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Synthesis and Evaluation of Carboxymethyl Glucoside as Montmorillonite Swelling Inhibitor

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Abstract: Methylglucoside (MEG) has been used in the water-based mud with fine montmorillonite (MMT) swelling inhibition, but it still has such shortages as large concentration and low thermostability. In this work, carboxymethyl glucoside (CMG) was synthesized with glucose and sodium chloroacetate and used as swelling inhibitor. The inhibition of CMG against clay swelling was investigated by MMT linear expansion test, mud ball immersing test and bentonite inhibition test. The results showed that the CMG has a good inhibition to the hydration swelling and dispersion of MMT. Under lower concentrations, the linear expansion rate of MMT in CMG solution is much lower than that of MEG, and the hydration expansion degree of the mud ball in the CMG solution was significantly inhibited. The characterizations of physical-chemical properties of particle, analyzed by thermogravimetric analysis and scanning electron microscopy revealed that CMG plays a great role in preventing water from absorbing and keeps MMT in large particle size.

Keywords: Carboxymethyl glucoside, inhibition, montmorillonite, swelling.

1. INTRODUCTION

Montmorillonite (MMT, $(Na,Ca)(Al,Mg)_6(Si_4O_{10})_3(OH)_6 \cdot nH_2O$, as shown in Fig. (**1**), is one of the general mineral group clays, in which the water content is variable depending on the environmental, and in fact when MMT absorbs water, it tends to swell to several times its original volume. The swelling and dispersal of MMT in water can generate great viscosity, so with this property it was used as the basic material in drilling fluid to keep a drill head cool during drilling and facilitate removal of rock fragment from the drill hole [1, 2]. On the other hand, during the drilling in oilfield, great quantities of water based mud are used. In this process, borehole stability problems such as bit balling, disintegration of cuttings, borehole wash-out and stuck pipe mostly occur in shale formations due to shale hydration and swelling [3-5]. It has been reported that, considering clays like semi-permeable membranes, presents osmotic pressure equations for the determination of the swelling properties [6]. Chenevert [7] stated that the main reason of instability during drilling by WBM (Water-based mud) systems is the swelling of clays, so montmorillonite swelling control is at the origin of well instability during the drilling. Steiger [8] found that potassium salts can inhibit the swelling of clay in water and consequently reduce the swelling pressure. Simpson showed that OBM (Oil-based mud) containing an emulsified water phase can prevent moisture and thus weaken the swelling of the clay [9]. Some hydrophilic organic compound, such as methylglucoside (MEG), has been used in WBM affording characteristics similar to those of OBM, such as lubrication and inhibition [9]. It has been proved by the experiments that MEG drilling fluid can stabilize shale by the similar mechanism of balance activity OBM. The MEG system is easy to formulate with better solid carry capacity and high lubrication. Besides, the MEG system is eco-friendly, so its application could reduce the cost of oil contaminated drilled cutting disposal [10]. Now, MEG has been applied in many Chinese drillings, but it was found that the dosage of MEG is relative high and the temperature resistance is relatively low, leading to a high cost. So the researchers have screened other organic additives with high thermostability and good capacity of swelling inhibition for WBM [11, 12]. In this work, carboxymethyl glucoside (CMG) was synthesized with glucose and sodium chloroacetate and used as a new montmorillonite swelling inhibitor with high thermostability. Both the inhibitive properties of synthesized inhibitor and the inhibitive mechanism were discussed in detail.

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2. EXPERMENTAL

2.1. Materials

The sodium montmorillonite (Na-MMT) SD-1005 was obtained from Zhejiang Sanding Technology Co., LTD. The chemical compositions of the sample were: SiO_2, 64.07%; Al_2O_3, 19.11%; CaO, 4.48%; MgO, 3.61%; Na_2O, 3.07%; Fe_2O_3, 2.64%; P_2O_5, 1.71%; K_2O, 0.72%. The anionic exchange capacity was 95 mmol/100g measured by the ammonium acetate method. MEG was provided by Sinopharm Chemical Reagent Co., Ltd, China. All the reagents were used without further purification.

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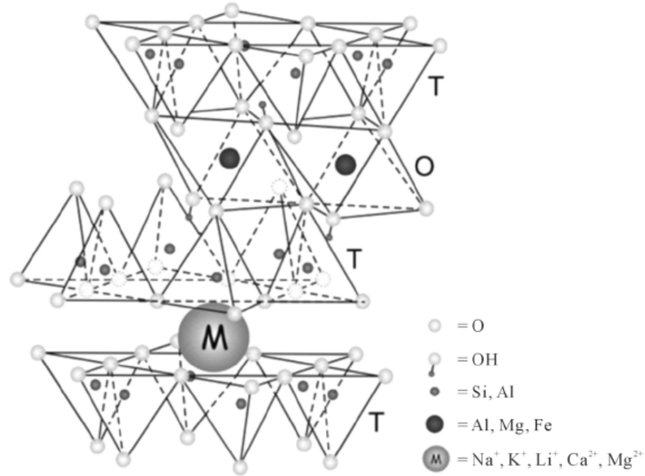
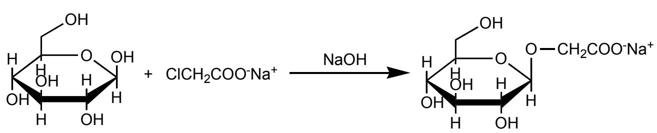


Fig. (1). The structure of montmorillonite.

