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Green synthesis of easy care and antimicrobial cotton fabrics

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ABSTRACT

Easy care characteristics and antimicrobial properties were imparted to cotton fabrics using aqueous multifinishing formulation consisting of butanetetracarboxylic acid (BTCA) and chitosan having different molecular weights. The latter were prepared by chitosanolysis using pectinase enzyme. Multifinishing treatment was carried out as per the pad-dry-cure method. Parameters affecting the magnitude of finishing viz. concentrations of BTCA and chitosan as well as curing time, temperature and their onset on fabric performance and antimicrobial activity were studied. Thus green synthesized fabrics were found to acquire high crease recovery with acceptable strength losses which can place them in the anticrease and easy care category of cotton finishing. Surface roughness and fabric stiffness imply that the multifinished fabrics retain their comfort. These fabrics display antimicrobial activity against gram-positive and gram-negative bacteria and yeast tested even after 10 washes. Mechanism of concurrent crosslinking of/and anchoring to cotton cellulose using BTCA is also reported.

1. Introduction

It has long been recognized that microorganisms can thrive on textile substrates. These microorganisms can cause fiber degradation by feeding on unreacted monomers and/or chemicals found in the fibers such as oils, dyes, finishes, and coatings. Natural fibers such as cotton are more susceptible than synthetics because their porous hydrophilic structures that retain water, oxygen, and nutrients, which provide a perfect environment for the growth of microorganisms (Hebeish et al., 2011).

Microbial infestation has unpleasant consequences such as foul odors, mold and mildew strains, discoloration and loss of functional properties (e.g. tensile strength and elasticity). Microbes can disrupt manufacturing processes, textile dyeing, printing and finishing operations through the reduction of viscosity, fermentation, and mold formation (Gupta, 2005).

A variety of antimicrobial finishes have been developed for application to textiles. These finishes acquire effective control of bacteria, molds, and fungi (Abdel-Halim, Fouda, Hamdy, Abdel-Mohdy, & El-Sawy, 2010; El-Shafei, Fouda, Knittel, & Schollmeyer, 2008; Fouda, El Shafei, Sharaf, & Hebeish, 2009; Fouda, Wittke, Knittel, & Schollmeyer, 2009). In this research work, chitosan samples is regarded as one of the most important antimicrobial finish due to its abundance, biocompatibility, biodegradability, renewability, nontoxicity, ease of application, environmental safety and cost-effectiveness (Fouda, Wittke et al., 2009). Chitosan is the deacetylated derivative of chitin which is the second most abundant polysaccharide found on earth next to cellulose. It is a linear hetero polysaccharide (Cabrera & Cutsem, 2005) consisting of β-(1,4)-2-amino-2-deoxy-D-glucopyranose unit (Fouda, 2005) with various degree of N-acetylation (Kittur, Kumar, Varadaraj, & Tharanathana, 2005) linked by β-(1,4)-glucosidic bonds (Chung & Chen, 2008).

The antimicrobial agents can be applied to the textile substrates by exhaustion, pad-dry-cure, coating, spray and foam techniques. The substances can also be applied by direct adding into the fiber spinning dope. It is claimed that the commercial agents can be applied online during the dyeing and finishing operations (Ramachandran, Rajendrakumar, & Rajendran, 2004).

Nowadays special focus on "green chemistry" by researchers is strongly created as a result of increasing awareness about the environment. Utilization of nontoxic chemicals, environmentally benign solvents and renewable materials are some of the key issues that merit important consideration in a green synthesis strategy (Desimone, 2002; El-Rafie et al., 2011; Poliakoff & Anastas, 2001).

With the above in mind, the present work is undertaken with a view to develop a green synthesis of multifinished

