Durable Antimicrobial Treatment of Cotton Fabrics Using N-(2-Hydroxy)propyl-3-trimethylammonium Chitosan Chloride and Polycarboxylic Acids

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ABSTRACT: *N*-(2-hydroxy)propyl-3-trimethylammonium chitosan chloride (HTCC), a water-soluble chitosan quaternary ammonium derivative, was used as an antimicrobial agent for cotton fabrics. HTCC has a lower minimum inhibition concentration (MIC) against *Staphylococcus aureus, Klebsiella pneumoniae*, and *Escherichia coli* compared to that of chitosan; however, the imparted antimicrobial activity is lost on laundering. Thus crosslinking agents were utilized to obtain a durable antimicrobial treatment by immobilizing HTCC. Several crosslinkers such as dimethyloldihydroxyethylene urea (DMDHEU), butanetetracarboxylic acid (BTCA), and citric acid (CA) were used with HTCC to improve the laundering durability of HTCC treatment by covalent bond formation between the crosslinker, HTCC and cellulose. The polycarboxylic acid treatment was superior to the DMDHEU treatment in terms of prolonged antimicrobial activity of the treated cotton after successive laundering. Also, the cotton treated with HTCC and BTCA showed improved durable press properties without excessive deterioration in mechanical strength or whiteness when compared to the citric acid treatment. With the addition of only 0.1% HTCC to BTCA solutions, the treated fabrics showed durable antimicrobial activity up to 20 laundering cycles. The wrinkle recovery angle and strength retention of the treated fabrics were not adversely affected with the addition of HTCC. Therefore, BTCA can be used with HTCC in one bath to impart durability of antimicrobial activity along with durable press properties to cotton fabric. J Appl Polym Sci 88: 1567–1572, 2003

Key words: crosslinking; fibers; FT-IR; mechanical properties

INTRODUCTION

Natural and synthetic fibers are susceptible to microorganisms, such as bacteria and fungi, which are nourished by sweat, sebum, and food stains, as well as the polymers themselves. When micro-organisms multiply in clothing, they not only cause physicochemical degradation such as discoloration, mechanical strength loss, and foul odor generation, but also may adversely affect human health in the cases of some microorganisms including *Tricophyton mentagrophetes*, *Candida albicans*, *Penicillium citrinum*, and *Stphylococcus aureus*, which cause athlete's foot, bedsores, allergies, and crossinfection in hospitals, respectively.[1,2] To overcome such problems, various antimicrobial agents were used to produce antimicrobial fibers: metals, inorganic particles containing metals, aromatic halogen compounds, quaternary ammonium salts, etc.[1] Recently, chitosan has also been studied as a new antimicrobial agent for textiles.[3,4] Protonated amino groups of glucosamine units in chitosan may inhibit growth of microorganisms by holding negatively charged cell walls.[5,6] However, the antimicrobial activity of chitosan may be reduced in neutral or alkaline conditions due to the insolubility of chitosan. Therefore, large amounts of chitosan need be applied to impart acceptable antimicrobial activity to textiles, which inevitably deteriorates their handle.

We previously reported the synthesis of a water-soluble chitosan derivative, *N*-(2-hydroxy)propyl-3-trimethylammonium chitosan chloride (HTCC), and evaluated the antimicrobial performance of the HTTC-treated cotton and HTCC/polyacrylonitrile blend fiber.[7–9] The chemical structure of HTCC is shown in Scheme 1 along with that of chitosan and cellulose. The antimicrobial activity of HTCC was much higher than that of chitosan because of the synergistic effect of the secondary amino groups and the quarternary ammonium groups of HTCC compared with the low effectiveness of primary amino groups in chitosan under neutral conditions. Only 0.025% of applied HTCC with respect to substrate was sufficient for 100% bacterial reduction, while over 2% of chitosan is generally required.[7] However, it is more difficult to achieve laundering durability in the case of HTCC compared with chitosan because of HTCC's inherently

