Simultaneous X-Linking and Antimicrobial Finishing of Cotton Fabric

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ABSTRACT: This research work tries to achieve a multifunctional finishing on the cotton fabric by using environmentally friendly chemicals. Chitosan and *N*-(2-hydroxy) propyl-3-trimethyl ammonium chitosan chloride (HTCC) with different crosslinking agents including citric acid (CA), butane tetra carboxylic acid (BTCA), and glutaraldehyde (GA) were coapplied on the cotton fabric. This improves the laundering durability of antimicrobial treatment by formation of covalent bond between the crosslinking agent, antimicrobial agent, and cellulosic chains. Furthermore, it helps to enhance the crease resistance properties of the treated samples. The antimicrobial activities of the treated samples were tested after 15 laundering cycles. The whiteness and wrinkle recovery angle of the treated fabric were also examined. The glutaraldehyde treatment was superior to CA treatment in terms of prolonged antimicrobial activity of the samples after successive laundering. Also, the treated samples with glutaraldehyde showed a higher wrinkle recovery angle with excessive deterioration in whiteness when compared with CA and BTCA. The treated samples with CA and BTCA show good antimicrobial activity after successive laundering and improved wrinkle recovery angle. However, BTCA indicates a higher durability in comparison with CA and same durability after repeated laundering with glutaraldehyde. This can be achieved without yellowing and unpleasant odor. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 178–185, 2007

Key words: cotton; chitosan; X-linking; antimicrobial; whiteness; durability

INTRODUCTION

It has been recognized for a long time that micro organisms, particularly bacteria, can grown on textile substrate. Cotton as a natural fiber is more susceptible than synthetic fibers due to its porous hydrophilic structure retaining water, oxygen and nutrients, and thereby providing a perfect environment for bacteria growth. Clothing such as footwear, sportswear and underwear, hospital healthcare textiles such as bedding, curtains, gowns, uniforms, towels, gloves and gauze, industrial clothing such as military garments, civil defense, protective garment, health care products such as latex examination gloves, and carpeting are excellent substrates for bacterial and fungal growth. They form a moist and warm environment and allow optimum growth conditions for the micro organisms. This microbial infestation has several unpleasant consequences. One of this is development of unpleasant odour when bacteria convert human perspiration into some foul-smelling substances such as carboxylic acid, aldehydes, and amines. The microbial textile infestations may also result in disease in those using textiles; for example, bacteria such as *Staphylococcus* on the underwear causes odour and acute purulence on human body, *Escherichia coli* causes odour and ulcers on the skin, and fungi such as *Aspergillus Niger* weaken and decolorize clothing. Mold and mildew stains may also be produced. As microbes often attack the finishing materials applied to textiles, color changes and loss of mechanical properties occur. Microbes may also severely disrupt manufacturing processes, dyeing, finishing, and printing operation through reduction of viscosity, fermentation, and mold formation. Microbial infestation cannot be removed in most cases even by frequent washing, except washing at boiling temperature. The treatment of textile materials with antimicrobial agents is necessary to avoid cross infection by pathogenic micro organisms, to control the infestation by microbes, to arrest metabolism in microbes to reduce odour formation, and to protect the textile products from staining, discoloration, and quality deterioration. The antimicrobial textiles can be classified into two categories, namely, biostatic and biocidal.[1–6]

Many antimicrobial agents used in textile industry are known from the food stuff and cosmetics sector. These substances are incorporated with textile substrates comparatively at lower concentrations. It must be ensured that these substances are not only permanently effective but also that they are compatible with skin and environment.

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Organic compounds such as Triclosan, a chlorophenol compound, inhibits growth of micro organisms by using an electrochemical mode of action to penetrate and disrupt their cell walls. Quaternary ammonium compounds, biguanides, amines, and glucoprotamine show poly cationic, porous and absorbent properties. These substances bind micro organisms to their cell membrane and disrupt the structure resulting in the breakdown of the cell.