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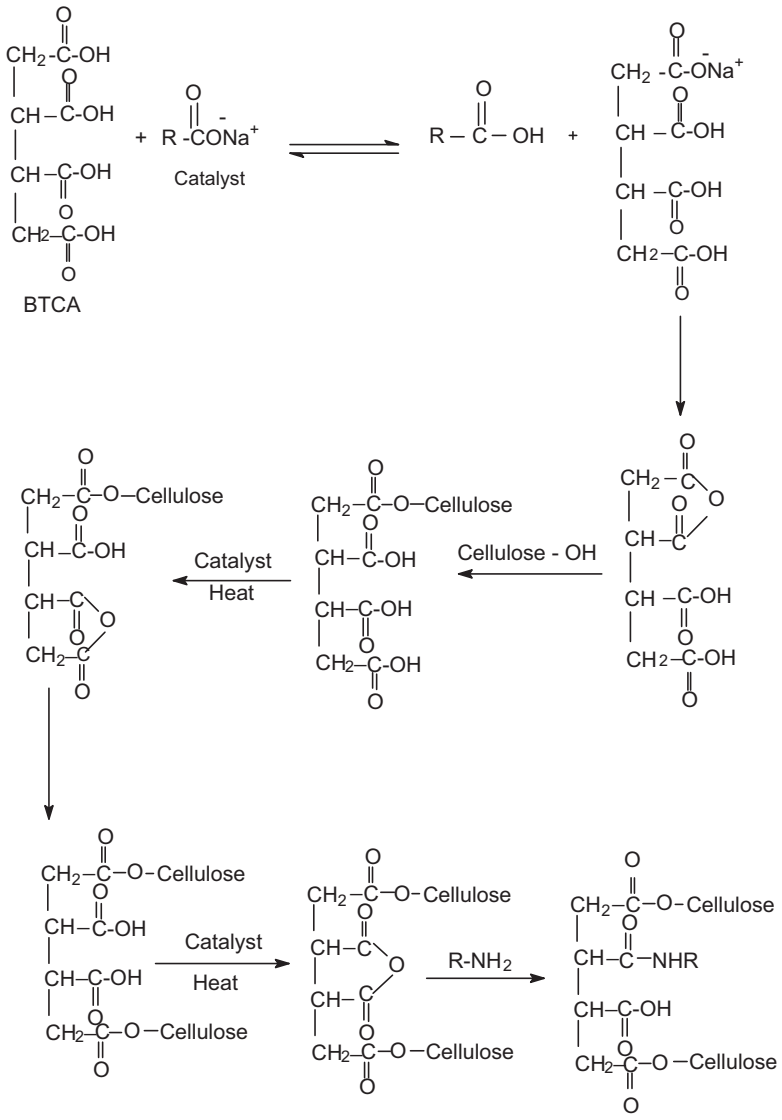

Fig. 1. The crosslinking mechanism of cotton cellulose using BTCA in presence of chitosan. (Catalyst, sodium acetate trihydrate; R–NH_2, chitosan.)

cotton fabric. The green synthesis is based on the use of chitosan having different molecular weights along with nontoxic 1,2,3,4,-butantetracarboxylic acid (BTCA). Variations in molecular weight are achieved by subjecting high molecular weight chitosan to enzymatic hydrolysis. BTCA is used to perform dual functions viz. as crosslinking agent and as anchor molecules for chitosan fixation on the cotton fabric. Ease of care characteristics and antimicrobial activity of the treated fabrics are evaluated together with other properties pertaining to fabric performance.

2. Experiment

2.1. Materials

Mill scoured, bleached and mercerized plain weave cotton fabric (169 g/m^2); supplied by Misr Company for Spinning and Weaving, Mehalla El-Kobra, Egypt was employed. The fabric was further purified in the laboratory by scouring at 100 °C for 60 min in a solution containing sodium carbonate (2 g/l). It was then thoroughly washed with boiling water followed by cold water and dried at ambient temperature. Chitosan with different molecular weights were prepared by chitosanolysis of high molecular weight chitosan (HMWC) via pectinase enzyme from *Aspergillus niger* (with activity 1.32 Units per mg protein). HMWC, pectinase enzyme and crosslinker 1,2,3,4-butanetetracarboxylic acid (BTCA) 99% were purchased from Sigma-Chemical Company, St. Louis, Mo, U.S.A. Other chemicals used in this study were of analytical grade.

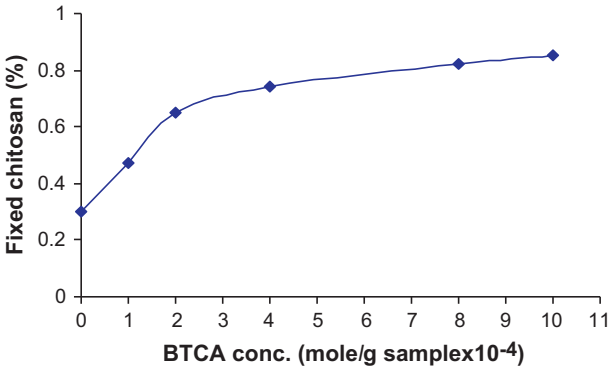

Fig. 2. Effect of BTCA concentration on the amount of chitosan fixed on to cotton.

