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A novel surface modification method for anhydrite whisker

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ABSTRACT

Calcium sulfate anhydrite whisker (CSAW, anhydrous-insoluble) was modified with inorganic-organic surface modification method. The modified-CSAW (M-CSAW) was investigated by field emission scanning electron microscope (FESEM), X-ray powder diffraction (XRD), Fourier transform infrared (FT-IR) spectroscopy, X-ray photoelectron spectroscopy (XPS) and thermogravimetric analysis (TG). The results indicate that trisodium phosphate and stearic acid have remarkable effects on CSAW. The contact angle of M-CSAW reaches up to 108.43°. Trisodium phosphate actives the surface of CSAW compared to traditional methods (acid or base activation approaches), and then chemical reaction occurs on the surface of CSAW between COO^- and Ca^{2+}. The M-CSAW can be potentially applied to whisker/polymer composite materials.

1. Introduction

Calcium sulfate whisker (CSW) has good thermal stability, chemical resistance, perfect structure, low cost, high strength and great stiffness [1]. It is widely used as a reinforcing agent in polymer [2–4], rubber [5], papermaking [6,7] and so on. CSW exists in three types: dehydrate, hemihydrates and anhydrite. The synthetic anhydrite whisker can be further divided into two types (anhydrous-soluble and anhydrous-insoluble). Among the three types, CSAW has the best physical and chemical performances, making itself a preferential filler than many other conventional fillers, such as calcium carbonate and natural fiber. However, the small dimension with high surface free energy leads to readily aggregation [8], which badly affects the performances of the target composites. It seems to be the dominated barrier for the interfacial interaction between whisker and polymer [9]. In order to overcome the aforementioned drawbacks, surface modification is utilized as an efficient way to manipulate the surface properties [10–12], enhance whisker dispersion, and reinforce the matrix [13,14]. The appropriate surface modification strategies and agents play an important role in making whisker/matrix more compatible.

Fatty acids (e.g. oleic acid, palm oil, and stearic acid) are often used as surface modification agents for fillers to provide a hydrophobic surface, aiming to increase the compatibility of filler and polymer. They act as a modifier in some particulate systems because of their intrinsic advantages, including low cost, ease of processing, etc. [15]. Meanwhile, modifying surface with fatty acids can reduce water absorption, prevent interaction from filler particles, and lower the surface energy. These advantages endow them more compatible and easily disperse in organic matrix. In addition, fatty acids provide a variety of benefits to the mechanical properties. K. Molnar et al. [16] have modified calcium sulfate with stearic acid, and investigated the characters of composite. The stearic acid coating gave rise to a drastic change of tensile properties and deformation behavior. J. Y. Liu et al. [17] have prepared polycaprolactone/CSW composite by coprecipitation methods. The flexural strength and impact strength were improved up to 21% and 22% with 15 wt% whiskers. CSAW has best mechanical property among the three types, but studies do not use CSAW as a filler so far, because CSAW is very stable, and the surface has low chemical activity. The inert surface is difficult to be modified with stearic acid directly, although stearic acid has lower surface energy and adhesive energy. If CSAW can be modified with stearic acid, the product could be expected as one of suitable fillers. The mechanical properties of as-prepare composite may be drastically improved accordingly. Finding new method to graft stearic acid onto the surface of CSAW is urgently needed and meaningful.

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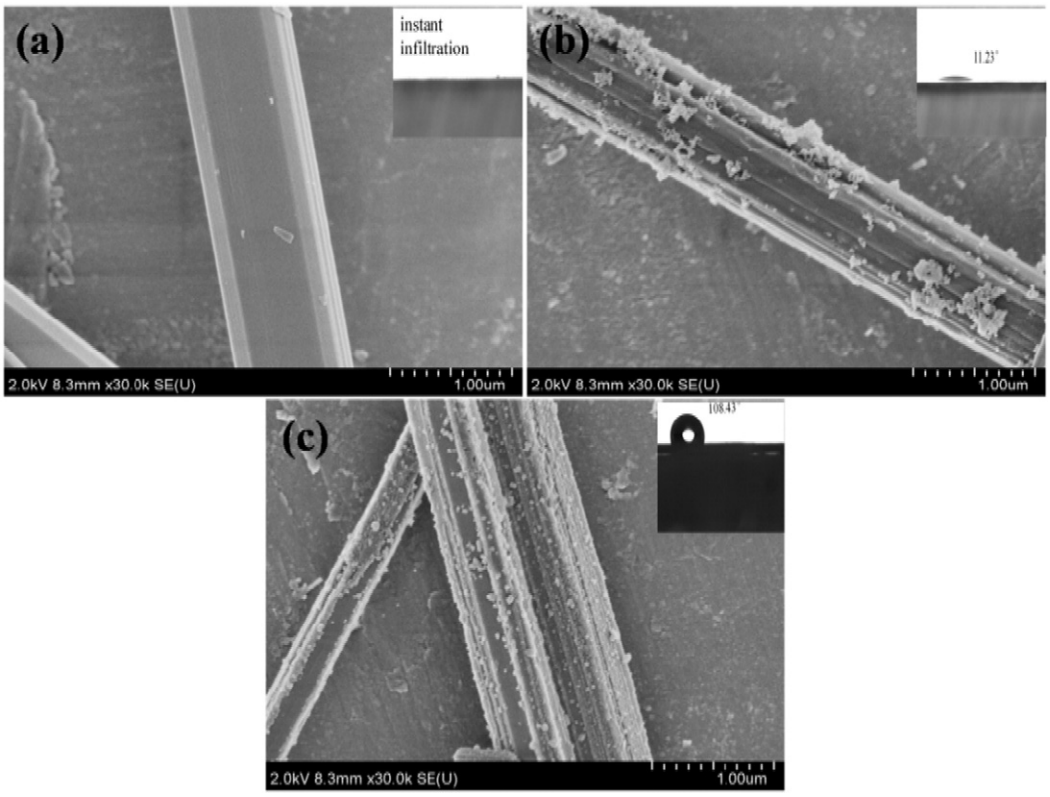

