Durable Antibacterial Finish on Cotton Fabric by Using Chitosan-Based Polymeric Core-Shell Particles

Weijun Ye,[1] John H. Xin,[1] Pei Li,[2] Kam-Len Daniel Lee,[2] Tsz-Leung Kwong[1]

[1]*Institute of Textile and Clothing, The Hong Kong Polytechnic University, Hung Hum, Kowloon, Hong Kong, People's Republic of China*
[2]*Department of Applied Biology and Chemical Technology, The Hong Kong Polytechnic University, Hung Hum, Kowloon, Hong Kong, People's Republic of China*

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ABSTRACT: Cotton fabric with excellent antibacterial durability was obtained when treated with chitosan-containing core-shell particles without any chemical binders. These amphiphilic nanosized particles with antibacterial chitosan shells covalently grafted onto polymer cores were prepared via a surfactant-free emulsion copolymerization in aqueous chitosan. Herein, two core-shell particles, one with poly (*n*-butyl acrylate) soft core and another with crosslinked poly(*N*-isopropylamide) hard core, were synthesized and applied to cotton fabric by a conventional pad-dry-cure process. Antimicrobial activity was evaluated quantitatively using a Shake Flask Method in which the reduction of the number of *Staphylococcus aureus* cells was counted. The results showed that treated fabric had an excellent antibacterial property with bacterial reduction higher than 99%. The antibacterial activity maintained at over 90% reduction level even after 50 times of home laundering. The fabric surface morphology as well as the effect of latex particles with different core flexibilities on fabric hand, air permeability, break tensile strength, and elongation was investigated. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 1787–1793, 2006

Key words: chitosan; core-shell polymers; antibacterial activity; nanoparticles; cotton fabric

INTRODUCTION

Since the first concept of ''antibacterial finishing for textiles'' emerged in 1941,[1] textile industry has made significant advances in developing antibacterial fibers and agents. In its early stage, antibacterial finishing focused only on the protection of the quality and integrity of textile substrates. People have not realized until recently that it is more important to protect wearers against the spread of bacteria and diseases. Today, textile materials are used widely in various environments, and antimicrobial treatment is rapidly becoming a prerequisite for textile goods used in hospitals, hotels, sports, and personal care industries. However, there is an increasing public concern for possible effects of antibacterial finishing on environmental and biological systems. An ideal textile antibacterial finishing should not only kill undesirable microorganisms and stop the spread of diseases, but also fulfill three other basic requirements.[2] First, safety: the product should not be excessively toxic to human and the environment and should not cause skin allergy and irritation. Second, compatibility: the product must not present negative influences to textile properties or appearances and must be compatible with common textile processing. Third, durability: the product should be able to endure laundering, drying, and leaching. Researchers are now focusing on safe, durable, and environmentally friendly natural substitutes.

Chitosan (CTS), a β-(1,4)-linked polysaccharide of D-glucosamine, is the deacetylated form of chitin, the second most abundant natural polymer in the world. Refined from the shells of crabs, shrimps, and other crustaceans, chitosan is nontoxic, biodegradable, and biocompatible, and has long been used as a biopolymer or a crude material in pharmaceutical and medical field, papermaking, and food processing.[3] Because of its polycationic nature, chitosan shows good antibacterial activity against various bacteria and fungi.[4] Experiments have proved that chitosan can stop the growth of a number of gram-positive and gram-negative bacteria by inhibiting the normal metabolism of microorganisms through the ionic interaction at cell surfaces and eventually killing the cell.[5]

As a natural renewable resource with unique property, chitosan is one of the safest and most effective antibacterial agents. A number of textile materials including cotton, silk, nylon, PET, and nonwoven polypropylene (PP) fabrics have been modified with chitosan or its derivatives, and excellent antibacterial activity as well as good mechanical properties after the

Correspondence to: J. H. Xin (tcxinjh@inet.polyu.edu.hk).
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treatment have been reported.[5–10] However, the lack of strong chemical bonding with textile substrates became the major drawback for chitosan antimicrobial application because of the problem in durability against repeated laundering. Chemical modification of chitosan with fiber-reactive groups[11,12] and the addition of polymer binder or crosslinker[13–15] in finish solution were reported to have a high durability, with over 80% bacterial reductions after 50 laundering cycles.