Table 1
Effect of different concentrations of BTCA used as crosslinker with chitosan on the amount of fixed chitosan along with major technical properties of the cotton fabrics.

Conc. of BTCA (mole/g sample) $\times 10^{-4}$	Fixed chitosan (%) After washing	TS (kg) W F		Elongation at Break (cm) W F		CRA (°) W F		Roughness (μm) W F		Stiffness (mg/cm^2) W F		AirPermeability (cm^3/S cm)	Water permeability (L/m^2 S)	WPU (%)
Control	–	61.5	51	18	24.08	68	56	14.1	14.6	1104	1170			
0	0.3	51.25	50	17.75	22.54	71	80	15	14.4	1114	1900	22.75	0.874	51.85
1	0.47	47.85	46.68	15.33	21.3	81	77	15.2	15.3	1530	2020	22.2	0.611	50.96
2	0.65	38.63	45.75	13.08	19.5	104	99	15.7	14.8	1600	2500	22.2	0.594	50.8
4	0.74	37.45	41.54	10.25	17.8	114	122	16.1	15	1890	2800	18.2	0.608	44.36
8	0.82	27.39	38.05	9	15	120	137	16.9	15.3	2400	3050	19.6	0.628	41.94
10	0.85	25.97	30.71	7.62	13.75	125	138	16.1	16.7	2501	3250	16.6	0.631	41.23
Blank	–	20.95	35.99	8.5	14	119	135	14.9	16	1100	3000	23	0.555	40.07

Reaction conditions: [Chitosan of MW 6×10^5], 1% (in 1% acetic acid; 0.6 mole of sodium acetate trihydrate catalyst) to 1 mole BTCA; treatment as per pad-dry-cure method: wet pick up 100%, drying at 80 °C for 5 min, curing at 160 °C for 2 min. Washing with 1% acetic acid to remove unbounded chitosan. Blank: cotton fabric treated with [BTCA], 8×10^{-4} mole/g sample only. Control: untreated fabric. Abbreviations: CRA, crease recovery angle; TS, tensile strength; W, warp direction of the fabric; F, filling weft direction of the fabric; WPU, water pick up.

2.2. Fabric treatment

2.2.1. Fixation of chitosan onto cotton fabrics

For crosslinking of chitosan to cotton fabrics; 1,2,3,4 butane tetracarboxylic acid (BTCA) was used as anchor molecule because of its low toxicity. The concentration range of anchor (BTCA) was from 1 to 10×10^{-4} mole/g fiber.

Chitosan samples of different molecular weights were dissolved in a solution of (0.1 M acetic acid/0.2 M sodium chloride) at temperature not above 70 °C, and left about 12 h with continuous stirring to obtain a 1% (w/v) solution. The chitosan solution was filtered to remove any undissolved matter.

Fabrics were padded in aqueous solution containing chitosan (1%), BTCA (1 mole) and sodium acetate trihydrate (0.6 moles) to a wet pick of 100%. The latter ingredient functions as a catalyst in terms of (a) facilitating epoxy groups formation through condensation in two steps of the four carboxyl groups of BTCA for anchoring of chitosan and/or crosslinking of the cotton fabrics and (b) moderating (lessening) the acidic effect of BTCA. At any event, however, the padded fabrics were then dried at 80 °C for 5 min and cured at 130–160 °C for 2–5 min. The finished fabrics were washed with water, followed by treatment in an aqueous solution of acetic acid 1%. Finally the fabrics were washed in cold water to neutral and dried at ambient temperature.

2.2.2. Evaluation of multifinished fabrics

Tensile strength (kg) and elongation at break (%) were carried out according to ASTM D-1682 using Tensile Strength Instron Corporation 4435 series IX Automated Material Testing System, USA.

Surface roughness (micron) test was carried out using Surface Roughness Measuring Instrument, Model SE1700, Japan, according to JIS-94.

Fabric stiffness test was carried out by making use of Shirley Stiffness tester according to ASTM D 1388.

