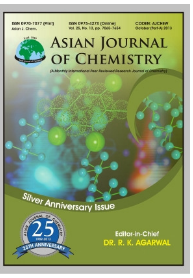
Asian Journal of Chemistry; Vol. 25, No. 14 (2013), 7971-7975

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2013.14882



Synthesis and Performances of Si-Carboxymethyl Starch Sodium as a Filtrate Reducer

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(*Received*: 27 November 2012; *Accepted*: 29 July 2013) AJC-13852

A new modified starch (Si-carboxymethyl starch sodium, Si-CMSS) as filtrate reducer for drilling fluid was synthesized by the reaction of silicate and carboxymethyl starch sodium(CMSS). The phase and structure of synthetic product were characterized by X-ray diffraction and Fourier transform infrared spectrum, silicon-hydrogen groups were found in the molecular structure of the product, indicating that silicate was involved in the reaction. As a filtrate reducer, Si-carboxymethyl starch sodium had good filtration control and environmental performance, more importantly, its temperature resistance performance was obviously increased to 150 °C. The filtering mechanism of Si-carboxymethyl starch sodium was analyzed and discussed for the first time.

Key Words: Si-carboxymethyl starch sodium, Silicate, Filtrate reducer, Temperature resistance, Mechanism.

INTRODUCTION

With the enhancement of environmental awareness and economic competition, standards of drilling fluid are more stringent[1]. Numerous studies of high performance, low cost and non-toxic drilling fluid have been carried out in laboratories, among which, the technology for preparing environmentally friendly drilling fluid additives is a sign of achievement[2]. And for filtrate reducer, one of the additives used for drilling fluid, the future research direction is use of the sources of rich, low cost and harmless natural materials, together with in-depth modification and simplifying the synthetic process[3].

Modified starch is considered as the most promising environment-friendly filtrate reducer, because starch is a natural green material which is rich, renewable and low cost and the modification process is very simple[4]. However, it is relatively poor resistance to temperature, easy to cause degradation or fermentation of lower molecular when the temperature increases[5]. So, its application was severely limited. To solve this problem, modified starch with the performance of anti-temperature has been studied.

At present, the studies of starch modification have been focused on grafting of acrylamide, acrylic acid, methacrylic acid and cationic monomer with amino substituent, which are mainly used for flocculants, retention aids and thickeners, but rarely applied in the oil industry[6]. In recent years, a number of new modified starch used for drilling fluid have been continuously developed. Fanta and Shogren[7], obtained high grafting efficiency product by adding the irradiated starch to acrylamide aqueous solution or acrylamide organic system. Khalil *et al.*[8] used $KMnO_4$-acid system to initiate the graft reaction of acrylic acid and the results showed that the grafting rate was relate to the type of the acid. Trimnell and Stout[9] prepared acrylic acid starch by using of starch treated with ultraviolet radiation. Liu *et al.*[10] prepared corn starch-acrylic acid copolymer by using photoinitiator. Li *et al.*[11] synthesized etherified starch as filtrate reducer, which can be used under high salinities and elevated temperature. Wang[12] synthesized acrylamide/acrylic acid/starch graft copolymer as filtrate reducer and the product has good filtration control property and anti-temperature performance. However, using environmentally friendly inorganic salt to improve the temperature resistance performance of modified starch has not been reported at present.

In this paper, carboxymethyl starch sodium (CMSS) was modified by silicate in alkaline reaction condition and a new modified starch (Si-CMSS) was prepared. As a filtrate reducer, Si-CMSS has good anti-temperature, filtration control and environmental performance.

EXPERIMENTAL

Corn starch and water-soluble sodium silicate were used as received without further purification. Anhydrous ethanol, sodium hydroxide and chloroacetic acid were analytical reagent(Kelong Chemical Reagents Co., China).

Synthesis of carboxymethyl starch sodium (CMSS): Added 8.1 g corn starch to the flask with thermometer and stirrer, took ethanol as dispersant and stirring evenly, dropwise added 8 mL sodium hydroxide solution (0.3 g/mL) and reacted at 45 ºC for 1.5 h; then added 5.67 g chloroacetic acid and continuously add sodium hydroxide solution dropwise for 12 mL and then reacted at 50 ºC for 2.5 h. After the synthesis reaction, the product was filtrated, collected and washed with distilled water, then dried in air and grinded, finally got yellow CMSS powder.

