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Controlled growth of magnesium hydroxide crystals and its effect on the high-temperature properties of cotton/magnesium hydroxide composites

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ABSTRACT

Controlled magnesium hydroxide particles were assembled successfully on the surface of cotton fibers for the improvement of flammability and thermal stability of cotton/magnesium hydroxide composites. Unlike previous researches where magnesium hydroxide particles have been blended into polymer matrix, self-assembly of particles onto the fiber surface demonstrated in this research provided substantially excellent properties. The morphology, structure and properties of cotton/magnesium hydroxide composites were characterized. Here, the fibers exhibited a swelling surface after the urea-modification, resulting in the more amounts of magnesium hydroxide crystals growing. Without the presence of sodium chloride, the particles self-assembled into lamellar-like structure on the surface of cotton fibers and into rod-like structures with the presence of sodium chloride thereby enabling us to control the growth of the particles. The vertical flammability test showed that the introduction of sodium chloride resulted in the change of morphology of magnesium hydroxide crystals, which had the important effect on the fire-proofing properties of cotton/magnesium hydroxide composites. The weight loss of origin fabrics, citric acid-modified cotton fabrics with $Mg(OH)_2$ crystals grew with salts and urea/citric acid-modified cotton fabrics with $Mg(OH)_2$ crystals grew with salts were 81.5%, 57.4% and 48.9% respectively when heated to a temperature of 500 °C.

1. Introduction

Magnesium hydroxide (MH) has increased research interests due to their huge surface area, smoke suppressibility, low cost, and low toxicity [1,2]. MH with specific morphologies, especially, has become the focus of considerable interest because of the expectation of novel properties [3]. Methods including solution precipitation, hydrothermal, and electroreduction are some of the approaches used to develop the structures of magnesium hydroxide crystals including rod-like, lamellar-like, belts-like and porous crystals [4–7].

In addition to the methods, the base precipitant, temperature, magnesium source and hydrothermal treatment have an important influence about the morphology, size and agglomeration of MH particles [8]. It has been shown that the chemical nature of the base precipitant is of prime importance. In another approach, the crystallite size, shape, and structure, can be controlled well by choosing different solvents and reaction conditions [9].

Especially, the polymer/magnesium hydroxide crystals composites have received more attention because the addition of the inorganic crystals can improve its properties and expand its applications [10–12]. Assembled of magnesium hydroxide crystals onto the surface of fibers can result in the more improvement of the properties of composites compared with the traditional method [13]. However, the ability to control the self-assembly of the magnesium hydroxide crystals into desired geometric shapes and sizes on the surface of fibers, although possible, has been challenging.

Cellulose, a homopolymer of β-1-4-linked D-anhydroglucopyranose unit, is the highest constituent of natural fibers. The skyrocketing interests on the natural fibers are not only for environmental concerns but also yielding a unique combination of high performance, reactive surface and processing advantages at relatively favorable cost [14]. However, broad substitution of cellulose is mainly thwarted by its poor fire-proofing properties. Many reports are available on obtaining cellulose fibers-based composites with excellent fire-proofing properties. To design and prepare the cellulose-based composites is desired for effectively overcoming the drawbacks of pure cellulose and developing the applications of cellulose.

We have successfully prepared the cotton fabrics/lamellar MH crystals composites by the secondary growth method, which exhibited excellent fire-proof properties compared with origin

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fabrics [15]. In this work, we developed a new simple method of adding salts in the crystal growth for the preparation of the cotton fabrics/MH crystals composites with controlled morphology of MH crystals, including lamellar-like and rod-like MH crystals. The morphology and structure of crystals on the fibers surface was analyzed. In addition, the flammability and thermal stability of original cotton and cotton/MH composites were also investigated. We expect our strategy to fabricate the fabrics coating with inorganic thin films will be of general interest and influence many other fields.

2. Experimental section

2.1. Materials

The cotton fabrics were purchased from Shanghai Textile Research Institute. The warp and weft density of plain weave fabrics was 173 threads/cm and 120 threads/cm respectively, and they were warp of 9.8 tex and weft of 14.75 tex. The cotton fabrics were washed with anhydrous ether in a Soxhlet Extractor at 45 °C for 5 h to remove the wax, grease or other chemicals before the modification.

Anhydrous ether, urea, citric acid, sodium hypophosphite, magnesium chloride hexahydrate, aqueous ammonia (37%), sodium hydroxide, and sodium chloride were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). All the chemical reagents used in the experiment were analytical grade and used without further purification.

2.2. The modification of the cotton fabrics

To introduce more polar groups on the surface of cotton fibers and swelling the cotton fibers for the crystal growth of magnesium hydroxide, the washed cotton fabrics were modified through two methods.