2.2. Synthesis of CMG

Carboxymethyl glucoside (CMG) was synthesized with glucose and sodium chloroacetate, as shown in Scheme **1**. A certain amount of glucose and 5% NaOH were dissolved in water at a certain temperature, and the sodium chloroacetate methanol solution was added dropwise. The reaction was stirred until the disappearance of glucose, as evidenced by thin-layer chromatography. The solvent was removed in vacuo and the residue was recrystallized in methanol, giving the title compound.



Scheme 1. Synthesis of carboxymethyl glucoside.

2.3. Swelling Inhibition and Mud Ball Immersing Test

The hydration swelling of Na-MMT is tested by a NP-01 shale expansion instrument according to API Procedure No.13B. Mud ball immersing test is as follows: montmorillonite (10 g) was used to make a mud ball and the mud ball was immersed in 100 mL tap water or other aqueous solutions for 36 h. Watch the details of the immersed mud balls, check whether there are cracks or dilapidation on the surface [13].

2.4. Bentonite Inhibition Test

400 mL of water containing 4 g inhibitor was treated by 4w/v% drilling fluid bentonite. After stirring for 30min, the dispersion was aged at 30 °C for 16 h. After that the equivalent amount of drilling fluid bentonite was added and the procedure was repeated until the dispersion became too viscous to be measured.

2.5. Physicochemical Property Analysis

TGA experiments were carried out using a TGA/SDTA 851^e thermal analysis machine (Mettler-Toledo, Switzerland) under a flow of nitrogen. The sample weight used was about 10 mg, and the temperature ranged from 25 °C to 400 °C with a ramping rate of 20 °C /min. The morphology of the MMT samples in the absence and presence of inhibitors was investigating using a Digital Microscope Imaging scanning electron microscope (SEM) at 20.0 kV. All micrographs of the specimen were taken at 5000 magnification.

3. RESULTS AND DISCUSSION

3.1. Synthesis of TGS

In this reaction, there are five hydroxyl groups in glucose, so the reaction between glucose and GTA may be very complex. In fact, among the five hydroxyl groups, the 1-α/β-OH is the most active one caused by the electro-withdraw effect of the other oxygen atom connecting to the same carbon (C_1) atom. In this reaction, the base, NaOH, plays the role of a catalyst. At the first step, the OH^- reacted with the most active proton (the hydroxyl group of C_1) producing a H_2O, and in this way the O atom was activated. Then the activated O attacked the α-C of sodium chloroacetate to substitute the Cl atom, producing the target molecule, carboxymethyl glucoside (CMG). The reaction condition was optimized by screening the molar ratio of sodium chloroacetate to glucose under refluxing, and the results were summarized in Fig. (**2**). From the results, it can be seen that the yield of CMG increases with the molar ratio, and the yield comes to the maximum of 84% at 1.2: 1 molar ratio of glucose to sodium chloroacetate. Further increasing the molar ratio leads to a decrease due to the side-reactions.

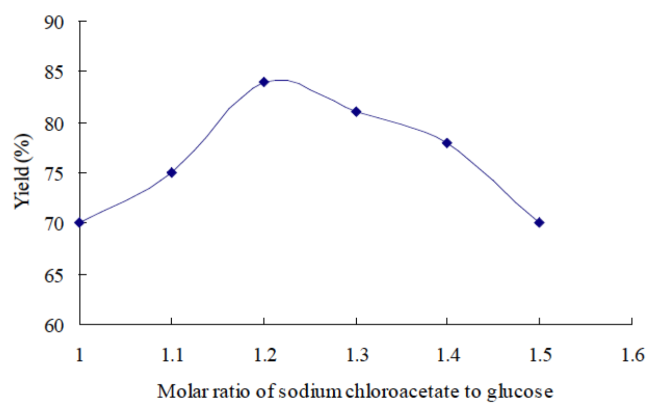


Fig. (2). The effect of molar ratio on the yield.

