Antibacterial Finishing of Tencel/Cotton Nonwoven Fabric Using Ag Nanoparticles-Chitosan Composite

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ABSTRACT

A silver nanoparticles-chitosan composite was prepared using a microcrystalline chitosan gelatinous water dispersion at ambient temperature and its aqueous solution was applied to the antibacterial finishing of Tencel/cotton nonwoven fabric. The size distribution of silver nanoparticles (AgNPs) was between 4 to 20 nm showed good stability in aqueous solution. The finished nonwoven fabric showed excellent water absorption ability, air permeability and antibacterial activity against *E.coli.*

Keywords: silver nanoparticles, chitosan, antibacterial activity, nonwoven

INTRODUCTION

Nonwoven fabric is one of the fastest growing technical textiles of the global textile industry and is widely used in medical textiles such as wound dressing. An ideal dressing should maintain an optimal physiologic environment to allow the wound to heal at a rapid rate, include prevention of bacterial infection, and provide a moist healing environment [1, 2]. One of the approaches for treating wound infection is the application of biocompatible antibacterial agents.

Chitosan, a bio-copolymer of glucosamine and N-acetylglucosamine units linked by 1-4 glucosidic bonds, is the second most abundant natural polymer after cellulose. It is widely derived from the exoskeletons of insects and shells of crustaceans. Chitosan is a biocompatible polymer exhibiting a great variety of useful biological properties such as anticholesteremic [3] and ionsequestering actions [4]. Also, chitosan inhibits the growth of a wide variety of bacteria and fungi, showing broad spectra of antibacterial activity, high killing rate, and low toxicity toward mammalian cells [5-7]. Chitosan applied to the textile industry, as an antibacterial agent, became popular due to its antibacterial activity coupled with good moisture retention [8-12]. Also, there are many studies showing that chitosan can accelerate wound healing in many clinical cases [13-16].

Silver has a long history as an antimicrobial agent, especially in the treatment of wounds. Silver nanoparticles (AgNPs) show strong inhibitory and antibacterial effects and limited toxicity to mammalian cells [17, 18]. Among the various synthetic methods of preparation of silver nanoparticles, chemical reducing method by using a reducing agent such as sodium borohydrate, citrate or ascorbate in a silver salt solution is most common [19,20]. Synthetic reducing agents are normally associated with environmental toxicity or biological hazards. Therefore the development of silver nanoparticles based on natural extracts is considered as most the appropriate method for environmental reasons. Chitosan was used to prepare AgNPs by reducing Ag^+ ions and AgNPs-chitosan composites were obtained [21-24]. Considering AgNPs attached to the polymer chains, the composite was dissolved and the antibacterial nanofiber nonwoven mats containing AgNPs were electrospun as in our previous work [24].

In this paper, AgNPs-chitosan composite was prepared with chitosan which was used as both the reducing agent and the stabilizing agent in an aqueous medium, and the structure and properties of the composites were characterized. Further, the solution of the composite was applied obtain an antibacterial spunlaced Tencel/cotton nonwoven fabric by a finishing method. The structure and properties of the treated nonwoven fabrics were studied.

EXPERIMENTAL

Materials

Chitosan, with viscosity-average molecular weight of 5.1×10^4 and deacetylation degree of 0.87, was provided by Zhejiang Ao-Xing Biotechnology Co. Ltd., (Zhejiang, and P.R.China). Silver nitrate ($AgNO_3$, 99.5%; Merck), acetic acid (99-100%; Merck), sodium hydroxide (98%; Merck) were used as received. A 35 gms nonwoven fabric of Tencel and cotton fibers was manufactured in TJPU Nonwoven Research Center.

Preparation of AgNPs-Chitosan Composite

Microcrystalline chitosan gelatinous water dispersion was prepared firstly as follows: proper quantities of chitosan flakes were dissolved in 2wt% acetic acid solutions at room temperature and the obtained solution was filtered to remove undissolved particles. Then NaOH solution was added slowly while stirred at 150 rpm with a homogenizer (BRT High-shear Emulsifier, Shanghai, P.R.China) until pH of the medium reach 10.0 to get 15wt% MCCh gelatinous water dispersion. AgNPs-chitosan composite was synthesized by adding 2 mL of freshly prepared 1.0×10^{-2} mol/L $AgNO_3$ solution into 50 ml of MCCh dispersion under constant stirring at room temperature. The reaction was kept for 60 min and the precipitate was filtered, washed with Milli-Q water [24].

The size of AgNPs was observed with a HITACHI H-7650 transmission electron microscope (TEM). The sample was prepared as follows: a drop of aqueous solution was dropped onto a carboncoated copper grids and air dried.

