement (GOC) which was provided by the Sichuan Jiajiang Cement Company, China. Mineral compositions and physical properties of class G oil well cement are presented in Table II. The other additives included dispersant (Chengdu, China), silica fume (Henan, China), sodium chloride (Shanghai, China), retarder

Table I. Factors and Levels of Orthogonal Experiment

Level	Factor				
	Monomer molar ratio AMPS:DMAA:AA:SA [A]	Mass fraction of initiator (%) [B] ^a	Temperature (°C) [C]	Reaction monomer concentration (%) [D] ^b	pH [E]
1	5:1.5:2.5:1	0.4	40	10	5
2	5:2:2:1	0.6	50	15	7
3	5:2.5:1.5:1	0.8	60	20	9
4	5:3:1:1	1.0	70	25	11

^aBased on the total mass of the monomer.

^bBased on the mass fraction of the solution.

Table II. Mineral Compositions and Physical Properties of Class G Oil Well Cement

C ₃ S (wt %)	C ₂ S (wt %)	C ₃ A (wt %)	C ₄ AF (wt %)	Specific density (kg/L)	Specific surface area (m ² /kg)
51.9	25.1	1.7	13.5	3.16	336

produced by OMIK (Chengdu, China), de-foamer produced in China by Chuanfeng (Chengdu, China) and filtrate reducer (WSP). The mix water was tap water. Cement slurry compositions having densities of 1.89 g/cm³ were prepared comprising the class G cement, water and the cement additives. According to API standard,²⁹ at first, the cement was dry blended with silica flour and drag reducer. Before cement/silica addition, the synthesized copolymer (WSP) was dissolved in the mixing running water. Then, within 15 s, the binder mixture was added to the mixing water placed in the cup of a Waring blender operated at 6000 rpm, and mixed for 30 s at 14,000 rpm.

Fluid Loss Test

The main parameter of interest in this respect is the volume of filtrate collected in static filtration test. The test parameter can be used to estimate the probable behavior of the cement slurry during cementing process (the placement process and no circulation in the well). The test was conducted in a GGS-71 High-Temperature and High-Pressure Water Loss Meter (Tongchun

analytical instrument factory of Qingdao, China). The system constituted by a filter cell involved by a heating jacket. The filtrate was collected in a measuring test tube. Before starting the test, the jacket was preheated over the test temperature and the cement slurry was homogenized in an atmospheric consistometer, OWC-9350 (Constant Pressure Thickening Instrument, Shenyang, China) about 20 min. And then, the cement slurry was poured into the filter cell, which was inserted in the jacket. The system was sealed and pressurized with nitrogen. The filtrate is collected over a period 30 min. As described by API RP 10B, the collected filtrate volume was doubled and regarded as API fluid loss (FL_(API)) of the corresponding cement slurry.

RESULTS AND DISCUSSION

Orthogonal Experiment Results

The orthogonal L₁₆ (4⁵) experiments are designed to optimize the synthesis conditions. As is shown in Table I, five key factors are studied including mole ratio (A), initiator concentration (B) reaction temperature (C), monomer concentration (D), and pH

Table III. L₁₆ (4⁵) Orthogonal Experimental Results

Sample no.	A	B	C	D	E	FL _(API) (mL) ^a
1	1	1	1	1	1	75.3
2	1	2	2	2	2	68.8
3	1	3	3	3	3	46.1
4	1	4	4	4	4	62.9
5	2	1	2	3	4	58.1
6	2	2	1	4	3	102.2
7	2	3	4	1	2	38.2
8	2	4	3	2	1	43.5
9	3	1	3	4	2	69.4
10	3	2	4	3	1	78.2
11	3	3	1	2	4	64.0
12	3	4	2	1	3	51.6
13	4	1	4	2	3	67.2
14	4	2	3	1	4	61.7
15	4	3	2	4	1	56.8
16	4	4	1	3	2	47.5
K ₁	63.275	67.500	72.250	56.700	63.450	
K ₂	60.500	77.725	58.825	60.875	55.975	
K ₃	65.800	51.275	55.175	57.475	66.775	
K ₄	58.300	51.375	61.625	72.825	61.675	
R	7.500	26.450	17.075	16.125	10.800	
Optimal level	A4	B3	C3	D1	E2	