Latex technology has long time been used for coating and painting applications. Narrow dispersed latex particles not only form a uniform and continuous coating on substrate surface but also provide a strong adhesive force due to the large surface area of particles. More and more textile finish processes utilize latex technology,[16] such as crease-resistance, water-repellency, and wet-strength treatment. Recently, we have reported a successful synthesis of latex particles with functional core-shell structures in which antibacterial chitosan was covalently linked to polymeric cores.[17] Herein, we used these nanoscaled particles as new antibacterial agents for cotton fabric antibacterial finish. The unique core-shell structure rendered excellent antibacterial durability to cotton fabric. Moreover, the treatment did not change fabric appearances and surface morphology. Cotton fabric with better air permeability was achieved.

EXPERIMENTAL

Materials

Chitosan (CTS, medium molecular weight 80,000, 75–85% deacetylation, Aldrich, St. Louis, MO) was dissolved in 0.6% acetic acid at 60°C followed by filtration to remove insoluble impurities. Scoured and bleached plain woven 100% cotton fabric (142 g/m^2) was washed with nonionic detergent and then rinsed with deionized water before finishing. Butyl acrylate (BA, Aldrich) was purified by distillation under reduced pressure. *N*-Isopropylamide (NIPAM, Aldrich) was recrystallized twice from hexane and toluene mixture (5 : 1) and dried in vacuum overnight. *N*-*N*′-Methylenebisacrylamide crosslinker (MBA) from BDH Chemical Ltd. (Poole, England) was used as received. *Tert*-Butyl hydroperoxide (TBHP) initiator was obtained from Aldrich as 70% aqueous solution and was further diluted to 20 m*M* as a store solution. Magnesium chloride (BDH Chemical Ltd.) and acetic acid (Riedel-de Haen, Seelze, Germany) were used without further purification. Fixapret® CL was from BASF, Germany. Freshly deionized and distilled water was used as the dispersion medium.

Synthesis of core-shell particle

Chitosan-poly(butyl acrylate) (CTS-polyBA) was synthesized followed our previously reported procedure.[17,18] For the preparation of chitosan-poly(*N*-isopropylamide) (CTS-polyNIPAM) particles, the procedure is similar except that 1 wt % of *N*-*N*′-methylenebisacrylamide crosslinker (MBA, based on the weight of NIPAM) was added as a core crosslinking agent.

Antibacterial finishing

The cotton antibacterial finish followed a pad-dry-cure method. Fabric specimens ($\sim 20 \times 40$ cm^2) were immersed into the polymerized latex solution for 3–5 min, and padded through a laboratory pad machine (Rapid Vertical Padder, Taiwan) under a nip pressure of 1 kg/cm^2 with a wet pick-up of $\sim$ 100%. After the dip-pad procedure was repeated one more time, the samples were dried in an oven at 100°C for 5 min and subsequently cured at 150°C for 4 min. After rinsed with running tap water, the treated samples were dried again for further tests.

Measurement and characterization

Mechanical properties of cotton samples before and after the treatment were measured with KES-FB instruments under standard temperature and moisture condition (20°C, 65% RH). Air permeability was performed with an automatic air-permeability tester (KES-F8-AP1, Kato Tech Co.) by measuring air-resistance of a constant air flow through a fabric specimen from and into the atmosphere. To evaluate fabric hand and stiffness property, bending rigidity and hystersis of bending moment were obtained from a Pure Bending Tester (KES-FB2, Kato Tech Co.). Testing samples were cut into 20 $\times$ 20 cm^2 in size. Tensile strength was carried out with an Instron Tensile Tester-4411. Breaking strength and elongation of test strips (2.5 cm in width) along both warp and weft directions were recorded.

Scanning electron microscopy (SEM) of particle and cotton fabric was obtained from a Leica Stereoscan 440 SEM. For particle samples, a drop of diluted latex solution ($\sim$ 200 ppm) was spread onto a clean glass surface and dried in a dust-free environment at room temperature. Cotton fabrics were cut into small pieces and fixed on a standard SEM sample holder by double-coated carbon conductive tab. All samples were sputter-coated with a thin layer of gold in vacuum before the SEM measurement.

To check the durability of antimicrobial treatment, accelerated wash fastness followed the AATCC Test Method 61-1996. An AATCC standard wash machine (Atlas Launder-Ometer) and detergent (AATCC Standard Detergent WOB) was used. Samples were cut into 5 $\times$ 15 cm^2 swatches and put into a stainless steel container with 150 mL of 0.15% (w/v) WOB detergent solution and 50 steel balls (0.25 in.

in diameter) at 49°C for various washing time to simylate 5, 20, and 50 wash cycles of home/commercial launderings.

