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Flocculation of submicron particles in water-based drilling fluids by CMC-g-DMDAAC

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ABSTRACT

During the process of recirculating drilling fluids, the removal of useless solids, especially submicron particles, in drilling fluids is the most problematic issue in drilling operations. The cost and efficiency of currently used technologies are the two issues that have to be addressed urgently. In this study, the novel flocculant CMC-*g*-DMDAAC was synthesized by grafting diallyl dimethyl ammonium chloride (DMDAAC) onto carboxymethyl chitosan (CMC). The physicochemical structure of the CMC-*g*-DMDAAC product was characterized by Fourier-transform infrared (FT-IR) spectroscopy, proton nuclear magnetic resonance (^{1}H NMR) spectroscopy, and determination of the ζ-potential. A kaolinite suspension, a bentonite suspension, and drilling fluids from an oilfield were selected to evaluate the flocculation performance of CMC-*g*-DMDAAC by testing the products' turbidities and particle size distributions. In comparison, the flocculation performances of chitosan, CMC, and commercial hydrolyzed polyacrylamide (HPAM) were also tested under the same conditions. The results showed that CMC-*g*-DMDAAC exhibited steady flocculation performances for all clay suspensions and drilling fluids at all pH ranges at low dosage. The scavenging capacity of submicron particles in drilling fluids was also excellent for the tested product.

1. Introduction

Drilling fluids are often used in modern oil and gas well drilling operations. In a drilling operation, drilling fluids provide a number of important functions, such as preventing the formation fluids from entering the wellbore, removing drill cuttings, suspending drill cuttings during pauses in drilling, and keeping the drill bit cool and clean (Fink, 2015; Hart and Snyder, 2006; Landis et al., 2013; Yan, 2012). Drilling fluids are generally composed of fluids (water, oil, or gas) and various additives including polymers, salts, and clays. Depending on the type of continuous phase, drilling fluids can be divided into water-based drilling fluids (WBM), oil-based drilling fluids (OBM), and gas-type drilling fluids; WBM are mostly used in onshore and offshore drilling operations. Once drilling fluids are introduced into a wellbore, their composition can change drastically because drill cuttings such as rocks, sand, shale, and other contaminations (called useless solids) can become suspended and mixed in the drilling fluids during the drilling operation. These solids inevitably become part of the fluids as the drilling fluids are returned to the surface (Hart and Snyder, 2006; Landis et al., 2013).

In conventional drilling operations, drilling fluids are recirculated after removing the useless solid contaminants from the fluid because drilling fluids are very costly and hazardous to the environment if discharged directly. Nevertheless, the most important task for the recirculation of drilling fluids is the removal of the useless solid phase from the returned fluids because the solid contaminants worse the performance of the drilling fluids by increasing the viscosity and friction and reducing the rate of penetration (ROP). It has been shown that the ROP was reduced by 10% when the solid content in drilling fluids was increased by 1% (Chen and Guan, 2011; Yan, 2012). Moreover, particles smaller than 1 μm, most of which are hydrated and dispersed clay particles, have a negative effect that is more than 10 times greater than particles larger than 1 μm, which are mainly sand, rocks, and other contaminations (Chen and Guan, 2011; Mitchell and Miska, 2011). Therefore, the key task during the recycling of drilling fluids is the separation of the solid particles in the fluids, especially the submicron clay particles.

The on-site removal of solids from drilling fluids is typically performed using a shaking screen. However, shaking screens can only remove solid particles that are larger than 74 μm (Engineers, 1999; Zhu and Zhang, 1999). Smaller solids may further be removed by additional processing equipment such as hydrocyclones, mud cleaners and centrifuges (Hart and Snyder, 2006; Landis et al., 2013). Hydrocyclones, which can be categorized into two types, desanders and desilters, are only able

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to remove particles greater than 54 μm and 8 μm, respectively (Chen and Guan, 2011). If centrifuges are used, it is possible to remove solid particles greater than 2 μm (Liu, 2006; Wang et al., 1998). However centrifuges do not only remove useless solid contaminants but also useful solid components such as barite and mud-forming clays. Hence centrifuges are not used frequently on site (Mitchell, 1995).

Since useless clay particles smaller than 2–8 μm cannot be efficiently removed from drilling fluids by mechanical methods, operators have turned to chemical methods. (Hart and Snyder, 2006) developed a mobile treatment process and apparatus that provides chemical precipitation and filtration to treat the drilling fluid waste for reuse. Alkaline treatment agents and a novel apparatus were applied for on-site treatment. This method requires additional equipment, which definitely increases the cost and requires the modification of the drilling fluid circulating system (DFCS). (Landis et al., 2013) invented a flocculation and dewatering system for recycling and reconditioning drilling fluids. In the same way, this invention involves additional equipment and modification of the DFCS involving considerable cost and time. Although many technologies and additives have been developed to remove unwanted materials, including nanoparticles in waste water, such as chitosan (Divakaran and Pillai, 2004; Zeng et al., 2008), polyacrylamide-acrylate copolymer (PAM) and polyethylene oxide (PEO) (Mpofu et al., 2004), the DNA-Chitosan complex (Zinchenko et al., 2013), and others (Du et al., 2017; Popowich et al., 2015; Yang et al., 2013; Zhu et al., 2015), few of these additives can be used to treat drilling fluids because most can only be used in a certain pH range and do not resist alkalis, salts, and other additives in drilling fluids. Thus, there is a need to develop an economical method for on-site treatment of drilling fluids that would allow the recirculation or reuse of these fluids after treatment.

