Antibacterial Modification of Cellulosic Materials

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The proliferation of bacteria on the surfaces of cellulosic materials during their use and storage can have negative effects on the materials themselves and on consumers. People's demands for materials with antibacterial properties have been satisfied in recent years because of the emergence of various antibacterial compounds. This paper reviews recent research and development progress in antibacterial modification of cellulosic fibers using various biocides such as N-halamines, quaternary ammonium salts, chitosan, triclosan, and nanoparticles composed of noble metals and metal oxides. Antibacterial mechanisms and treating methods for antibacterial cellulosic materials are also involved in this paper.

Keywords: Antibacterial; Cellulose; Fibers; Biocides

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INTRODUCTION

In our daily lives, microorganisms (bacteria, virus, and fungi) can be found everywhere in the atmosphere, and they multiply quickly when nutrients, temperature, and moisture are suitable. There are some differences between the various types of microorganisms. Bacteria, single-celled or noncellular spherical or spiral or rod-shaped organisms lacking chlorophyll that reproduce by fission, are important as pathogens and exist widely in soil, water, and organisms. Viruses are a kind of ultramicroscopic infectious agents that replicate themselves only within cells of living hosts. They do not have complete cell structures, only with a piece of nucleic acid (DNA or RNA) wrapped in a thin coat of protein. Many of them are pathogenic. Fungi (yeast) are made of eukaryotic cells containing cytoderm structure and are reproduced by spores. Some of them are pathogenic to organisms and are difficult to remove.

Microorganisms are widely distributed in water, soil, atmosphere, and organisms. Normally, microorganisms in the atmosphere cannot reproduce due to a lack of nutrition and suitable temperature, and they are easily killed by sunlight in a relatively dry atmosphere. There are more microorganisms indoors, especially in hospitals, outpatient services, *etc*., than outdoors. Textiles can also act as media for the growth of microorganisms because nutrients and moisture is present in textiles containing natural fibers (Purwar and Joshi 2004). Humid environment (relative humidity 75 to 95%) and suitable temperature provide a desirable living environment for the growth of bacteria, fungi, and molds. The dirt, dander, and spilled food on fabrics provide nutrition for the growth of bacteria, and can accelerate the bacterial reproduction. Natural fibers, such as cotton, linen, wool, and silk, are easily stained by microorganisms. As for microorganisms living in textiles, the quantity is different with each other according to the type of textiles and the wearing period. So it is hard to compare the number of microorganisms on textiles and in environments. The growth of harmful microorganisms on the surface of textiles can have bad effects, such as unpleasant odors, stains, and reduction in fabric mechanical strength, affecting both the fabric itself and the users. Thus, antibacterial modification of textiles, the topic of this review, can be highly desirable for their long term use and storage. This review emphasizes antibacterial modification of cellulosic materials by various antibacterial agents including N-halamines, quaternary ammonium salts, chitosan, triclosan, and nanoparticles of noble metals and metal oxides. Also considered are the antibacterial mechanisms of each agent, and the application methods into cellulose substance, such as traditional pad-dry-cure process, dip-coating process, novel microcapsule, and hydrogel process, making this paper different from other review papers (Yuan and Cranston 2008; Simoncic and Tomsic 2010).

Cotton fabrics, made from natural cellulosic fibers consisting of β-1,4-D-glucose, are easily contaminated by microbes, which affects the health of wearers and even causes infection in hospitals where cotton fabrics are widely used (Stana-Kleinschek *et al*. 1999; Ren *et al*. 2008a). Cellulose possesses numerous –OH groups in amorphous regions, and such groups can react with many reactive groups. Thus, the modification of cellulose material is easy and feasible.

In recent years, a large number of antibacterial treatments of textiles have been applied on cotton fabrics, and many researchers have been working to find biocides and treatments to confer durable antibacterial properties to cotton textiles. Antibacterial modification of cellulose materials has provided potential opportunities to expand the application in different fields such as medical, engineering, and food industries (Li *et al.* 2010; Anany *et al.* 2011). This article summarizes some of the most recent research developments in antibacterial modification of cellulose. Many studies have focused on synthesis of novel antibacterial agents with excellent durability and antibacterial ability. Progress related to N-halamines, quaternary ammonium salts, chitosan, triclosan, and nanoparticles of noble metals and metal oxides is presented in this review.

N-halamine

N-halamines are defined as compounds containing one or more nitrogen-halogen bonds. As one of the most effective biocides, N-halamine compounds have attracted much interest from researchers due to their favorable properties, such as rechargeability, non-toxicity to humans, and antimicrobial activity against a broad spectrum of microorganisms (Eknoian *et al.* 1999; Sun and Sun 2001a,b, 2002, 2003, 2004; Liang *et al.* 2006b; Liang *et al.* 2007b; Liu and Sun 2008a,b; Dong *et al.* 2011a; Li *et al.* 2013). Also, cytotoxicity of bacteria-killing triazine-treated cotton fabric was tested, and the result showed that this treatment was not toxic (Ma *et al*. 2014). When exposing N-halamine precursors to NaClO solution, chlorinated nitrogenous structures with antibacterial activity are produced. The oxidative chlorine can be released into the environment, reacting with receptors in the cells of bacteria to finally inactivate microorganisms (Chen *et al.* 2007). After inactivation of bacteria, oxidative chlorine atoms can be regenerated by being exposed to a certain concentration of sodium hypochlorite solution. The rechargeability is a unique feature, which differs from other biocides. It is perhaps for this reason that N-halamines are used in a broad range of applications, such as hospitals, medical devices, and water purification (Dong *et al.* 2011b; Kocer *et al.* 2011a). Most recently, N-halamine compounds were reported as being used in antibacterial modification of cotton fabrics (Sun and Sun 2001c; Liu and Sun 2006, 2008c).