Inorganic compounds such as metallic complex compounds based on metals like cadmium, silver, copper, and mercury cause inhibition of the active enzyme centers (inhibition of metabolism). Among these, silver compounds are very popular and have already been used in the preparation of antimicrobial fabric.[7] Recently a durable platform technology has been developed that introduces copper, with potent biocidal activities, into cotton fibers and other polymeric materials.[8]

Also, natural herbal and dyes can be used for antimicrobial finishes since, there is a tremendous source of medicinal and dye plants with antimicrobial composition to be the effective candidates in bringing out antimicrobial textiles. Recently, the uses of these materials reported as antimicrobial agents on to the wool fabrics.[9]

Chitosan is a natural nontoxic biopolymer and is biocompatible, derived by deacetylation of chitin, a major component of the shells of crustacea such as crab, shrimp, and crawfish. It has received considerable attention for its commercial applications. Coatings of chitosan on conventional fibers appear to be the more realistic prospect since they have been used in several applications such as thickening agents in pharmaceutical and cosmetic formula and it is also known that this biopolymer has antimicrobial and wound healing properties.[10–14] The reported antimicrobial activity with chitosan was only shown in acidic medium because of its poor solubility above pH 6.5. This is a limitation for its application as an antimicrobial agent for textile finishing. The water-soluble quaternary ammonium salts of chitosan are soluble in both acidic and basic physiologic circumstances, so they might be good candidates as polycationic antimicrobial agents. The other kind of quarternized chitosan, which is synthesized by the reaction of chitosan with glycidyl trimethylammonium chloride, has been reported to have a good moisture-retention capacity, but relatively little work has been reported on its antimicrobial activity.[15–21] These studies investigate the action of chitosan-*N*-(2-hydroxyl)-propyl trimethyl ammonium chloride on the growth of microorganisms, to assess the potential for using it as a natural antimicrobial agent in advanced textiles.

Kim et al.[16] applied 0.25 g/L of *N*-(2-hydroxy) propyl-3-trimethyl ammonium chitosan chloride (HTCC) on the cotton fabric with 75% of pick-up and found that the finished fabric has good antimicrobial properties but it was not durable during washing and it could be easily removed from the fabric after two laundering process. They suggested using a crosslinking agent in combination with HTCC for producing a durable antimicrobial finished fabric. They used 80 g/L of dimethyloldihydroxyethylene urea (DMDHEU) with HTCC and found that this crosslinking agent was not effective to improve the durability. They also used 1 g/L of HTCC with 80 g/L of either citric acid (CA) or butane tetra carboxylic acid (BTCA) and understood that BTCA and CA make the finished fabric durable on 20 times of home laundering.[19] Lim and Hudson worked on a fiber-reactive chitosan derivative. They applied *O*-acrylamidomethyl-*N*-[(2-hydroxy-3-trimethyl ammonium) propyl] chitosan chloride (NMA-HTCC) on to cotton fabrics by a cold pad-batch method in the presence of an alkaline catalyst and evaluated its use as a durable antimicrobial textile finish. The antimicrobial activities of the NMA-HTCC-treated cotton fabrics were evaluated quantitatively against *Staphylococcus aureus*. The cotton treated with NMA-HTCC at a concentration of 1 wt % of fabric showed 100% bacterial reduction. The activity was maintained over 99% even after being exposed to 50 consecutive home laundering conditions.[21]

Glutaraldehyde as a crosslinking agent is a bifunctional crosslinking agent that is one of the probable successors of formaldehyde containing crosslinker of cellulosic materials[22–24] that can crosslink chitosan alone[25] and chitosan with cellulose.[13] Also, poly carboxylic acids such as CA and 1,2,3,4-butane tetracarboxylic acid are mentioned as cotton crosslinking agents that are environmentally friendly and could be good substitutes for methylol containing X-linkers.[26,27] The chemical structures of different X-linking agents are illustrated in Figure 1.