3.2. Swelling Inhibition Evaluation

To investigate the influence of CMG with the swelling inhibition of MMT, the swell rate of MMT with time in different concentration of CMG solution was recorded. As shown in Fig. (**3**), the water adsorption rate increased dramatically during the initial 10 min and then was followed by a slow increase in any cases, while the swelling rate of MMT in CMG solution is much lower than that of other solutions indicating that the water affinity of the MMT was inhibited by CMG. The influence of CMG concentration to its swelling inhibition behavior is similar with all of the inhibitors that low swelling rate can be obtained in the presence of high inhibitor concentration because the swelling rate is a function of inhibitor dosage. In our research, the inhibition performance of MEG, a common inhibitor as suggested before, has also been investigated for comparison. The results show that the swelling ratios of MMT are 59.02%, 56.46%, 54.55% and 55.23% at the CMG concentration of 1.0%, 2.0%, 5.0%, and 10.0% respectively within 40 min, while the swelling ratio in 10% MGE, 65.48%, is much higher than that of CMG solutions.

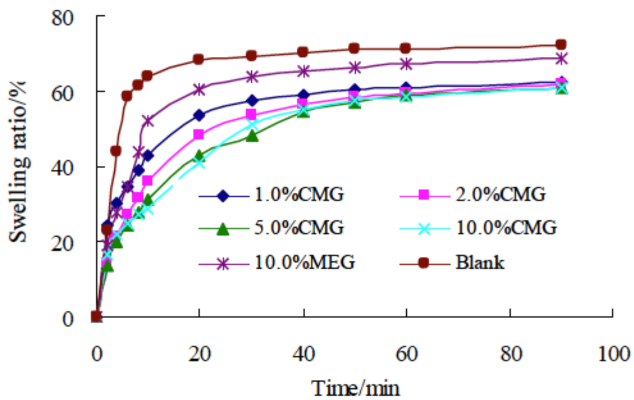


Fig. (3). The inhibition of CMG (left) and GTA (right) to clay.

3.3. Mud Ball Test

The mud ball immersing test provides a more intuitive way to describe the inhibitive property. In our research, the mud balls were immersed into water and 2% CMG respectively. Fig. (**4**) shows the status of the mud balls after being immersed for 48 hours. From the results, it can be seen that the morphology of mud ball in the presence of water is greatly changed and cracked into pieces due to the swelling of MMT. In contrast, there is almost no status change found when the mud ball was immersed in CMG solution indicating that the swelling of MMT by hydration is slight so as to make the surface of the mud smooth ball without any cracks. This observation could be explained by the hydrophobic film resulting from CMG, which blocks the water penetration into the interlayer of MMT and then prevents it from hydrating the swelling.

Fig. (4). The status of mud balls immersed in water (left) and 2% CMG (right) solution for 48 h.

3.4. Bentonite Inhibition Test

The test was designed to simulate the incorporation of yielding clays into a drilling fluid, which usually occurs when drilling water intrude into sensitive shales in the stratum. As shown in Fig. (**5**), the yield point increases sharply with the addition of bentonite in fresh water due to the hydration and dispersion of clay. On the contrary, the yield point increases slowly in the inhibitor systems, which means CMG performed a good inhibitive capacity.

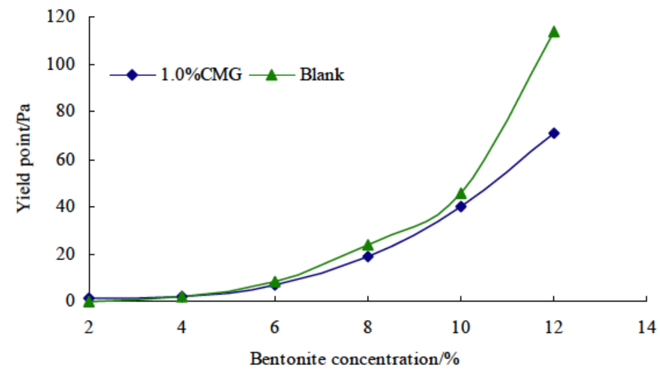


Fig. (5). Bentonite inhibition test comparing the yield point of 2% CMG with the base fluid.

3.5. TGA Analysis

For further investigation, thermogravimetric analysis (TGA) was used to describe the thermal stability of MMT after being modified by different additive, and the result was shown in Fig. (**6**). From the pattern, we can see that there is a long mass loss step in the process of decomposition of MMT modified by water and CMG solution. Before 200 °C, the mass loss is assigned to the dehydration of physically adsorbed water and water molecules around hydrated Na^+ anions on exchangeable sites in MMT [14, 15], which is very slight in both of samples, less than 5%. The weight loss at above 200 °C is contributed to the release of structural water. In case of CMG modified MMT, the mass loss above 200 °C due to structural hydroxyl groups is less than that of the water modified sample, which indicates the adsorption of water into the interlayer regions between silicate sheets of MMT was greatly weakened after modified with CMG.