Fig. 1. FESEM images of (a) CSAW, (b) inorganic M-CSAW and (c) inorganic-organic M-CSAW.

In our study, M-CSAW was fabricated via a novel simple method. First, trisodium phosphate was selected to active CSAW surface, and then stearic acid was utilized to modify the surface of CSAW. M-CSAW exhibits remarkable hydrophobic property. The resulting M-CSAW was studied by SEM, FT-IR, XPS and TG to reveal the preparation mechanism.

2. Experiment

2.1. Experimental materials

The main raw materials used in this work including $CaSO_4 \cdot 2H_2O$ and stearic acid were purchased from sinopharm chemical reagent Co., Ltd.; trisodium phosphate and Ethanol were purchased from Beijing chemical reagent plant and Tianjin chemical reagent plant respectively. All chemicals in the experiment were of analytical grade and used directly without further purification.

2.2. Synthesis of CSAW

3.0 g $CaSO_4 \cdot 2H_2O$ was mixed with 60 mL distilled water in a 100 mL stainless steel autoclave. The autoclave was sealed, heated at 140 °C for 2 h, then cooled down to room temperature quickly, filtered, washed and dried in air at 100 °C. The product was dried, and calcinated at 800 °C for 4 h in muffle furnace.

2.3. Surface modification of CSAW

2 g CSAW was dispersed in 100 mL 0.015 mol/L trisodium phosphate solution and under ultrasonic for 2 min. The homogeneous solution was stirred for 10 min, filtered off and washed. The product was dispersed in 100 mL ethanol, and 0.12 g stearic acid was added into the slurry of CSAW heating at 90 °C in the oil bath with magnetic stirring for 5 min, filtered and washed with plenty of ethanol to remove excessive stearic acid. Then the M-CSAW was dried at 100 °C for 1 h.

2.4. Characterization

Water contact angle instrument DSA30, Kruss, Germany. Drops of deionized water (3 μL) were deposited on five different spots of the surface. The values are averages of five measurements. The morphology of CSAW and M-CSAW was conducted with a SU8010/Aztec(X-MaxN) field emission scanning electron microscope (FESEM) from Hitachi Limited using an acceleration voltage of 2.0 kV. X-ray powder diffraction (XRD) pattern was determined by a Philips X'Pert X-ray spectrometer using Cu Kα radiation with a tube voltage of 40 kV and a tube current of 35 mA. FT-IR spectra were obtained on a Nexus infrared spectrometer (Thermo Nicollet. USA), the wave-number range was set from 4000 cm^{-1} to 400 cm^{-1}. X-ray photoelectron spectroscopy (XPS) measurement was carried out by using Thermo escalab 250Xi multifunction electron spectrometer (Thermo Electron Corporation) equipped with an Al Kα X-ray source. The thermogravimetric analysis (TG) experiments were performed on a Netzsch STA-449 F3 apparatus under identical

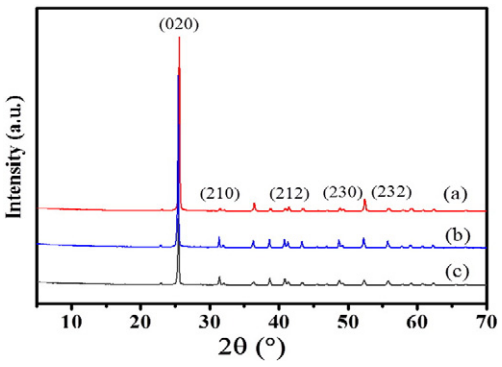

Fig. 2. XRD patterns of (a) CSAW, (b) inorganic M-CSAW and (c) inorganic-organic M-CSAW.