Antibacterial activity

The antibacterial activity was evaluated quantitatively using a shaking flask method developed by Dow Corning Corp.[19] This method is specially designed for specimens treated with nonreleasing antibacterial agents under dynamic contact conditions. The test determines the reduction in the number of bacterial cells in 1 h, shaking flask containing treated specimen. A gram positive bacterium, *S. aureus* (ATCC 6538), commonly found on the human body, was chosen as the testing bacterium. A typical procedure is as follows: a 1 ± 0.1 g sample fabric, cut into small pieces in a size around $0.5 \times 0.5\ cm^2$, was dipped into a flask containing 50 mL of 0.5 m*M* PBS (monopotassium phosphate, pH = 5.0) culture solution with a cell concentration of 1.0–1.5 $\times 10^4$/mL. The flask was then shaken at 250 rpm on a rotary shaker at 37°C for 1 h. Before and after shaking, 1 mL of the test solution was extracted, diluted and spread onto an agar plate. After 24 h of incubation at 37°C, the number of colonies formed on the agar plate was counted, and the number of live bacterial cells in the flask before and after the shaking was calculated. Antimicrobial efficacy was determined based on duplicated test results. Percentage bacterial reduction was calculated according to the following equation:

$$R = (B - A)/B \times 100\%$$

where R is the percentage bacterial reduction, B and A are the number of live bacterial cells in the flask before and after shaking.

