Characteristics of Cotton Fabrics Treated with Epichlorohydrin and Chitosan

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ABSTRACT: Cotton fabrics treated with a crosslinking agent, epicholorohydrin, in the presence of chitosan (CEC) provide many possible reactive sites for reactive dyes and antimicrobial properties of the grafted chitosan to the cellulose structure. This process was applied by means of the conventional mercerizing process. The chitosan finishing and durable press finishing of the cotton fabrics occurred simultaneously in the mercerization bath. ECH is expected to react with hydroxyl groups in cellulose and chitosan or with amino groups in chitosan to form alcohol crosslinking by the Belfast process. The fixed chitosan content in the CEC was calculated by the nitrogen percentage of an Elemental Analyzer. The color strength (K/S) of the reactive dyes of the treated cotton fabrics did not significantly change with an increase of chitosan; however, the degree of swelling of the treated cotton fabrics decreased with an increase of chitosan and ECH. These performances were retained through 20 washing and tumble drying cycles. J Appl Polym Sci 117: 623–628, 2010

Key words: antibacterial activity; chitosan; cotton; epichlorohydrin (ECH); mercerizing

INTRODUCTION

Cellulosic fiber is one of the most abundant natural fibers with characteristics, such as, biosynthesis, a hydrophile property, and biocompatibility. Although cotton has many advantages as a biocompatible polymer, it needs to be treated and finished due to low levels of resiliency, bad durability after laundering, and low-antimicrobial activity. If these two properties can be improved by one treatment with a natural finishing agent, the finishing will be environmentally acceptable.[1]

Chitosan, a polysaccharide comprising copolymers of glucosamine and *N*-acetyl-glucosamine, is obtained by alkaline deacetylation of the chitin derived from the exoskeletons of crustaceans and arthropods.[2–4] Because chitosan has various practical properties, such as, microbial resistance, nontoxicity, biodegradability, and metal-ion adsorption, many investigators have concentrated on applying chitosan to a wide variety of textiles. Cotton textiles have poor resistance to microorganisms, so the antimicrobial finishing of cotton fabrics is an economical way to prevent harm to the human body.[4]

The epicholorohydrin (ECH) known as a cellulose crosslinking agent for Belfast wash-and-wear finish is applied with the assistance of sodium hydroxide. Cotton fabric is padded in succession with the agent and then the catalyst and then, in its wet state, is allowed to lie for a few minutes, during which the crosslinking takes place primarily to give wet crease resistance.[5,6] On the other hand, many researchers have studied about chitosan crosslinking using ECH. The ECH crosslinks chitosan molecules by reacting mostly with the hydroxyl group of chitosan.[7–9]

Generally, cotton is treated with chitosan by dissolving the chitosan in a dilute acetic acid solution, but this method does not create any firm chemical bonds between chitosan and cellulose and, thus, is not durable in repeated laundering.[10] The purpose of this study is to make improvement of the functional property of cotton by a simple mercerizing process. The crosslinking of cotton fabric and chitosan by ECH in a mercerizing process, which is essential for cotton, can improve physical properties. In addition, crosslinking between chitosan and chitosan and between chitosan and cellulose by an application of chitosan endows cotton fabrics with antimicrobial activity, deodorization, greater affinity on acid dye, and easier finishing. It is a very economical way to conduct mercerizing and crosslinking successively. The influences of the crosslinking agent in the presence of chitosan as well as the finishing conditions on the performance properties and the

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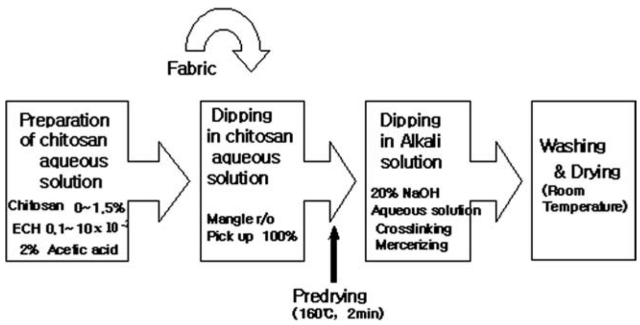

Figure 1 Scheme diagram of chitosan crosslinking.

antimicrobial activity of the chitosan treated cotton fabrics were discussed in this study. The dyeability of the cotton fabrics treated with a crosslinking agent, epicholorohydrin, in the presence of chitosan (CEC) by the reactive dyes was also studied.

