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Research Article

Synthesis of a Biglucoside and Its Application as Montmorillonite Hydration Inhibitor

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A biglucoside (BG) was synthesized with glucose and epichlorohydrin as raw materials. The inhibition of BG against montmorillonite swelling was investigated by various methods including montmorillonite linear expansion test, mud ball immersing test, thermogravimetric analysis, and scanning electron microscopy. The results show that the BG has good inhibition ability to the hydration swelling and dispersion of montmorillonite. Under the same condition, the linear expansion ratio of montmorillonite in BG solution is much lower than that of MEG. The particle distribution measurement, thermogravimetric analysis, FT-IR, and scanning electron microscopy results all prove the efficient inhibition of BG.

1. Introduction

Montmorillonite is a 2 : 1 montmorillonite, which has two tetrahedral sheets sandwiching a central octahedral sheet (as shown in Figure 1). The particles are plate-shaped with an average diameter of approximately one micrometer. The water content of montmorillonite is variable and it increases greatly in volume when it absorbs water. The hydration and expansion will lead the viscosity to increase, which may be a disadvantage for its application [1–3]. So the hydration and expansion should be controlled in some degree using some human friendly hydration inhibitors. In fact, methylglucoside (MEG) has been used as an environmental friendly montmorillonite hydration inhibitor [4–7]. But the inhibitive ability is relatively weak compared with other inhibitors. So the researchers have screened other organic additives with high thermostability and good capacity of swelling inhibition [8–10]. In this work, a biglucoside (BG) was synthesized with glucose and epichlorohydrin as a new montmorillonite swelling inhibitor. The inhibitive properties were evaluated through linear expansion, mud balls, thermogravimetric analysis, and scanning electron microscopy.

2. Experimental Procedure

2.1. Materials. The sodium montmorillonite (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 cationic exchange capacity was 95 mmol/100 g measured by the ammonium acetate method. MEG was provided by Sinopharm Chemical Reagent Co., Ltd., China. All the reagents were used without further purification.

2.2. Synthesis. The biglucoside (BG) was synthesized with glucose as shown in Scheme 1. A certain amount of glucose and base were dissolved in water at a certain temperature, and the epichlorohydrin was added dropwise. The mixture was stirred until the disappearance of glucose, as evidenced by thin-layer chromatography. The solvent was removed in vacuo and the residue was recrystallized, giving the title compound.

2.3. Swelling Inhibition and Mud Ball Immersing Test. The hydration swelling of shale is tested by an NP-01 shale

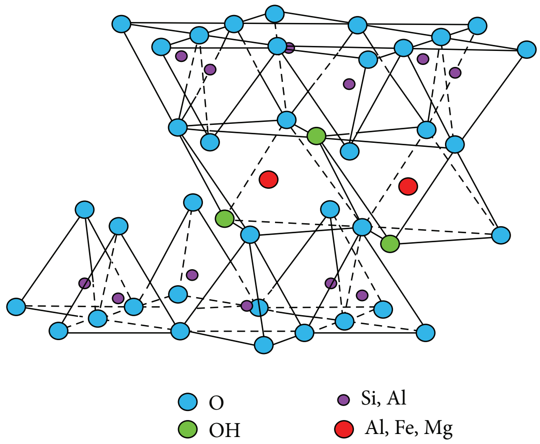
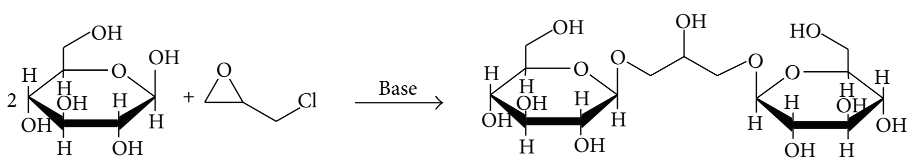


Figure 1: The structure of montmorillonite.



Scheme 1: Synthesis of trimethylsilyl glucoside (BG).

expansion instrument according to API Procedure number 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 [11].

2.4. FT-IR Characterization. The Fourier transform-infrared (FT-IR) spectrophotometer (Nicolet Nexus 670, USA) was used to identify the surface group over the MMT.

2.5. TGA Analysis. TGA experiments were carried out using a Q600 SDT thermal analysis machine (TA Instruments, USA) under a flow of nitrogen. The sample weight used was about 10 mg, and the temperature ranged from 25°C to 930°C with a ramping ratio of 20°C/min.