Several N-halamine siloxanes are shown in Fig. 1. The compounds 5,5-dimethyl-3-(3'-triethoxysilylpropyl) hydantoin (Fig. 1a), 3-(3-triethoxysilylpropyl)-7,7,9,9-tetramethyl-1,3,8-triazaspiro decane-2,4-dione (Fig. 1b), 4-(3-triethoxysilyl-propoxyl)-2,2,6,6-tetramethylpiperidine (Fig. 1c), and 3-triethoxysilylpropyl-2,2,5,5-tetramethylimidazolidin-4-one (Fig. 1d) have been successfully synthesized and introduced into cotton fabrics, which made them efficient against a wide spectrum of bacteria (Barnes *et al.* 2006, 2007; Liang *et al.* 2005, 2006b, 2007a,b; Ren *et al.* 2008b). Polymeric N-halamine siloxane was synthesised through a hydrosilylation reaction of poly(methylhydrosiloxane) and tert-butyl acrylate, and the coated cotton with the polymer was stable toward washing (Chen *et al.* 2012). A new N-halamine acrylamide monomer was copolymerized with a tethering siloxane monomer, and cotton treated with this copolymer can inactivate 8-logs of both Gram-negative and Gram-positive bacteria within 5 min contact time (Kocer *et al.* 2011c). Even though these siloxanes can be covalently bonded onto cellulose surface *via* a flexible method, most of them are insoluble in water solution, which makes them not practicable in industrial applications. However, some N-halamine polymers containing N-halamine groups and quaternary ammonium salt groups have potential for industrial application due to their solubility in water (Liang *et al.* 2006a).

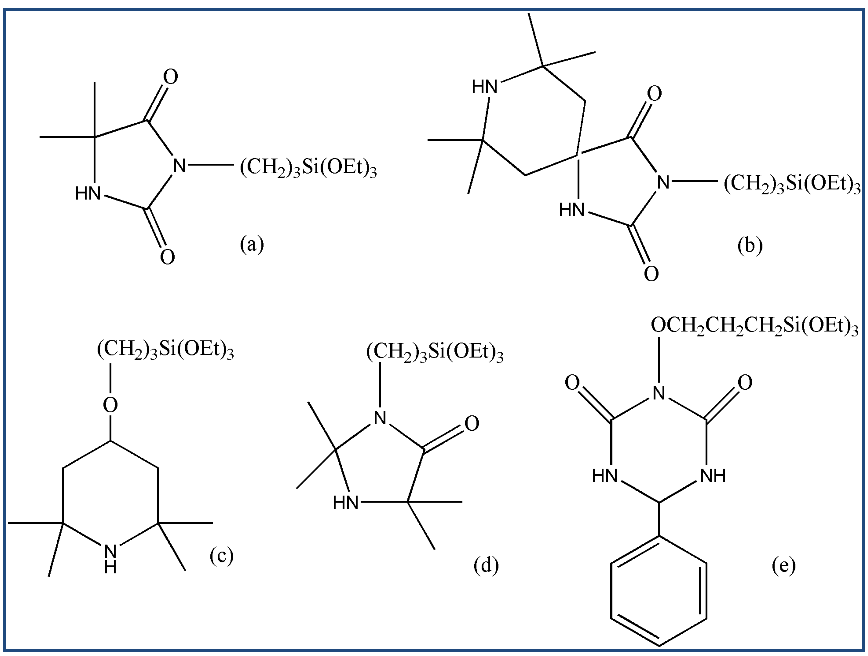

Fig. 1. Chemical structures of N-halamine siloxanes

An N-halamine that contains diol groups can also react with cellulosic fibers *via* a traditional pad-dry-cure process. 3-(2,3-dihydroxypropyl)-7,7,9,9-tetramethyl-1,3,8-triazaspiro(4,5)decane- 2,4- dione was bonded onto cotton. After chlorination, the treated cotton exhibited excellent antibacterial ability, and the chlorine loadings and surface hydrophobicities had effects on the antibacterial efficacies (Ren *et al.* 2009). N-halamine epoxides can also be tethered to cotton surfaces through covalent ether linkages. Also there have been studies using N-halamine epoxides for antibacterial treatment of cotton fabrics (Kocer *et al.* 2011b; Cerkez *et al.* 2012a; Ma *et al.* 2013). Most of these epoxides have relatively low activity toward cellulose materials, and the mechanical strength of cotton could decrease if cross linking agents, such as BTCA, were used.