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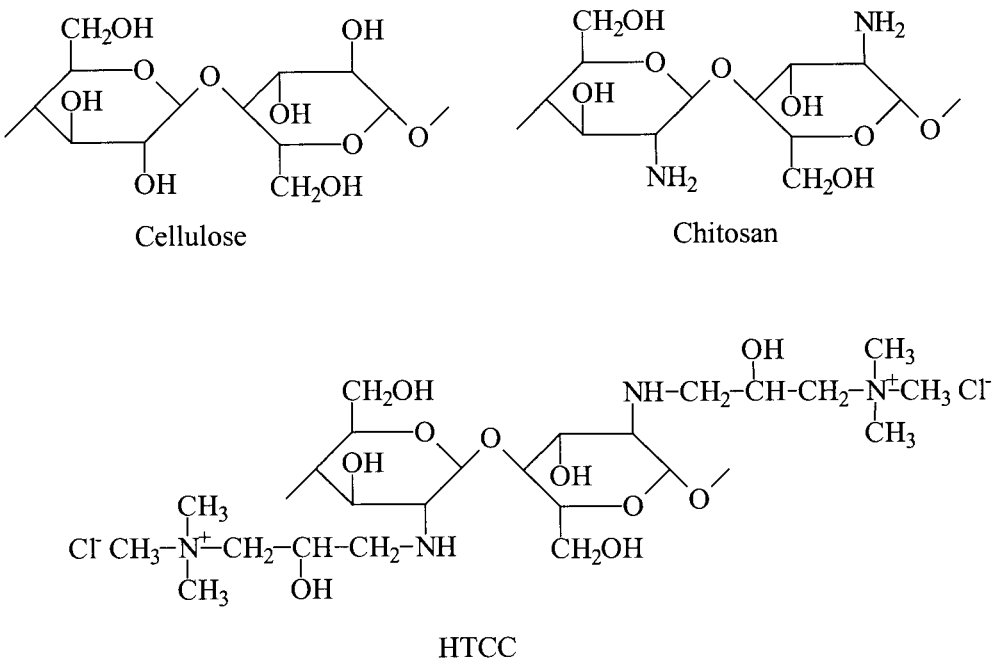

Scheme 1 Chemical structure of cellulose, chitosan, and HTCC.

excellent water solubility. Therefore, HTCC should be modified to introduce new groups capable of reacting with cotton or should be treated with appropriate binders.

On the other hand, cotton fabrics are generally treated with crosslinking agents to impart anticrease and durable press property, which is called resin finishing. Crosslinkers react with hydroxyl groups in cellulose and crosslink cellulose molecules with primary chemical bonds. HTCC is a chitosan derivative, so its chemical structure is similar to that of cellulose in that it also has hydroxyl groups. Therefore, crosslinking agents that are used for cellulosic fibers may react with HTCC also. The crosslinks, if formed, between cellulose and HTCC, can improve the laundering durability of the antimicrobial activity. For this purpose, dimethyloldihydroxyethylene urea (DMDHEU), a most popular conventional resin finishing agent, was selected in this study and the feasibility of forming crosslinks between cellulose and HTCC was investigated.

Some polycarboxylic acids such as butanetetracarboxylic acid (BTCA), citric acid (CA), and maleic acid, can crosslink cellulosic materials via esterification of hydroxyl groups in cellulose, resulting in improved shape retention properties of cotton without releasing formaldehyde.[10,11] BTCA with sodium hypophosphite catalyst have been widely recognized for excellent performance including durability in repeated laundering. In this study, BTCA and CA were also selected and their effectiveness on the laundering durability of the microbial activity of HTCC was evaluated.

Resin finishing usually deteriorates mechanical strength of the treated cotton fabrics. The presence of HTCC may cause further deterioration of some physical properties. Wrinkle resistance, mechanical strength, and whiteness of the fabrics treated with selected crosslinkers and HTCC were, therefore, evaluated.

EXPERIMENTAL

Materials and reagents

Desized, scoured, bleached, and mercerized 100% cotton fabrics (125g/cm^2) were used as untreated textiles. Degree of substitution for (2-hydroxy)-propyl-3-trimethylammonium chloride group and molecular weight of HTCC were 0.96 and ca. 150,000 g/mol, respectively. The synthesis and characterization of HTCC were described in our previous article.[8] Reagent grades of BTCA and CA were obtained from Aldrich. Sodium acetate (Junsei Chemical Co. Ltd, Japan) and sodium hypophosphite (Duksan Pure Chemicals Co. Ltd, Korea) were used as catalysts for the reaction of cellulose with BTCA and CA, respectively. For the BTCA treatment, sodium acetate instead of sodium hypophosphite was used as a catalyst because of environmental concerns such as the eutrophication effect and the potential phosphin generation of sodium phosphite and cost effectiveness of sodium acetate.[12,13] For dimethyloldihydroxyethylene urea (DMDHEU) Fixapret CL (BASF, Germany) with 80% solid content was used. Triton X-100 (Shinyo Pure