In this research work, the quaternary ammonium salt of chitosan was prepared by chemical modification of chitosan with glycidyl trimethyl ammonium chloride. Glutaraldehyde (GA), CA, and 1,2,3,4-bu-

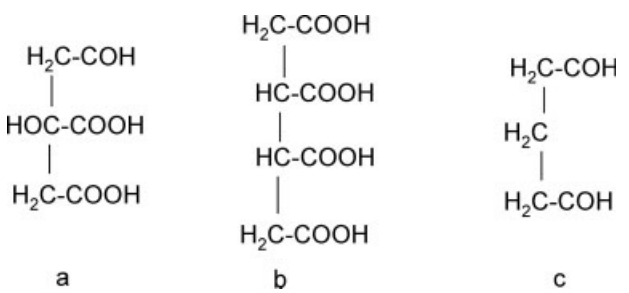

Figure 1 Chemical structures of different crosslinking agents (a) citric acid (CA), (b) butane tetracarboxylic acid (BTCA), and (c) glutaraldehyde (GA).

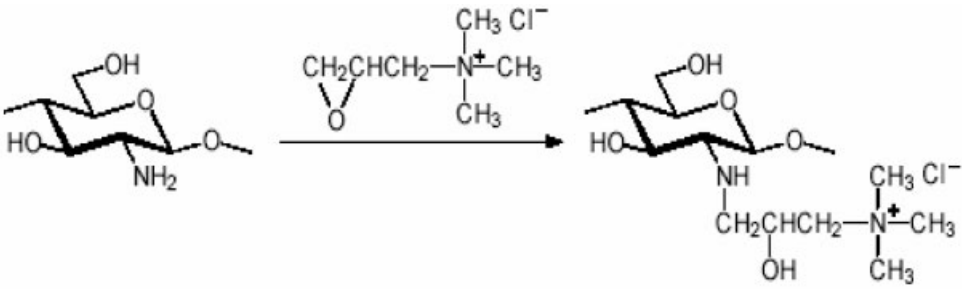

Figure 2 Reaction of chitosan with GTMAC for synthesis of HTCC.

tane tetracarboxylic acid (BTCA) were chosen as free formaldehyde crosslinking agents in combination with HTCC and chitosan to produce fabric with durable antimicrobial and also crease-free properties.

EXPERIMENTAL

Material

Chitosan was produced by Chitotech Co. (Iran) with degree of deacetylation of 82%. GTMAC (Fluka, Switzerland), GA (25%), CA, BTCA, acetone, sodium hypophosphate (SHP) of analytical grade and commercial grade of $MgCl_2$ were used. The bleached cotton fabric used was of 170 g/m^2 weight.

HTCC synthesis

Purified native chitosan (1.0 g) was dispersed in 40 mL water, GTMAC (10 mL) was added, and the mixture was stirred at boiling temperature for 9 h. The reaction products were filtered, precipitated in acetone, and allowed to remain for 24 h and then the solid material was extracted and washed again with acetone. After 24 h, the solid material was separated and then extracted with acetone by Soxhlet for 6 h. The material dried in 70°C oven. The reaction between GTMAC and NH_2 groups in chitosan is shown in Figure 2. The synthesized material was investigated by FTIR spectroscopy (Fig. 3).

Fabric treatment

Cotton samples were padded with solutions of HTCC alone, HTCC with different concentrations of crosslinking agent (GA, CA, and BTCA) and required catalyst ($MgCl_2$ for GA and sodium hypophosphite (SHP) for CA and BTCA) and chitosan alone with 80% wet pick-up according to the Table I. The padded samples were then dried and cured.

Durability test

To evaluate the durability of HTCC and chitosan alone and HTCC with different crosslinking agents on the fabrics against home laundering, swatches of 5 × 10 cm^2 were washed according to AATCC Test Method 61(2A)-1996 using an ATLAS Launder-Ometer. In this method, one cycle of laundering is equal to five launderings of medium or warm washing at