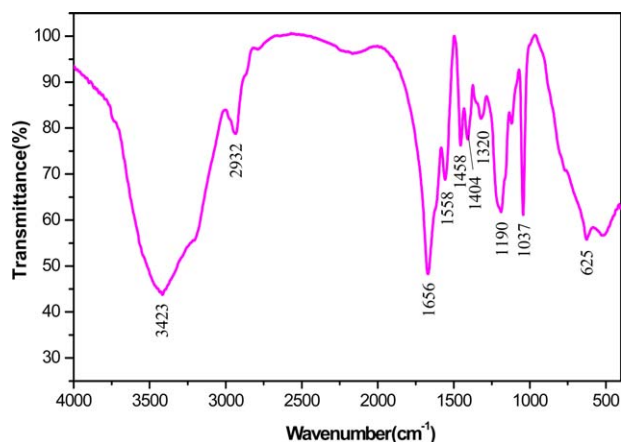
^a FL_(API) test condition: 90°C, 6.90 MPa.

^b K_i^A = (∑ the FL_(API) value of synthesized polymer at A_i)/4.

^c R_i^A = max(K_i^A) - min(K_i^A).

Table IV. The Optimal Experiment Condition and the Performance of WSP

Monomer molar ratio AMPS:DMAA:AA:SA	Mass fraction of initiator (%)	Temperature (°C)	Monomer concentration (%)	pH	FL _(API) (mL)
5:3:1:1	0.4	60	20	7	32.6

**Figure 2.** FTIR spectrum of the synthesized copolymer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

value (E) were selected. The optimized conditions can be obtained according to the minimum value of the filtration loss of the fresh water cement slurry with the prepared polymer (4% BWOC-By Weight of Cement) at 90°C. Table III shows the results of the orthogonal tests. The results show that mass fraction of initiator and temperature play an important role in the reduction of the filtration loss than other factors. The dosage of the initiator has the greatest influence on the free radical polymerization because of the induced decomposition and the cage effect.³⁰ According to Pan,³¹ less initiator leads to low efficiency

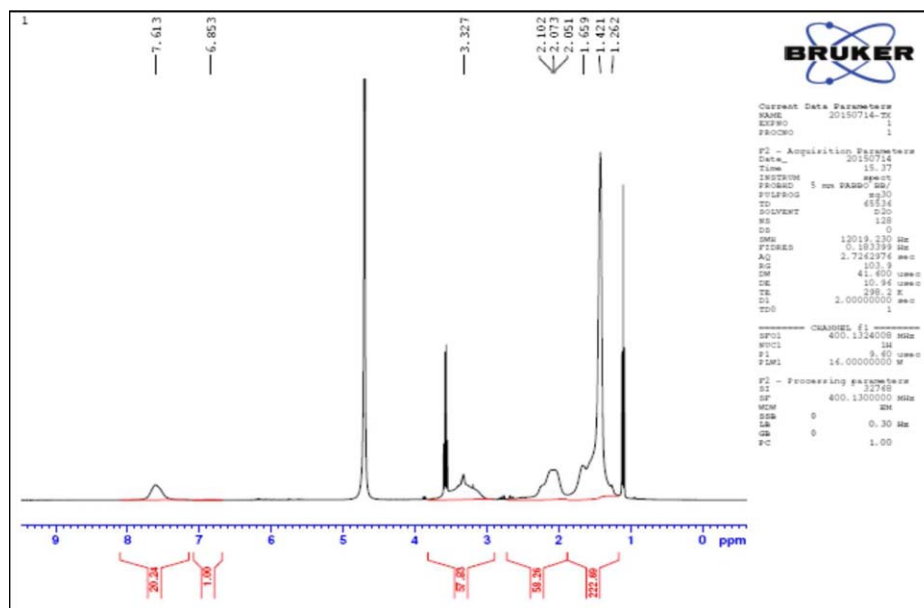
and slow polymerization rate. The order of the influence on the filtration loss is B > C > D > E > A. Table IV lists the optimal experiment condition from the orthogonal test and the performance of the synthesized copolymer (WSP), which was obtained under the optimal condition.