Several vinyl monomers containing amide bonds were grafted onto cotton by the radical polymerization method (Liu and Sun 2006, 2008c). A kind of vinyl N-halamine acrylamide monomer was polymerized with monomers containing silane-, epoxide-, and hydroxyl groups. After hydrolysis of alkoxy groups, the copolymer can react with cotton fabrics with the formation of silyl ether bonding. The coated fabrics can obtain good antibacterial activity after chlorination. The coatings can inactivate six logarithmic units (base 10) of activity of *S. aureus*, and *E. coli* O157:H7 within a few minutes of contact time (Cerkez *et al.* 2012b). The monomer 3-(4'vinylbenzyl)-5,5-dimethylhydantoin (Fig. 2) can be attached to cotton by admicellar polymerization technology with the help of cationic surfactant (Ren *et al.* 2008a). The monomers can also be applied into many other fabrics due to the active vinyl groups, thus expanding the application of N-halamine compounds.

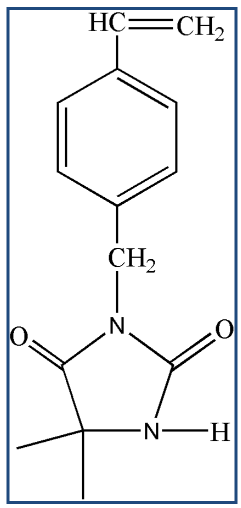

Fig. 2. Chemical structure of 3-(4'vinylbenzyl)-5,5-dimethylhydantoin

Polymeric N-halamines without reactive groups, such as poly(2,2,6,6-tetramethyl-4-piperidyl methacrylate-co-acrylic acid potassium salt) and poly(2,2,6,6-tetramethyl-4-piperidylmethacrylate-co-trimethyl-2-methacryloxy-ethylammonium chloride), have been coated onto cotton fabric *via* a layer-by-layer deposition method without using covalently bonding tethering groups; this approach has broadened the use of N-halamine in numerous fields (Cerkez *et al.* 2011). Ionic precursors are soluble in water which avoids the use of organic solvents. However, the layer-by-layer deposition method may be time-consuming relative to industrial applications.

Quaternary Ammonium Salts

Cationic surfactants, particularly quaternary ammonium salts, are important antibacterial agents that have been widely used in textiles for many years. Quaternary ammonium salts have excellent antibacterial activity toward a broad spectrum of bacteria such as *S. aureus* and *E. coli* (Mahltig *et al.* 2005; Laatiris *et al.* 2008; Massi *et al.* 2009; Murguía *et al.* 2008; Yuan and Cranston 2008).

Two kinds of interaction between quaternary ammonium salts and microbes can occur: a polar interaction caused by cationic nitrogen and a non-polar interaction caused by the hydrophobic chain. The cationic ammonium group of quaternary ammonium salts can attract the negatively charged cell membrane of bacteria. This attractive interaction causes the formation of a surfactant-microbe complex, and this can subsequently interrupt the activity of proteins, including all of the important functions in the cell membrane and even bacterial DNA. Additionally, hydrophobic groups can penetrate into the microorganism and interrupt all of the key cell functions. With the increase of the length of the alkyl chain, the antibacterial ability of quaternary ammonium salts also increased (Gilbert and Moore 2005; Marini *et al.* 2007; Tiller *et al.* 2001). However, there is evidence of skin sensitization for silane quaternary ammonium compounds (NICNAS, 2007).

Quaternary ammonium salts containing silicon groups can be tethered to cellulose *via* covalent bonds. DC-5700 (Fig. 3), a reactive silane quaternary ammonium salt, is widely used in modification of textiles (Sauvet *et al.* 2000). The toxicity experiment with DC-5700 indicated that the median lethal dose (LD50) is 12.27 g/kg ± 0.116 g/kg, and it cannot be absorbed into the body through contacting the treated fabrics. This finding indicates that DC-5700 is probably a safe antibacterial agent (Li *et al.* 2012). And DC-5700 has been used in industry for many years.

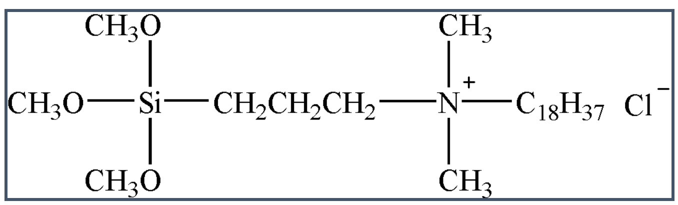

Fig. 3. Chemical structure of DC-5700

Another quaternary ammonium salt, sulfopropylbetaine, which contains the reactive alkoxysilane group, was synthesized and then was covalently bound onto cotton fabrics (Chen *et al.* 2011). The treated fabrics showed durable antibacterial activity against *S. aureus*, *E. coli*, and *C. albicans*. This antibacterial agent is a perfect candidate for environmentally friendly antibacterial treatment of textile.

Polymeric quaternary ammonium salts were also synthesized and used for textile treatment. Polymeric organosilicon was achieved by reacting polysiloxane-bearing chlorohydrocarbon with tertiary amine (Fig. 4) (Shao *et al.* 2003; Summers *et al.* 2003; Lu *et al.* 2007; Owusu-Adom and Guymon 2008; Caillier *et al.* 2009).