Finishing of Tencel/Cotton Nonwoven Fabric with AgNPs-Chitosan Composite

AgNPs-chitosan composite was dissolved in 0.25wt% acetic acid solution to get a transparent solution. Its zeta (ζ) potential value was determined using a Delsa™ Zeta Potential Particle Analyzer.

The Tencel/cotton nonwoven fabric was impregnated in AgNPs-chitosan composite solution and squeezed between rollers to get 80%wet pick up, then the fabric was dried at 80 ℃ and baked at 140℃for 4min.

Structure and Properties

X-ray photoelectron spectroscopy (XPS) was recorded using a BRUKER AXS D8 DISCOVER X-ray photoelectron spectroscopy employing amonochromated Al-Ka X-ray source, survey spectra were recorded with a pass energy of 200 eV, and high resolution spectra with a pass energy of 50 eV. The bending length of the nonwoven fabric was tested according to DIN EN ISO 9073-7 (1998-10) with the sample size of 40×200 mm. The air permeability property was tested following the standard of DIN EN ISO 9237 (1995-12) using an YG461 air permeability tester. The water absorption ability of the samples was calculated by extra weight ratio through dipping into the physiological saline and removal of excess liquor.

E.coli (KCTC 1041) was selected to evaluate its antibacterial activity. The test method is described as follows: *E. coli* bacterium culture was incubated at 37 °C and controlled at 10^5-10^6 CFU/mL, and then 10 mL of bacterium culture were added to three flasks containing 90 mL of sterilized water, respectively. The finished fabric was placed into one of the flasks and an original nonwoven fabric was added to another. The third one was tested as a blank control. All the flasks were stirred with an orbital shaker at 37°C and then bacterium culture was diluted to 10^{-5} of initial concentration. 1 mL of each diluted solution was seeded into a Petri dish. After pouring Luria-Bertain agar into each dish, the plates were incubated at 37 °C for 12 h. The counts of bacterial colonies were the surviving numbers of *E. coli*.

RESULTS AND DISCUSSION

Characterization of AgNPs-Chitosan Composites

It is widely known that silver nanoparticles (AgNPs) exhibit strong antibacterial activity and have no negative effect on human cells [25]. With the binding interaction between macromolecules and the metal nanoparticles, many polymers were successfully used for nanoparticles synthesis [18, 26, 27]. In the nanoparticles synthesis process, polymer chains act as stabilizer in the form of metal nanoparticles-polymer composite.

Chitosan is an oxygen-rich natural carbohydrate (polysaccharide) consisting of anhydroglucose units joined by an oxygen linkage to form a linear molecular chain which is similar to cellulose. Chitosan was reported as both stabilizer and reducing agent to form AgNPs and AgNPs-chitosan composites formed [28-30]. In the process, when $AgNO_3$ was mixed with chitosan solution, silver atom concentration was primarily reduced and rapidly

complexed with a silver ion to form a dimer cluster, and then the dimer combined with another dimer cluster to be tetramer cluster. Continuous reduction of the Ag^+ solution causes the aggregation of tetramer clusters into nanoparticles [31-32]. The silver clusters and nanoparticles formed are capped by the chitosan chains. The bonds of Ag-C, Ag-N and Ag-O bonds may contribute to the formation of AgNPs-chitosan composites [28]. The size of AgNPs was affected by the parameters of the synthesis process such as the concentration of Ag^+, pH value.

The morphology of AgNPs of the study was observed using TEM and the diameters of particles were calculated with the aid of Digital Micrograph™ software (Gatan, Inc). The selected TEM figure and the histogram of the size distribution are showed in *Figure 1*. As can be seen from this figure, all Ag nanoparticles were homogeneously dispersed and no aggregation was found. The particles showed spherical shape with the particles size distribution of 4-20 nm.