EXPERIMENTAL

Materials

A desized, scoured, and bleached cotton print cloth (115 g/m^2, 89 epi, and 79 ppi) used in the experiments. The fabric was further purified by washing with warm water and nonionic detergent of 1 g/L (Kierlon NB-MFB, BASF) in a home laundering machine (LG, Ltd.). After washing, the fabric was rinsed with warm water thrice and was oven-dried at 40°C for 24 h. The chitosan (Taehoon-Bio Co., Korea) was deacetylated about 95% and had a molecular weight of ~ 21,000.[11] The ECH, acetic acid, and sodium hydroxide used in all experiments (Junsei Chemical, Co.) were reagent grade.

Finishing and dyeing

Figure 1 shows a schematic drawing of the finishing process used in this study. A padding solution was prepared by 0–1.5% owb chitosan and 0.1–5 ($\times 10^{-2}$ [M]) ECH in 2 wt % aqueous acetic acid solution. The cotton fabrics were first dipped in the padding solution for 1 min at 20°C, and then were pressed by a mangle roller to control the pick-up ratio (~ 100% of weight). Subsequently, the fabrics were predried on a pin frame at 160°C for 2 min, and then were mercerized in 20 wt % aqueous NaOH solution. A possible mechanism at a strong alkali condition is shown in Figure 2.[7–9] Three possible products were resulted from this process; however, Case 3 (crosslinking between chitosan and cotton) may be dominated under a strong alkali condition.

Finally, the fabrics were washed thoroughly with distilled water and dried at the room temperature.