Dry Creasy Recovery Angle was determined according to AATCC Technical Manual test method vol. 70, 1998.

The amount of chitosan fixed onto the treated fabric was evaluated in term of nitrogen content values estimated as per a standard Kjeldahl method (Vogel, 1975) and then the amount of fixed chitosan % was calculated from the equation: fixed chitosan % = N% × 161/14.

Antimicrobial potentialities of the multifinished fabrics under investigation were determined by disc diffusion test (Abdel-Halim et al., 2010). The effectiveness of the antimicrobial activity of the treated cotton fabrics was evaluated using different species of bacteria, yeast and fungi. Which were obtained from the culture collection of the microbial chemistry laboratory, NRC, Cairo, Egypt, as follows:

Bacterial species were grown on nutrient agar and include:

(A) Gram-negative, *Escherichia coli*, (B) Gram-positive, *Staphylococcus aureus*, *Bacillus subtilis* and *Bacillus cereus*.

Yeast species were cultivated on glucose agar and include: *Saccharomyces cerevisiaea*, *Candida albicans*, *Saccharomyces chevallii*, *Candida pseudotropicalis*, *Rhodotorula minuta*, *Saccharomyces cerle*.

Fungi species were grown on Czapk's Dox agar and include:

Aspergillus niger, *Maccrophomina phaseoli*, *Trichoderma viride* and *Fusarium oxysporium*.

To test the antimicrobial spectrum; disks of the fabric with diameter 0.8± cm were transferred to the surface of agar media plates, previously inoculated with the test organisms. The diameter of inhibition zone was measured after 24 h for both bacteria and yeast and after 48 h for fungi.

The durability of the multifinished cotton fabrics against repeated laundering were evaluated by washing these fabrics as per the modified AATCC Test method 61(2A)-996. The fabrics were laundered 15 cycles using soap detergent in a washing machine

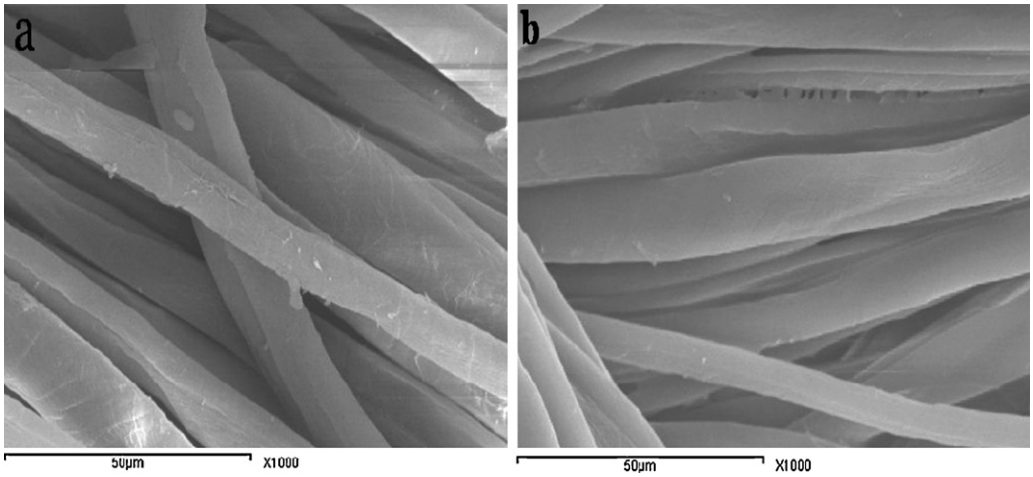

Fig. 3. SEM for (a) untreated fabric; (b) fabric treated with the multifinishing formulation.

with full water level at 40 °C for 8 min and dried for 45 min at 50 °C in an oven and sterilized by heat at 105 °C.

3. Results and discussion

3.1. Mechanism of current crosslinking and chitosan fixation

Chitosan with expectable multi-functional finishing effects when used for treatment of cotton fabrics along with BTCA and sodium acetate trihydrate (catalyst) in one-step process are the subject of current studies. The crosslinking mechanism of cotton cellulose using BTCA in precence of chitosan is shown below in Fig. 1 (El-Tahlawy, El-Bendary, El-Hendawy, & Hudson, 2005).