To address the above-mentioned issues associated with the removal of solid particles from drilling fluids, especially submicron particles, in this study, a cationic polyelectrolyte flocculant, CMC-*g*-DMDAAC was prepared through the grafting reaction of carboxymethyl chitosan (CMC) with diallyl dimethyl ammonium chloride (DMDAAC). The chemical structure and ζ-potential of the CMC-*g*-DMDAAC were characterized in detail. Its flocculation performance and mechanisms were evaluated and analyzed in clay suspensions and drilling fluids and were compared with the results for chitosan, CMC, and commercial hydrolyzed polyacrylamide (HPAM), which is applied widely as a flocculant in oilfields. In this experiment, 1:1 type kaolinite and 2:1 type bentonite were selected to simulate the submicron clay particles in the drilling fluids (Tombácz and Szekeres, 2006; Yan, 2012).

2. Material and methods

2.1. Materials

Chitosan (viscosity: 100–200 mpa·s, deacetylation degree > 95 mol %) and superfine kaolinite (average particle diameter: 3.5 μm) were purchased from Aladdin Chemistry Co., Ltd. (China). Bentonite (sodium form) was acquired from Alfa Aesar (China). Monochloroacetic acid (AR) and the redox initiators (GR) were supplied from J&K Scientific Ltd. (China). DMDAAC (60% in water) was obtained from Energy-Chemical (China). All of the p.a. grade chemicals used in the carboxylate content analysis (NaOH, HCl, acetone, and ethanol) were purchased from Sinopharm Chemical Reagent Co., Ltd. (China) and used without further purification. Commercial-grade HPAM (hydrolysis degree 20–30%) with a molecular weight of 5 million and other experimental chemicals were purchased from domestic reagent companies. Deionized water was used throughout the experiments.

2.2. Synthesis of CMC-g-DMDAAC

Firstly, CMC was prepared in our laboratory based on the method reported by (Liu et al., 2000) and (Chen and Park, 2003). To synthesize the CMC-*g*-DMDAAC, a certain amount of CMC was dissolved in 200 mL of a 1 wt% HCl solution. After 30 min of stirring under an N_2 atmosphere, a certain amount of redox initiator was added. The solution was maintained for 3 min of pretreatment with the initiator to suppress the formation of a DMDAAC homopolymer. Then the DMDAAC monomer aqueous solution was added dropwise to the solution. Subsequently, the reaction was performed for 3 h under an N_2 atmosphere at a temperature of 50 °C and the final sample was precipitated in ethanol. The obtained solid product was filtered and extracted using ethanol as the solvent in a Soxhlet apparatus for 36 h to remove the impurities and was dried in an oven at 80 °C. The synthesis pathway of CMC-*g*-DMDAAC is shown in Fig. 1.

2.3. Preparation of stock suspensions and solutions

A clay suspension was prepared using deionized water without a dispersing agent. Two grams of kaolinite (kao), bentonite (ben) and ben-kao 1:1 mixture were separately dispersed in 1 L of deionized water under stirring for 10 min. The resulting suspension was adjusted to the chosen pH using 0.1 M NaOH or 0.1 M HCl solutions and then equilibrated for 24 h prior to use.

Because chitosan is not soluble under neutral pH conditions, a 1 wt% chitosan stock solution was prepared in a 0.01 M HCl solution. It took about 2–3 h to dissolve the chitosan completely under stirring at room temperature.

Subsequently, 1.0 g of CMC and 1.0 g of CMC-*g*-DMDAAC were separately added to 100 mL of deionized water under vigorous stirring for 5 min, followed by preserving at room temperature for 2 h to obtain a transparent and viscous solution.

2.4. Characterization

Fourier-transform infrared (FT-IR) spectroscopy. The FT-IR analyses were conducted with a Magna-IR 560 spectrometer (Nicolet, USA) with a wavelength range of 400–4000 cm^{-1} and a resolution of 4 cm^{-1}.

Proton nuclear magnetic resonance (^1H NMR) spectroscopy. The ^1H NMR spectra were recorded at room temperature on a Bruker Avance 400 spectrometer (Bruker, Switzerland), in which D_2O was used as the solvent and the spectra were calibrated using the residual protons of the solvent.

ζ-Potential analysis. The ζ-potential of the stock suspensions and solutions were measured by a Zetasizer Nano ZS (Malvern, England) at various pH values at room temperature. The pH values of the stock suspensions and solutions were modified using 0.1 M NaOH or 0.1 M HCl solutions, and the pH was measured by a FE20 pH Meter (Mettler Toledo, Switzerland).

Particle size. The particle size distribution curves were recorded by a Mastersizer 2000 laser particle size analyzer (Malvern, England). The suspensions were sonicated at room temperature for 30 min by an ultrasonicator prior to the measurements.

Scanning electron microscopy (SEM). The SEM analyses were performed by a Quanta 200F scanning electron microscope (FEI Company, USA),

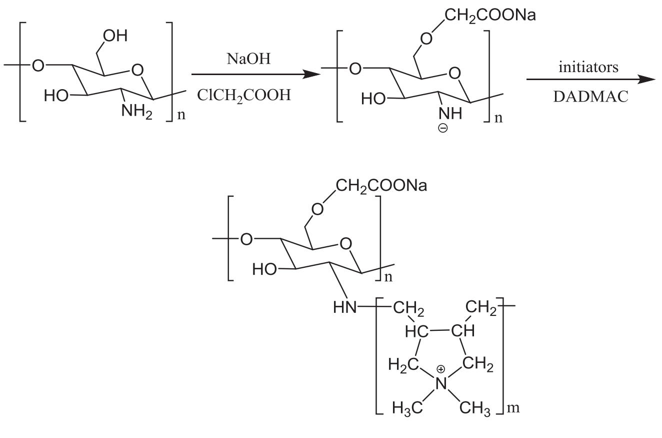

Fig. 1. Synthesis pathway of CMC-*g*-DMDAAC.