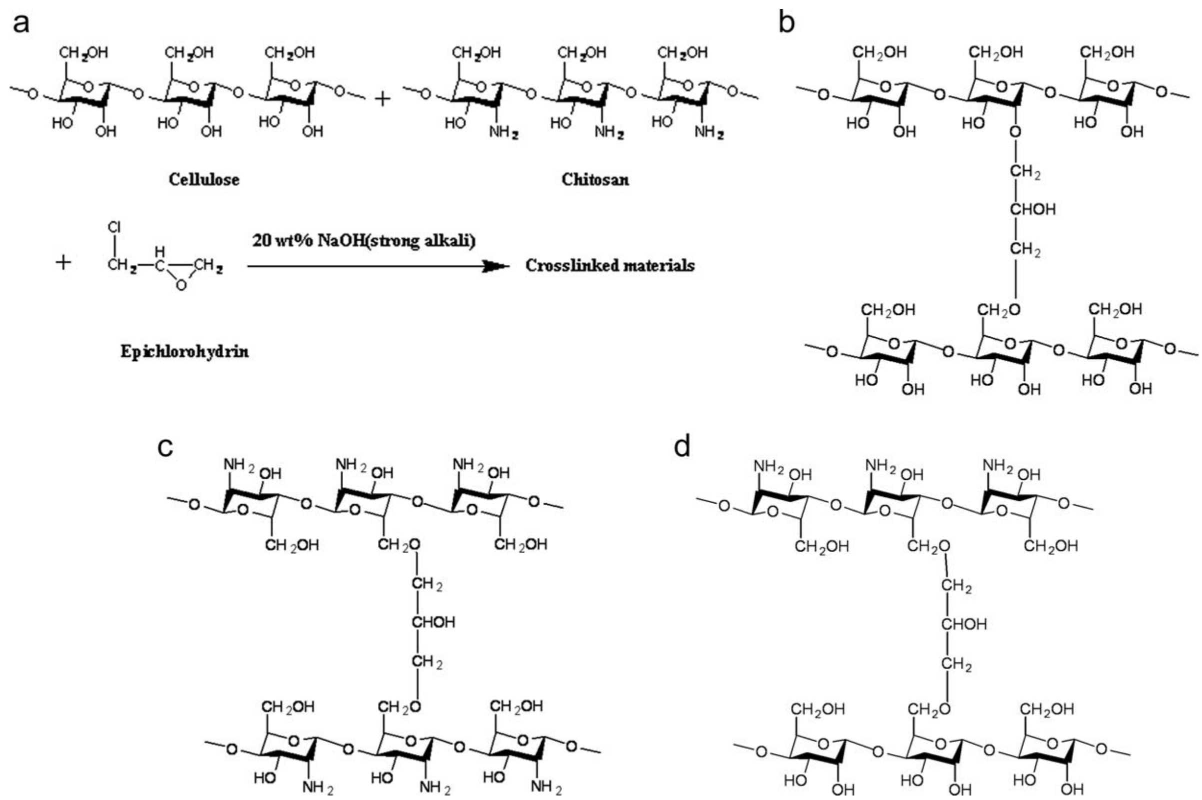

Figure 2 Mechanism and products of crosslinking between chitosan and cellulose. (a) General mechanism of crosslinking of cellulose and chitosan. (b) Case 1, crosslinking of cellulose and cellulose. (c) Case 2, crosslinking of chitosan and chitosan. (d) Case 3, crosslinking of chitosan and cellulose.

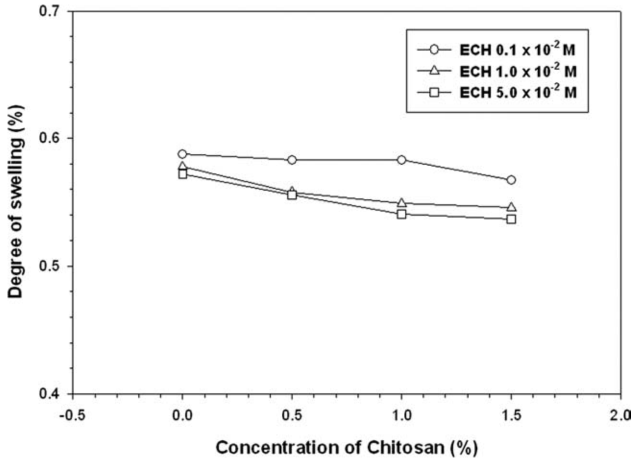

Figure 3 Relationships between concentration of chitosan and degree of swelling of cotton fabrics treated with chitosan and ECH dissolved in 2% acetic acid solution.

The reactive dyes (C.I. Reactive Yellow 15, C.I. Reactive Red 45, and C.I. Reactive Blue 21) were used for the dyeing of the CEC fabrics. In this study, the various dye concentrations were used in the range from 0.05 to 1.0% owf. The samples were labeled as COD-0.05, COD-0.10, COD-0.50, and COD-1.00 (0.05, 0.10, 0.50, and 1.00 means the concentration of the dye). The dyeing bath solution contained severally 0.05, 0.1, 0.5, or 1.0% of a dye (owf), 2.5 g/L sodium of carbonate, and 60 g/L of sodium sulfate. The dyeing process was performed at 40°C for 20 min with constant stirring. The cotton fabrics were then continuously dyed at 60°C for 60 min with material-to-liquor ratio of 1 : 20. After the dyeing process, the fabrics were cooled down to 25°C and thoroughly washed with detergent and dried at 90°C.

Measurement

The fixed chitosan content in the CEC was calculated by the nitrogen percentage from an Elemental Analyzer (EA 1108, Fisions Instruments S.P.A, Italy). Dye uptake (henceforth, K/S) was calculated by standard reflectance obtained from a maximum absorption wavelength using a Computer Color Matching System (CCM, Color Quest XE, Hunterlab, USA). The wash-and-light fastness were measured by KS K 0430 A-1 and ISO 015 B02 (63°C, 20 h, water-cooled xenon-arc lamp, and continuous light), respectively. Antimicrobial activity was evaluated by the Shake Flask Method using standard bacteria *Staphylococcus aureus* (ATCC 6538) and *Klebsiella pneumoniae* (ATCC 4352). The antibacterial rates were calculated by the following method using a colony count.

$$\text{Bacteria reduction rate (\%)} = [(\text{A} - \text{B})/\text{A}] \times 100,$$

where A and B are the surviving cells (CFU/mL) for flasks containing test samples (CEC) and the control (blank cotton), respectively.

TABLE I
Chitosan Content of CEC

Conteration of chitosan applied (% owb)-Concentration of ECH applied ($\times 10^{-2}$ [M])	Fixed chitosan content into the CEC (wt %)
0–0	0
0.5–5	0.65
1.0–5	0.99
1.5–5	1.33
2.0–5	1.70
1.5–1	1.31

RESULTS AND DISCUSSION

Degree of swelling

For measuring the degree of swelling, it was necessary to make a series of gravimetric measurements to determine the weight percentage as a function of the chitosan concentration. The degree of swelling of ECE treated fabric was decreased with the degree of crosslinking. The degree of swelling of the chitosan treated cotton fabric in this study is given by

$$\text{Degree of swelling (\%)} = [(\text{WW} - \text{DW})/\text{DW}] \times 100$$

where, WW is wet weight after centrifuge (g) and DW is dry weight (g).