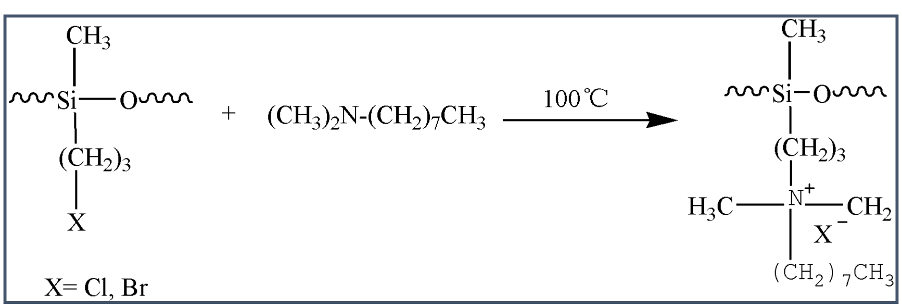

Fig. 4. Quaternization of poly((3-chloropropyl) methylsiloxane) with dimethyloctylamine

The polymer can be coated onto cotton fabric with good antibacterial activity (Sauvet *et al.* 2000; Fortuniak *et al.* 2011). The introduction of antibacterial monomers during polymerization process is a promising approach in the development of non-leaching antibacterial materials. Moreover, the synthesized quaternary ammoniums showed significant antimicrobial activities, which could be exploitable in the development of a wide variety of bactericidal materials.

In recent years, nanoparticles have caught the attention of many researchers. Quaternary ammonium nanoparticles containing sodium alginate and 3-(trimethoxysilyl)-propyl-octadecyl-dimethylammonium chloride with an average size of 99 nm were synthesized by the method of ionic gelation (Fig. 5). The nanoparticles were loaded onto cotton fabrics *via* a pad-dry-cure method. The treated cotton can inactivate >99.99% *E.coli* and *S. aureus* even after 30 laundry cycles (Kim *et al.* 2010). The efficient antibacterial activity of the coatings makes this kind of nanoparticles to have potential in future industrial application.

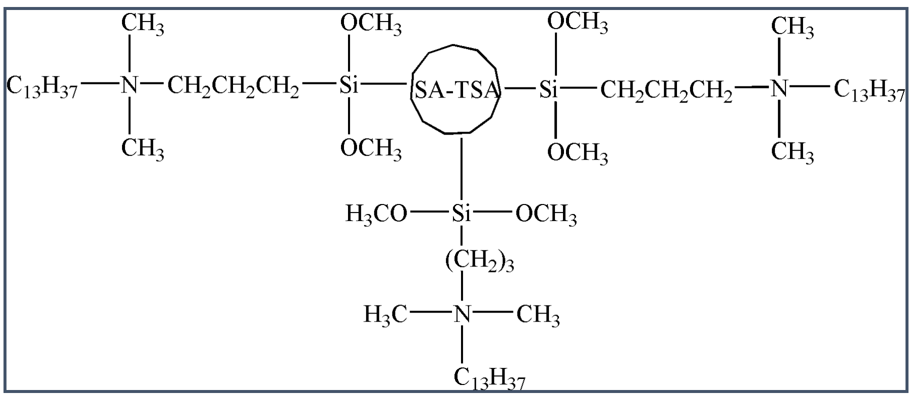

Fig. 5. Chemical structure of SA-TSA nanoparticles

Quaternary ammonium groups have also been attached onto chitosan and N-halamine compounds in order to improve the antibacterial activity of quaternary ammonium salts. N-(2-hydroxy)propyl-3-trimethyl ammonium COS chloride (Fig. 6) and

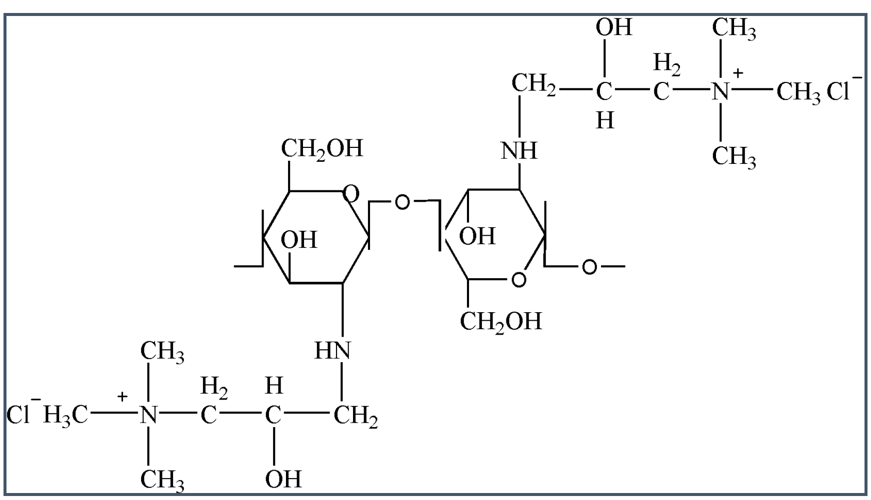

Fig. 6. Chemical structure of N-(2-hydroxy)propyl-3-trimethyl ammonium COS chloride