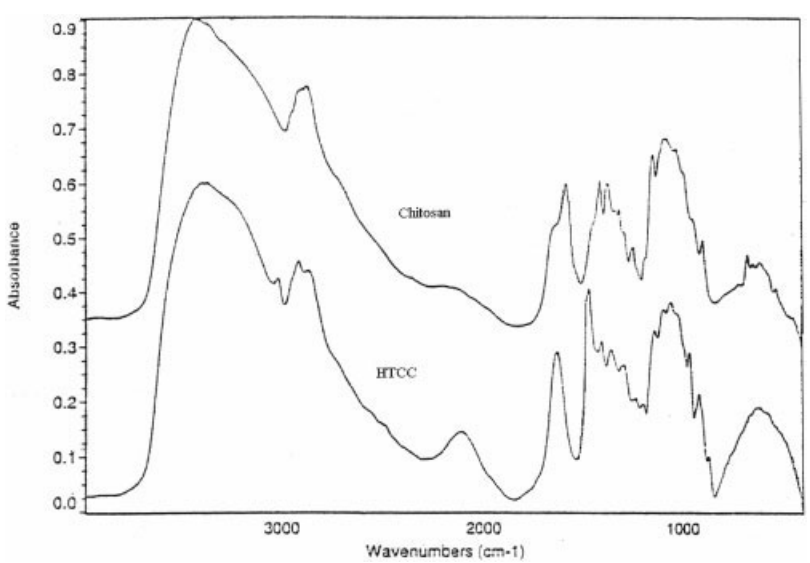

Figure 3 FTIR spectrum of chitosan and HTCC.

TABLE I
Preparation of Different Samples

Sample no.	Contents	Drying conditions	Curing conditions
1	HTCC (0.1%)	At 100°C for 3 min	At 150°C for 2 min
2–4	HTCC (0.1%) + CA (3, 5, 8%), SHP	At 100°C for 3 min	At 150°C for 2 min
5	Chitosan (1%)	At 100°C for 3 min	At 150°C for 2 min
6–8	Chitosan (1%) + CA (3, 5, 8%), SHP	At 100°C for 3 min	At 150°C for 2 min
9–11	HTCC (0.1%) + BTCA (3, 5, 8%), SHP	At 100°C for 3 min	At 170°C for 2 min
12–14	Chitosan (1%) + BTCA (3, 5, 8%), SHP	At 100°C for 3 min	At 170°C for 2 min
15–17	HTCC (0.1%) + GA (3, 5, 8%), $MgCl_2$	At 100°C for 3 min	At 150°C for 2 min

the temperature range of (38 ± 3)°C. Each cycle lasted 45 min at 50°C with 42 rpm and nonionic detergent.

Antimicrobial test of treated fabrics

Antimicrobial effectiveness of treated samples was evaluated using AATCC 100-1999. The *Staphylococcus aureus* was used as the bacterium due to its popularity of being selected as a test organism and its resistance to common antimicrobial agents. Fabric samples were contacted with 1 mL of bacterial inoculum in a 250-mL glass vessel. The inoculum was a nutrient broth culture containing about 1.4×10^4/mL colony forming units (cfu) of bacteria. The samples that were contacted with bacteria for 18 h and then 100 mL of distilled water was poured into vessel and vigorously shaken. The aliquot of the solution was diluted to serial of one-tenth and 100 mL of each dilution stated on a nutrient agar and incubated for 18 h at 37°C. To evaluate antimicrobial activities of the treated samples, the reduction in colony number between the treated and untreated fabric after incubation was compared. The results are expressed as the log reduction of *S. aureus*. A one-log reduction equals a 90% kill of bacterium and a six-log reduction is equivalent to a 99.9999% kill. The percentage reduction of bacteria (R, %) is calculated by following equation:

$$R(\%) = 100(N_1 - N_2)/N_1$$

where N_1 and N_2 are the average numbers of bacteria recovered from the untreated and treated fabric swatches respectively.

Other testing

The crease recovery angle (CRA) was measured according to AATCC test method 66-1989 and the Whiteness Index was measured using Hunter Lab D25M. The values of L* (Lightness), a* (redness–greenness), and b* (yellowness–blueness) was determined by using computer color matching system.

RESULTS AND DISCUSSION

Analysis of HTCC

The synthesized HTCC was swollen immediately and dissolved in water. This property differs verily from chitosan. With increase of pH to 10, the solubility of HTCC was not changed. In neutral medium, the hydroxyl groups of chitosan are not so reactive that they can be involved in an open ring reaction with epoxy groups of GTMAC but the amino groups can react.[16,28] The higher mole ratio of GTMAC and temperature of the reaction leads to increase in the yield production of water soluble HTCC.[16] Also, FTIR spectroscopy studies showed the peaks at 1480 cm^{-1} that corresponded to C—H bond (Fig. 3). This peak and the others at 1640 cm^{-1} are characteristic of GTMAC. The disappearing of the peak of chitosan at 1596 cm^{-1} related to N—H bending and 1650 cm^{-1} relating to C=O stretching of amide groups confirm that NH_2 groups are replaced by 2-hydroxy propyl-3-trimethyl ammonium chloride groups.