FTIR Analysis of the Synthesized Copolymer

FTIR spectrum of the synthesized copolymer is shown in Figure 2. The broad peak around 3423 cm⁻¹ is assigned to the N—H stretching band. The absorption bands at 2932 and 1458 cm⁻¹ can be attributed to the C—H stretching vibration of methyl. The peaks at 1656 and 1558 cm⁻¹ are assigned to C=O stretching band in DMAA and AMPS. The absorption band around 1404 cm⁻¹ can be attributed to deformation vibrations of methyl groups and to valence vibrations of free carboxylate groups present in AA. The peak at 1320 cm⁻¹ is assigned to the C—N stretching band. The absorption peaks of sulfonic groups present in AMPS and SA were present at 1190, 1037, and 625 cm⁻¹. No double bond is formed in the molecules because there is no absorption peak in the range of 1620–1635 cm⁻¹. The presence of these typical absorption bands in the FTIR spectra indicates the occurrence of copolymerization of the fed monomers.

¹H-NMR Analysis of the Synthesized Copolymer

The ¹H-NMR spectrum of the synthesized copolymer is shown in Figure 3. The peaks at 7.613 and 6.853 ppm correspond to the proton vibration peaks of the N—H second amide group of AMPS. The methyl protons of DMAA as well as the methylene

**Figure 3.** ¹H NMR spectrum of the synthesized copolymer, measured in D₂O. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

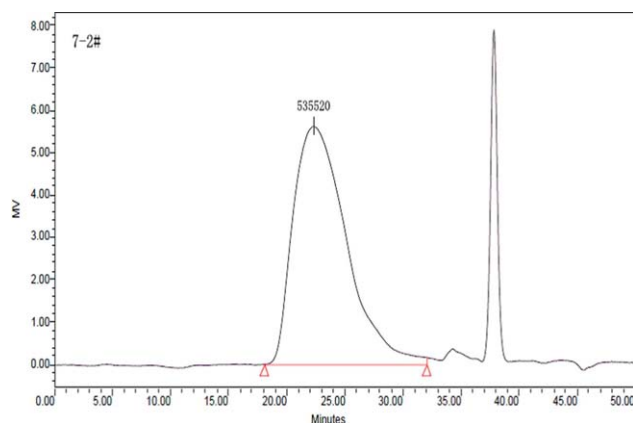


Figure 4. GPC curve of the synthesized copolymer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

protons of AMPS and AS are indicated by the broad peak at 3.327 ppm. Small broad overlapping peaks between 2.102 and 2.051 ppm correspond to the proton vibration peaks of the C—H of the main chain. The broad peak between 1.262 and 1.659 ppm can be assigned to methylene protons present in the backbone of the polymer and to methyl protons of AMPS monomer.

GPC Analysis of the Synthesized Copolymer

GPC result is shown in Figure 4 and Table V. As seen from Table V, the number average molecular weight (M_n) is 86,692, the weight average molecular weight (M_w) is 468,689, and polydispersity index (PDI) of the prepared sample is 5.406. The relatively high molecular weight and the broad polydispersity index are typical for a radical polymerization. Combined with FTIR and $^1\text{H-NMR}$ results, the WSP is successfully synthesized.

TG–DTG Analysis of the Synthesized Copolymer

The specimen used to test the thermostability is synthesized under the optimized conditions as described in the orthogonal test. The thermogravimetry–differential thermogravimetry (TG–DTG) thermal analysis technology is applied to study the thermal behavior of the synthesized copolymer, and the respective curves are shown in Figure 5. The process of the thermal decomposition of the synthesized copolymer includes three stages from the thermoanalysis curves shown in Figure 5. From the TG curve, it can be seen that the first stage is about 83.5 °C, and 2.4% mass losses, it is mostly due to water gradually volatilization. The drastic weight loss occurs near 289 °C in the TG curve, which ends at about 384.3 °C and a wave hollow appears in the DSC curve, which is related to the decomposition of the synthesized copolymer. Moreover, the mass loss of the synthesized copolymer quickly reaches 29.5%. The third stage is around 460.8 °C. In the TG curve of the synthesized copolymer, the mass loss declines constantly, 17.6% mass is left when the

temperature reaches 483.5 °C. A large number of mass losses are caused by the thermal degradation of C—C in the main chain at higher temperature. Bai *et al.*³⁰ reported the synthesis of AM/AMPS/DMDAAC/SSS, the results showed the thermal degradation of the quadripolymer was not obvious before 273.2 °C. Guo *et al.*³² investigated the thermal degradation of the fluid loss additive HTF200C, and the result showed there was no apparent thermal degradation when the temperature was lower than 280 °C. Combined the above analysis, the synthesized copolymer (WSP) shows no significant mass loss below 289 °C, the results show the WSP itself has a good characteristics of temperature resistance.

