

# Fabrication and surface properties of hydrophobic barium sulfate aggregates based on sodium cocoate modification



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## ABSTRACT

Hydrophobic barium sulfate aggregates were fabricated by the direction of cocoate anions. At 30 °C, when the weight ratio of sodium cocoate to BaSO<sub>4</sub> particles was 2.0 wt.%, the active ratio of the product reached 99.43% and the contact angle was greater than 120°. This method could not only simplify the complex modification process, but reduce energy consumption. The surface morphology, chemical structure and composition of BaSO<sub>4</sub> aggregates were characterized by SEM, XRD, and FTIR. The results indicated that the as-synthesized BaSO<sub>4</sub> particles were almond-liked and were composed of many interconnected nanoballs and that their surfaces were affected by cocoate anions. The adsorption of cocoate anions reversed the charge and weakened the surface polarity of BaSO<sub>4</sub> particles, driving the formation of aggregates. And cocoate anions induced a change of the BaSO<sub>4</sub> particles surface from hydrophilic to hydrophobic by a self-assembly and transformation process. Due to the self-assembled structure and the surface hydrophobicity, when adding the hydrophobic BaSO<sub>4</sub> into PVC, the mechanical properties of PVC composite materials were significantly improved.

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## 1. Introduction

Barium sulfate, which is commonly referred to as barite, has attracted a great deal of attention and been widely used in many areas due to its high specific gravity, opaqueness to X-rays, inertness and whiteness [1,2]. Barite is one of the most important fillers used to produce polymer composites such as plastics, rubber, paint, and ink. For these industrial applications, the strong polarity of BaSO<sub>4</sub> surface and the weak particle-polymer affinity lead to the phase separation of composites and deterioration of the polymer properties. So various surface modification techniques have been developed to improve the compatibility between BaSO<sub>4</sub> and polymers [3–6].

The extent of hydrophobicity of materials surface is one of the most important properties that affect the final application of the products made from it. Studies have discovered that the hydrophobicity of solid surfaces is controlled by both surface microstructure and chemical composition [7–10]. Consequently, increasing surface roughness and lowering surface polarity can dramatically enhance surface water repellency. During the past decades, tremendous routes have been devoted to the design and controlled fabrication of

hydrophobic materials with functional properties, such as sol–gel method [11,12], situ modification [13,14], layer-by-layer assembly [15,16], chemical deposition [17] and physical coating [18]. Among them, situ modification has been attracting great interest for its great importance in both fundamental research and potential industrial applications.

At present, the industrial preparation procedures of hydrophobic BaSO<sub>4</sub> are as follow: keep the reaction temperature at 30 °C in the precipitation process; then heat the BaSO<sub>4</sub> suspension up to 80 °C in the surface modification process, which uses sodium stearate as modifying agent [19,20]. The processes are energy-consuming for the complex steps. According to the factory data, when the temperature of the BaSO<sub>4</sub> suspension increases from 30 °C to 80 °C, the energy consumption is  $1.3 \times 10^6$  kJ per ton [21] and the durability of surface hydrophobicity is also a great problem. And because the price of stearic acid is rising steadily, substituting friendly modifying agent for stearic acid is extremely promising. The friendly modifying agent should possess the following primary characteristics: (1) make the modification process carry out under the low temperature as possible; (2) have the hydrophilic group and hydrophobic hydrocarbon chain; (3) be safe and friendly to environment. In this paper, provided that the hydrophobic BaSO<sub>4</sub> particles can be prepared in situ with sodium cocoate at 30 °C, it can not only simplify the complex process, but reduce energy consumption as well. For a factory with usual yield of twenty thousand ton

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hydrophobic BaSO<sub>4</sub> particles, this method can save  $7.5 \times 10^6$  kWh on electricity. And the sodium cocoate is a reproducible resource. Therefore, the sodium cocoate is environmentally friendly modifying agent.

Hydrophobic BaSO<sub>4</sub> aggregates of new forms were successfully prepared at 30 °C by a self-assembly and transformation process controlled by cocoate anions. Results from SEM, XRD, FTIR spectra have been gathered together and used to present an investigation of the hydrophobic behavior. And hydrophilic BaSO<sub>4</sub> surface can be modified into hydrophobic by the direction of cocoate anions. The specific properties of the head group and hydrocarbon chain of cocoate anions are strongly related to the formation of hydrophobic surface and play the role of affinity adsorbent during the combination of the BaSO<sub>4</sub> particles with polymer materials [22–24]. Therefore, in this work we focused on studying the formation process of BaSO<sub>4</sub> aggregates in order to examine the specific surface properties of BaSO<sub>4</sub> aggregates. New insights and mechanism schematic models were given.