Synthesis of Si-carboxymethyl starch sodium (Si-CMSS): Added 3 % (by weight of corn starch) water-soluble sodium silicate to first step of CMSS synthesis, the remaining processes were the same with else steps of CMSS synthesis.

Characterization of Si-CMSS: Si-CMSS was purified by three times extraction with acetone and then NICOLET MX-1E (Nicolet, USA, in the range from 4000-400 cm^{-1}) Fourier infrared spectrometer and D/max-rB X-ray Diffraction (Japan) were used to characterize the structure of Si-CMSS. Mettler Toledo thermo gravimetric and differential thermal combined analyzer of type TGA/SDTA851e was used to checkout the performance of Si-CMSS under high temperature.

RESULTS AND DISCUSSION

Characterization of Si-CMSS: The XRD patterns of Si-CMSS, CMSS-Na_2SiO_3 mixture, CMSS and Na_2SiO_3 were shown in Fig. 1. Fig. 1a is the XRD diffraction pattern of Si-CMSS, which is dispersion diffraction peaks and there are two sharp peaks at 32 and 46º diffraction direction, these peaks belong to the crystalline compounds of organic silicon confirmed by JCPDS card, indicating that organic silicon compounds had been formed by introducing water-soluble sodium silicate and chemically reacting with CMSS. Fig. 1c is the XRD diffraction pattern of CMSS. Compared with Fig. 1a, it is found that there is no organic silicon crystal compounds diffraction peak in Fig. 1c. Fig. 1b is the XRD diffraction pattern of the mixed system of CMSS and Na_2SiO_3, this pattern is the simple overlying of Fig. 1c and 1d, which shows that Si-CMSS could not be synthesized if simply mixed CMSS and Na_2SiO_3.

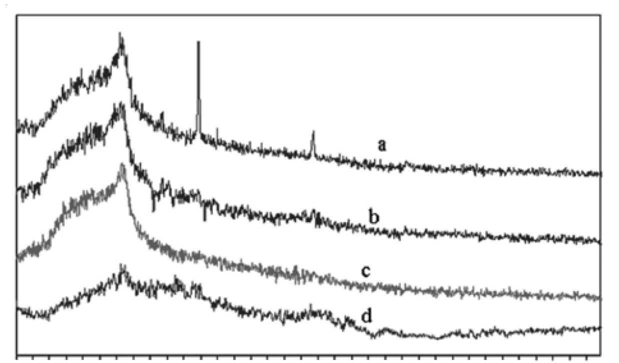

Fig. 1. XRD patterns of Si-CMSS (a), CMSS-Na_2SiO_3 mixture (b), CMSS (c) and Na_2SiO_3 (d)

FTIR analysis: The FTIR spectra of Si-CMSS, CMSS-Na_2SiO_3 mixture, CMSS and Na_2SiO_3 were shown in Fig. 2. The FTIR spectra of Si-CMSS and CMSS characteristic bands are basically the same from Fig. 2a and 2c, but there is a significant sharp peak (2362.45 cm^{-1}) in Fig. 2a, it is a stretching vibrational absorption peak corresponding to Si-H bonds, however, this characteristic peak does not appear in Fig. 2b, it further demonstrated that the silicon participated in the reaction and formed organic silicon compound.

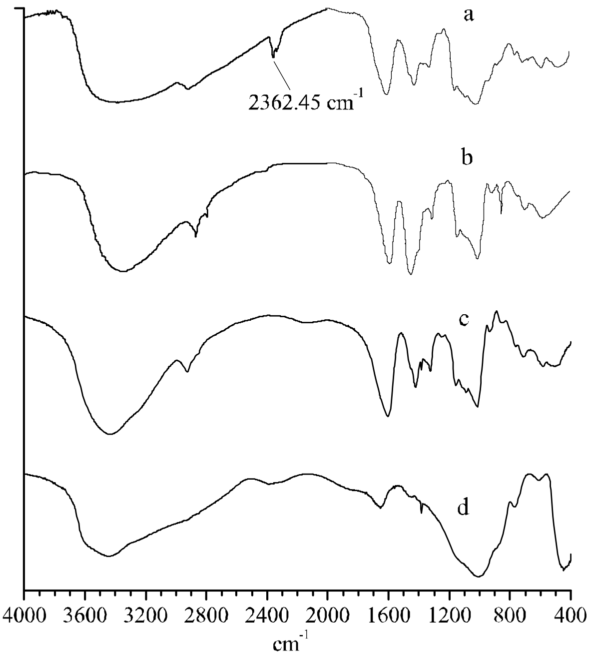

Fig. 2. FTIR spectra of Si-CMSS (a), CMSS-Na_2SiO_3 mixture (b), CMSS (c) and Na_2SiO_3 (d)