Antimicrobial properties of HTCC, chitosan alone and coapplied with different crosslinking agents

Table II shows the influence of different treatment based on chitosan and cationized chitosan on the antibacterial properties of the treated fabrics. It is clear that all the treated fabrics by chitosan and its derivative (HTCC) alone and in combination with different crosslinkers showed good antibacterial properties. This is due to the action of chitosan as an antimicrobial agent. The proposed action of chitosan includes: interaction of polycationic structure of chitosan with anionic components resulting in changes in permeability and then causing death of the cell by inducing leakage of intermolecular components or preventing of nutrients from entering the cell by formation of polymeric membrane on the surface of the cell or adsorption of electronegative substances in the cell and disturbing the physiological activities of the microorganism that causes death of the cell.[29]

The results also show that three different crosslinking agents used with chitosan and HTCC have no influence on the antimicrobial properties of the

TABLE II
Reduction of Bacteria R (%) Before and After 15 Cycles of Laundering

Sample no.	Treatment	R (%)	
		Before laundering	After 15 cycles of laundering
0	Untreated	0	0
1	HTCC (0.1%)	99	UD
2	HTCC (0.1%) + 3% CA	99.99	UD
3	HTCC (0.1%) + 5% CA	99.99	UD
4	HTCC (0.1%) + 8% CA	99.99	90
5	Chitosan (1%)	99	UD
6	Chitosan (1%) + 3% CA	99.99	UD
7	Chitosan (1%) + 5% CA	99.99	UD
8	Chitosan (1%) + 8% CA	99.99	90
9	HTCC (0.1%) + 3% BTCA	99.99	UD
10	HTCC (0.1%) + 5% BTCA	99.99	90
11	HTCC (0.1%) + 8% BTCA	99.99	99
12	Chitosan (1%) + 3% BTCA	99.99	UD
13	Chitosan (1%) + 5% BTCA	99.99	UD
14	Chitosan (1%) + 8% BTCA	99.99	99
15	HTCC (0.1%) + 4% GA	99.9999	90
16	HTCC (0.1%) + 8% GA	99.9999	90
17	HTCC (0.1%) + 16% GA	99.9999	99

UD, no log reduction was detected.

treated cotton fabrics. Table II shows the effect of coapplication of different crosslinking agents with various concentrations on the durability of the antimicrobial properties of the treated cotton fabrics. The poly carboxylic acid reagents such as BTCA can produce a cyclic anhydride as a result of heat and