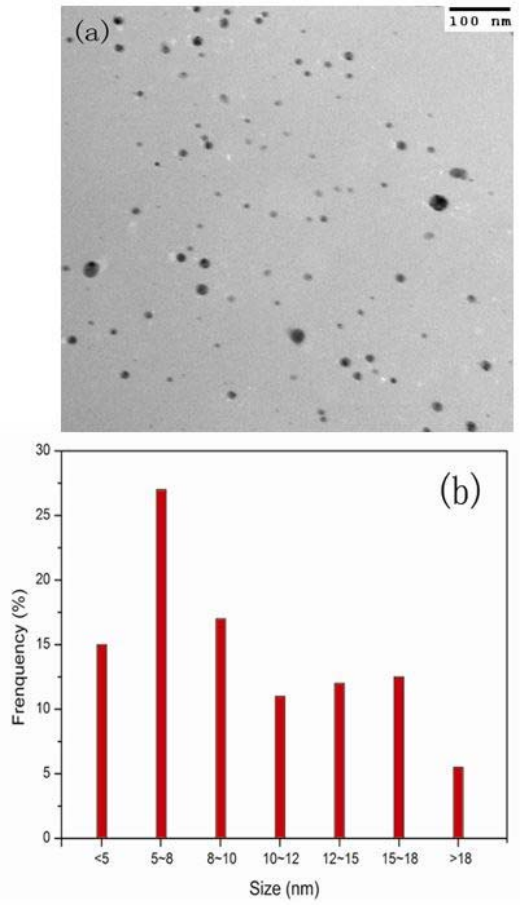

FIGURE 1. TEM image (a) and histograms size distributions (b) of AgNPs.

When the AgNPs-chitosan composite was dissolved in acetic acid solution, a yellow transparent solution was obtained. Its UV–vis spectrum is shown in *Figure 2*. An absorption peak is observed at about 428.4 nm which belongs to surface plasmon absorption band (SPB) of AgNPs [23].

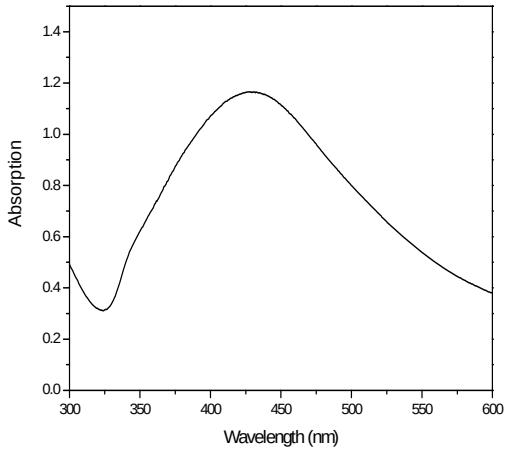

FIGURE 2. UV–vis absorption of Ag-chitosan nanoparticles.

Zeta (ζ) potential is a parameter characterizing electric properties of interfacial layers in dispersions, emulsion, porous bodies and provides useful information about the stability of the systems. As ζ value approaches zero, particles tend to aggregate. The ζ value of the solution was 37.77 mV (*Figure 3*) which indicated the stability of the solution.

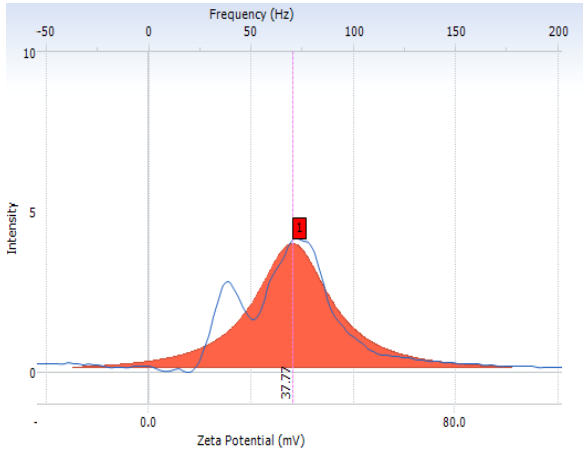

FIGURE 3. The tested results of zeta potential value.

The Structure of Finished Nonwovens

The structure of the samples was characterized by XPS and the Ag 3d spectrum is shown in *Figure 4*. The binding energies of the Ag 3d5/2 and Ag 3d3/2

peaks are 374.2ev and 368.1ev, respectively [33]. The peak positions are practically independent of the Ag concentration and are characteristic of metallic silver. The existence of Ag ensures the antibacterial activity of finished nonwoven. The C (1s), O (1s) and N (1s) spectral peaks are also observed in wide scan spectrum (*Figure 5*).

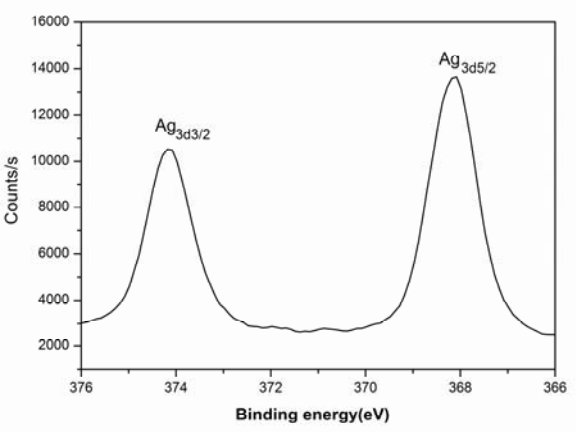

FIGURE 4. Ag 3d XPS spectrum of silver nanoparticles.