Filtrate Performance of the Synthesized Copolymer

The FL_{API} of the fresh water, 18.5 and 37% By Weigh of Water (BWOW) salt water cement slurries ($\rho = 1.89 \text{ g/cm}^3$) with different WSP dosages at 90 °C/6.9 MPa are evaluated. The influence of the WSP dosage on the filtrate volume of cement slurry is shown in Figure 6. As is shown in Figure 6, the results demonstrate that the filtration loss of the fresh water cement slurry rapidly decreases with the increasing of the WSP dosage. When the dosage of the WSP is 3% of the cement in fresh water cement slurry, the FL_{API} is 58 mL. And if the dosage is more than 3%, only small improvements are made in fluid loss efficiency. At last, the fluid loss can be controlled within 40 mL.

The WSP addition shows an outstanding fluid loss control property, which can be explained as follows: cement slurries are colloidal suspensions. The electro-kinetic charge of a cement particle is positive even though the actual cement surface is most likely composed of positive “patches” separated by neutral and negative “patches.”^{5,33} The synthesized copolymer (WSP) contains $-\text{SO}_3^-$ and $-\text{COO}^-$ functional groups, which carries an anionic charge. So, the charged surfaces of a cement particle attract oppositely charge that are firmly attached to the surface of the particle,³⁴ which form an absorption layer of high elasticity, viscoelasticity, and glutinous macromolecular. It could change the particle size distribution of cement slurry. Under differential pressure (ΔP), the viscoelastic material is pressed into the gap of cement particles and glued between cement particles. The filtering passage of filter cake is fully filled and stopped up.^{13,35,36} A schematic diagram of adsorption and filtrate cake mechanisms of WSP on the surfaces of cement particles is shown in Figure 7. At the same time, the groups [$-\text{SO}_3^-$, $-\text{COO}^-$, $-\text{OH}$, and $-\text{CON}(\text{CH}_3)_2$] of the WSP can adsorb on the surface of cement particles through hydrogen band, could produce a hydrated layer, which make the cement particles easily squeeze into the pores among the cement particles. Under differential pressure (ΔP), the channels of fluid loss were blocked. And then, the filter cake becomes dense, the permeability reduces, which can contribute to reduce the filtration loss.

Table V. Molecular Weight and its Distribution of the Synthesized Copolymer

Sample no.	Elution volume (mL)	Retention time (min)	Adjusted RT (min)	M_n	M_w	M_p	PDI M_w/M_n
7#	13.384	22.316	22.316	86,692	468,689	535,520	5.406