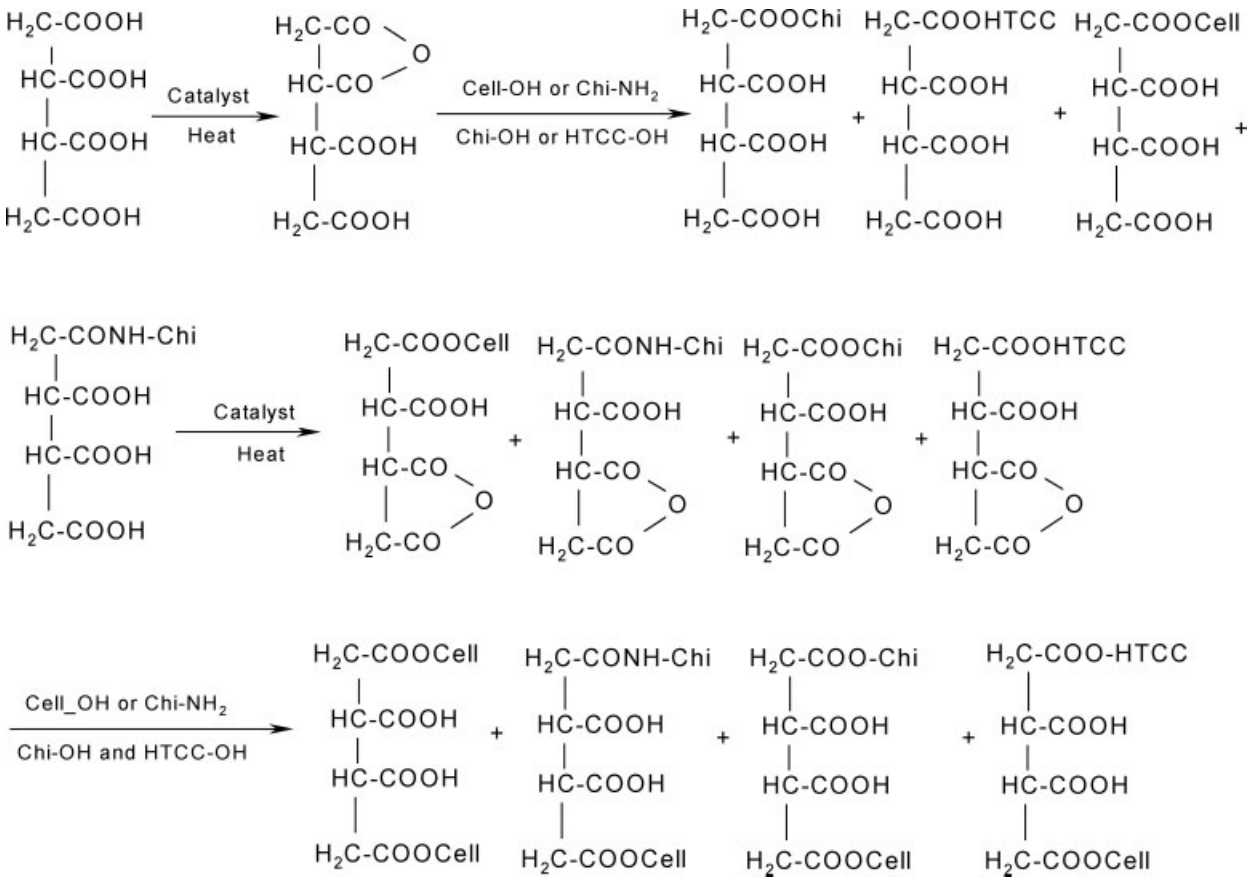

Figure 4 Crosslinking mechanism of cellulosic chains, cellulose-chitosan, and cellulose-HTCC by BTCA in presence of catalyst and heat.

