Nanocomposite of Chitosan and Silver Oxide and Its Antibacterial Property

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ABSTRACT: An aqueous emulsion of chitosan nanoparticles encapsulating silver oxide is prepared from silver nitrate and chitosan. The nanoparticles are positively charged with an average diameter of 300 nm. The dried particle has a spherical shape with a 100 nm diameter. The emulsion is applied onto cotton and delivers a durable antibacterial activity against *S. aureus* and *E. coli*, after 20 washings. The coefficient of friction of the treated fabric is similar to that of the untreated cotton fabric. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 108: 52–56, 2008

Key words: nanochitosan; chitosan; antibacterial textile; silver oxide; nanocomposite

INTRODUCTION

The antibacterial property of silver and its derivatives has been extensively studied.[1–3] The materials generally have a long-term biocidal activity, low volatility, and low toxicity to mammalian cells.[4,5] Many of these materials have been prepared using doping techniques.[6–12] A uniform and stable emulsion is believed to be useful in many fields, for instance, direct coating of biomaterials, devices, and medical textiles.

Chitosan, a natural polysaccharide, is a derivative of chitin that comes from the shells and exoskeletons of some crustacea. The polymer is antibacterial, nontoxic, biodegradable, and biocompatible.[13–19] Research work has been done on the preparation of chitosan/silver nanocomposites in solid forms, such as fibres, powders, and films.[19–23]

We have recently developed a new aqueous emulsion of pure chitosan nanoparticles.[24] The emulsion has only chitosan and water, which render its applications when other additives may be undesirable. We report in this article our work on the nanocomposite of chitosan and silver oxide and its application in textiles, specifically the antibacterial performance. Functional finishes are typically applied onto textiles using water as a medium; therefore, the nanocomposite is designed in an emulsion form. It is also known that silver compounds may alter the shade of textiles. To overcome the colour problem, we have tried to obtain the composite with a minimum quantity of silver oxide that is still effective in the bacterial reduction. The durability of the finish on the textile is also considered in the experimental design. Our result indicates that the finish is very long lasting and is still effective after 20 washings.

EXPERIMENTAL

Materials

Chitosan (degree of deacetylation: 95%, molecular mass: 500,000 g mol^{-1}) was purchased from Haidebei (China). The other chemicals were analytical grade from Aldrich without further treatment.

Preparation of the chitosan encapsulating silver oxide nanoparticles

Typically, silver nitrate (5 mL, 5% (w/v) in water) was dropped into 150 mL (w/v) chitosan solution (0.5% w/v in 1% acetic acid) under magnetic stirring. After 4 h, black precipitates were obtained after the addition of sodium hydroxide (5% aqueous solution (w/v)). The precipitates were filtered and rinsed with deionised water until neutral. The precipitates were then dispersed in deionised water (250 mL).[24]

Morphology characterization

The emulsion was characterized with laser scanning, using a Zetasizer 3000HSA; each sample was measured 30 times and the average size and zeta potential were calculated. Scanning electron microscopy (SEM) analyses were performed using a JOEM JSM

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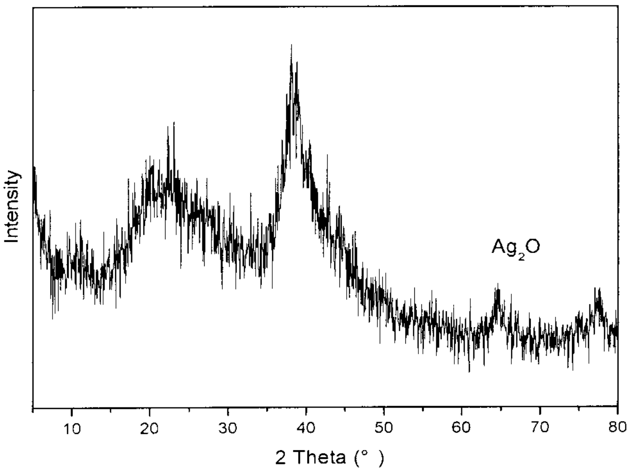

Figure 1 XRD spectrum of the chitosan/silver oxide nanoparticles.

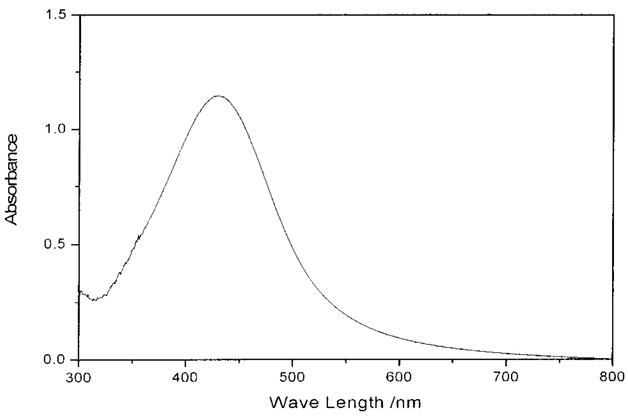

Figure 2 UV–visible spectrum of the emulsion of the chitosan/silver oxide nanoparticles.