TGA-SDTA analysis: Fig. 3 is the TGA-SDTA gram of Si-CMSS, which shows that the thermal decomposition process of Si-CMSS can be divided into three stages. First stage, physical adsorbed water and chemically combined water were released in the structure at 50-220 ºC, seen from the prolapsed part of the curve; Second stage, macromolecular glycoside bonds, C-O bonds and C-C bonds in the Si-CMSS structure occurred to break, generating new products at 220-310 ºC, it is a rapid weight loss stage and the rate of weight loss is *ca.* 38 %, indicating that the decomposition temperature of Si-CMSS is *ca.* 220 ºC. The third stage, temperature is higher than 400 ºC, the residual part of the product began to change into aromatic ring materials, then gradually formed a graphite structure. A sharp exothermic peak at about 463 ºC can be seen from the SDTA curve in Fig. 3, which is a decomposition peak of the organic silicon compounds.

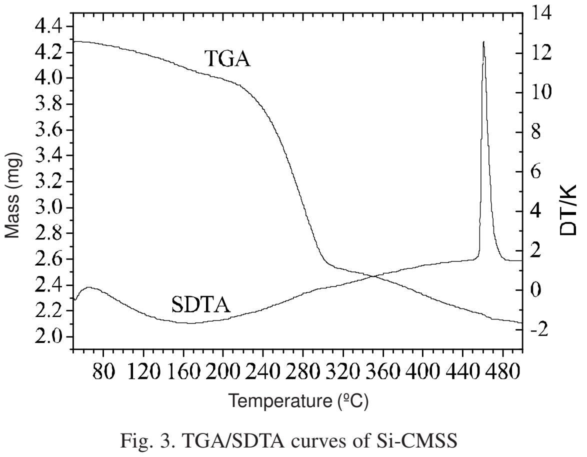

Fig. 3. TGA/SDTA curves of Si-CMSS

Performance evaluation of Si-CMSS

Filtration control performance: As a filtrate reducer, the filtration control performance of Si-CMSS was evaluated according to the standard of API RP 13B-1 and the relation curves between filter loss(FL) and filtrate reducer concentration, apparent viscosity(AV) and filtrate reducer concentration were shown in Fig. 4. Seen from Fig. 4, the filter loss is only 10 mL and the apparent viscosity is 45 mPa s when the corresponding dosage of Si-CMSS is 1.19 g/L, which shows that Si-CMSS filtrate reducer has good filtration control performance.

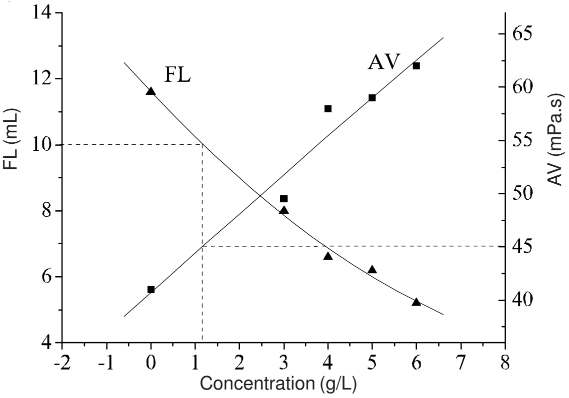

Fig. 4. Diagram of filter loss and apparent viscosity relate to filtrate reducer concentration

Table-1 is the performance comparison of CMSS and Si-CMSS added in basic slurry. Adding 0.4 % filtrate reducer (based on basic slurry) can obviously decrease the filter loss of fresh-water slurry, meanwhile, the apparent viscosity and yield point are significantly increased; the filter loss of the basic slurry added Si-CMSS has decreased 7.8 % compared with that added CMSS, it is because the water-soluble sodium silicate inhibited the polymerization degree decrease of corn starch in the modification reaction.Temperature resistance performance: Placed the two samples that, respectively composed of basic slurry with 0.4 % CMSS and basic slurry with 0.4 % Si-CMSS in the roller heating furnace and hot aging for 16 h at 110, 130, 150 and 160 ºC separately, then measured the filter loss, the results were shown in Fig. 5. It is clear in Fig. 5 that the basic slurry added Si-CMSS has good temperature resistance performance, because the increase rate of filter loss is small with the rise of temperature; the filter loss of CMSS increases obviously while temperature rises and the filter loss is 18.7 mL when the temperature reaches to 130 ºC, which means that CMSS filtrate reducer has been invalidated; however, the filter loss of basic slurry added Si-CMSS is only 15.2 mL at 150 ºC, that means the temperature resistance performance of Si-CMSS is better than CMSS.