TABLE I
Minimum Inhibitory Concentration (MIC) of Chitosan and HTCC against Bacteria

Bacteria	MIC (ppm)		
	HTCC	Chitosan in 1% acetic acid	100% Acetic acid
Staphylococcus aureus (A.T.C.C. No. 6538)	125	500	0.5
Klebsiella pneumoniae (A.T.C.C. No. 4352)	125	500	0.5
Escherichia coli (A.T.C.C. No. 25922)	125	250	0.5

Chemicals Co. Ltd, Japan) was used as a wetting agent. Nutrient broth and trypton glucose extract agar (DIFCO Laboratories, USA) were used as the bacteria cultivating reagents for the antimicrobial activity test. All the other chemicals were of reagent grades and used without further purification.

Assessment of antimicrobial activity

Minimum inhibitory concentrations (MICs) of HTCC and chitosan against *Staphylococcus aureus* (American Type Culture Collection (A.T.C.C. No. 6358), *Klebsiella pneumoniae* (A.T.C.C. No. 4352), *and Escherichia coli* (A.T.C.C. No. 25922) were determined by the approved standard method M07-A3 of NCCLS and the bacteria were incubated at 37°C for 24 h using Muller-Hinton Broth. The antimicrobial activity of the treated cotton fabric was evaluated using the AATCC Test method 100-1988. Nutrient broth and tryptone glucose extract agar were bacteria cultivating reagents and *Staphylococcus aureus*, a Gram-positive bacterium, was the test bacterium.

Antimicrobial treatment of cotton fabric

The treatment bath consisted of an aqueous solution with differing amounts of HTCC and 8% polycarboxylic acids (BTCA or CA) or DMDHEU, a catalyst, and 0.1% (w/v) Triton X-100. Sodium acetate and sodium hypophosphite were used as catalysts at concentrations of 0.6 mol ratio to BTCA and CA concentrations, respectively. 2% (w/v) $MgCl_2$ was used for the catalyst of the DMDHEU treatment.

Cotton fabric was impregnated to give an approximate 70 ± 2% wet pickup via two successive steps of padding through the treatment bath and squeezing under pressure. For the polycarboxylic acids, the padded fabric was dried at 100°C for 3 min and subsequently cured at 170°C for 3 min in a Mathis (Switzerland) curing oven. In the case of the DMDHEU treatment, drying and curing were carried out at 100°C for 3 min and at 150°C for 4 min, respectively. The treated fabric was washed several times with water and finally dried at 100°C for 3 min.

Laundering durability and other analysis of durable antimicrobial cotton

The laundering durability of the antimicrobial cotton fabric was tested using JIS L 0217-103 with a commercial washing machine (Samsung SEW-50X1, Korea). The ratio of washing solution to goods was 30 : 1 including 0.2% nonionic detergent and a dummy load. One laundering cycle was comprised of 5-min laundering and subsequent 2-min rinsing, followed by another 2-min rinsing.

The standard methods used to evaluate performance properties of the treated cotton fabrics were the following: conditioned wrinkle recovery angle by AATCC 66-1984, breaking force by ASTM D 5035-90 (raveled strip), and Elmendorf tear resistance by ASTM D 1424-83. The whiteness index of the treated fabric was measured using a reflectance spectrophotometer (Color-Eye 3000, Macbeth, New Windsor, NY). FTIR spectra of the treated fabric were obtained with a FTIR spectrometer (Midac Co., Irvine, CA) using the potassium bromide pellet technique. To identify ester links, the treated cotton fabric was neutralized with 0.1*N* NaOH solution at room temperature for 2 min, which can shift the carbonyl stretching peak of unreacted carboxylic acids at 1720 cm^{-1} to the carbonyl stretching peak of carboxylates at 1580 cm^{-1}.[14]

RESULTS AND DISCUSSION

Antimicrobial activity of HTCC and chitosan

Synthesized HTCC was water soluble and showed excellent antimicrobial activity without any crosslinking treatment, while unmodified chitosan is not soluble in neutral and alkaline aqueous solutions. The minimum inhibitory concentrations (MICs) of HTCC and chitosan as they related to three kinds of bacteria are shown in Table I. The MICs of HTCC were 125 ppm irrespective of the type of bacteria, while chitosan can kill the bacteria at the concentration range of 250 to 500 ppm in the presence of acetic acid. However, the 100% acetic acid alone can kill the bacteria even at 0.5 ppm because the optimum pH for bacterial multiplication is usually located in the range of pH

