

Synthesis of Attapulgite Colloid Nanoparticles and its Application on Castor Silk Fibers

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Abstract:In order to develop the multifunctional performance of castor silk, it was finished by attapulgite (ATP) colloid nanoparticles. The structure and antibacterial properties of the castor silk fibers before and after finished were characterized by means of scanning electron microscope (SEM) and antibacterial experiment. The results indicated the ATP particles were rod-shaped with the size of 100 nm, its crystal beam is short and relatively uniform. When the concentration of ATP solution was 10%, the finished silks have good antibacterial property, with the inhibition rate of *Staphylococcus aureus* and *Escherichia coli* were respectively 88.9% and 84.3%. After washing 20 times, it respectively remains 71.4% and 68.5% to *Staphylococcus aureus* and *Escherichia coli* .

Introduction

Attapulgite (ATP, or palygorskite as it often be called) is a kind of crystalline hydrated magnesium aluminum silicate with unique three dimensional structures and has a fibrous morphology with exchangeable actions and reactive -OH groups on its surface[1]. Castor silkworm, known as a kind of India silkworm, has highly adaptable and multi-feeding features, It also no diapause period under optimum conditions. Therefore, the silk of castor silkworm are resourceful, and its economic benefits are very considerable [2,3].

In previous studies of castor silk properties, Wei-Qing Jiang and Bin Zhou make the fiber degumming under the high temperature and high pressure processing condition to improve the ecology of castor silks[4]. Lei Mao has used ATP solution to modify the antibacterial property of mulberry silk and cotton fabrics, and improve their multifunctional requirement[5]. In this paper, castor silk fibers were modified by ATP solution, and its structure and properties were tested. This method can improve the antibacterial property of castor silk, and increase the additional value of castor silk products.

Experiments

Materials

The degumming of castor silks were conducted in laboratory. Purified ATP, glacial acetic acid, ammonia, sodium hydroxide and sodium hexametaphosphate were purchased from Shanghai Chemical Reagent Co, Ltd. *S.aureus* (ATCC 6538) and *E. coli* (ATCC 8099) were obtained from of Department of chemical engineering, Yancheng Institute of Industry Technology(China).

Preparation of the nano ATP particles and the ATP treated castor silk fibers

The experimental technique adopted for nano ATP colloidal solution was as follows: a certain amount of ATP clay were added to the sodium hexametaphosphate aqueous solution(0.5g/l) to obtain the ATP colloidal solution with 1 wt.%, 2 wt.%, 5 wt.%, 10 wt.% and 20 wt.% concentrations. The pH value of the ATP colloidal solution was neutralized to 7.0 with glacial acetic, and then the solution was kept stirring at 30°C for 30 min. At the end, the solution was dealt with ultrasonic oscillations at 30°C for 30 min, and the nano ATP colloidal solution was obtained.

The castor silk fibers were immersed in the ATP colloid solution (with the bath ratio of 1:50)with constant stirring for 30min at 30°C,then washed with tap water several times to remove unfixed materials. The resulting castor fibers were air-dried at ambient temperature to produce the ATP finished castor fiber.

Test methods for the ATP clay and its treated castor silk fibers

Model JSM scanning electron microscope (SEM) was not only used to observe the particles size and morphology of ATP, but also used to the morphology nanoparticles on the surface of castor silk .X-ray photoelectron spectroscopy (XPS) measurements were carried out on VG ESCALAB MkII with an Al Ka X-ray source. The antibacterial activity and the durability of the ATP treated castor fibers were tested against *E. coli* and *S. aureus* by using a shaking flask method according to FZ/T 73023-2006 (China). This method is specially designed for specimens treated with the antibacterial agents under dynamic contact conditions. The percentage reduction was determined as follows:

$$\text{Reduction in cfu (\%)} = \frac{A - B}{A} \times 100. \quad (1)$$

where, A and B are the bacterial colonies of the original castor fibers and ATP treated castor fibers, respectively.

Results and discussion

Synthesis of the ATP Colloidal Nanoparticles

ATP has the structural formula $\text{Si}_8\text{O}_{20}\text{Mg}_5(\text{Al})(\text{OH})_2(\text{H}_2\text{O})_4 \cdot 4\text{H}_2\text{O}$ and its ideal structure is studied by Bradley early in 1940 [6].The chemical structure of the ATP is given in Figure 1. To verify the ATP colloidal nanoparticles on the castor silk fibers, elemental composition analysis were initially carried out via energy-dispersive X-ray spectroscopy (EDS) in Figure. 2. The resulting EDS spectrum shows strong carbon, oxygen, and copper peaks as expected. Carbon and oxygen arise from the castor silk fibers. Three peaks of Mg, Al and Si in the spectrum indicate the existence of ATP Colloidal Nanoparticles in the castor silk fibers.