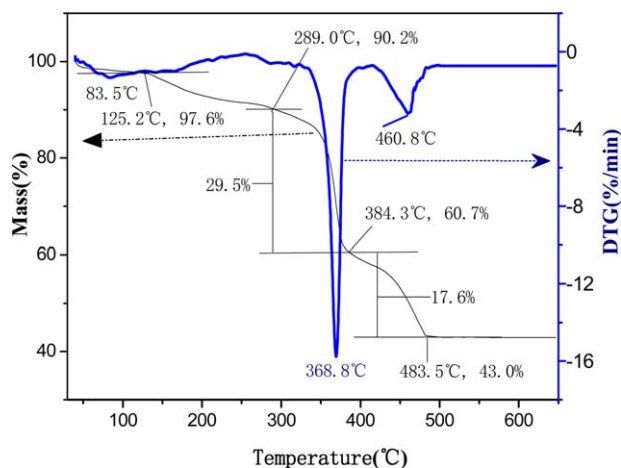


Figure 5. TG and DTG of the synthesized copolymer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Also presented in Figure 6 is the influence of the WSP dosage on the filtrate volume of 18.5 and 37% BWOW salt water cement slurries. The filtration loss also presents a gradually decreased with the increase of WSP dosages. Apparently, the FL_{API} is larger than that in fresh water cement slurry at the same concentrations of the WSP. The reason is that cement slurries are strong alkaline suspensions, including different kinds of salt ions. The salt ions have the screening effect in the cement slurry suspension, which makes the molecular chain of the WSP twisting,³⁰ especially in 37% BWOW salt water cement slurry. But when the WSP concentration increases to 5%, the FL_{API} is less than 90 mL for the 37% BWOW salt water cement slurry. The salt solution is a kind of strong electrolyte solution and the fluid loss of brine cement slurry is difficult to control. The abilities of fluid loss control of many kinds of filtrate reducer will be weakened and even disappear in brine cement slurry.^{32,37} The test results indicate that the WSP has excellent salt-tolerance property because a lot of monomers with stable

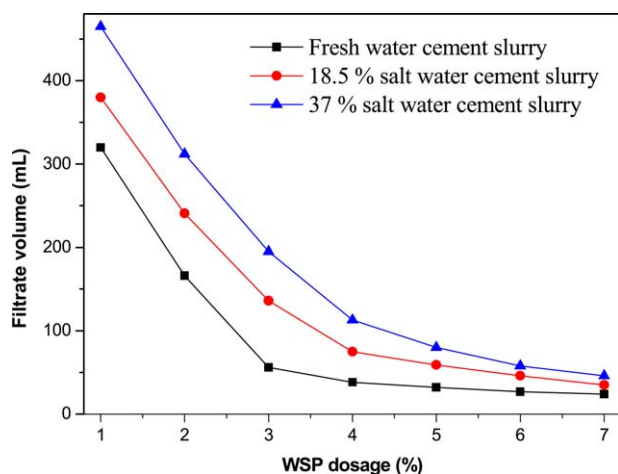


Figure 6. Influence of the WSP dosage on the filtrate volume of the three investigated cement slurries. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

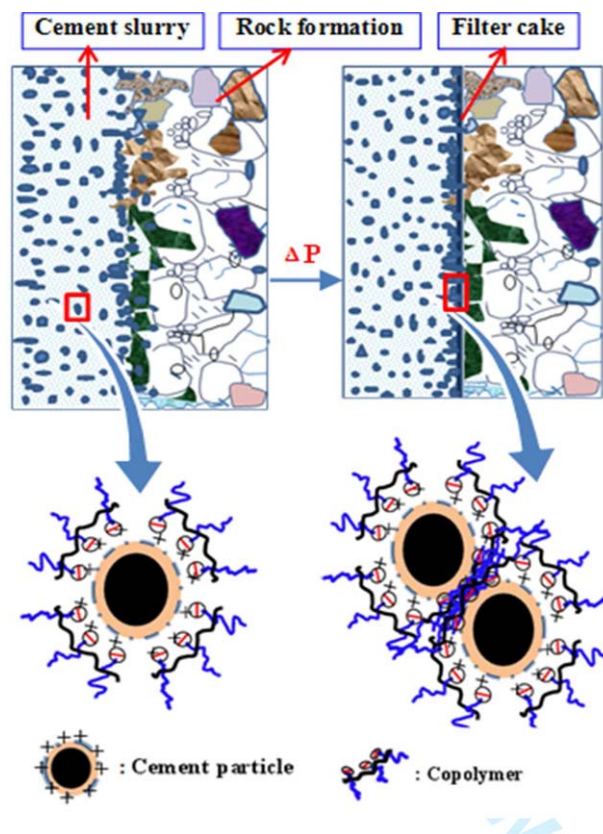


Figure 7. Schematic diagram of adsorption and filtrate cake mechanisms. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

sulfonic acid group ($-\text{SO}_3^-$) are introduced in the WSP, which is not sensitive to the salt ions.