Factors affecting the treatment such as BTCA concentration and chitosan concentration as well as temperature and curing time and the onset of this on fabric performance and antimicrobial properties are discussed in the following sections:

3.2. Crosslinking agent (BTCA) concentration

3.2.1. Fixed chitosan

In order to pursue concurrent easy care and antimicrobial finishing, cotton fabrics were treated in aqueous finishing formulations consisting of chitosan and BTCA at different concentrations along with sodium acetate trihydrate as a catalyst using the pad-dry cure method. No other additives were included in the finishing bath.

Fig. 2 shows the effect of BTCA concentration on the amount of chitosan fixed on the cotton fabric by the multifinishing treatment under investigation. Obviously, the amount of fixed chitosan increases by increasing the concentration of BTCA within the range studied. This could be interpreted in terms of greater availability of BTCA molecules in the vicinity of the hydroxyl groups of cotton cellulose. It is understandable that reaction of BTCA via crosslinking with cotton cellulose relies on availability of BTCA molecules in the proximity of the cellulose hydroxyl groups which are immobile. That is, higher BTCA concentration would work in favour of greater amount of BTCA molecules in the proximity of the immobile hydroxyl groups of cotton cellulose.

In absence of BTCA the amount of fixed chitosan is much lower than in its presence. For instance at BTCA concentration of 10^{-3} mole/g sample, the fixed chitosan attains a value of 0.85%. This is against a value of 0.3% in absence of BTCA.

The foregoing results are rather a manifestation of the ultimate products brought about by cotton cellulose-chitosan-BTCA-sodium acetate trihydrate-water system. In such a complex system several interactions occur among its components. Of these interactions mention is made of the chemical attachment of chitosan through bridging by BTCA. The latter reacts with the hydroxyl group of cotton thereby forming one end of the bridge and with the chitosan hydroxyl on the other end of the bridge. In both cases bridging occurs via esterification reactions.

3.2.2. Technical properties

The multifinished fabrics were monitored for their major technical properties, namely, tensile strength (TS), elongation at break, crease recovery angle (CRA), stiffness, air permeability, water permeability and water pick up (WPU %). The results obtained are summarized in Table 1.

Table 1 shows that the tensile strength of the multifinished fabrics decreases by increasing the BTCA concentration in the finishing formulation. For instance fabric treated with BTCA at concentration of 10^{-3} mole/g sample exhibits a warp tensile strength of 25.97 kg as compared with 37.45 kg for similarly treated fabric but using BTCA at concentration of 4×10^{-4} mole/g sample.

Table 2
Effect of molecular weight of chitosan used in treatment of cotton fabrics on chemical, physical and mechanical properties of treated fabrics.

MW of chitosan used in fabric treatment ($\times 10^5$)	Fixed chitosan %	Tensile Strength (kg)		Elongation at break (%)		Crease recovery		Roughness		Stiffness	
		w	f	w	f	w	f	w	f	w	f
Untreated sample	–	61.5	51	18	24.08	68	56	14.1	14.6	1104	1170
6	0.86	34.4	26.3	8.5	14.8	140	150	16.8	17	2420	4162
4	0.87	32.8	24.8	7.3	16.4	140	147	16.1	15.5	1958	3204
1.5	0.90	34	25.8	7.4	13.9	135	144	15.3	15.1	1335	1032
1.2	0.92	28.6	26.3	7.6	16.1	134	140	15.1	14.1	1140	1961
0.9	0.94	31.3	20.6	7.9	14.4	127	135	14.1	14.9	1083	1925
0.19	0.95	33.2	25.7	7.9	14.9	125	134	14	14	1014	1712

Reaction conditions: [Chitosan], 1% (in 1% acetic acid) Pad-dry-cure method; wet pick up 100%; drying at 80 °C for 5 min curing temperature at 160 °C for 4 min.

Table 3
Effect of molecular weight of chitosan on the antimicrobial activity of treated cotton fabrics.