6335F; samples were cast on the surface of a prewashed silicon wafer for the test. Transmission electron microscopy (TEM) analyses were performed using a Philips CM-20 TEM; atomic force microscopy (AFM) analyses were performed using a Seiko SPM-2.

Finishing of cotton fabrics and performance tests

The emulsion was applied onto cotton, using a padding method. Cotton fabrics were soaked in the emulsion for 3 min, and then pressed with a pair of revolving rubber rollers at a predetermined pressure. The pick-up of the fabrics was 80%. The fabrics were then dried at 100°C for 3 min and cured at 150°C for 3 min subsequently. The Flask-Shake Method (ASTM E 2149-01) was used for the antibacterial test against *E. coli* and *S. aureus*. The durability to home laundry was performed according to AACTT 63 option 1. The yellowness of the fabric was measured with a Datacolor Elrepho 2000 spectrophotometer according to ASTM E 313 and ASTM D 1925. The coefficient of friction was determined with a Kato Tech KESFB fabric objective tester.

RESULTS AND DISCUSSION

Characterization of the chitosan/silver oxide nanoparticles

The particle analysis indicates that the emulsion has an average diameter of 300 nm with a narrow size distribution (polydispersity: 0.325) and zeta potential of +70 mV. The pH of the emulsion is 6.5, which is similar to the pH of the water used in the preparation. Previous work has reported the stable structure of the hydrogen bonds between water molecules and the amino groups of chitosan, as the water molecules

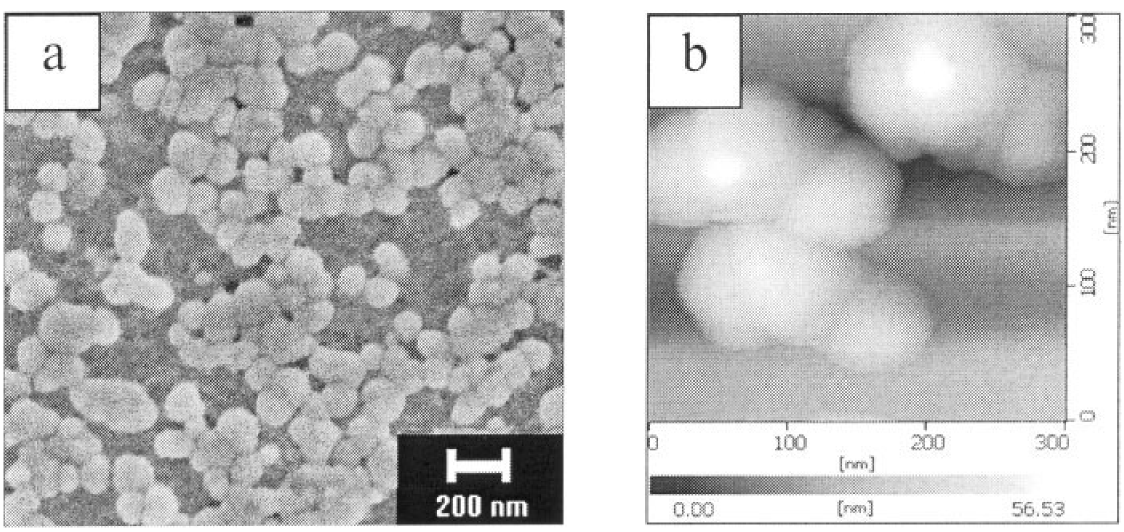

Figure 3 (a) SEM micrograph of chitosan-AgO composite; (b) AFM micrograph of chitosan-AgO composite.