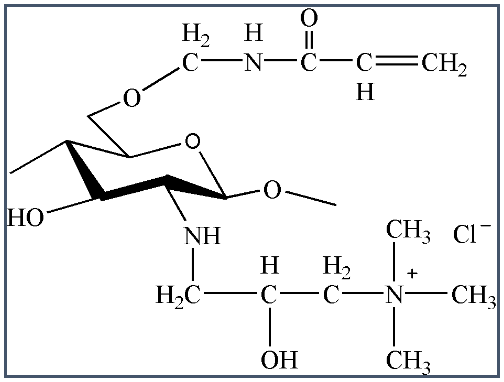

Fig. 7. Chemical structure of *O*-acrylamidomethyl-*N*-((2-hydroxy-3- trimethylammonium) propyl) chitosan chloride

O-acrylamidomethyl-*N*-((2-hydroxy-3- trimethylammonium) propyl) chitosan chloride (Fig. 7) were coated onto cotton, which then exhibited good antibacterial activity. However, the hand feeling of cotton could be affected after being treated by chitosan derivatives (Seong *et al.* 2000; Lim and Hudson 2004a). A series of polymeric quaternary ammonium salts containing N-halamine groups have been synthesized (Fig. 8), and they showed good solubility in water and antibacterial activity against a wide range of bacteria (Kou *et al.* 2009; Cerkez *et al.* 2011).

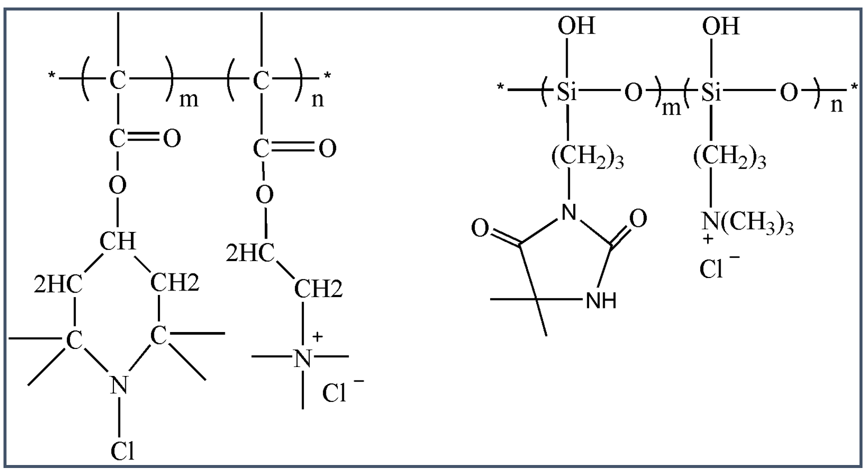

Fig. 8. Chemical structure of polymeric quaternary ammonium salts containing N-halamine

A novel wastewater treatment agent, a water-soluble quaternized cellulose derivative, was synthesized and exhibited high flocculation capacity and effective antibacterial activity. The agent (Fig. 9) was effective in flocculating of montmorillonite

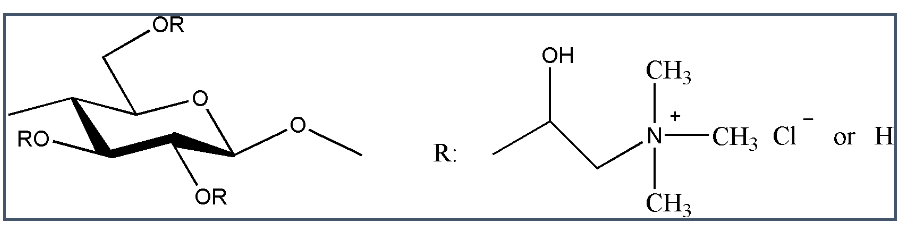

Fig. 9. Chemical structure of quaternized cellulose

suspensions over a wide range of pH values and had the ability of strongly inhibit the growth of *E. coli* and *S. aureus* (Song *et al.* 2009) which makes it have potential application in water treatment.

Chitosan

Chitosan, designated as poly-β-(1-4)-D-glucosamine or poly-(1,4)-2-amido-deoxy-β-D-glucose, is a deacetylate of chitin, which is mainly derived from shells of shrimps and other sea crustaceans (Fig. 10). The main mechanism for antibacterial ability of chitosan is charge interaction between cationic amino groups of chitosan and negatively charged molecules on the bacteria cell surface in acidic aqueous solutions, resulting in the disruption of the cell membrane. This interaction affects the permeability of cell and ceases intracellular transport or leakage of intracellular biomaterial (Lim and Hudson 2003). Also, chitosan can interact with DNA of microorganisms to inactivate essential proteins. As a result, bacteria will be inhibited or killed (Chung and Chen 2008; Dodane *et al.* 1999). Another possible mechanism has been studied as complexation between amino groups on chitosan and trace metals outside bacteria cells, which is essential for the growth of microorganisms (Martínez-Camacho *et al.* 2011).

