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Antimicrobial coating of modified chitosan onto cotton fabrics

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ABSTRACT

Chitosan has been applied as an antibacterial agent to provide biocidal function for textiles but has limitations of application condition and durability. In this study, a new N-halamine chitosan derivative was synthesized by introducing N-halamine hydantoin precursor. The synthesized chitosan derivative 1-Hydroxymethyl-5,5-dimethylhydantoin chitosan (chitosan-HDH) was coated onto cotton fabric with 1,2,3,4-butanetetracarboxylic acid (BTCA) as a crosslinking agent. The coatings were characterized and confirmed by FT-IR and SEM. The treated cotton fabrics can be rendered excellent antimicrobial activity upon exposure to dilute household bleach. The chlorinated coated swatches can inactivate 100% of the *Staphylococcus aureus* and *E. coli* O157:H7 with a contact time of 5 min. Almost all the lost chlorine after a month of storage could be recharged upon rechlorination. The crease recovery property of the treated swatches improved while the breaking strength decreased compared with uncoated cotton.

1. Introduction

Cotton is one of the important textile materials applied in healthcare and medical garments. However, cotton can provide suitable media for the growth of microorganisms due to its hydrophilic property retaining moisture, oxygen and nutrients [1]. Until now, a large quantity of antimicrobial agents are incorporated into materials to prevent the infection of pathogenic microorganisms, including quaternary ammonium salts [2–4], metal ions [5,6], N-halamines [7–13]. Besides their excellent biocidal efficacies, some of these antimicrobial agents show different degrees of toxicity to humans. Furthermore [14–16], their easy decomposition is also harmful to the environment [17].

Chitosan, a cationic polymer derived from chitin in the nature, can be as a promising antimicrobial agent due to its biocompatibility, biodegradability, non-toxicity and versatility [18,19]. However, the lack of strong bonding forces between chitosan with textiles results in poor durability [20]. The chemical cross-linked method has been applied to improve the wash durability by using polycarboxylic acid [17,21,22], glutaraldhehyde [23], and genipin [24]. Moreover, UV-curing technology in the field of photocrosslinking and photografting has attracted attention in the chitosan treating [25–27]. Chitosan is a typical pH-sensitive polymer, and cationic nature of chitosan can inactive a variety of bacteria and fungi [28]. It loses antimicrobial activity under alkaline conditions [29]. Many researches have been conducted to overcome the problems and enhance the antimicrobial properties of chitosan through chemical modifications [30–34]. Chemical modification of chitosan can lead to development of a multifunctional finishing of textiles. The modification can be carried out in the C_2-amine groups of chitosan. Hydroxymethyl is a very active group and can react with amide [35] and hydroxyl [36].

In this work, we synthesized a novel N-halamine chitosan derivative. The N-halamine structure enhanced the antimicrobial activity toward different microorganisms as well as the stability of chitosan in wide range of pH. Moreover, the durability of the chitosan derivative has enhanced significantly. The synthesized chitosan derivative was attached onto cotton fabrics using BTCA as a crosslinking agent, which provided cotton with antimicrobial and durable-press functionalities. Compared with other coating methods, the crosslinking finishing process can also improve the washing durability of the textiles. The coating was rendered biocidal function upon dilute household bleach treatment [37]. We have demonstrated synthesis and characterization of the chitosan derivative and application of the antimicrobial agent onto cotton fabrics. In addition, tensile strength and storage stability were also investigated.

2. Experimental

2.1. Materials

Chitosan with a molecular weight of 200 kDa and deacetylation degree of 95% was purchased from Zhejiang Aoxing Biochemical

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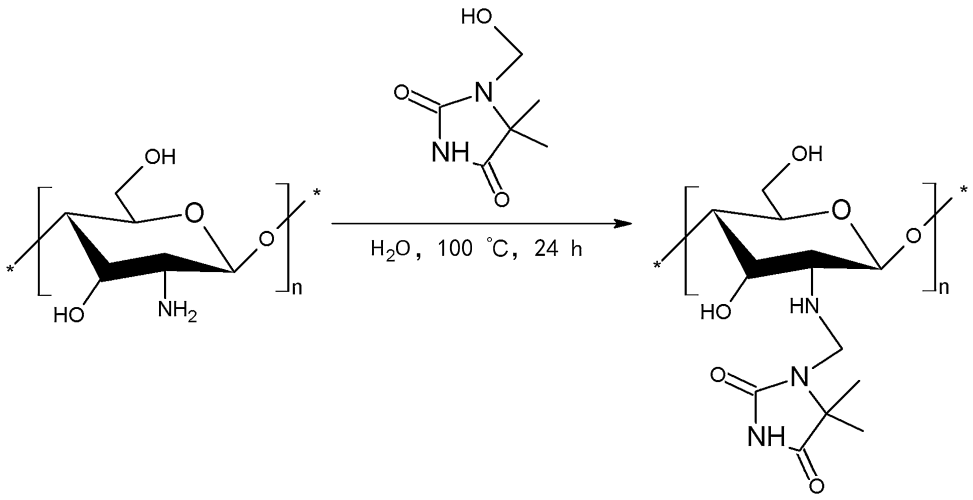

Scheme 1. The schematic description of synthesis of chitosan-HDH.