2.6. Scanning Electron Microscopy. The surface morphology of the sample under study in the absence and presence of inhibitors was investigated using a Digital Microscope Imaging scanning electron microscope (model SU6600, serial number HI-2102-0003) at accelerating voltage of 20.0 kV. Samples were attached on the top of an aluminum stopper by means of carbon conductive adhesive tape. All micrographs of the specimen were taken at 5009 magnification.

3. Results and Discussion

3.1. Synthesis. Epichlorohydrin is a bifunctional compound with a –Cl group and an epoxide group, which is a highly reactive compound and is a versatile precursor in the synthesis of many organic compounds. In this reaction, there are five hydroxyl groups in glucose, so the reaction between glucose and epichlorohydrin may be very complex. In fact, among the five hydroxyl groups, the 1-α/β-OH is the most active one due to the electro-withdraw effect of the other O atom connecting to the same C (C1) atom. In the first step, the base bonds to the H of 1-α/β-OH and the activated O can attack the epoxide group from the opposite side of –Cl due to the stereochemistry, as a result, a O^- anion intermediate produced. The anion captured H^+ from H_2O to produce another intermediate. Then, by a typical substitution reaction, the intermediate reacts with another glucose molecule to form the target compound (biglucoside, BG). The reaction process was shown in Figure 2.

The reaction condition was optimized by screening the temperature and molar ratio, and the results were summarized in Figures 3 and 4. The yield of BG increases as the molar ratio of epichlorohydrin to glucose increases, and at 2.2 the yield comes to the maximum, and further increasing leads to a decrease. So the molar ratio of epichlorohydrin to glucose was selected as 2.2. With the optimized molar ratio, the effect of the temperature on the yield indicates that low temperature is suitable for the high yield, and higher temperature leads to higher yield. But, as the temperature increases up to 80°C, the yield begins to decrease, which may be due to the side reactions at high temperature. So we select 80°C in the following synthesis.

3.2. Swelling Inhibition. In order to investigate the influence of BG to the swelling inhibition of montmorillonite, the swell ratios in different concentrations of BG solution were recorded. As shown in Figure 5, the water adsorption ratio increases dramatically at the initial 10 min, followed by slow