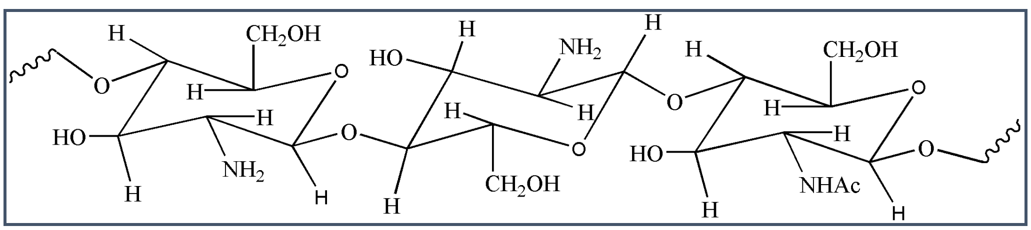

Fig. 10. Chemical structure of chitosan

In addition to antimicrobial activity, chitosan has some essential advantages such as non-toxicity, biocompatibility, and biodegradability, which make it an ideal material for antibacterial treatment of textiles. Chitosan can be used as an additive for spinning antimicrobial fibers (Kumar *et al*. 2004; Fan *et al.* 2006; Haider *et al.* 2010) and as a finishing agent for surface modification of cellulose, cellulose/polyester, and wool fibers (Öktem 2003; Huang *et al.* 2008; Sadeghi-Kiakhani *et al.* 2013).

The technology of microcapsules has been used to attach chitosan to cotton fabrics. Chitosan-based microcapsules were grafted onto cellulose by a novel non-toxic procedure. Cellulose was irradiated by UV light followed by functionalization with chitosan emulsion. The treated cellulose with enhanced antibacterial property can inactivate 100% of *S. aureus* and *E. coli* within 48 h contact time (Alonso *et al.* 2010). Another kind of polyelectrolyte-multilayer microcapsule was made by a layer-by-layer (LbL) deposition method, and the capsule was very efficient to kill *E. coli* (Cui *et al.* 2010).

Besides the above technology of microcapsules, a traditional pad-dry-cure process was also used for antibacterial treatment of cotton by chitosan. Chitosan was modified by cationic hyperbranched dendritic polyamidoamine containing terminal methyl ester end groups, and the modified chitosan was applied onto cotton fabric using a padding method. The treated cotton fabric was found to have a good antibacterial activity, compared to unmodified chitosan (Klaykruayat *et al.* 2010). Core–shell nanoparticles of nano silver as core and chitosan-O-methoxy polyethylene glycol as shell were made and successfully coated onto cotton using the conventional pad-dry-cure method. Fabrics treated with core-shell nanoparticles showed excellent antibacterial activity against *E. coli* and *S. aureus* (Abdel-Mohsen *et al.* 2012). Nanoparticles of chitosan were synthesized and coated onto cotton *via* traditional pad-dry-cure process with the help of crosslinking agent (Hu *et al.* 2012; Hebeish *et al.* 2013). However, the mechanical strength could be affected due to the involvement of the crosslinking agent. Multifunctional cotton fabrics were made by using chitosan/AgCl-TiO_2 colloid *via* a pad-dry-cure process. The Antibacterial test showed that chitosan with AgCl–TiO_2 colloid has good antibacterial activity and inactivates 100% of *S. aureus* and *E. coli* at concentrations of 4 g/L and 10 g/L of chitosan/AgCl–TiO_2 colloid, respectively (Arain *et al.* 2013).

In recent years, stimuli-responsive polymeric systems have been made in the modification of textiles. Also, hydrogels can be used in cotton fabrics in very thin layers (Nacer Khodja *et al.* 2013). The stimuli-responsive hydrogel PNCS nanoparticles with size of about 85.2 nm have been used for modification of cellulose fabrics in the presence of BTCA as crosslinking agent (Bashari *et al.* 2013). As a disadvantage, chitosan's weak solubility in water solution might inhibit its potential use in industry (Channasanon *et al.* 2007; Gupta and Haile 2007; El-Shafei *et al.* 2008). For improvement of its water solubility, a reactive quaternized form of chitosan has been prepared by introducing acrylamidomethyl groups, which can react with cellulose by forming covalent bonds under alkaline conditions (Fig. 11) (Lim and Hudson, 2004b).

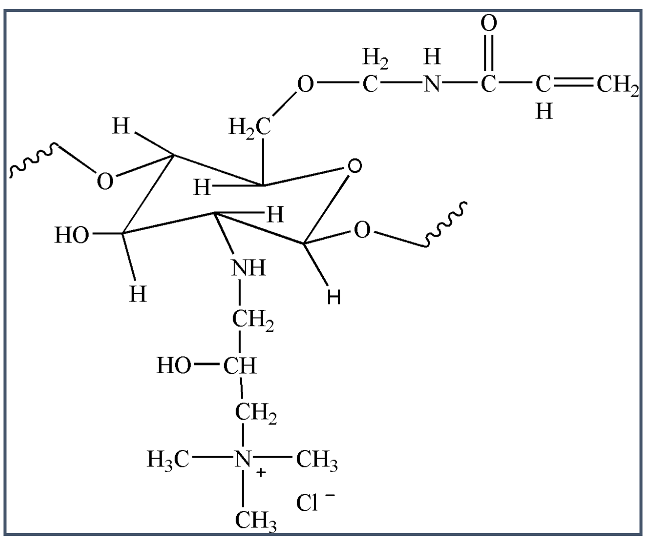

Fig. 11. Chemical structure of reactive O-acrylamidomethyl-N- (2-hydroxy-3- trimethyl ammonium)propyl chitosan chloride