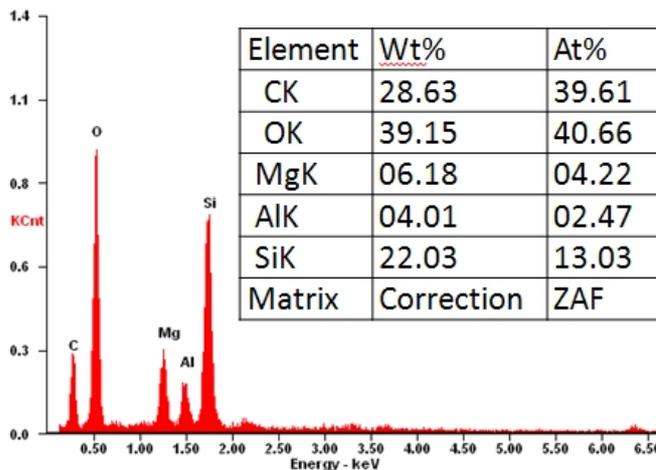
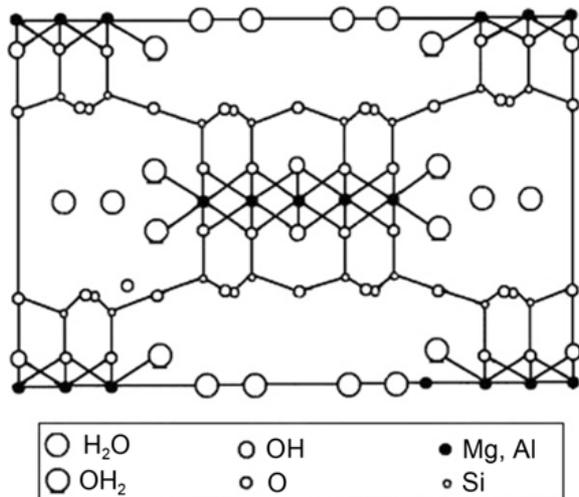


Figure 1. The chemical structure of the ATP.

Figure 2. EDS of the ATP.

The SEM images of the purified ATP nanoparticles in Figure 3. As shown in Figure 3, the ATP nanoparticles showed a rod-shaped structure with diameter of around 100 nm and with length of approximately a few microns, which were typical one-dimensional nano material[7]. The dispersion stability of the nano ATP solution could be characterized by means of distribution and size of the nano particles .Figures 4 showed the three different concentration of ATP nanoparticles solution. When the concentration of ATP was lower than 10wt%, the average particle size was under 100nm.And the concentration of ATP was 15wt%, the nanoparticles aggregated and the size of particle distributed between 500nm to 1000nm.

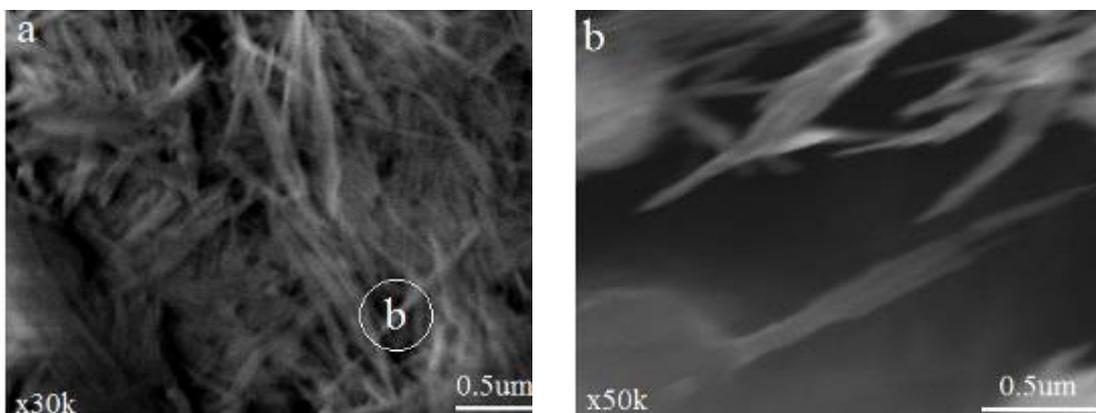


Figure 3. The SEM images of the ATP particles: (a) with magnification 30000 and (b) with magnification 50000.