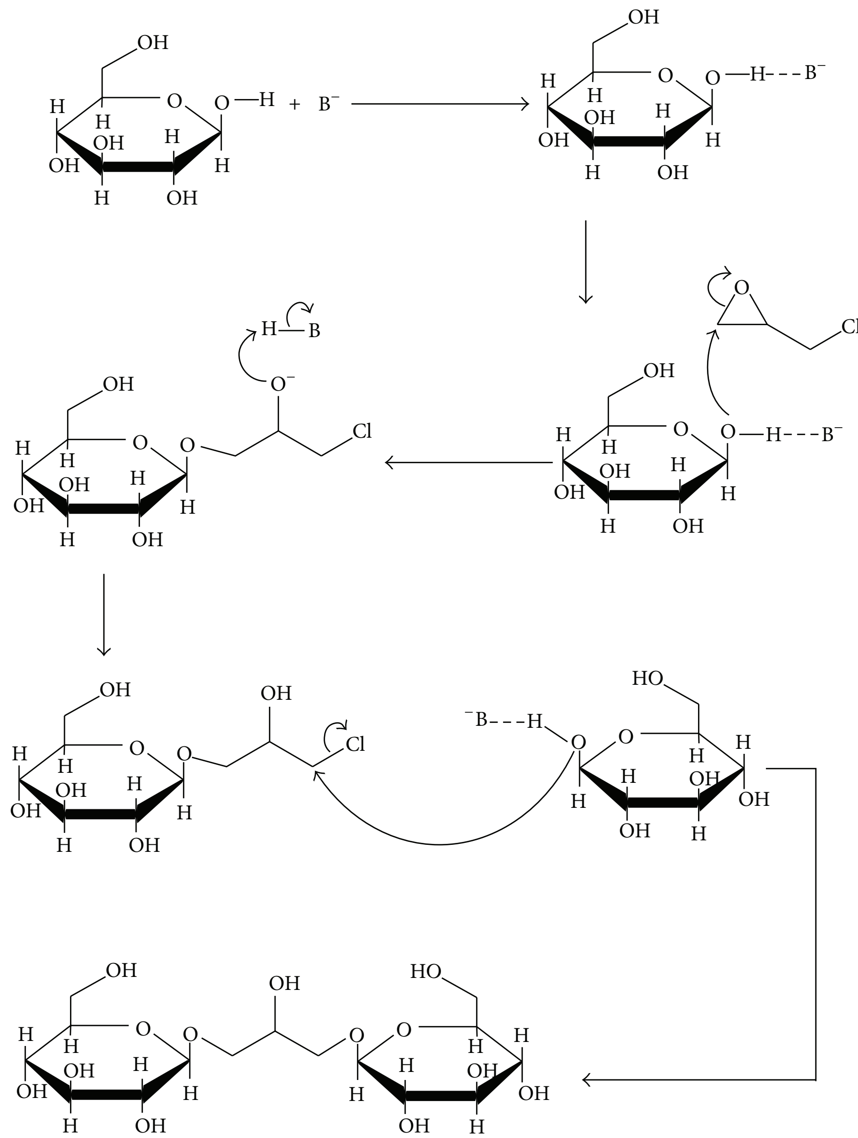


FIGURE 2: The reaction process of glucose and epichlorohydrin.

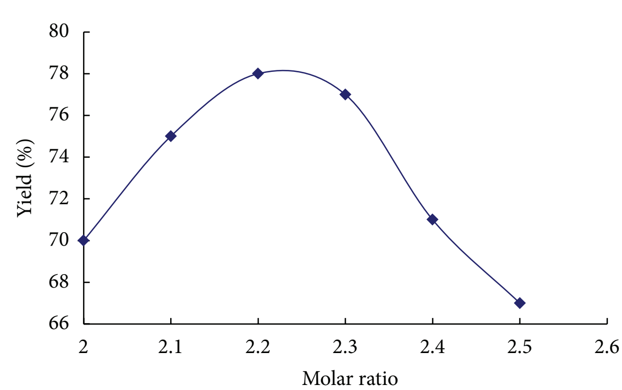


FIGURE 3: The effect of molar ratio on the yield.

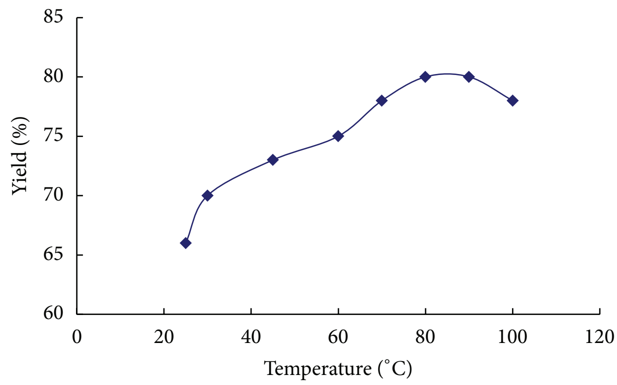


Figure 4: The effect of temperature on the yield.

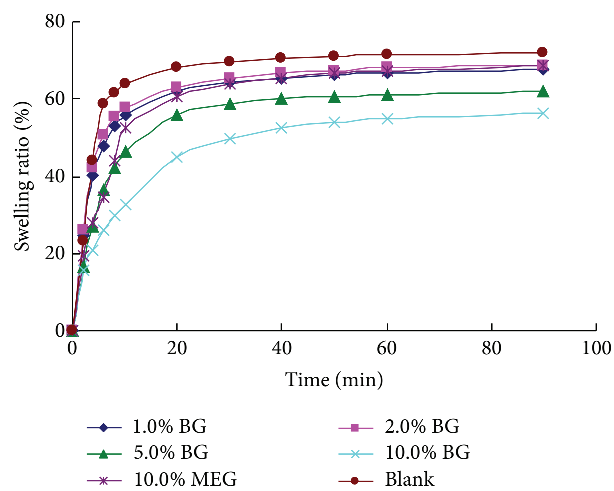


Figure 5: The linear expansion ratio of montmorillonite in BG solution.

increase. Compared with the control test, the swelling ratio of montmorillonite in BG solution is much lower, indicating that the water affinity of the montmorillonite was inhibited by BG effectively. Generally, the higher the concentration of the BG, the lower the swelling ratio that was obtained. And the inhibition of BG is much effective compared to that of MEG with the concentration of 10%, and the swelling ratios are 56.4% and 68.5%, respectively.