Triclosan

2,4,4'-trichloro-2'-hydroxydiphenyl ether (triclosan) has been found to be one of the most efficient antimicrobials. The compound has been used for more than 30 years and exhibits a broad range of antimicrobial activity in the modification of numerous consumer products such as soaps, creams, and toys (Goetzendorf-Grabowska *et al.* 2004; Orhan *et al.* 2012; Ibrahim *et al.* 2013a,b). After contact with a microorganism, triclosan inhibits the active site of enoyl-acyl carrier protein reductase enzyme (ENR), which is essential to the fatty acid synthesis of bacteria and the building of the cell membrane

(Ocepek *et al.* 2012; Perumalraj 2013). It has been shown that triclosan can result in skin irritation (Hahn *et al*. 2010).

Numerous methods have been used for application of triclosan onto cotton textiles. Mostly, the traditional pad-dry-cure process has been used widely. Cotton fabrics have been used for single-stage antimicrobial finishing by various concentrations of DMDHEU and triclosan. With the increase of DMDHEU and triclosan concentration, the antimicrobial activity also increased (Perumalraj 2013). The commercially available triclosan has been used for durable antibacterial finishing of cotton/polyester fabrics by the dip-dry-cure process. Factors of pH, triclosan concentration, curing temperature, and curing time have been investigated (Ibrahim *et al.* 2010). The antibacterial property against *S. aureus*, and *E. coli* was tested before and after 10 washing cycles. Results showed that fabrics treated under softening finishing formulation exhibited higher antimicrobial activity and slightly lower K/S values (Ibrahim *et al.* 2010).

Triclosan has been coated onto cotton fabrics by two different ways. In the first method, triclosan had been dissolved into β-cyclodextrin solution, and then β-cyclodextrin was grafted onto cotton. The second method was that cotton was immersed in triclosan water–ethanol solution and then grafted by β-cyclodextrin derivative. An antibacterial test showed that fabrics treated with the first method had a more durable antibacterial activity than the second method (Peila *et al.* 2013).

A kind of microencapsulated biocide containing melamine–formaldehyde polymer wall and triclosan core was successfully prepared and was used as antibacterial modification agent of cotton fabrics by the screen printing method. The treated fabrics were tested against *S. aureus* and *E.coli*. The results showed that microcapsules with triclosan had good antibacterial activity, and they can be applied onto cellulose successfully without changing the fabric properties (Ocepek *et al.* 2012).

Nanoparticles of Noble Metals and Metal Oxides

Recently, some organic biocides have been reported to be harmful to a certain extent (Friedrich *et al.* 1998; Chen *et al.* 2006; Dimitrov 2006). Application of noble metals and metal oxide nanoparticles would be an ideal alternative by virtue of their low corrosion rates and low toxicity (Christensen *et al*. 2010), favorable mechanical properties, and good biocompatibility (Shiraishi *et al.* 2009).

Some of these noble metals and metal oxides that have been used for antibacterial activity are TiO_2, ZnO, CaO, MgO, CuO, Ag_2O, Al_2O_3, and CeO_2 (Yonezawa and Kunitake 1999; Stoimenov *et al.* 2002; Xiong *et al.* 2003; Yeo *et al.* 2003; Nersisyan *et al.* 2003; Jeong *et al.* 2005; Park *et al.* 2006; Nirmala Grace and Pandian 2007; Zhang *et al.* 2008; Rai *et al.* 2009; Raghupathi *et al.* 2011). Among these, TiO_2 particles have been shown to be very effective in inactivating bacteria including Gram-positive and Gram-negative bacteria (Sato and Taya 2006; Skorb *et al.* 2008; Kangwansupamonkon *et al.* 2009). TiO_2 can obtain good oxidizing ability when illuminated under UV light (Huang *et al.* 2000; Rincón and Pulgarin 2003; Schmidt *et al.* 2006). An electron hole pair is generated on the TiO_2 surface because of the photon energy. After adsorbing hydroxide ions or water onto the TiO_2 surface, the hole in the valence band can react with them, and finally a hydroxyl radical is produced. Furthermore, an electron in the conduction band can reduce O_2 to generate superoxide ions. Both electron holes and hydroxyl radicals are extremely reactive when in contact with organic substrates (Kangwansupamonkon *et al.* 2009). Studies of TiO_2 as a photocatalyst for photolysis of microbial organisms, such as viruses, bacteria, and cancer cells have been reported, and its potential use in the sterilization of medical devices, food packaging, sanitary ware surfaces, as well as textiles was also widely studied (Sunada *et al.* 1998; Blake *et al.* 1999; Nonami *et al.* 2004; Maneerat and Hayata 2006).