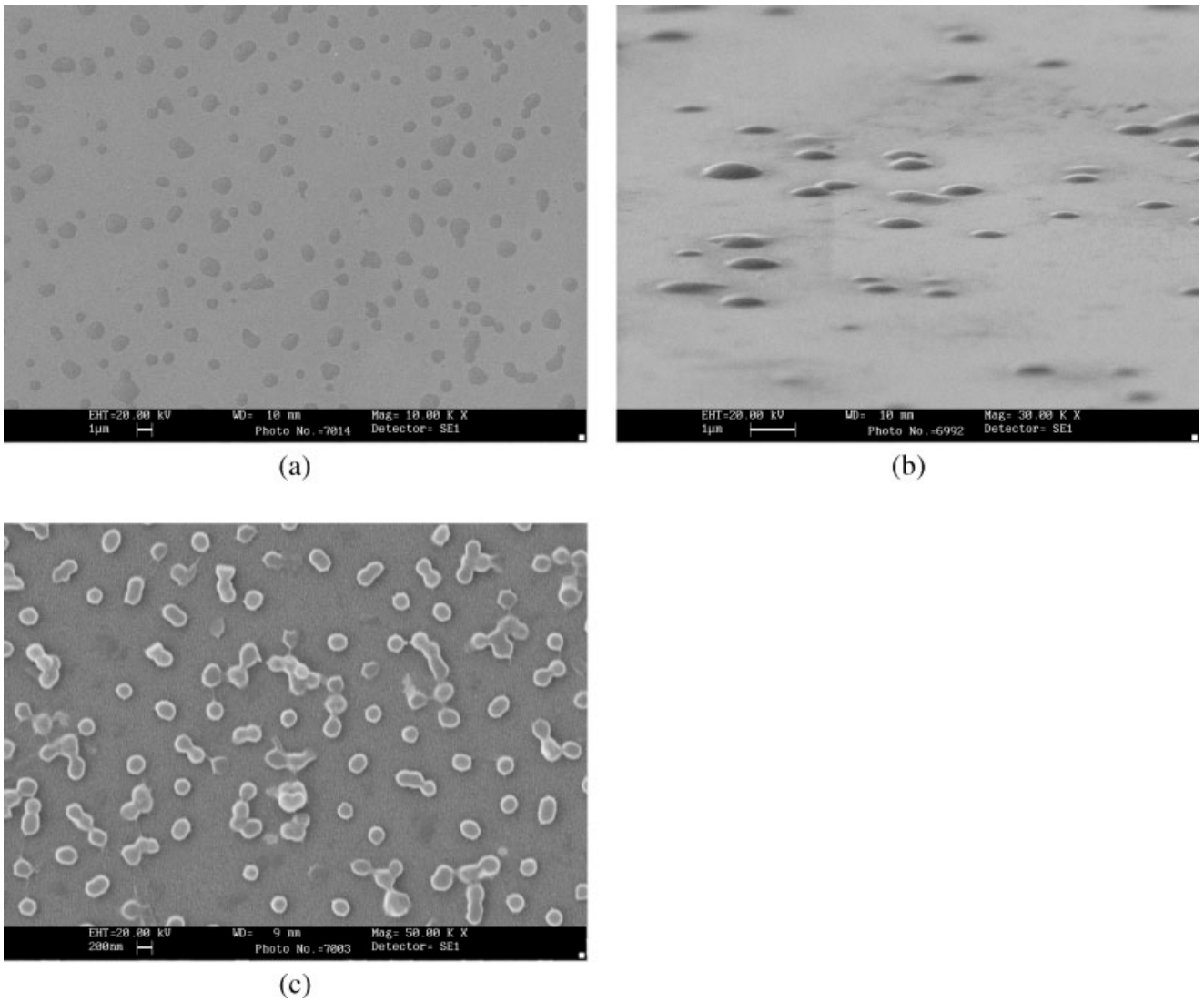

Figure 1 SEM micrographs of CTS-polyBA (a, b) and CTS-polyNIPAM (c) latex particles. (a) CTS-polyBA, top-view; (b) CTS-polyBA, 80° side-view; (c) CTS-polyNIPAM, top-view.

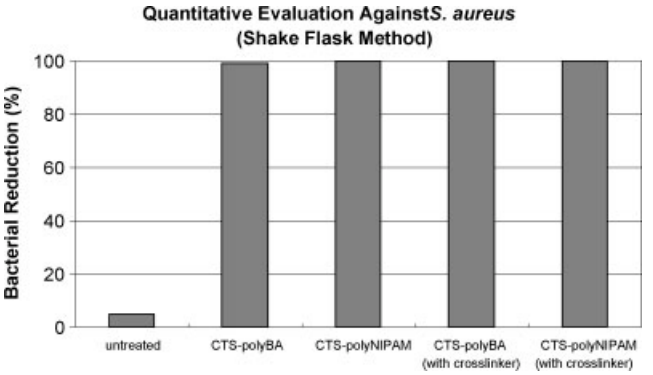

Figure 2 Bacterial reductions of antimicrobial treated and untreated cotton specimens.

RESULTS AND DISCUSSION

Core-shell particles

In this study, two polymers were chosen as the core material. One is poly(*n*-butyl acrylate) (polyBA), a soft polymer with a low glass transition temperature (T_g) of −49°C. At room temperature, polyBA is in rubbery state and polymer chains are mobile. Another is crosslinked poly(*N*-isopropylamide) (polyNIPAM), a hard-core material with thermosensitive behavior.[20] By comparing the core-shell particle with different core flexibilities, we explored the impact of the treatment on fabric surface morphology, hand, and antimicrobial durability.

In our previous dynamic light-scattering study, we have found that these particles were in nanoscale with an average diameter around 300 nm. NMR, TEM, and *zeta*-potential measurements have shown that they had a well-defined core-shell structure in which antibacterial chitosan shells were covalently grafted onto the polymer cores.[17] Here, SEM micrographs (Fig. 1) show that the soft CTS-polyBA particles deformed on solid surfaces. Because of the mobility of polyBA chains, the particles flattened onto the substrate with an enlarged size of around 700 nm in diameter [Fig. 1(a)]. On SEM with 80° side-view, these flattened particles looked like pancakes [Fig. 1(b)]. In contrast with the CTS-polyBA particles, the hard-core CTS-polyNIPAM particles remained spherical with no change in particle size [Fig. 1(c)].

Antibacterial activity of treated fabrics

In most cases, polymerized emulsions were directly applied to cotton fabrics without further treatment. Both CTS-polyBA and CTS-polyNIPAM lattices were stable colloids, with an average particle size around 300 nm.[17] To check whether the addition of chemical binder could improve the fabric antibacterial durability, we also added 0.3 wt % Fixapret CL with a catalytic amount of magnesium chloride (0.075 wt %) into some latex solutions. The main component of Fixapret CL is dimethylolhydroxyetheneurea (DMDHEU), a conventional crosslinking agent that is able to link hydroxyl and amino groups in cellulose and chitosan.[21]

Figure 2 is antibacterial result of all treated and untreated cotton samples. As expected, the cotton fabrics before the treatment had a negligible bacterial reduction of less than 10%, while all padded specimens, either from CTS-polyBA or CTS-polyNIPAM, with or without the crosslinker in the finish solutions, showed over 99% bacterial reduction. The result indicated that core-shell particles with chitosan antibacterial shells had excellent antimicrobial activity and it was not affected by the addition of the Fixapret CL crosslinker. This observation was consistent with most published results,[6,10,21] although some reports mentioned that the addition of dimethylolhydroxyetheneurea could decrease the chitosan inhibitory ability against the growth of *S. aureus*.[22] The surface positively charged core-shell particles could interact with negatively charged bacterial membrane, and eventually destroyed the normal cell metabolism.