Co., Ltd., China. 1-Hydroxymethyl-5,5-dimethylhydantoin (HDH) was purchased from TCI, Shanghai; household bleach (the active chlorine content was 5%) and acetic acid (analytical grade) were purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai. All reagents were used as received without further purification. Bleached cotton fabric ($133 \times 72/40^{S} \times 40^{S}$) was supplied by Zhejiang Guandong dyeing and Garment Co., Ltd. The bacteria employed were *Staphylococcus aureus* (ATCC 6538) and *Escherichia coli* O157:H7 (ATCC 43895) (American Type Culture Collection, Rockville, MD). The Trypticase soy agar was from Difco Laboratories, Detroit, MI.

2.2. Instruments

The FT-IR spectra of chitosan, chitosan-HDH and chitosan-HDH-Cl were recorded by a Nicolet Nexus 470 spectrometer in the optical range of 400–4000 cm^{-1} by averaging 32 scans at a resolution of 4 cm^{-1}. All samples were prepared as potassium bromide pellets. The ^{13}C NMR spectrum of chitosan-HDH was recorded on a Bruker AV-300 spectrometer. The SEM images were obtained by SU-1510 field-emission scanning electron microscope (Hitachi, Tokyo, Japan).

2.3. Synthesis of chitosan-HDH

The chitosan-HDH was prepared by procedure as below. 15.9 g (0.1 mol, 97%) of 1-Hydroxymethyl-5,5-dimethylhydantoin (HDH), 16.1 g (0.1 mol, 98%) of chitosan, and 100 ml distilled water were added in a 250 ml round-bottom flask. The mixture was stirred at 100 °C for 24 h. After the reaction, the solvent was removed by filtration, and the precipitate was washed with distilled water thoroughly. Then the product was dried in a vacuum oven at 45 °C for 24 h. The solid powder was weighed to calculate grafting ratio. The synthesis of chitosan-HDH is depicted in Scheme 1.

2.4. Chlorinated procedure of the chitosan-HDH

The chitosan-HDH was soaked in 10% solution of household bleach at pH 7 (adjusted with 1N H_2SO_4) at ambient temperature for 60 min. After chlorination, the samples were washed thoroughly with distilled water to remove free chlorine. The resulting solid powder was dried at 45 °C for 24 h to remove any unbonded chlorine from the coated cotton. The chlorine concentrations loaded onto the samples were determined by the iodometric/thiosulfate titration procedure. The weight percent Cl^+ on the samples was calculated by the following formula:

$$Cl^+\% = (35.45NV)/(2W) \times 100\% \quad (1)$$

where Cl^+ (%) is the weight percent of oxidative chlorine on the samples, N and *V* are the normality (equiv/L) and volume (L) of the titrant sodium thiosulfate, respectively, and *W* is the weight of the sample in grams.

2.5. Coating and chlorinated procedure of cotton fabric

The chitosan-HDH was first dissolved in 3% acetic acid solution at a concentration of 3 wt% with the addition of BTCA and sodium hypophosphite at concentrations of 5 and 6 wt%, respectively. The mixture was stirred to produce a uniform solution at 85 °C for 30 min. Cotton swatches were soaked in the solution for 30 min, and then padded through a laboratory wringer. Two dips and two nips were used to get a wet add-on of 100 wt%. Then the swatches were dried at 100 °C for 3 min and cured at 170 °C for 2 min. After curing, the swatches were soaked in a 0.5% detergent solution for 15 min, washed several times with distilled water to remove unbonded antimicrobial agent, and dried at room temperature. The treated swatches were chlorinated by the procedure described in Section 2.4.

2.6. Biocidal efficacy testing

The biocidal efficacies of the coatings against *S. aureus* and *E. coli* was evaluated by suspensions in pH 7 phosphate buffer solution (100 mM) according to AATCC Test Method 100 standard. An aliquot of 25 μL bacterial suspensions were added to the center of a 2.54 cm square fabric, and then the suspension was sandwiched between two identical swatches by sterile weights. At the contact times of 5, 10, 30 and 50 min for the bacteria, the swatches were quenched with 0.02N sodium thiosulfate solution to remove any oxidative chlorine. Ten-fold serial dilutions were made to all samples and each dilution was plated on Trypticase agar plates, and all plates were incubated for 24 h at 37 °C. Bacterial colonies were enumerated and recorded for biocidal efficacy analysis.

2.7. Stability testing

The storage stability of the covalently bound chlorines on the swatches was evaluated by examine the remaining chlorine on the fabrics. The swatches were stored for 5, 10, 15, 20, 25 and 30 days at

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