Cotton fabrics deposited and grafted by nanoparticles with self-cleaning property have been successfully prepared *via* an aqueous sol process at low temperature. And these TiO_2-coated cotton fabrics presented permanent self-cleaning properties, such as photocatalytic decomposition of dyes and antibacterial activity after photodegradation (Wu *et al.* 2009). A well-adherent surface of titanium oxide nanoparticles was produced on cellulosic fibers at low temperature from an aqueous titania sol, which was obtained *via* hydrolysis and condensation reactions of titanium isopropoxide in water. SEM images of the formed titania films revealed a semi-spherical particle morphology with grain size of about 10 nm in diameter. The coated substrates showed substantial bactericidal properties under different testing conditions. Possible mechanisms for the antibacterial activity have been discussed (Kangwansupamonkon *et al*. 2009; Pasqui *et al*. 2011). The stability of the titania coatings was investigated by comparing the UV transmission of coated fibers before and after repeated washing (Daoud *et al.* 2005).

TiO_2 has been coated onto the cotton surface by a dip-coating process. Apatite-coated TiO_2 was coated onto cotton textiles by dip-coat technique, and their antibacterial performance against *S. aureus, E. coli*, and *Micrococcus luteus* was detected under black light, visible light, and dark conditions. In addition, the coated cotton fabrics were found to be nontoxic to human dermal fibroblasts (Kangwansupamonkon *et al.* 2009). And another study indicated that cotton fabrics with antimicrobial, self-cleaning, UV-protective properties were achieved by dip-coating (pad-dry) and a solvothermal (exhaustion) sol-gel processes with silica and titania sols. Antibacterial properties of the coated fabrics against *S. aureus* were detected (Onar *et al.* 2011).

Nanoparticles of noble metals and metal oxides have created a new potential field in scientific research for continuous investigations because of their ideal properties. The application of noble metals and metal oxides nanoparticles has already been demonstrated as being practical for use in nanoparticle biocides. Considering the significant role of textiles in our daily life, the use of nano-materials has been very much welcomed.

COMPARISON

N-halamines are biocides that are active against a broad spectrum of microorganisms, such as bacteria, fungi, and viruses. They have many favorable properties such as rechargeability and non-toxicity to humans. In addition to the covalently bonded N-halamine compounds, some N-halamine materials have adsorbed halogens (*e.g.* chlorine) on the surface of the treated fabrics which might produce an unpleasant odor and limit their applications in some specific areas (Li 2003).

Quaternary ammonium salts are also active against a broad spectrum of microorganisms. The antimicrobial activity of quaternary ammonium salts depends on the length of alkyl chain, the number of cationic ammonium groups, and other specific groups. Some quaternary ammonium salts could leach out from textiles due to lacking of reactive functional groups, and the treated fabrics have poor wash durability.

Chitosan has many advantages such as non-toxicity, biocompatibility, and biodegradability. But chitosan has week adhesion ability to cellulose. Crosslinking agents have been used to enhance the binding ability to cellulose fibers. But the treatment has a negative effect on the mechanical strength and hand feeling of cotton fabrics.

Triclosan is a broad spectrum antimicrobial agent with a relatively low MIC against many common bacteria. However, it could cause bacterial resistance and break down to toxic polychlorinated dioxins (Larsen 2006). Owing to health and environmental issues, some retailers as well as governments in Europe have banned the use of triclosan.

Nanoparticles of noble metals and metal oxides can inactivate microbes at very low concentrations either in free state or in metal oxides. Silver is by far the most widely used in textiles as well as in wound dressings (Hermans 2006). However, silver nanoparticles could be used for skin-contact uses and so people can potentially be exposed to the nanoparticles through dermal, oral, or inhalation pathways (Windler *et al*. 2013).

CONCLUSION

Increasing attention has been focused on antibacterial cotton textiles because of the threats from numerous pathogenic bacteria and viruses nowadays. Customers are seeking comfortable, health-saving, and good-looking textiles. Given all of these demands, numerous producers in textiles industries and researchers have been studying the modification of cotton textiles with antibacterial properties. Antibacterial cotton textiles modified by biocides such as silver, quaternary ammonium salts, and triclosan at finishing stage are already available on the market. The use of some other biocides, such as chitosan and N-halamine, is still in the development stage.

While antibacterial cotton textiles provide advantages in protection of wearers from bacterial attack, drug resistance and toxicity of breakdown products to the environment also need to be taken into account. It has been reported that the long historical use of Ag has led to measurable background concentration in the aqueous environment, between 0.03 and 1000 ng/L (Luoma 2008; USEPA 2010). However, various studies have revealed that nano-Ag and triclosan in the environment are easily removed by wastewater treatment, and quaternary ammonium salts are biodegradable and are also expected to rapidly hydrolyze (USEPA 2007, 2008b). The long-term advantages and potential disadvantages caused by antibacterial cotton textiles should be considered at the same time. Nowadays, developing new kinds of antibacterial composites with efficient inactivity property is still in urgent need. It is hoped that antibacterial cellulosic materials can be used in various applications in people's daily life and protect individuals from microorganisms attack from such microbes as bacteria, fungi, and viruses.

With continuous emergence of new pathogenic microorganisms and expanded drug resistance, further developing a new antimicrobial material with superior performance, lack of drug resistance, and stronger antibacterial efficacies is still necessary. With the increase of people's healthcare awareness, how to develop antibacterial textiles with long durability, high safety, and good antibacterial efficacy, and how to apply the antibacterial textiles in a wider area will be the theme of future antibacterial materials industry.

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