



Preparation and controlled release behavior of halloysite/2-mercaptobenzothiazole nanocomposite with calcined halloysite as nanocontainer

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ABSTRACT

2-Mercaptobenzothiazole was loaded in calcined halloysite to prepare nanocomposite through vacuum loading and polyelectrolyte layers coating. The microstructure and morphology of treated nanotubes and synthetic composite were characterized by X-ray diffraction, Fourier transform infrared spectroscopy, scanning electron microscopy, transmission electron microscopy and automatic gas adsorption analyzer. The total loading and release behavior of 2-mercaptobenzothiazole in tubes with and without polyelectrolyte shell were investigated with the help of UV–Vis spectrophotometer.

Results show that calcination keeps the basic tube structure, expands the inner diameter and shortens the tube length. Halloysite treated at 550 °C has the maximum loading of 8.2 wt%. The release time of inhibitor in uncoated halloysite is 3–10 days, which is closely related to the calcination temperature, and the release rules conform to the first order kinetic model. Polyelectrolyte shell makes it controlled and sustained for composite to release 2-mercaptobenzothiazole under the same condition. When the environmental pH changes from neutral to acidic or alkaline to dissociate the polyelectrolyte layers, 2-mercaptobenzothiazole will be released at different rates immediately. It is concluded that 550 °C treated halloysite is a worthy candidate to prepare halloysite/2-mercaptobenzothiazole composite.

1. Introduction

Coatings are widely used in marine engineering to prevent the structures and ships from seawater corrosion. However, partial destruction of conventional coating not only destroys the appearance and continuity of coating but also causes more and more serious corrosion, leading to a series of economic losses. With the development of science, more and more researches are focused on the preparation of corrosion resistant coating with self-healing ability. Among them the study of nanocontainer/inhibitor composite with feedback mechanism takes a significant part [1–4]. The nanocontainers, whose size is small enough to maintain coating continuity, is capable of supporting inhibitor so as to avoid its direct interaction with coating matrix or external environment. In order to obtain the sustained and controllable release of inhibitors, reservoirs are usually coated with polyelectrolyte shells or blocked openings by stoppers, which are sensitive and responsive to the changes of pH or ion concentration in environment [5–8].

Compared with other nanocontainers like carbon nanotubes, nanoparticles and polyelectrolyte capsules [9–13], halloysite nanotubes

(HNTs) are excellent in many characteristics. Halloysite is an economically viable clay material which has a large storage for industrial production. In addition, it is harmless to creatures and has a hollow tubular structure [14]. With a length of 500–1500 nm, an outer diameter of 40–50 nm and an inner diameter of 15–20 nm, HNTs are able to load active ingredient and belong to mesoporous material [15,16]. When the value of n is 2 in the chemical formula $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot n\text{H}_2\text{O}$, a monolayer of water molecules exists between two curved layers and the interlayer spacing is 10 Å. After the dehydration of halloysite at a certain calcination temperature range, the spacing reduces to 7 Å and the value of n changes to 0 [17,18]. When pH is 4–8, the negative zeta potential of halloysite on the surface is close to the zeta potential of SiO_2 located on the surface layer. Substances with dissimilar charges attract each other, based on which the polyelectrolyte multilayers can be alternately manufactured on the surface of halloysite [19–26]. Studies find that alloy plate coated with a film doped by inhibitor-loaded halloysite show a better corrosion resistance than the specimen coated with blank film in the corrosive NaCl solution. If the coating is damaged to motivate corrosion, the pH

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value or ion concentration around will be easily affected, leading to the dissociation of polyelectrolyte shells or stoppers. Then, the corrosion inhibitor stored in tube will be immediately and freely released to form a new self-repairing film locally to prevent further corrosion [27,28].

Recently, the nanocomposites, inhibitor-loaded halloysite nanotubes with shell or stopper, have attracted much attention in the academic community and industrial sector [29–34]. Nevertheless, from the present research situation, the storage and release capacity of these materials mainly depends on a familiar method that changing the composition of external shell or stopper to modify electrostatic interaction. Furthermore, natural form is the advantage of halloysite, but this advantage also brings limitations and challenges to its further research and application. Since the formation depends on natural conditions to a large extent, compared with the synthetic nanomaterials, halloysite nanotubes from different regions are inhomogeneous and contain different amount of sheet-like impurities. The loading and releasing ability of halloysite is largely conditioned by its tube size. It is found that the total loading of original halloysite for usual inhibitors, benzotriazole (BTA) and 2-mercaptobenzothiazole (MBT), is about 5 wt % [23,35]. With the inner diameter of 15–20 nm, halloysite nanotubes are not large enough to accommodate macromolecular substances, such as some enzymes, proteins and so on. To solve this problem, acid treatment was studied to etch the layer of aluminum oxide at varying temperatures, processing time and acid concentrations. Lumen size increased to 21.5 ± 2.0 nm after removal of 20% aluminum and further expanded to 36.3 nm upon 65% dealumination at 50 °C. The effect of acid etching to enlarge the inner diameter of halloysite is obvious [36,37]. However, because of the complexity and corrosivity of the processes, acid treatment is not propitious to the demand of wholesale industrialization. Researchers have tried to use heat treatment as pretreatment to modify halloysite. During the temperature range of 400–550 °C, the chemical water of nanotube loses due to dehydroxylation and the crystalline structure transforms into amorphous structure. After calcination at 550 °C, halloysite having both the moderate strong acid site and the strong acid site becomes an excellent support for acidic catalyst. The integrity of the tube structure after heat treatment shows a good thermal stability of halloysite [38].