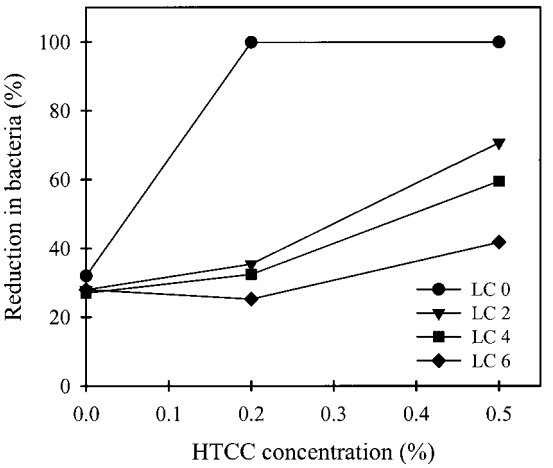

Figure 1 Laundering durability of DMDHEU(8%)/HTCC-treated cotton fabrics. LC; laundering cycle.

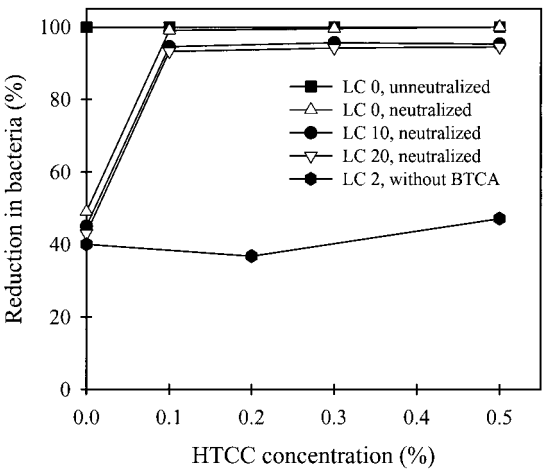

Figure 2 Laundering durability of BTCA(8%)/HTCC-treated cotton fabrics.

6.5–7.0, which suggests the MIC values of chitosan in an acid solution may not be as low as 250 ppm. HTCC shows higher antimicrobial activity than unmodified chitosan because the introduction of trimethylammonium groups in addition to the amino groups of HTCC may synergistically increase antimicrobial activity. However, cotton fabrics treated with HTCC alone had no appreciable antimicrobial activity even after a single laundering.

Laundering durability of crosslinked cotton with crosslinkers and HTCC

The degree to which a simultaneous one-bath treatment of DMDHEU/HTCC with increasing HTCC application levels increased the antimicrobial activity of the treated cotton can be seen in Figure 1. However, only two successive washings were enough to remove the water-soluble HTCC, suggesting that the DMDHEU treatment cannot immobilize HTCC onto cotton. The reduced reaction between methylol groups of DMDHEU and hydroxyl group of HTCC may result from the electrostatic repulsion of the carbonium/immonium intermediate of DMDHEU and the trimethylammonium group of HTCC.

Two polycarboxylic acids were employed to bind the HTCC to cotton via the esterification of hydroxyl groups of cellulose and HTCC. Unexpectedly, polycarboxylic acid treatment with BTCA or CA can exhibit acceptable antimicrobial activity in the absence of chitosan or HTCC (Figs. 2 and 3). An addition over 0.1% was enough to achieve approximately 100% reduction in bacteria irrespective of the kinds of polycarboxylic acids. However, the antimicrovial activity of the crosslinked cotton with polycarboxylic acids cannot be observed when the residual free carboxylic acid groups were neutralized with 0.1*N* NaOH solution. It implies that the free carboxylic acids can dissociate in the presence of water and release hydroxonium ions having a bactericidal effect because many kinds of bacteria survive only in the pH region of 5 to 7.