TABLE I
Bending Rigidity (*B*) and Bending Hysteresis (2HB) of Untreated and Treated Samples

	Warp		Weft	
Sample	*B* (gf cm^2/cm)	2HB (gf cm/cm)	*B* (gf cm^2/cm)	2HB (gf cm/cm)
Untreated	0.0353	0.0360	0.0720	0.0658
CTS-polyBA	0.0604	0.0310	0.1756	0.0796
CTS-polyNIPAM	0.1375	0.0916	0.3754	0.2314
CTS-polyBA (with crosslinker)	0.0878	0.0518	0.2576	0.1396
CTS-polyNIPAM (with crosslinker)	0.1425	0.1191	0.3620	0.2835
CTS	0.0783	0.0508	0.2860	0.1361
CTS (with crosslinker)	0.1436	0.1007	0.3294	0.2195

Given are the mean values.

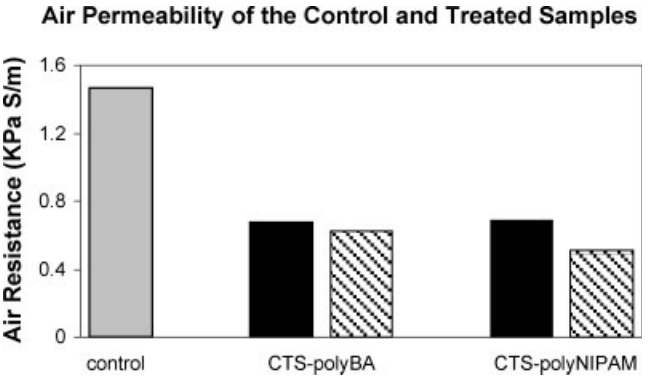

Figure 3 Air resistance of untreated and treated samples; black, without crosslinker; shadow, with crosslinker.

Mechanical properties

To assess the effect of the latex treatment on cotton fabric mechanical property, we performed several tests on fabric hand, air permeability, and tensile strength. Bending rigidity (B) and hysteresis of bending moment (2HB) are two parameters related to fabric stiffness and difficulty of fabric deformation under bending. Results (Table I) showed that the latex treatment increased both B and 2HB values in machine (warp) and cross (weft) directions, indicating that the condensation of latex particles on cotton surfaces could make the fabric stiffer. Nevertheless, depending on the core flexibility and the padding solution with or without the crosslinker, the change in fabric stiffness was quite different.

Previous SEM (Fig. 1) shown that the CTS-polyBA particles are much softer than the CTS-polyNIPAM particles, it is reasonable that the cotton fabric coated with the soft-core CTS-polyBA presented a better fabric hand than the fabric modified with the hard-core CTS-polyNIPAM particles. Moreover, it is worth mentioning that the CTS-polyBA treated samples even had a better fabric hand than fabrics treated with chitosan. We performed the same antibacterial treatment on cotton using 0.5 wt % aqueous chitosan as the finish solution (the same amount of chitosan content as in the latex emulsions). Regardless of the solution with or without the Fixapret CL crosslinker, this time both bending rigidity and hysteresis of bending moment in warp and weft directions were measured larger than the corresponding CTS-polyBA treated values, but smaller than the CTS-polyNIPAM treated ones (Table I). The results indicated that coating with CTS-polyBA soft-core particles could provide fabric with relatively good fabric hand, and the fabric hand could be adjusted by the core flexibility. However, adding crosslinker in padding solution could make fabric much stiffer (Table I).

Figure 3 is air-resistance (R) of treated and untreated specimens. R presents the air pressure needed for a constant airflow penetrating a fabric surface. A small resistance value means a better air permeability. Significant decreases in air resistance were observed after the latex treatment, indicating that both CTS-polyBA and CTS-polyNIPAM nanoparticles could smooth fiber surface and let airflow transfer more easily through the fabric. Lee et al.[23] observed the same improvement of air permeability after chitosan coating on some natural fabrics of cellulose, silk, and wool. Figure 3 also shows that cotton padded with the crosslinker had a slightly better air permeability than the one without the crosslinker. Most likely it is because the crosslinking made cotton fibers more compact and less swellable.