The weight of the completely dried sample was measured directly, and the sample was dipped into a glass beaker filled with distilled water for 24 h at 20°C. The weight of the swollen fabric was measured by centrifuge (20,000 rpm for 5 min.).

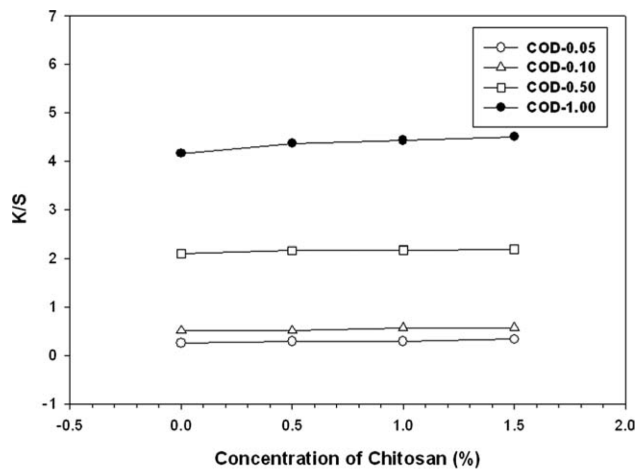

Figure 4 Relationships between concentration of chitosan and K/S value of C. I. Reactive Yellow 15 with 5×10^{-2} [M] ECH.

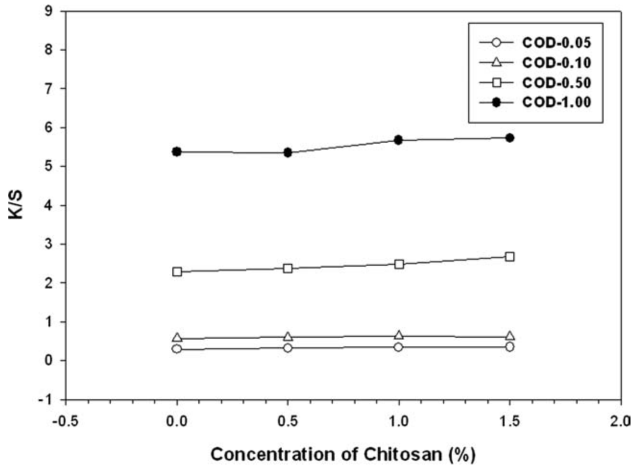

Figure 5 Relationships between concentration of chitosan and K/S value of C. I. Reactive Red 45 with 5×10^{-2} [M] ECH.

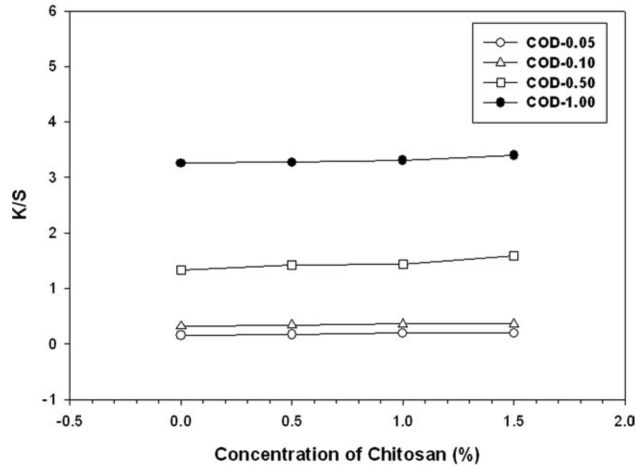

Figure 6 Relationships between concentration of chitosan and K/S value of C. I. Reactive Blue 21 with 5×10^{-2} [M] ECH.

According to Gupta and Jabrail,[12] the degree of swelling in the chitosan microsphere changed significantly on crosslinking with crosslinking agent, glutaraldehyde or glyoxal. On the other hand, ECH crosslinks chitosan molecules by connecting mostly with the hydroxl group of chitosan.[7–9] The degree of swelling of the chitosan treated cotton fabric is shown in Figure 3. It was found that the degree of swelling slightly decreased with the addition of the chitosan and ECH. This result may be explained by reporting that the diminishing of degree of swelling of chitosan treated cotton fabrics was due to the reduction of the amine group (chitosan) and the hydroxyl group (cotton and chitosan) with crosslinking by ECH.