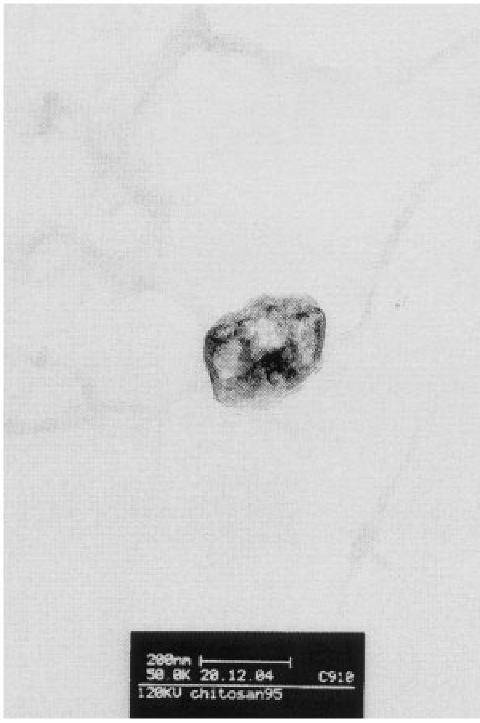

Figure 4 TEM micrograph of chitosan-AgO composite.

act as the providers of proton and the amino groups are the receivers.[25–28] Positive charge of the nanoparticles in the emulsion suggests that the emulsion is stabilized by the hydrogen bond between chitosan and water. When the emulsion is heated above 90°C, the nanoparticles in the emulsion aggregate because of the breakage of the hydrogen bond. Figure 1 shows the XRD spectrum of a dried sample of the emulsion. Two strong peaks at 10° and 20°, which are due to the crystalline region of chitosan,[29,30] are observed. Another two peaks at about 65° and 78° are from crystalline silver oxide.[31–34] Also, The UV–vis spectrum shown in Figure 2 displays a single peak at 440 nm, which is due to the plasma vibration of silver.[19,22,23]

Figure 3(a) shows the SEM micrograph of the nanocomposites. The average diameter of the composite particle is about 100 nm; the particle size is also uniform. The AFM micrograph in Figure 3(b) gives a closer view of the particle. The TEM micrograph in Figure 4 shows the silver oxide nanoparticles are encapsulated into the chitosan nanoparticles; there is more than one silver oxide particle in the nanoparticle. The composite is formed as chitosan molecules entangle with silver oxide during the precipitation in the nanocomposite preparation. The affinity between silver oxide and chitosan is high because of the chelate formation between silver oxide and the amino group of chitosan.[19]

The stability of the emulsion has been monitored with the particle analyzer. There was no PPT and big change in particle size during a 2-month storage at room temperature.

Treated cotton fabric and its antibacterial property

Figure 5 shows the SEM micrographs of the emulsion-treated cotton. The nanoparticles formed rough layers on the surface of cotton fibres. Figure 6 summaries the antibacterial activities of the control sample, the treated sample and the treated sample after 20 washings. The cotton fabric finished with the emulsion of chitosan-silver oxide nanocomposites has a 100% bacterial reduction to *S. aureus* and *E. coli*, respectively. The bacterial reduction remains

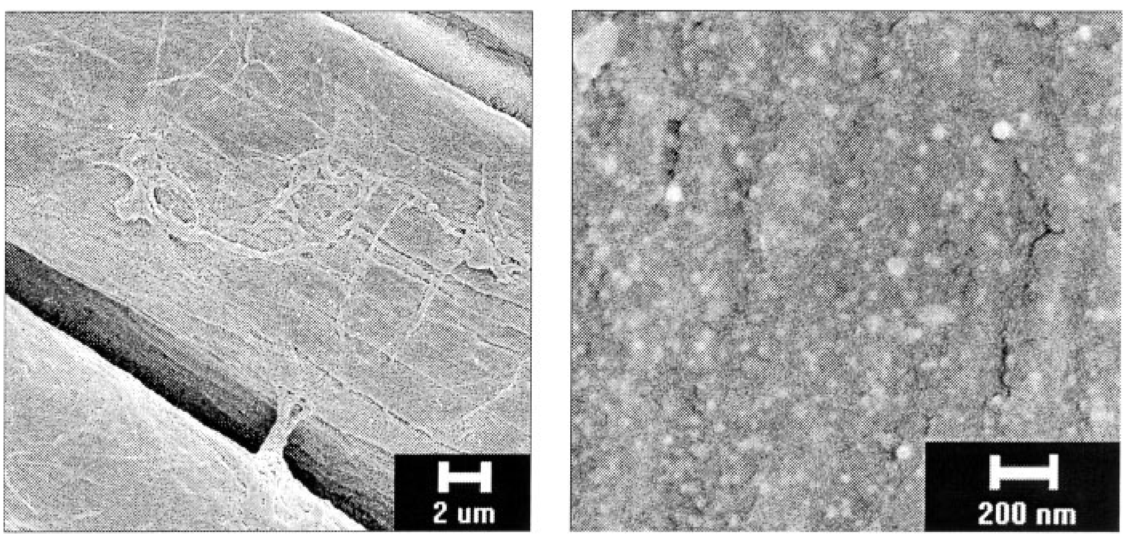

Figure 5 SEM micrographs of the surface of finished cotton fabrics.