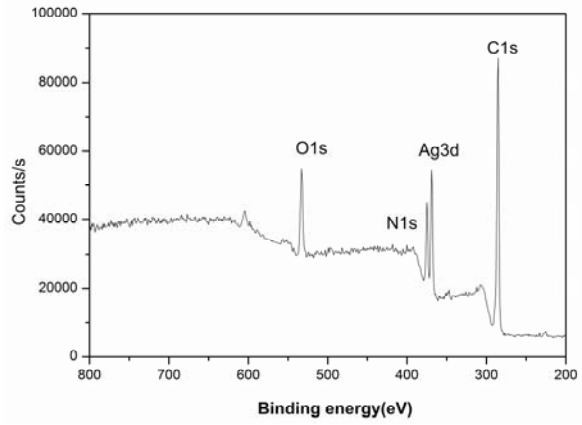

FIGURE 5. The XPS wide scan spectrum of the finished nonwoven fabric.

The Properties of the Finished Nonwovens

Softness, air permeability and water absorption properties are important parameters to evaluate the comfort of the obtained textile. The properties of the finished nonwoven fabric are listed in *Table I*. As we know, cotton and Tencel fibers have an inborn good water absorption property. Besides, the wicking effect enhances their water absorption ability. The value of the original nonwoven was tested as 94.82%. On the other hand，the value of the finished fabric increased to 99.79% which benefits from the good hygroscopicity of chitosan. Air permeability of the finished fabric was slightly increased. The reason is may be due to the structure of the nonwoven fabric being slightly destroyed in the process because the fibers were rather loosely entangled. On the other hand, the bending length increased after treatment which indicates the fabric became more rigid to some extent.

TABLE I. The properties of the nonwoven fabric.

Samples	Bending length (cm)	Permeability ($L \cdot m^{-2} \cdot s^{-1}$)	Water absorption ability (%)
Original	2.05	2285	9482
Finished	2.24	2408	9979

Figure 6 shows a typical antibacterial test result of the nonwoven fabrics against *E.coli* as determined by the viable cell colony count method. As shown in the figure, the *E.coli* viable cell count of the medium with finished nonwoven fabric decreased by 6 log cycles within 8 hours of cultivation compared to the control without which showed significant antibacterial activity.

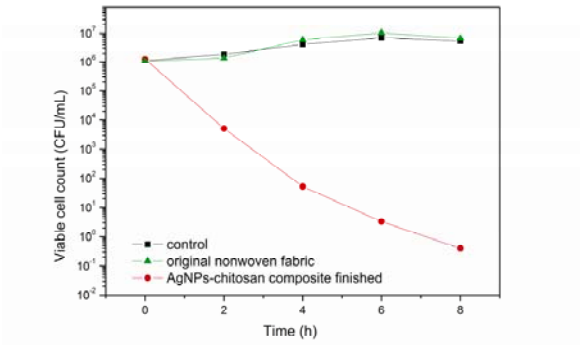

FIGURE 6. Antibacterial effects of the finished nonwoven fabric against *E. coli.*

Chitosan is known to have strong antibacterial properties with MBC value against *E. coli* in the range of 0.0075-1.0% (w/v) [34]. Also previous researches investigated the growth inhibition effect of AgNPs against bacteria, and the MIC (minimum inhibitory concentration) of AgNPs stabilized by poly-(N-vinyl-2-pyrrolidone) (PVP) were 5 and 10 ppm for *S. aureus* and *E. coli* [35], and the MBC (minimum bactericidal concentration) of AgNPs capped by mercaptoacetic acid was 56.5μg mL^{-1} against *E. coli* [36]. The AgNPs-chitosan composite, which has the advantages of both soluble

and unsoluble anti-bacterial agents, proved to be more efficient than either AgNPs or chitosan alone for deactivating bacteria [25], possibly due to the synergistic effect of both the AgNPs and chitosan in the composite. This result indicates that the AgNPs-chitosan composite is a promising antibacterial agent of combining nanotechnology and biotechnology.

CONCLUSIONS

Chitosan and silver nanoparticles are both commonly antibacterial agent used in textile. In this article, silver nanoparticles-chitosan composite was prepared using a green method and was applied to develop an antibacterial nonwoven fabric. The finished nonwoven fabric showed excellent antibacterial activity against *E.coli* as well as good air permeability and water absorption properties. The results indicate that this nonwoven fabric may have great potential for use as a medical dressing material.

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