Chitosan content of CEC

The amount of chitosan in the CEC was measured by the nitrogen contents using the Elemental analysis. Table I shows the relationship between the chitosan concentrations in the CEC in the treatment solution. The amount of fixed chitosan increased with the chitosan concentration of treatment condition, the chitosan content in the CEC was 0.99% at the concentration of chitosan applied at 1.0% owb. Whereas when the concentration of chitosan was over 1.0% owb, the chitosan content in the CEC smoothly increased. From the results, it can be assumed that the chitosan has some degree of interaction (such as, cotton–chitosan crosslinking, chitosan–chitosan crosslinking, etc.) with cotton fabric by ECH. On the other hand, the chitosan content in the CEC for 1.5% concentration of chitosan applied (owb) are 1.31, 1.33 at 1×10^{-2} [M] and 5×10^{-2} [M] of ECH concentrations, respectively. This result leads to the conclusion that the ECH did not affect the chitosan content of the CEC within the extent of this study.

Dyeing properties

It is difficult to achieve cotton yarn or fabric dyed in deep and bright shades at a low cost. Because cotton

TABLE II
The Wash Fastness of Dyes[a] on Cotton Fabric Treated with Chitosan[b] and ECH[c]

			Yellow	Red	Blue
Untreated cotton fabric	Change		4–5	4–5	4–5
	Staining	Cotton	4–5	4–5	4–5
		Wool	4–5	4–5	4–5
Chitosan treated cotton fabric	Change		4–5	4–5	4–5
	Staining	Cotton	4–5	4–5	4–5
		Wool	4–5	4–5	4–5

[a] Concentration of dye 1.0% owf.
[b] Concentration of chitosan 1.0% owb.
[c] Concentration of ECH 5 ($\times 10^{-2}$ [M]).

fabric has been significantly functionalized by the application of modified chitosan, it could be expected that its dyeing behavior had also been modified. Hence, anionic and cationic dyes were applied to chitosan treated cotton to study the treatment color strength (K/S) obtained and the fastness of dyes to wash and light.[13]

Three reactive dyes, C.I. Reactive Yellow 15, C.I. Reactive Red 45, and C.I. Reactive Blue 21, were evaluated in this work. Figures 4–6 show color strength (K/S) of dyes (Yellow, Red, and Blue) as a function of the concentration of chitosan and dye. It is well-known that crosslinking reduced the dyeability of cellulosic fabrics[14–16]; however, the K/S value of chitosan treated cotton fabrics in Figures 4–6 did not change with the concentration of applied chitosan increased in the concentration of each dye. All dyes (reactive dyes of an anionic type) used in the study shows similar K/S values on chitosan treated cotton comparing with those on untreated cotton samples.

An explanation for this could be based on the forces of repulsion and attraction expected to occur during the dyeing process. These forces arise due to the presence of free hydroxyl groups and amino ions in chitosan treated cotton cellulose and anionic groups present in dyes. When dyeing with anionic dyes, the presence of amino groups on chitosan treated cotton reduces the repulsion between the free hydroxyl groups of cellulose and the anionic groups of dyes. As a result, chitosan treated cotton fabrics showed high-color strength after dyeing with these dyes.[17]

All dyeing for fastness tests was carried out with dye 1% owf. Table II shows the results of the wash fastness tests for reactive dyes (Yellow, Red, and Blue) on cotton fabrics. All dyes showed good to excellent wash fastness. As shown in Table II, the wash fastness of the chitosan treated cotton fabrics was the same in grade with the untreated cotton fabrics. This result leads to the conclusion that the chitosan does not affect the wash fastness of dyes, within the extent of this study. Table III gives the results of the light fastness. As shown in Table III, the light fastness of the cotton fabrics was nearly the same in grade. This suggests that the crosslinking of cotton and chitosan by ECH hardly affects the light fastness of dyes, within the extent of this study.

TABLE III
The Light Fastness of Dyes[a] on Cotton Fabric Treated with Chitosan[b] and ECH[c]

	Yellow	Red	Blue
Untreated cotton fabric	4–5	4	4
Chitosan treated cotton fabric	4–5	3	4

[a] Concentration of dye 1.0% owf.
[b] Concentration of chitosan 1.0% owb.
[c] Concentration of ECH 5 ($\times 10^{-2}$ [M]).