In order to simplify the synthesis process, increase the loading capacity and optimize the controlled release behavior, we researched the effect of varying calcination temperature on the characteristics of halloysite and tried to use them as nanocontainers to prepare the smart HNT/MBT nanocomposite in this paper. The characteristics of the treated halloysite nanotubes and synthetic composites were investigated by series of instruments. The total loading and the release behavior of composites before and after being encapsulated by polyelectrolyte multilayers under simulative conditions were researched. Through analysis and comparison, we obtained the optimum calcination temperature for halloysite as container in preparing halloysite/2-mercaptobenzothiazole nanocomposite.

2. Materials and methods

2.1. Reagents

Halloysite was obtained from Shanghai Gu Yan Industrial Co., Ltd. 2-mercaptobenzothiazole (MBT, AR) was provided by Tianjin Yuan Li Chemical Corp. Sodium hydroxide (AR) and sulphuric acid (AR) were supplied by Tianjin Jiang Tian Chemical Technology Co., Ltd. Poly (styrene sulfonate) (PSS, $M_w \sim 10,000$) and Poly (ethylenimine) (Polymin P, $M_w \sim 75,000$) were obtained from Alfa Aesar (China) Chemicals Co., Ltd. All solutions used in experiments were prepared with distilled water.

2.2. Preparation

2.2.1. Thermal treatment

According to the thermal analysis results of original halloysite, heated temperature was determined preliminarily. In a fiber resistance furnace (SX3-4-13, China), the calcination of halloysite was carried out at selected temperatures for 3 h, after which the samples were cooled in air and marked.

2.2.2. Nanotube loading

The solution of 0.5 g MBT in 25 ml ethanol placed on magnetic stirring apparatus (DF-101Z) was stirred enough time to completely dissolve. Then the treated halloysite sample of 0.6 g was added in the solution and stirring continued to form uniform suspension. The obtained suspension was placed in a PC-3 plastic vacuum desiccator and the sealed device was vacuumized for a period of 50 min using a 2XZ-2 vacuum pump. After the vacuum degree of $1.325E3$ Pa was obtained for 10 min, vacuum pump and vacuum valve were closed to keep the pressure constant for 10 min. The purpose of this step was to make the internal MBT evenly distributed and avoid the accumulation at tube ends. Then, these two steps were repeated again. Finally, vacuum valve was opened to connect the inside with outside for 10 min and return the internal pressure to atmospheric pressure. After this whole cycle of operation, the resulting solution was stirred until the uniform suspension was formed again, and the next cycle was repeated. A complete evacuation process required consisted of 4 cycles of the above, after which the suspension was centrifugalized at a high speed for 1 min in the centrifuge (DT5-1), washed three times to remove the residue of MBT by distilled water, dried at 50 °C for 24 h in the vacuum oven (DGB/20-002) and finally ground into powder.

2.2.3. Polyelectrolyte encapsulation

Loaded samples were immersed in the prepared Polymin P solution at a concentration of 2 mg/ml for 15 min. Subsequently, the solution was centrifuged and washed three times to remove the excess polyelectrolyte. The obtained samples was similarly immersed in PPS solution of the same concentration, centrifuged and cleaned. Finally, 4 polyelectrolyte layers with dissimilar charge were formed alternately.

2.3. Characterization

Thermal analyzer (DSC/TG STA 449 F3 Jupiter made in NETZSCH from Germany) was employed to study the thermal stability of original halloysite with a temperature range of 50–900 °C at a heating rate of 10 °C \cdot min $^{-1}$. The surface morphology of treated halloysite was observed by scanning electron microscopy (Hatchi S-4800 and Genesis XM2 energy spectrometer made in EDAX) at an accelerating voltage of 5 kV. All the samples were sputter-coated with gold-palladium for 30 s before SEM observation. The microstructure of halloysite and composites were characterized by transmission electron microscopy (JEM-2100F). The measurements were performed at 200 kV accelerating voltage. The X-ray diffraction patterns of halloysite, MBT and the composite were measured by an X-ray diffractometer (Rigaku D/MAX 2500X) with a Cu target ($\lambda = 1.54$ Å), at voltage of 40 kV and current of 40 mA. And the 2θ range was from 5 to 80° with a scan speed of 5 ° \cdot min $^{-1}$. The FTIR spectra of halloysite, MBT and the composite were tested as KBr pellets using a BIO-RAD 3000 spectrophotometer in the 4000–400 cm^{-1} region. The specific surface areas and average pore diameter of samples were obtained from N_2 absorption-desorption isotherms at 77 K, measured on an automatic gas adsorption analyzer (ASAP-2050).

2.4. Loading and release behavior

The total loading and release behavior of MBT were investigated by UV–Vis spectrophotometer (UV-3600) in the test range of 200–400 nm.

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