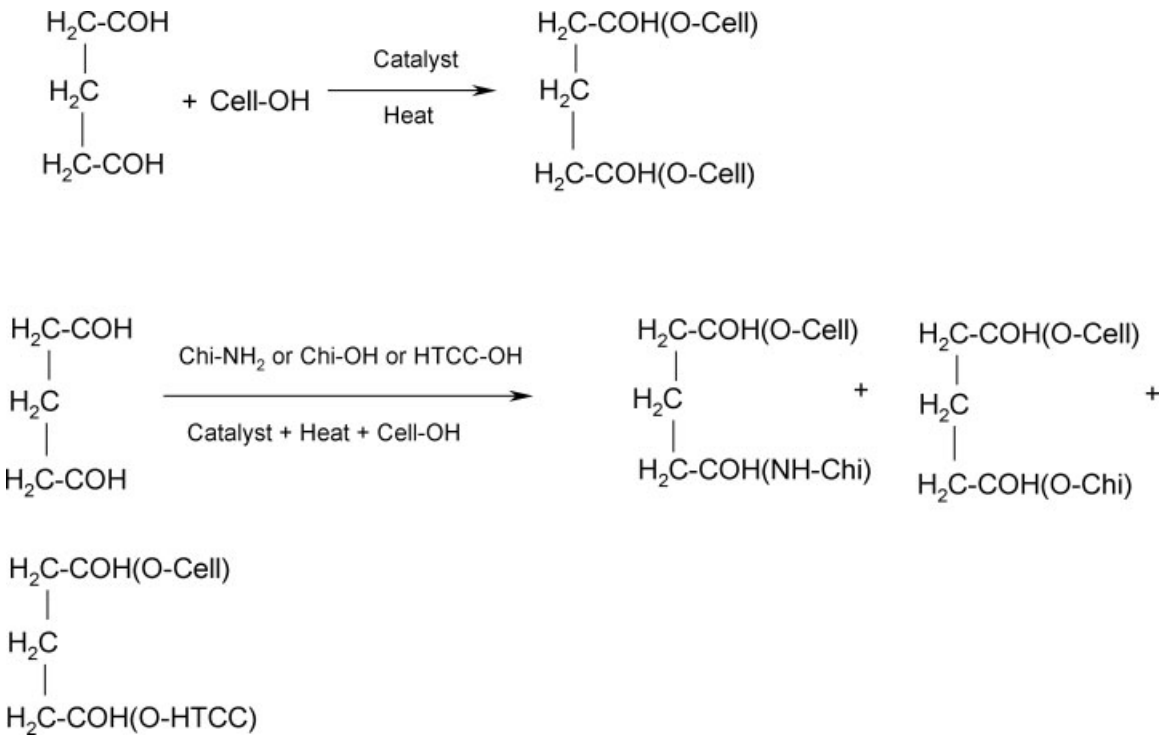

Figure 5 Crosslinking mechanism of cellulosic chains, cellulose-chitosan, and cellulose-HTCC by glutaraldehyde in presence of catalyst and heat.

catalyst and then esterify the cellulosic chains. However, chitosan and HTCC can be also esterified by the poly carboxylic acid. This could result in a crosslinking between cellulose and chitosan or HTCC as well as crosslinking between cellulosic chains. The mechanism of crosslinking between cellulose, chitosan, and HTCC by BTCA is illustrated in Figure 4. The mechanism action of CA is the same as that of BTCA. Also, the crosslinking mechanism of cellulose, chitosan, and HTCC by GA is indicated in Figure 5.

Sample no. 1 that was treated with HTCC successfully showed antibacterial properties while there is no sign of reduction of bacteria growth on the untreated sample. Also, the sample no. 5 has antibacterial properties due to the antimicrobial effect of chitosan. All of the different treated samples showed 100% inhibition rate of growth of *S. aureus* before laundering (Table II).

The results of accelerated laundering showed about 90% inhibition of growth of *S. aureus* for samples nos. 4, 8, 11, 14, 16, and 17. This means that the different crosslinking agents act very well and build a linkage between the antimicrobial agent and fabric, which was stable during repeated laundering processes. The crosslinking effect of GA on chitosan was investigated by Nakatsuka and Andrady.[25] Application of GA and chitosan on cotton fabric was also investigated by Zhang et al.[13] and they found that chitosan can be linked to the cellulose chain by the GA intermediate. Hence, it might be elucidated that the un-replaced NH_2 groups still remaining in HTCC can react with GA. The major restricting property of GA is its yellowing effect and mall odor of unwashed samples. However, this deficiency could be compensated by washing with detergent. Anyway the use of GA has the risk of toxic chemicals that must be mentioned.

By using CA or BTCA in the pad-bath, the antimicrobial properties of the treated cotton samples retain after laundering. However, BTCA shows a higher durability in comparison with CA and produces the same durability as GA after repeated laundering. This can be achieved without yellowing and unpleasant odor.

The results of wrinkle recovery angle (WRA) are demonstrated in Table III. Chitosan and HTCC alone have no significant impact on the WRA of the fabric. Using X-linking agent may improve laundering durability of the treated sample as well as WRA. The impact of different X-linking agents on WRA of the treated fabric is differing. In this study, GA shows better performance as regards amount of fabric WRA. This may be due to the higher amount of GA used in the pad-bath. However an increase in the concentration of the X-linking agent in the pad-bath leads to a higher fabric WRA.

The BTCA and CA also demonstrated the same trend. However BTCA produces a fabric with higher

fabric WRA in comparison with CA, which is in agreement with works of others.

The results also indicated that the amount of WRA decreases after repeated laundering. This is the same for all three X-linking agents used in this experiment. However, the values of WRA are still significant as regards recovery from creasing when an optimum amount of X-linking agent used.