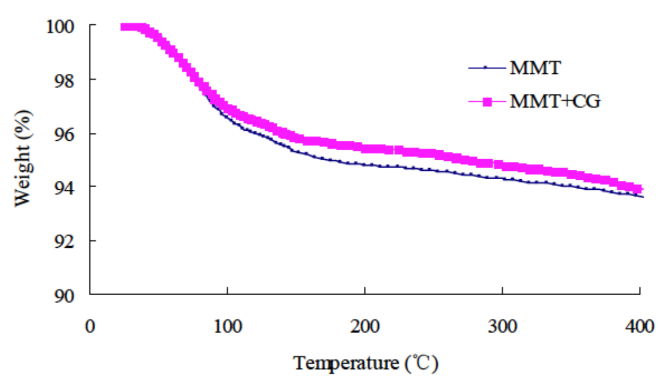
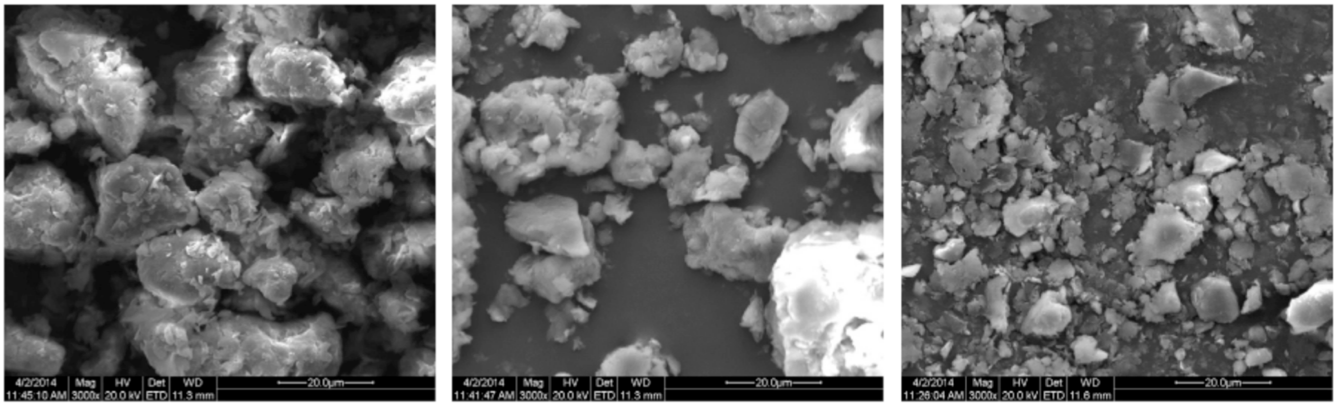


Fig. (6). The TGA of the montmorillonite treated by water and CMG solution.

3.6. Scanning Electron Microscopy

Scanning electron micrographs (SEM) of MMT in the absence and presence of inhibitors have been recorded in order to get insight into the particles morphology. Fig. (**7a**) shows an SEM image of the virgin MMT particles without any treatment, and the morphology of the MMT particles after being immersed in 1% CMG solution for 12 h has been



(**a**) Virgin MMT
Average particle sizes=35μm

(**b**) MMT treated with CMG solution
Average particle sizes=22μm

(**c**) MMT treated with water
Average particle sizes=13μm

Fig. (7). SEM of montmorillonite treated with different ways.

shown in Fig. (**7b**). For comparison the SEM image of MMT particles after being immersed in water for 12 h has also been measured in Fig. (**7c**). From the three micrographs, it can be found that large aggregates of oriented platelets are present in the untreated montmorillonite sample. After being immersed in water or CMG solution, the MMT particles aggregated clusters particles still remain, which are still larger than that of the MMT immerged in water, indicating the inhibition of CMG to the swelling of MMT.

CMG containing 4 hydrophilic –OH groups and a carboxyl group is favorable for the absorption of CMG on the surface of MMT by the hydrogen bonds between CMG and MMT as suggested by vanOlphen [16]. As a result, the space between the MMT layers was blocked by the absorbed CMG molecules, which inhibits the entering of H_2O molecules into the layer of MMT. On the other hand, the stability of MMT in water was greatly enhanced by the film on the MMT surface formed from CMG, which plays a great role to protect MMT against hydration.

CONCLUSION

Carboxymethyl glucoside (CMG) was synthesized for the use of MMT swelling inhibitor. The MMT swelling tests showed that CMG exhibits great inhibition to the MMT linear expansion by keeping 59.02% of swelling ratio within 40 min event under a 1.0% concentration, which is much effective than that of MEG with the swelling rate of 65.48% under 10% concentration. Furthermore, the hydration expansion degree of the mud ball in the CMG solution is significantly weaker and it also has a good performance in bentonite inhibition test. The thermogravimetric analysis and scanning electron microscopy results all consist with the inhibition results.

CONFLICT OF INTEREST

The authors confirm that this article content has no conflict of interest.

ACKNOWLEDGEMENTS

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