2.2.1. The citric acid-modification

The washed cotton fabrics were treated with citric acid/sodium hypophosphite solutions (the weight (%) of cotton fabrics, citric acid, sodium hypophosphite and water was 3.25:1.8:1.2:97) for 1 h, then took out and washed extensively with double-distilled water and cured at 135 °C for 5 min. The citric acid-modified cotton fabrics were obtained and named as CCF.

2.2.2. The urea/citric acid-modification

The washed cotton fabrics were immersed in the urea and sodium hydroxide solutions (the weight (%) of cotton fabrics, urea, sodium hydroxide and water was 3.25:12:8:80) for 1 h, then took out and washed extensively with double-distilled water and cured at 80 °C for 2 min. Then, the urea-treated cotton fabrics were treated with citric acid/sodium hypophosphite solutions (the weight (%) of cotton fabrics, citric acid, sodium hypophosphite and water was 3.25:1.8:1.2:97) for 1 h, then took out and washed extensively with double-distilled water and cured at 135 °C for 5 min. The urea/citric acid-modified cotton fabrics were obtained and named as UCCF for simplicity.

2.3. Growth of $Mg(OH)_2$ crystals on CCF and UCCF

2.3.1. The crystal growth without salts

Magnesium chloride hexahydrate solutions (0.05 mol/L) and aqueous ammonia solutions (0.2 mol/L) were loaded into a flask at a rate of 4 mL/h. The reaction was continued at 25 °C for 4 days. The CCF and UCCF with MH crystals were obtained and named as CCF—$Mg(OH)_2$ and UCCF—$Mg(OH)_2$, respectively.

2.3.2. The crystal growth with salts

To study the effect of salts on the growth of MH crystals, magnesium chloride hexahydrate solutions (0.05 mol/L), aqueous ammonia solutions (0.2 mol/L) and sodium chloride (80 g/L) were loaded into a flask at a rate of 4 mL/h. The reaction was continued at 25 °C for 4 days. The fabrics with MH crystals were obtained and named as CCF—$Mg(OH)_2$/NaCl and UCCF—$Mg(OH)_2$/NaCl, respectively.

2.4. Measurement and characterization

2.4.1. Scanning electron microscopy (SEM)

The surface morphology of the fibers surface was investigated in a Hitachi S-4800 SEM at an accelerating voltage of 10 kV after sputter coating the samples with gold-palladium.

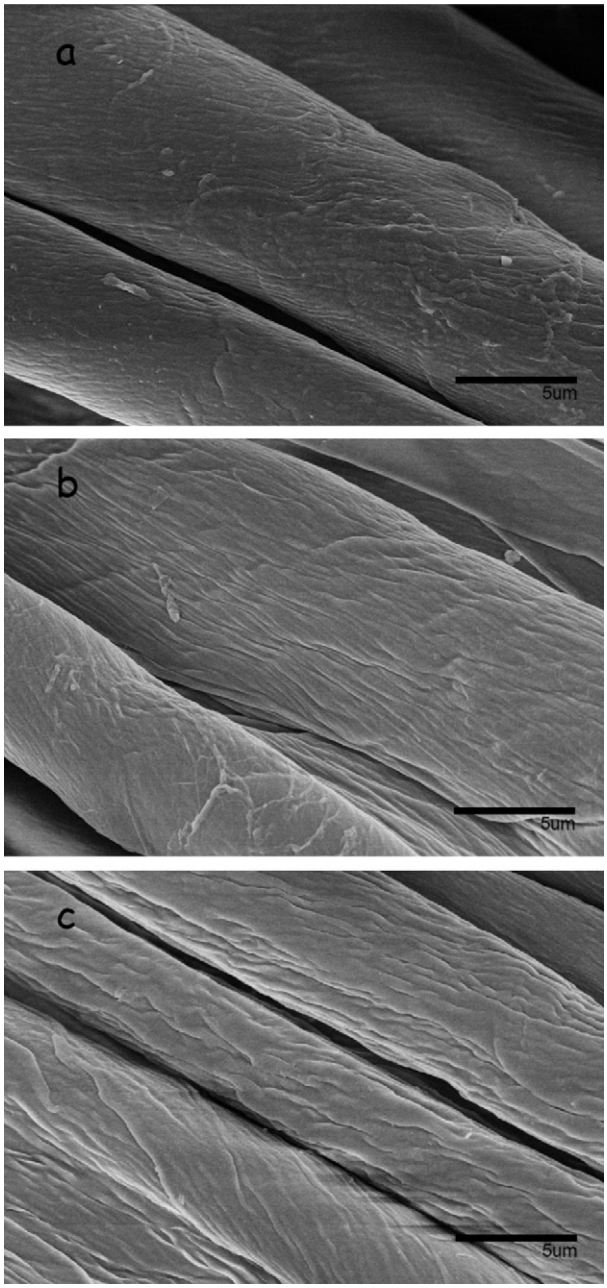

Fig. 1. SEM images of (a) cotton fibers, (b) the fibers with citric acid treatment and (c) the fibers with urea/citric acid treatment.