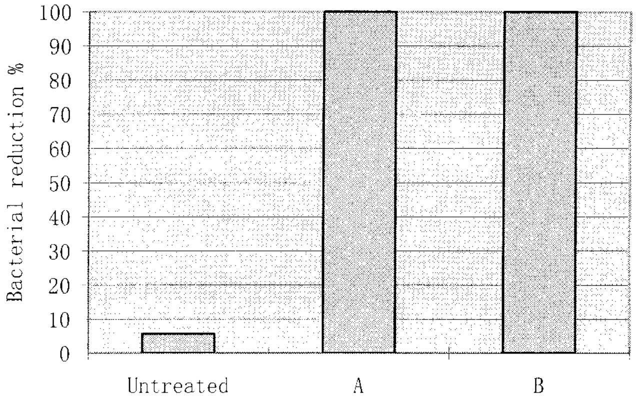

Figure 6 Comparison of bacterial reduction: Sample A - cotton fabric finished with the chitosan/silver oxide nanoparticles, Sample B – Sample A after home laundry of 20 times.

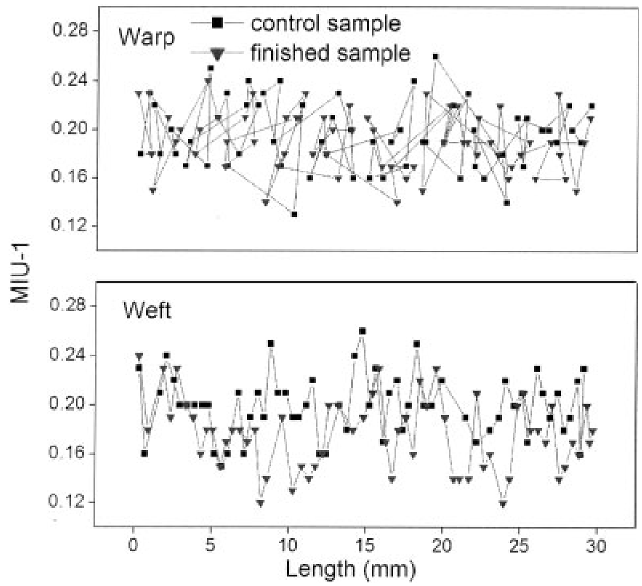

Figure 7 The coefficients of friction of the control and the chitosan-treated fabrics in the warp and weft directions, respectively.

unchanged after 20 washings. A control experiment is performed with chitosan only. The bacterial reduction of the control after 20 washings is 92.1%. However, the bacterial reduction of the nonocomposite-treated sample is still 100%. Therefore, the nanocomposite is effective as an antibacterial agent. Its high durability indicates that affinity between chitosan and cotton is very high. Chitosan and cotton are both polysaccharides, using the ''like dissolves like'' principle, they have similar intermolecular attraction forces, and thus, their affinity to each other is high. Also, chitosan does not dissolve in neutral and alkaline conditions, thus most chitosan on the fabric is not affected during washing. Table I summarizes the yellowness of the untreated and the treated fabrics. The yellowness of the treated fabric is higher than that of the untreated but the change is small. In other words, the visual appearance of the treated sample is similar to that of the untreated. Figure 7 shows the coefficients of friction of the chitosan-treated and the control fabrics, it is discovered that their values are similar, in order words, the effect of chitosan on the fabric handle is small, this can be explained by the low add-on of chitosan onto the fabric, which results in only a small change in the physical performance of the fabric.

TABLE I
Yellowness Indexes of the Control and the Chitosan-Treated Fabrics

Samples	Illum/obs.	ASTM-E 313	ASTM-D 1925
Control sample	C/10	6.957	7.914
	C/2	5.300	6.632
Finished sample	C/10	7.374	8.471
	C/2	5.749	7.202

Illum, illuminant; obs., observer.

CONCLUSION

The chitosan-silver oxide emulsion is effective in bacterial reduction. The emulsion can be easily applied onto textile fabrics using the conventional pad-dry-cure process. The finish is durable and washfast; it remains effectively after 20 washings. As chitosan is not soluble in alkaline conditions, the nanoparticles on the fabric do not dissolute during laundry (the pH of laundry detergents in water is higher than seven; depending on the detergents, the pH can be as high as 10.5). The synergy of chitosan and silver oxide in bacterial reduction enables a very low add-on process. The Kawabata fabric-objective-measurement suggests that the treatment does not affect the handle of the cotton fabric. This is anticipated as the amount of the chemical used is only very small. The high effectiveness is also due to a large surface of the nanocomposite on the fabric surface. The chitosan-silver oxide emulsion may offer another antibacterial finish option for the textile industry.

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