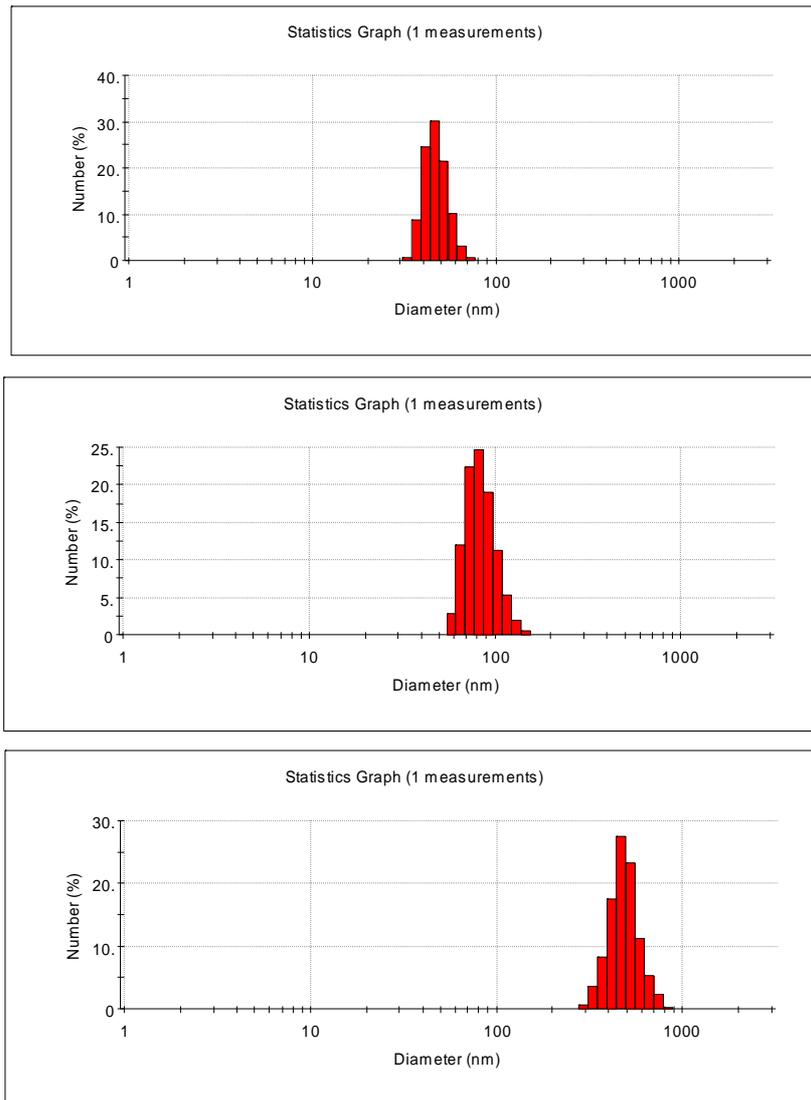


Figure 4. The size distribution of the nano ATP particles; (a) 5 % with dispersion, (b) 10 % with dispersion, (c) 15 % with dispersion

Morphology of the ATP treated castor silk fibers

The morphology and size of the ATP nanoparticle had a greater influence on the structure and performance of the treated fibers. Figure 5 showed the SEM images of the castor fiber' surface before and after treatment by the nano ATP colloidal particles. It could be seen from Figure 5(a) that the untreated castor fiber surface was clean and smooth. However, it became rough and was covered by nano ATP colloidal particles in Figure 5(b),(c) and (d). The particles distributed uniformly on surface of the treated castor silk, which may cause the castor fiber with the possibility of antibacterial ability. The above results showed that the nano ATP colloidal particles could be treated onto the surface of the castor fiber.

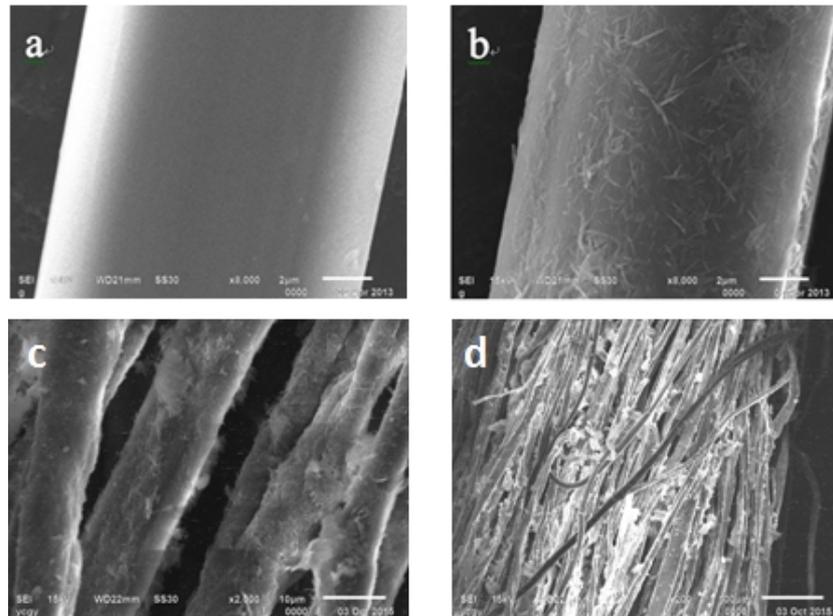


Figure 5. SEM micrographs of the castor silk fibers: (a) untreated sample, (b) (c) (d) treated sample by the 5 wt% ATP colloidal solution which was respectively amplified 8000, 2000 and 200