The results of colorimetric properties of the untreated and different treated fabric samples illustrated in Table IV. These results indicated that coapplication of X-linking agents with HTCC and chitosan leads to a decrease in the fabric whiteness and an increase in the amount of b*, which represents the yellowing. However, the rate of reduction in the fabric whiteness varies and depends upon the type of the X-linking agents used. In this study, GA shows the highest and BTCA the lowest influence on the fabric whiteness. The changes in the b* also show the same trend which means an increase in the concentration of GA leads to produce a yellow fabric. The presence of residual aldehyde groups was known as a main cause of fabric yellowing when the fabric was treated with GA.[30] Also when CA was coapplied with antimicrobial agents, CA might release aconitic acid, which is known as a source of yellowing.[31]

CONCLUSIONS

The FTIR spectroscopy and water solubility above pH 7 confirmed synthesis of HTCC. All of the treated fabrics showed inhibition of the *Staphylococcus aureus* growth. The wash fastness properties of the HTCC treated fabric can be improved by addition of any of the three X-linking agents used in this research. However GA shows a higher durability during repeated laundering. The problem with GA is fabric yellowing of treated samples and unpleasant odor, which can be reduced by washing; using of GA may help to improve the wash fastness properties of antimicrobial finishes and also make the cotton fabric crease-resistant. The washing durability of the treated samples can be also be achieved by using CA or BTCA in the pad-bath. However, BTCA shows a higher durability than CA and produces the same durability as GA after repeated laundering. This can be achieved without yellowing and unpleasant odor.

TABLE III
Wrinkle Recovery Angle (WRA) of Cotton

Treatment	WRA (°)	
	Before laundering	After 15 cycles of laundering
Untreated	101	103
HTCC (0.1%)	103	102
HTCC (0.1%) + 3% CA	130	126
HTCC (0.1%) + 5% CA	160	144
HTCC (0.1%) + 8% CA	182	170
Chitosan (1%)	102	105
Chitosan (1%) + 3% CA	130	124
Chitosan (1%) + 5% CA	158	145
Chitosan (1%) + 8% CA	181	166
HTCC (0.1%) + 3% BTCA	170	152
HTCC (0.1%) + 5% BTCA	194	181
HTCC (0.1%) + 8% BTCA	210	196
Chitosan (1%) + 3% BTCA	160	150
Chitosan (1%) + 5% BTCA	190	174
Chitosan (1%) + 8% BTCA	206	196
HTCC (0.1%) + 4% GA	180	165
HTCC (0.1%) + 8% GA	210	180
HTCC (0.1%) + 16% GA	226	198

TABLE IV
***L**, **a**, **b**, and Whiteness of Untreated and Different Treated Cotton Fabric Samples Before and After 15 Cycles of Laundering*

Treatment	*L**	*a**	*b**	Whiteness
Untreated	89.23	2.46	−3.67	92.17
HTCC (0.1%)	89.90	2.16	−3.14	90.92
HTCC (0.1%) + 3% CA	90.30	0.97	0.67	73.79
HTCC (0.1%) + 5% CA	89.82	0.56	2.59	63.30
HTCC (0.1%) + 8% CA	89.89	0.23	4.18	56.17
Chitosan (1%)	87.18	1.26	1.02	65.54
Chitosan (1%) + 3% CA	89.15	0.58	2.83	60.98
Chitosan (1%) + 5% CA	89.16	0.11	5.26	49.30
Chitosan (1%) + 8% CA	88.89	−0.25	6.48	42.79
HTCC (0.1%) + 3% BTCA	90.70	1.39	−1.01	82.62
HTCC (0.1%) + 5% BTCA	90.16	1.20	−0.09	77.16
HTCC (0.1%) + 8% BTCA	90.50	0.62	2.73	64.48
Chitosan (1%) + 3% BTCA	88.74	0.78	2.06	63.73
Chitosan (1%) + 5% BTCA	89.33	0.03	4.10	55.23
Chitosan (1%) + 8% BTCA	89.25	0.11	5.25	49.07
HTCC (0.1%) + 4% GA	90.04	0.67	3.93	57.73
HTCC (0.1%) + 8% GA	88.53	0.18	8.97	29.96
HTCC (0.1%) + 16% GA	84.38	1.19	18.42	−27.11

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