3.3. Mud Ball Test. The mud ball immersing test was employed to describe the inhibition of BG for wet montmorillonite. The mud balls were immersed into water and 2% BG solution, respectively. Figure 6 shows the status of the mud balls after immersing for 48 hours. The mud ball immersing in water swelled obviously, and cracks appeared on the surface, while it changed in BG solution. The mud ball immersing in BG solution swells slightly and the surface is very smooth with no cracks on the surface. It is clear that BG has significantly strong montmorillonite hydration swelling inhibition. This observation could be explained by the film resulting from absorption of BG on the surface, which blocks the water penetration into the montmorillonite to prevent it from hydration swelling [12, 13].

3.4. FT-IR Analysis. FT-IR spectra were used to confirm the adsorption of BG on MMT, and the IR of "MMT + water" and "MMT + 2% BG + water" was shown in Figure 7. In the IR of MMT, the peaks at 3460 cm^{-1} and 1650 cm^{-1} are attributed to the stretching and bending vibrations of physically adsorbed water on the clay particles, respectively. In the IR of BG modified MMT, it is clear that the intensity of the two peaks was depressed, which indicates that the absorption of H_2O molecules to MMT was inhibited.

3.5. TGA Analysis. Thermogravimetric analysis (TGA) was used to probe the thermal stability of montmorillonite treated with water and 2% BG solution, and the result was shown in Figure 8. Generally, several mass loss steps are observed in the process of decomposition of both montmorillonite samples. Before 200°C, the mass loss is assigned to the dehydration of physically adsorbed water and water molecules around metal cations such as Na^{+} and Ca^{2+} on exchangeable sites in montmorillonite [9, 10], which is very slight in the two samples, less than 3%, and they are quite similar. From the temperature of 200°C to 800°C, the two samples keep losing weight, and it is obvious that the weight loss of BG treated

(a) (b)

Figure 6: The status of mud balls immersed in water (a) solution and 2% BG (b) solution for 48 h.

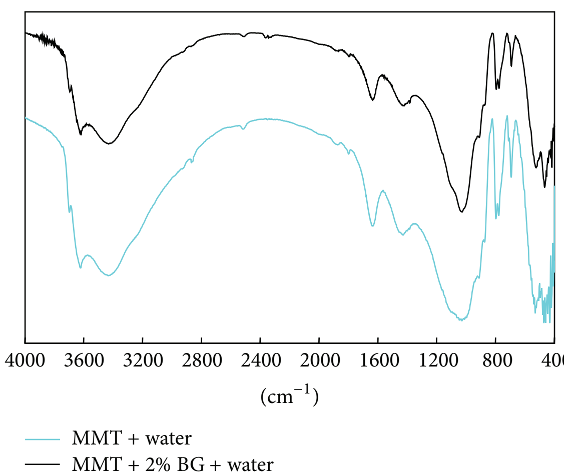


Figure 7: The FT-IR of the montmorillonite treated by water and BG solution.

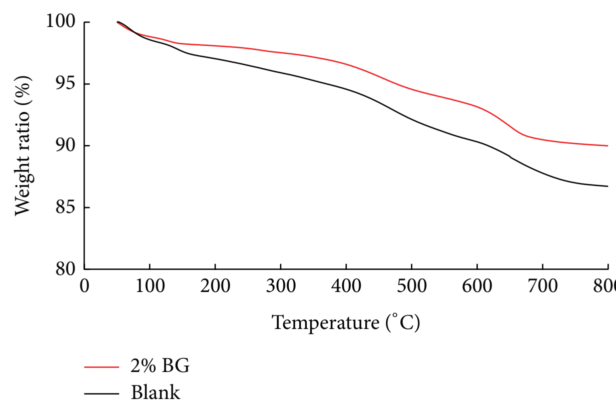


Figure 8: The TGA of the montmorillonite treated by water and BG solution.