Influence of Temperature on the Filtrate Volume

To evaluate the property of temperature-resistance of the synthesized copolymer (WSP), the fluid loss at different temperatures was tested according to the API specifications. The influence of temperature on filtrate volume of the three

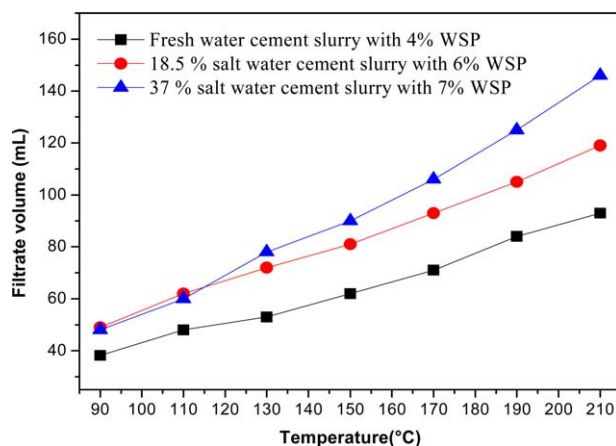


Figure 8. Influence of temperature on filtrate volume of the three investigated cement slurries. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table VI. The Fluid Loss of WSP, HTF200C, and BS-100L

	Cement slurry		
	Fresh water cement slurry + 4% WSP	Fresh water cement slurry + 4% HTF200C	Fresh water cement slurry + 4% BS-100L
FL _(API) (mL)	38.2	42 ³²	48.6

investigated cement slurries is shown in Figure 8. As is shown in Figure 8, The FL_{API} of cement slurries appear an increasing trend with temperature increasing. Generally, under high temperature, the degradation of function groups and the rupture of molecule chain are happen, the property of fluid loss additive will get greatly weaken with the increase of temperature, owing to the adsorption and hydration abilities of the WSP on the cement particles decreasing with the increasing temperature. However, the fluid loss of fresh water cement slurry with 4% WSP can be still controlled within 100 mL at the temperature of 210 °C. The fluid loss of the 37% BWOW salt water cement slurry with 7% WSP can be still controlled within 150 mL at the temperature of 210 °C. As is shown in Figure 2 (FTIR), the main structure of the WSP is as follows: the main bond is the anti-temperature C—C bond, and the main functional groups contain —SO₃⁻ and —COO⁻, which have strong ionicity coordination and strong chelation. The molecular structure of the synthesized copolymer (WSP) is beneficial to the property of temperature-resistance.

Comparative Test between WSP and Other Filtrate Reducer for Oil Well Cementing

BS-100L is the commercialized products generally used in oil well cementing. But the detailed composition of BS-100L is unknown because of the commercial secrecy. Cement filtrate reducer HTF200C was reported by Guo³² and synthesized using the monomers of AMPS, DMAA, and a new compound with double carboxyl. Both BS-100L and HTF200C are AMPS-based copolymers for oil field cementing. The two filtrate reducer additives (WSP and BS-100L) are added into the fresh water cement slurry with the same copolymer amount (4% BWOC), and the density of all cement slurries is 1.89 g/cm³. The fluid loss of cement slurries are measured at 90 °C and 6.9 MPa. The results are listed in Table VI. As can be seen in Table VI, the fluid loss of WSP addition is 38.2 mL, which is smaller than other two products, while those of HTF200C and BS-100L are about 42 and 48.6 mL, respectively. Compared with a commercial filtrate reducer BS-100L and a reported copolymer HTF200C, the WSP has better performance.

CONCLUSIONS

A new water-soluble polymer is synthesized as a filtrate reducer for oil well cementing through free radical aqueous solution polymerization. And the optimal polymerization conditions are obtained. The molecule structure of the water-soluble polymer is characterized by FTIR and ¹H-NMR. The molecule weight of the synthesized copolymer (WSP) is determined by gel permeation chromatography (GPC). The results show that the WSP contains all the designed functional groups, and the filtrate reducer is successfully synthesized. TG analysis proved that the

thermal degradation of the WSP is not obvious before 289 °C. The performance of the WSP in the fresh water, 18.5% and 37% BWOW salt water cement slurries is evaluated. Besides, a commercial filtrate reducer BS-100L and a reported copolymer HTF200C was also testes. All results indicated that the prepared copolymer as a filtrate reducer possessed excellent properties such as thermal stability and fluid loss control ability.

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