TABLE-1
PERFORMANCES OF BASIC SLURRY, DRILLING FLUID SYSTEMS OF CMSS AND Si-CMSS

Sample	Apparent viscosity (mPas)	Plastic viscosity (mPas)	Yield point (Pa)	Filter loss (mL)
Basic slurry	10.00	5.00	5.00	21.50
Basic slurry+0.4 % CMSS*	22.25	6.50	15.75	9.00
Basic slurry+0.4 % Si-CMSS*	21.25	5.50	15.75	8.30

*Mass fraction was 0.4% (based on basic slurry).

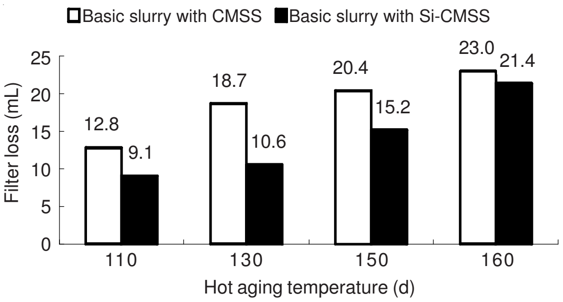

Fig. 5. Filter loss of the samples before and after hot aging at different temperatures

Evaluation of biological toxicity: Aqueous solutions of Si-CMSS and CMSS were prepared, respectively (the mass fraction was 0.4 %), then carried on the biological toxicity evaluation to them according to ASTM D5660-1996 (2004) combining the characteristics of photobacterium phosphoreum[13]. The results of biological toxicity test in Table-2 show that Si-CMSS and CMSS are non-toxic. It is because the raw materials and the introduced modifier are non-toxic to environment. Furthermore, the basic structure unit of CMSS and Si-CMSS is glucose, which can promote the bacteria's generation and propagation, so the relative luminosities are both more than 100 %.

TABLE-2
RESULTS OF BIOLOGICAL TOXICITY TEST

Sample	Relative luminosity (%)	Basis of toxicity grade	Toxicity grade
CMSS	113	Relative luminosity >100%	Non-toxic
Si-CMSS	107		Non-toxic

Analysis of filtering mechanism

Relationship between filtration control performance and zeta potential: According to DLVO theory[14], there are two opposing forces exist between clay particles, namely attraction and repulsion force, the repulsive force consists of electrostatic repulsion and solvolytic membrane repulsion. Electrostatic repulsion is directly proportional to the square of ζ potential. It is shown in Fig. 6 that the potential of Stern surface is ζ potential, which is generally negative and the more negative the ζ potential value is, the more stability the system is[15-17].