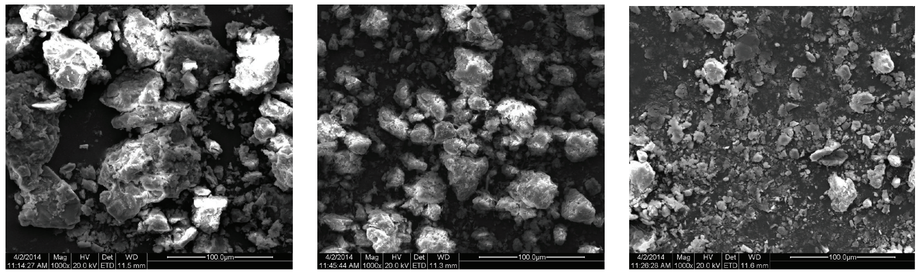
montmorillonite is less than that of the control sample, which indicates that the BG treated montmorillonite contains less water than that of the control one. From this test, it can be concluded that BG can inhibit the water absorption of montmorillonite effectively.

3.5.1. Scanning Electron Microscopy. In order to evaluate the montmorillonite particles treated by different ways, SEM was carried out. Figure 9(a) shows an SEM image of the virgin particles without any treatment. Figure 9(b) shows SEM image of the particles after being immersed in 2% BG solution for 12 h, and Figure 9(c) shows the particles after being immersed in water for 12 h. From the three micrographs, it can be found that, after being immersed in water or BG solution, the particles dispersed and changed to smaller particles. It also can be seen that the particle size of montmorillonite treated with BG solution is much larger than that of the one treated with water, which also means that BG inhibited the hydration and dispersion of montmorillonite.

3.5.2. Mechanism. BG is a molecular with plenty of –OH groups and without any charge. So it can be absorbed on the surface of MMT by the hydrogen bonds between the –OH groups of BG and MMT, as suggested by Van Olphen (shown in Figure 10) [13]. The absorbed BG molecules can block the space between the MMT layers and inhibit the H_2O molecules from entering the layer. The hydrogen bond between the BG molecules can form a film covering on the surface of MMT.

4. Conclusions

In this work, a biglucoside (BG) was synthesized with glucose and epichlorohydrin for the use of montmorillonite swelling inhibitor. The inhibition was investigated by linear expansion test, mud ball immersing test, thermogravimetric analysis, and scanning electron microscopy. The results showed that BG can inhibit the montmorillonite linear expansion more effectively than MEG with the swelling ratio of 56.4% and



(a) Virgin montmorillonite. Average particle sizes = 35 μm

(b) Montmorillonite treated with BG solution. Average particle sizes = 28 μm

(c) Montmorillonite treated with water. Average particle sizes = 13 μm

Figure 9: SEM of montmorillonite treated with different ways.

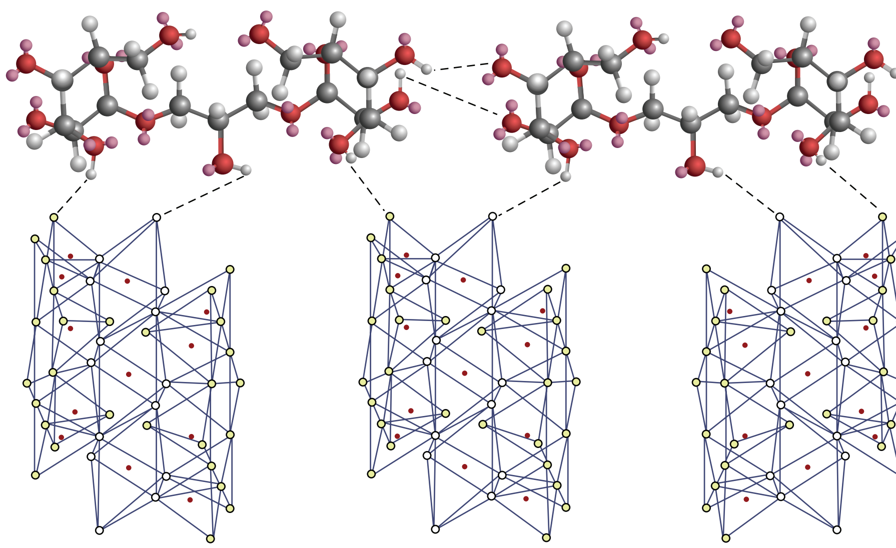


Figure 10: The possible interaction of BG and MMT.

68.5%, respectively. The hydration expansion degree of the mud ball in the BG solution was significantly weaker than that of MEG. The FT-IR, TGA, and SEM results also prove the efficient inhibition of BG to the hydration and dispersion of montmorillonite.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

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