Antibacterial activity of the ATP Treated Castor Silk

The count of *S. aureus* bacterial colonies of the castor fibers treated by ATP particles were shown in Table 1. Upon increasing the concentration of ATP colloidal solutions from 1 % to 20%, the *S. aureus* bacterial colonies of the ATP treated castor fibers decreased in Figure 3. The bacterial reduction rates increased significantly from 63.4% to 88.9 % to *S. aureus*, and 55.4% to 84.3 % to *E. coli*, when the concentration of the ATP colloidal solution increased from 1 % to 10% .However, the concentration of the ATP colloidal solution increased furtherly, the antibacterial ratio changes little. Therefore, when the mass fraction of the ATP colloidal solution was 10%, the finished castor silk had good antibacterial property.

Table 1 The antibacterial properties of the finished castor silk

Antibacterial parameter sample	The count of bacterial colonies [cfu/ml]		The ratio of antibacterial activity [%]	
	<i>S. aureus</i>	<i>E. coli</i>	<i>S. aureus</i>	<i>E. coli</i>
Blank sample	2.68×10^6	1.21×10^6	—	—
1% ATP	9.80×10^5	5.4×10^5	63.4	55.4
2% ATP	7.60×10^5	4.01×10^5	73.9	66.9
5% ATP	6.54×10^5	3.26×10^5	75.6	73.1
10% ATP	2.95×10^5	1.89×10^5	88.9	84.3
20% ATP	2.7×10^5	1.56×10^5	89.9	87.1

The antibacterial activity of the ATP treated castor fibers after repeated washings

As one of the most important factors to consider for the antimicrobial finish of castors silk fibers is its durability against repeated launderings. The castor silk fibers treated by the concentration of 10% ATP colloidal solution, which were laundered 5 times, 10 times, 20 times. The results are given in Table 2.

Table 2 The antibacterial properties of the ATP treated castor fibers after repeated washings

Antibacterial parameter Washing times	The count of bacterial colonies[cfu/ml]		The ratio of antibacterial activity [%]	
	S.aureus	E. coli	S.aureus	E. coli
0	2.95×10 ⁵	1.89×10 ⁵	88.9	84.3
5	6.98×10 ⁵	3.37×10 ⁵	73.9	72.1
10	7.34×10 ⁵	3.62×10 ⁵	72.6	70.1
20	7.64×10 ⁵	3.81×10 ⁵	71.4	68.5

When washed 5 times, the ratio of antibacterial activity decreased obviously, from 88.9% to 73.9 % to S.aureus, and 84.3% to 72.1 % to E. coli. With the laundering cycles increased furtherly, the antimicrobial ratio have a little change, it still maintained 71.4 % to S.aureus and 68.5 % to E. coli after 20 laundering. The results indicated that increasing laundering cycles over 5 washings only has a small negative impact on the retained antimicrobial activities of the ATP treated castor silk fibers. According to the literature[8], there were broken bonds occurring on the surface of the ATP particles due to the nanostructure, and there were biochemical reactions between the broken bonds and the bacteria, resulting in an inhibition of the bacteria. Furthermore, the strong absorbability of the nano ATP particles reduced the nutrition of the bacteria, which also resulted in an inhibition of the bacteria.

Conclusion

In summary, the ATP nanoparticles showed a rod-shaped structure with diameter of around 100 nm and with length of approximately a few microns, which were typical one-dimensional nano material. When it used to modify the castor silk fibers, the treated fibers have good antibacterial property and the ATP nanoparticles distributed uniformly on the surface of it. With the increase of the concentration of ATP colloidal solutions, the antibacterial ability of the treated fibers were improved significantly. When the concentration of the ATP colloidal solution was 20%, the antimicrobial ability of castor fibers respectively reached 88.9 % to S.aureus and 84.3 % to E. coli. After washed 5 times, the ratio of antibacterial activity decreased to 73.9 % for S.aureus and 72.1 % for E. coli. Upon increasing laundering of ATP treated castor silk fiber from 5 to 20, antimicrobial activities change a little, so it has a small negative impact on the retained antimicrobial property of the ATP treated castor silk fibers.

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