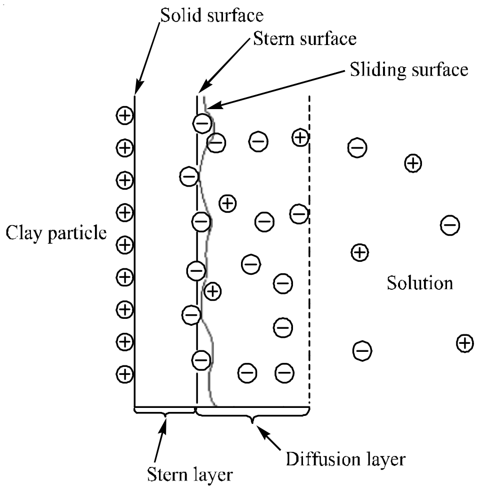

Fig. 6. Model of Stern double layer

The basic slurry, drilling fluid systems of CMSS and Si-CMSS in Table-1 were aging for 24 h, then their zeta potentials were measured, respectively and the results were shown in Table-3. In Table-3, the absolute value of ζ potential of the drilling fluid systems added CMSS and Si-CMSS increase obviously, it is because CMSS and Si-CMSS filtrate reducer adsorb or wrap on the clay surface and the polymer molecules in CMSS and Si-CMSS contain powerful hydrated carboxylic acid groups (-COO-), making the increase of negative charge density on the clay surface and thickening the solvent membrane (hydration film), therefore the absolute value of ζ potential is improved and the stability of clay particles is increased. Meanwhile, there are many hydroxyl groups (-OH), ether bonds (-O-) in CMSS and Si-CMSS molecules, so hydrogen bonds can be formed between oxygen or hydroxyl groups on the clay and the filtrate reducers. In addition, the two filtrate reducers both can form space grid structure adsorbing clay particles that attribute to the characteristics of the helical molecular structure and the high molecular weight, which will also help to improve the coalescence stability of clay particles and filtration control performance of the filtrate reducer[18].

TABLE-3
ZETA POTENTIALS OF BASIC SLURRY, DRILLING FLUID SYSTEMS OF CMSS AND Si-CMSS

Sample	ζ (mV)
Basic slurry	-21.4
Basic slurry + 0.4 % CMSS	-45.6
Basic slurry + 0.4 % Si-CMSS	-42.3

Relationship of morphology and performance: Fig. 7 are SEM images of corn starch, CMSS and Si-CMSS. As seen from Fig. 7a, corn starch presents as granular distribution and the particles have smooth surface and different sizes. Fig. 7b shows that the original starch granules have been deformed and mutually adhered after modifying into CMSS and present as continuous distribution state and have some pits on surface; due to the introduction of the hydrophilic carboxylic acid group (-COO-), this continuous distribution is conducive to the formation of the dense and small permeability fluid layer. It is shown in Fig. 7c that many lamellar and needle-like crystals are distributed on the surface of Si-CMSS, they are probably crystalline forms of organosilicon compounds and the pits on the surface of Si-CMSS were filled by them, so a space network structure has been formed, which is more conducive to the irregular polymer coils' retention into the gap of filter cake with the help of "bridge-action" and it further reduces the filter cake's permeability. At the mean time, the organosilicon compounds formed in the structure of Si-CMSS making it has good temperature resistance performance.

Reasons of temperature resistance enhancement: The temperature resistance of CMSS was increased by modification of water-soluble sodium silicate for two reasons: First, when adding soluble sodium silicate into the reaction system, the high-temperature degradation and alkaline degradation of the starch were inhibited by powerful inhibitive ability of the sodium silicate, a higher degree of polymerization and a bigger molecular weight were maintained in the reaction stage, so the temperature resistance was improved[19]. Second, which is the main reason, sodium silicate in the alkaline environment firstly reacts as follows:

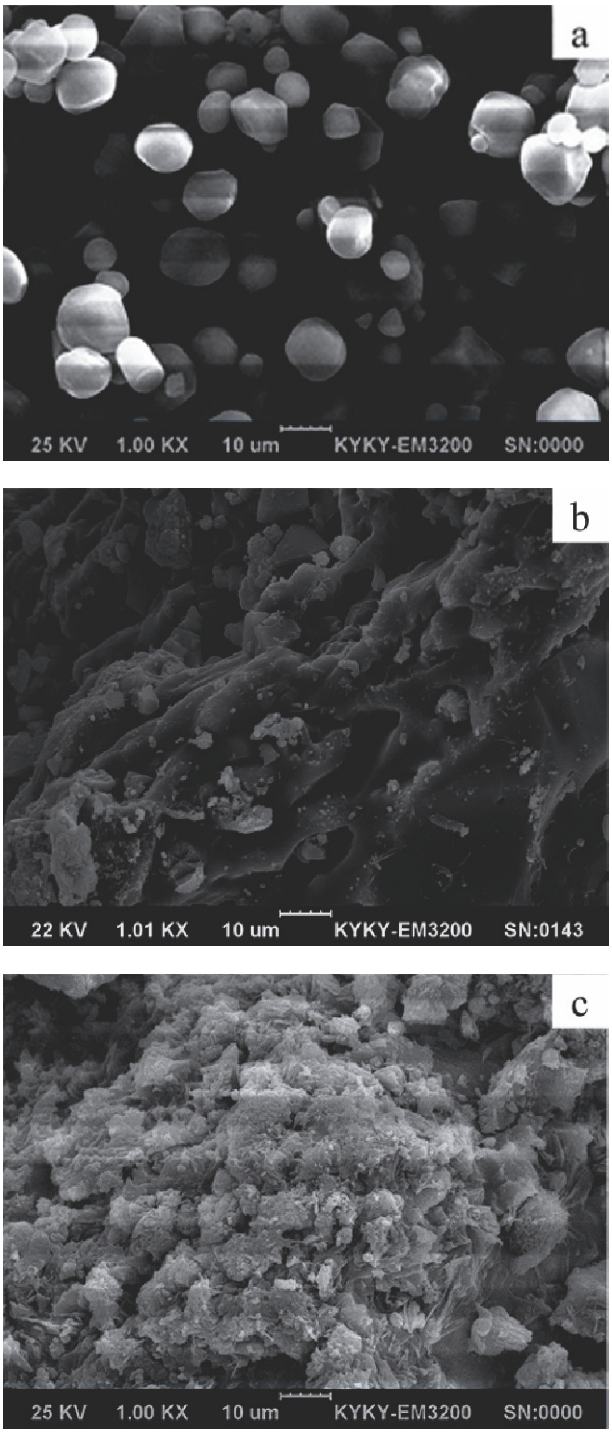

Fig. 7. SEM images of starch (a), CMSS (b) and Si-CMSS (c)

$$Na_2O\cdot SiO_2 + NaOH + H_2O \rightarrow 3NaOH + SiO_2$$

Then, silicon-hydrogen groups were formed in starch molecular by the reaction of SiO_2 and CMSS (Fig. 8). It is shown in Fig. 8 that the introduction of silicon making the formation of C-Si-C bond chain between two glucose units, that strengthened the link of glucose units and induced their resistance to heat fracture, thereby increased the temperature resistance performance.

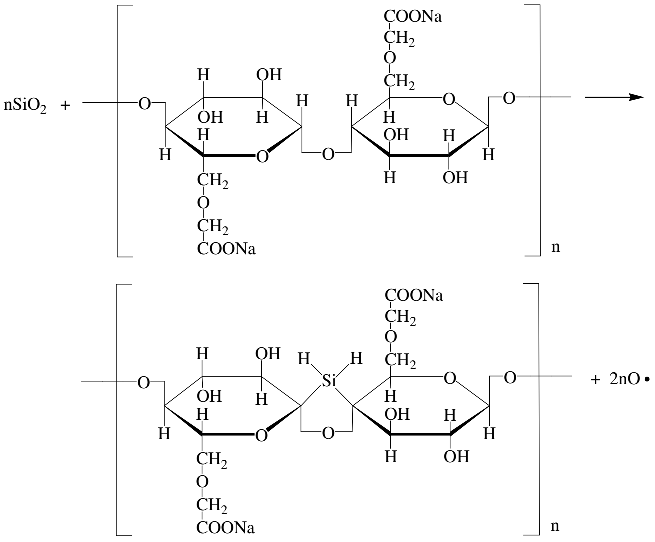

Fig. 8. Reaction of SiO_2 and CMSS

Conclusion

Carboxymethyl starch sodium was modified by water-soluble sodium silicate in alkaline reaction condition, the structure of synthetic product was characterized by X-ray diffraction and Fourier transform infrared spectrum proving that Si-CMSS had been synthesized.

As a filtrate reducer, the temperature resistance performance of Si-CMSS was up to 150 ºC, which was significantly improved compared with CMSS. The thermal decomposition temperature was known up to 220 ºC through TGA-SDTA analyzing and the filtration control performance was also improved; at the mean time, Si-CMSS maintained a good performance of environmental protection.

The thickness of hydration films of the clay was increased by Si-CMSS filtrate reducer in the drilling fluid system; meanwhile, Si-CMSS filtrate reducer enhanced clay coalescence stability and showed good filter loss control property. Many lamellar, needle-like crystals of organic silicon compounds were found on the surface of Si-CMSS by electron microscope, which is a reason for the enhancement of its temperature resistance performance.

The degradation of starch molecules was inhibited and higher degree of polymerization was retained by introducing silicate in the synthesis process of CMSS. Moreover, the introduction of silicon-hydrogen groups in the polymer molecules was very important to the temperature resistance performance of Si-CMSS, because it strengthened the links of polymer chains, making them not easy to break at high temperatures.

ACKNOWLEDGEMENTS

The authors acknowledged the grant from Innovative Research Team of Southwest Petroleum University, Chegdu, P.R. China (2012XJZT002).

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