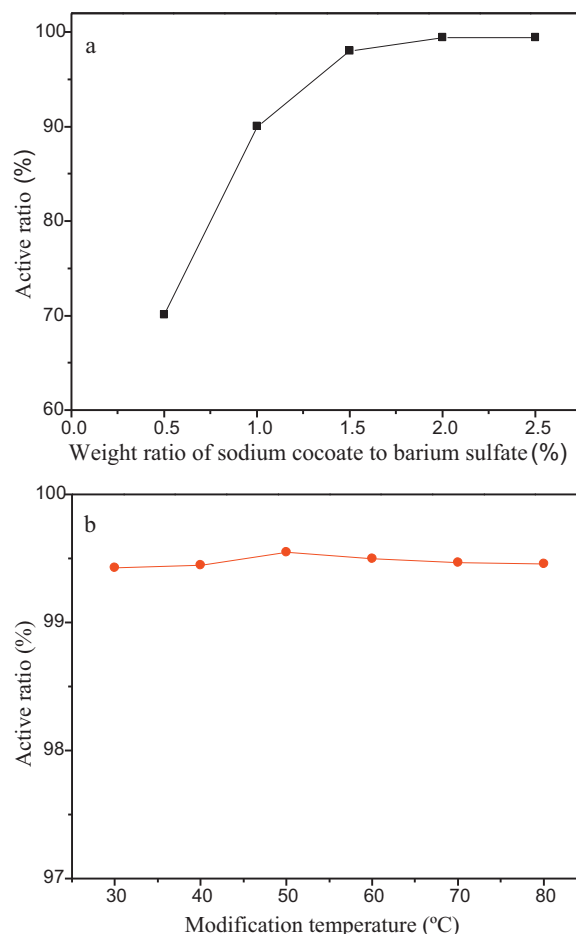
## 2. Experimental

### 2.1. Synthesis of hydrophobic BaSO<sub>4</sub>

Sodium cocoate was obtained by a certain amount of cocinic acid dissolving in 1 mol L<sup>-1</sup> NaOH solution. A facile synthesis procedure employed for hydrophobic BaSO<sub>4</sub> was as follows: The reaction temperature was 30 °C controlled by a constant temperature instrument. The sodium cocoate was added into 100 mL of 0.5 mol L<sup>-1</sup> BaCl<sub>2</sub> solution with vigorously stirring. The weight ratio of sodium cocoate to BaSO<sub>4</sub> particles was 2.0 wt.%. Then, 100 mL (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> solution with the concentration of 0.5 mol L<sup>-1</sup> was added dropwise into the above solution and at the steady drop rate of 40 drops min<sup>-1</sup>. The pH of the mixture solution was altered to 7–8 using NH<sub>3</sub>·H<sub>2</sub>O. The pH value was controlled by pH meter. Several minutes later, the mixture turned turbid gradually and the white precipitate appeared. After finishing the reaction, the mixture was kept under static conditions for 12 h. Finally, the white precipitates were separated from mother liquid by filtration and washed several times with deionized water, dried in an oven at 100 °C for 4 h. The desired products were slightly pestled and put through a 220 mesh sieve for studies.

### 2.2. Characterization

Contact angle (CA) measurements were conducted at room temperature using sessile drop method on OCA-30 Micro (DataPhysics Instruments GmbH, Filderstadt, Germany) with 2 μm droplet of distilled water as an indicator. Surface morphology was examined with scanning electron microscopy (SEM) micrographs by a Hitachi S-4800 spectrometer at 15 kV. For SEM analysis, the samples were dispersed in ethanol absolute, dropped onto carbon-covered copper grids placed on filter and dried at room temperature [25]. Particle size distribution was performed by Laser particle size analyzer (LS-POP, OMEC, China) using water as measure medium. Fourier transform infrared spectra (FTIR) were recorded in the range 400–4000 cm<sup>-1</sup> on a VECTOR-22 FTIR spectrometer (Bruker, Germany) with a resolution of 8 cm<sup>-1</sup> by embedding the prepared powders in KBr pellets. X-ray diffraction (XRD) measurement data of power samples were recorded on a D/MAX-2000/PC diffractometer (Rigaku Corporation) equipped with (Cu Kα) at 40 kV and 200 mA. The zeta potential of BaSO<sub>4</sub> particles at various aging time were measured by a Zetasizer 3000 HS (Malvern) equipped with a microprocessor unit. The unit automatically calculated the electrophoretic mobility of the particles and converted it to the zeta potential using the Huckel and Smoluchowski equation. The



**Fig. 1.** The effect of weight ratio of sodium cocoate to barium sulfate (a) and reaction temperature (b) on the active ratio of BaSO<sub>4</sub> product.

simple-supported beams impact testing machine (ZBC-4) was used for studying the mechanical properties of samples. For mechanical properties analysis, the hydrophobic BaSO<sub>4</sub> particles were added to PVC and the weight ratio of BaSO<sub>4</sub> particles to PVC was about 10:100.

## 3. Results and discussion

### 3.1. Surface hydrophobicity

The active ratio and contact angle of product are often used to measure the extent of hydrophobicity of solid surfaces. Fig. 1 presents the effect of weight ratio of sodium cocoate to BaSO<sub>4</sub> and reaction temperature on the active ratio of BaSO<sub>4</sub> product (AR-BaSO<sub>4</sub>), respectively. Experiments were carried out at different weight ratio of sodium cocoate to BaSO<sub>4</sub> and the AR-BaSO<sub>4</sub> is presented in Fig. 1a. The AR-BaSO<sub>4</sub> is improved with the increase of weight ratio of sodium cocoate to BaSO<sub>4</sub>. When adding sodium cocoate (>2.0 wt.%), the AR-BaSO<sub>4</sub> remains nearly constant. The weight ratio of sodium cocoate to BaSO<sub>4</sub> was now kept constant at 2.0 wt.% and the influence of reaction temperature on the AR-BaSO<sub>4</sub> was investigated. Fig. 1b shows the obtained results. Despite of increasing reaction temperature from 30 °C to 80 °C, a slight increase in AR-BaSO<sub>4</sub> is observable. At 30 °C, the AR-BaSO<sub>4</sub> has reached 99.43%. While using sodium stearate as modifying agent, the AR-BaSO<sub>4</sub> was only 30.03% at the same conditions. Not until the temperature rose to 80 °C did AR-BaSO<sub>4</sub> was 99.42% (picture not presented).

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