The disappearance of antimicrobial activity after neutralization substantiated the temporal bacteriacidal action of polycarboxyic acids. Hence all the following antimicrobial evaluations were carried out after neutralization to minimize the influence of the polycarboxylic acids. In the treatment bath without HTCC, the bacterial reduction value of BTCA- and CA-treated fabrics after neutralization were 49.0 and 38.5%, respectively, indicating negligible antimicrobial activity. The HTCC/polycarboxylic acids treatment made the bacterial reduction value more than 91% even after 20 launderings, irrespective of the kind of polycarboxylic acid. Only 0.1% HTCC was sufficient to impart antimicrobial activity even after 20 launderings when used with BTCA or CA. The bacte-

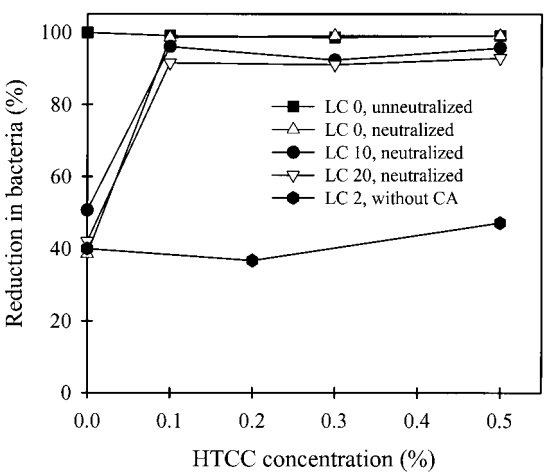

Figure 3 Laundering durability of CA(8%)/HTCC-treated cotton fabrics.

rial reduction values after 10 and 20 launderings implied that HTCC was durably immobilized by polycarboxylic acids: BTCA or CA reacted not only with cellulose but also with HTCC forming ester linkages to make crosslinks between HTCC and cotton.

The existence of ester linkage was verified by FTIR analysis (Fig. 4). In the IR spectrum (b) of the antimicrobial cotton, which was crosslinked with BTCA and HTCC, ester C═O stretching band at 1724 cm^{-1} appeared after the neutralization of cotton with a 0.1*N* NaOH solution. However, it was difficult to identify the ester carbonyl stretching resulting from the reaction between HTCC and BTCA because of negligible amounts of HTCC. Therefore, the mixed formulation of HTCC and BTCA was cured in the absence of cotton at the same curing condition and subsequently the cured mixture was poured into excess water to dissolve unreacted BTCA, HTCC, and sodium acetate catalyst. Figure 4(c) is the IR spectrum of the water-insoluble fraction, the reaction product of BTCA and HTCC. Two small peaks at 1406 and 1470 cm^{-1} correspond to the C—H scissoring vibration of the reacted BTCA and C—H antisymmetric deformation of the N-trimethyl group of the HTCC component, respectively. The presence of ester was demonstrated by C═O stretching at 1734 cm^{-1}.[13] The shoulder peaks at 1850 and 1780 cm^{-1} were assigned to symmetric and asymmetric stretching of residual cyclic anhydrides in the reacted BTCA component.[15]

Durable press performance of antimicrobial cotton

It is well known that cellulose molecules can be crosslinked with polycarboxylic acids containing three or more carboxylic acid groups via two step reactions: cyclic anhydride formation between adjacent carboxylic groups and subsequent ester bond formation between hydroxyl groups in cotton.[16] Crosslinks between cellulose molecules can impart elastic property and wrinkle resistance to cotton. The influence of the HTTC addition on the wrinkle recovery angle (WRA) of the crosslinked cotton is shown in Figure 5. At the same application level of polycarboxylic acids, both polycarboxylic acids significantly increased WRA and the improvement was far higher in the case of BTCA than CA, probably because of the facile anhydride formation of BTCA compared to that of CA. The presence of HTCC during crosslinking did not decrease wrinkle resistance but slightly increased it, indicating the reaction between the polycarboxylic acid and HTCC did not deter ester crosslinks between cellulose molecules.

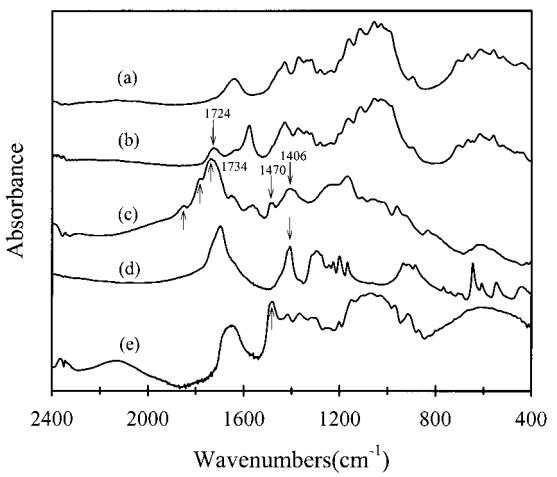

Figure 4 FTIR spectra of (a) cotton, (b) BTCA/HTCC-treated cotton, (c) BTCA/HTCC-cured product, (d) BTCA, and (e) HTCC.