To evaluate fabric resistance to stretching or pulling force, we performed fabric strip test to investigate the effect of antibacterial treatment on fabric breaking and elongation. Since acetic acid was used for the preparation of chitosan-containing core-shell particles, the finish solutions were acidic with a pH value of around 4.3. As expected, in both warp and weft directions, fabric tensile strength decreased after the latex modification (shown in Table II). However, the change was not significant as all fabrics still maintained at least 75% of their original tensile strength in warp or weft direction. It seems that the treatment did not cause much difference in fabric break elongation. As a result of adding Fixapret CL crosslinker, greater loss in fabric tensile strength was observed. This is understandable, as crosslinking increases the rigidity of fabric cellulose molecules, reduces the mobility of cellulose chains,

TABLE II
Break Tensile Strength and Elongation of Treated and Untreated Cotton Fabrics

	Warp			Weft		
Sample	Break force (N)	Strength maintained (%)	Break strain (%)	Break force (N)	Strength maintained (%)	Break strain (%)
Untreated	377.5	–	17.8	219.2	–	15.0
CTS-polyBA	364.6	96.6	20.7	168.6	76.9	12.3
CTS-polyNIPAM	361.8	95.8	19.5	210.6	96.1	14.1
CTS-polyBA (with crosslinker)	305.1	80.8	16.9	164.4	75.0	13.5
CTS-polyNIPAM (with crosslinker)	356.8	94.5	18.6	197.9	90.3	13.9

and therefore prevents the redistribution of applied stress.

Surface morphology

Figure 4 are SEM micrographs of cotton fabrics before [Fig. 4(a)] and after the treatment [Figs. 4(b) and 4(c), without the crosslinker]. Compared with the one before the treatment, the treated surface did not show much difference. Both treated and untreated cotton displayed smooth fiber appearances. No individual particles or deposits were found even under high SEM magnifications. Fabric reflective FTIR has proved the latex particles coated onto the fabric surface.[17] All these evidences implied that during the particle condensation, the nanosized particles were packed closely to form a thin film on fabric surface instead of individual particles.

Laundering durability

One of the biggest concerns of antibacterial finish in today's textile industry is durability. An ideal antimicrobial finish should be effective for the entire lifetime of a textile article. Generally, if a textile material can maintain at least 80% of its inhibitory activity after twenty times of home laundering, it will be acceptable as a ''durable antibacterial finish.''[24]

We performed wash fastness test on cotton fabric based on AATCC standard Method 61-1996. The efficacy was determined by measuring the fabric bacterial reductions after 0, 5, 20, and 50 repeated wash cycles. Table III shows the wash fastness result of the percentage of reductions in the number of *S. aureus* cells. All washed samples maintained high antibacterial efficacy even after 50 times of repeated laundering regardless of the Fixapret CL corsslinker. We also performed the wash fastness test in acidic