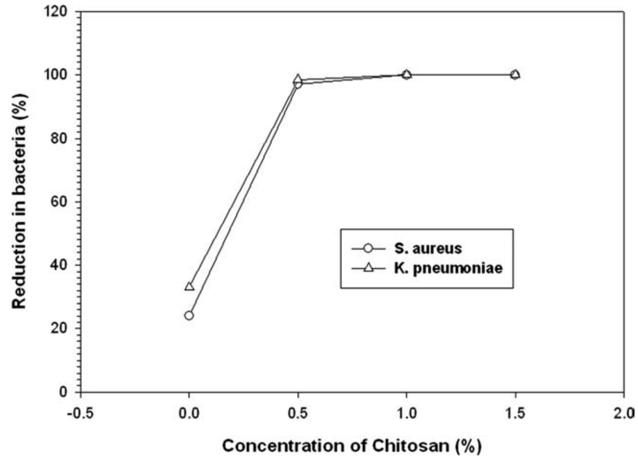

Figure 7 Relationships between concentration of chitosan and antimicrobial activity of cotton fabric treated with chitosan dissolved in 2% acetic acid solution and 5×10^{-2} [M] ECH.

Antimicrobial properties

It is widely known that the antimicrobial property of cotton treated with chitosan is attributed to the chitosan amino group, which converts to ammonium salt in a dilute acid solution. This salt then makes contact with the negatively charged protoplasm of the microorganism and destroys the cell wall.[18,19] Figure 7 shows the effect of chitosan concentration on the antimicrobial activity of *S. aureus* and *K. pneumoniae*. All chitosan treated cotton fabrics showed very high activities with almost 100% reduction. The activity increased as the amount of chitosan applied increased, and complete 100% reduction was obtained at the concentration of 1.0% owb. Figure 8

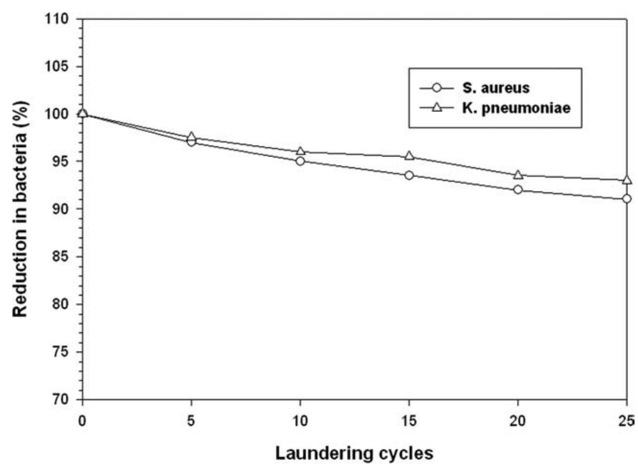

Figure 8 Durability of antimicrobial activity of cotton fabric treated with the solution of 2% acetic acid, 1.0 wt % chitosan, and 5×10^{-2} [M] ECH.

shows the durability of antimicrobial activities during repeated laundering. After the 25th laundering cycle, the bacteria reduction of *S. aureus* and *K. pneumoniae* reached more than 91% and 93%, respectively. These results verify that chitosan is firmly linked to the cotton by ECH.

CONCLUSIONS

Cotton fabrics were closslinked with the ECH in the presence of chitosan to provide good dyeability and antimicrobial properties to the fabrics. The amount of fixed chitosan increased with the chitosan concentration of the treatment condition; the chitosan content into the CEC was 0.99% of the concentration of chitosan applied at 1.0% owb. Whereas when the concentration of chitosan was over 1.0% owb, the chitosan content in the CEC smoothly increased. The degree of swelling of the treated cotton fabric slightly decreased with the addition of the chitosan and ECH. The K/S value of chitosan treated cotton fabrics dyed with reactive dyes did not significantly change with increasing the concentration of the applied chitosan. The wash fastness and light fastness of the chitosan treated cotton fabrics were nearly the same in grade with that of untreated cotton fabrics. A high antimicrobial property level was obtained by chitosan treated cotton fabrics with ECH, and despite repeated laundering, the antimicrobial properties remained at over 91%.

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