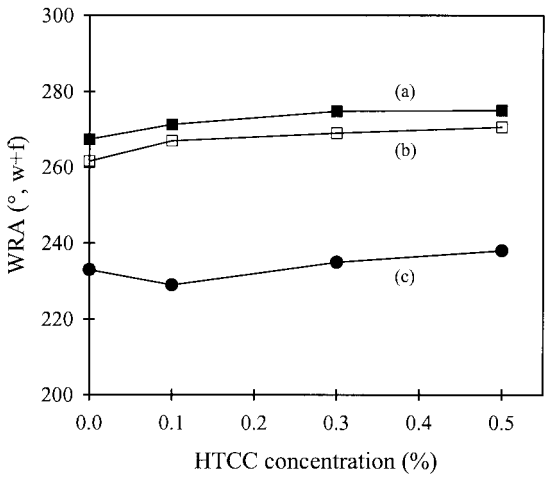

Figure 5 WRA of durable antimicrobial cotton fabric; (a) CA(8%)/HTCC cured at 170°C, (b) BTCA(8%)/HTCC cured at 170°C, and (c) BTCA(8%)/HTCC cured at 160°C.

Mechanical strength of crosslinked cotton can be adversely affected by polycarboxylic acids treatment, which can be attributed to irreversible acid degradation and reversible cellulose crosslinking.[17] Table II represents the effect of HTCC addition on tensile strength, tearing strength, and whiteness of the durable antimicrobial cotton. The polycarboxylic acids treatment alone showed decreases in both tensile and tearing strength retentions. However, HTCC, the antimicrobial agent, in the formulation did not deteriorate the strength until 0.5% application level, which is mirrored by the effect on the WRA. The HTCC addition slightly decreased the whiteness of the crosslinked fabric irrespective of the kinds of crosslinkers. Superior performance of BTCA compared to CA was also pronounced in whiteness of the treated fabric. In the citric acid treatment, noticeable yellowing of the crosslinked cotton has been previously reported where unsaturated carboxylic acids such as aconitic acid, citraconic acid, and itaconic acid were inevitablely generated.[17] Therefore, BTCA would be a better choice in imparting both durable

TABLE II
Performance Properties of Durable Antimicrobial Cotton Fabrics

HTCC concentration (%)	Tensile strength retention (%)			Tearing strength retention (%)			Whiteness index		
	CA (8%)	BTCA (8%)		CA (8%)	BTCA (8%)		CA (8%)	BTCA (8%)	
	Cured at 170°C	Cured at 160°C	Cured at 170°C	Cured at 170°C	Cured at 160°C	Cured at 170°C	Cured at 170°C	Cured at 160°C	Cured at 170°C
0	64.8	76.8	74.2	57.0	44.0	42.4	63.4	70.9	69.2
0.1	63.9	76.5	75.1	57.7	48.9	45.6	63.0	70.3	68.5
0.3	63.0	76.8	74.7	58.6	49.9	47.1	61.1	69.7	67.9
0.5	65.0	74.9	74.6	58.0	52.1	48.8	61.9	68.4	66.8

antimicrobial activity and wrinkle resistance to cotton without significantly impacting mechanical strength or whiteness via a single application.

CONCLUSION

Water-soluble HTCC, *N*-(2-hydroxy)propyl-3-trimethylammonium chitosan chloride, was an excellent antimicrobial agent effective against *Staphylococcus aureus, Klebsiella pneumoniae*, and *Escherichia coli* when compared to chitosan irrespective of the presence of acetic acid as indicated in the MIC analysis. The DMDHEU/HTCC treatment was not effective in immobilizing HTCC on cotton resulting in the loss of antimicrobial activity only after two laundering cycles. However, the simultaneous treatment of HTCC and polycarboxylic acids, particulary BTCA, imparted durable antimicrobial activity to cotton fabric. The imparted laundering durability of antimicrobial cotton fabrics was because of the introduced covalent bond formation between the cellulose molecule and HTCC via the esterification of BTCA catalyzed by sodium acetate as ascertained by FTIR analysis. The bacterial reduction values of the fabrics treated with 8% BTCA and 0.1% HTCC were greater than 90% even after 20 laundering cycles. Also, the durable antimicrobial treatment introduced an excellent durable press property to cotton without severely impairing mechanical strength or whiteness. It is concluded from the results that BTCA can be used with HTCC in one bath to impart durability of antimicrobial activity along with durable press property to cotton fabric.

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