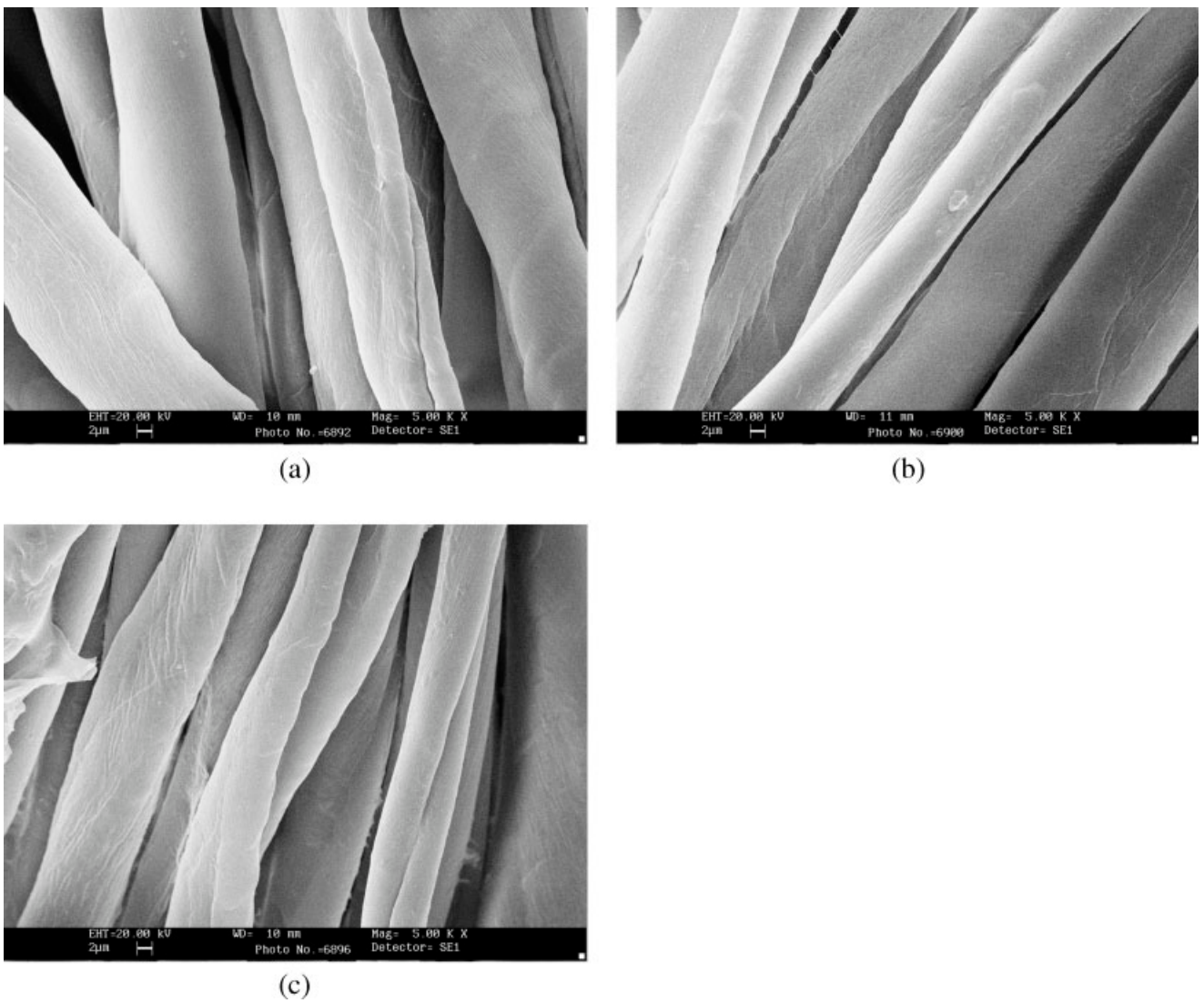

Figure 4 SEM images of treated and untreated cotton fabrics; (a) untreated; (b) CTS-polyBA treated; (c) CTS-polyNIPAM treated.

TABLE III
Antibacterial Activity of Treated Specimens in terms of Bacterial Reduction (%) after Different Laundering Cycles

	Bacterial reduction (%) after wash cycles			
	0	5	20	50
CTS-polyBA	99.0	89.2	100	98.7
CTS-polyNIPAM	100	98.3	100	99.5
CTS-polyBA (with crosslinker)	100	100	99.8	96.7
CTS-polyNIPAM (with crosslinker)	100	97.7	99.8	98.2

human sweat with a pH of 4.5 for 20 and 50 wash cycles, and the same high antibacterial activity of over 90% bacterial reductions was observed. Such an excellent antimicrobial durability means that with no aid of a chemical binder, the chitosan component on fabric surface could not be washed away, even in a chitosan-soluble acidic environment. These core-shell nanoparticles adhered themselves firmly onto the cellulose surface, most likely not only by physical interactions but also by certain chemical bindings.

CONCLUSIONS

In this study, we developed a novel antibacterial finish on cotton fabric using chitosan-based core-shell particles. Two types of chitosan-shelled nanospheres with different core flexibilities were synthesized and applied to cotton fabric by pad-dry-cure method. Quantitative antibacterial tests revealed an excellent and durable fabric antibacterial activity with 99% bacterial reductions after the treatment and over 90% reductions after 50 times of laundering cycles. Experiments found that the treated fabrics had better air permeability and the reduction in fabric tensile strength was not significant. The treatment did not cause much change in fabric appearance and surface morphology. Fabrics coated with soft-core particles could have a better fabric hand than could these treated with hard-core particles.

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