Molecular weight of fixed chitosan $\times 10^5$	Fixed amount of chitosan onto cotton fabrics (%)	Antimicrobial activity expressed as inhibition zone (mm)								
		Tested organisms								
		Bacteria				Yeast				
		Gram negative	Gram positive			*Saccharomyces cerevisiaea*	*Candida albicans*	*Saccharomyces chevallii*	*Candida pseudotropicalis*	*Rhodotorula minuta*
			Staphylococcus aureus	*Bacillus subtilis*	*Bacillus cereus*					
6	0.86	19	20	20	22	17	18	21	18	18
4	0.87	20	21	20	22	18	18	22	20	20
1.5	0.90	22	21	21	23	19	19	23	18	15
1.2	0.92	24	20	23	25	23	19	23	19	22
0.9	0.94	27	25	27	27	27	22	25	22	25
0.19	0.95	30	29	26	29	27	28	29	25	27

Reaction conditions: [Chitosan], 1% (in 1% acetic acid), BTCA (8×10^{-4} mole/g sample), and 0.6 mole of sodium acetate trihydrate to 1 mole BTCA was used

Treatment of cotton fabric with the finishing formulation containing chitosan only without BTCA decreases also the tensile strength; the latter in the warp direction decreases from 61.5 kg for the untreated fabric to 51.25 kg for the treated fabric. Most probably, chitosan diffuses into the microstructure of cotton cellulose of the fabric and, in so doing, causes rigidity of the fibrillar structure of cotton, thereby decreasing the tensile strength. Similar trend is observed with the weft tensile strength. The tremendous losses in tensile strength upon treatment with BTCA in absence of chitosan are in accordance with previous reports (Liu et al., 2006) which ascribed this to molecular degradation of cotton cellulose under the action of BTCA and catalyst along with rigidity conferred on the cotton structure under the influence of crosslinking. Presence of chitosan lessens the severity of the treatment thereby improving the tensile strength. In no case, however, such improvement could outweigh the high losses in tensile strength.

Results of elongation at break of the cotton fabrics before and after treatment with BTCA in presence and absence of chitosan or in presence of chitosan without BTCA bring into focus a trend which is similar to that brought about by the results of tensile strength discussed above. Hence they can be explained on similar lines.

Table 1 depicts that treatment of cotton fabrics with BTCA with or without chitosan causes significant improvement in the crease recovery angle (CRA). The CRA displays values (warp + filling) of 254° and 257° upon using BTCA (8×10^{-4} mole/g sample) alone and together with chitosan respectively. This is against value of 124° for the untreated fabric. Chitosan-treated fabric without BTCA exhibits CRA of 151°. It can, therefore, be concluded that cotton cellulose, BTCA, chitosan and sodium acetate trihydrate catalyst interact as previously described to yield finished fabrics. These fabrics could be placed under the finishing category of anticrease and easy-care cotton fabrics.

Enhancement of CRA could be associated with crosslinking caused by reaction of BTCA with two adjacent hydroxyl groups of cotton cellulose as well as to formation of hydrogen bonds between the different ingredients involved in the crosslinking treatment and the cotton cellulose of the fabrics (El-Tahlawy et al., 2005).

Table 1 shows that fabrics treated with the finishing formulation in question acquire marginal increment in roughness especially at higher BTCA concentrations, but not reached to the level which affects their smoothness and, therefore, comfort. That is, the multifinishing treatment in question did not detract from the comfort of the treated fabrics.

It is also obvious (Table 1) that the air permeability values of the treated fabrics are lower than that of the untreated fabric. Formation of coating layer of the chitosan on the surface of the cotton fabric, acts as a barrier which detracts from the role of pore size on the fabric surface in air permeability. Indeed the SEM images shown in Fig. 3 are in conformation with this. The treated samples appear with smooth coating in contrast with the untreated sample where surface irregularities of the untreated fibers are observed. It is as well to emphasize that the decrement in the air permeability is not reflected on the comfort of the fabric since the water permeability of the treated fabric increases and water pick-up is not affected greatly. It is also seen that the stiffness of the treated fabric shows significant increase with high BTCA concentrations (with HMWC) but this undesirable property is not observed (with LMWC) as will be described later.

3.3. Chitosan concentration

Cotton fabrics were subjected to aqueous multifinishing formulations that contain different chitosan concentrations and fixed amount of BTCA together with sodium acetate trihydrate. Thus treated fabrics were monitored for the fixed chitosan %.

Table 4
Effect of washing on the fixed amount of chitosan add-on fabrics.

Before washing	After 5 washes		After 10 washes		After 15 washes	
Fixed amount of chitosan %	Fixed amount of chitosan %	Retention%	Fixed amount of chitosan %	Retention%	Fixed amount of chitosan %	Retention%
0.5	0.44	88	0.39	78	0.34	68
0.7	0.6	85.7	0.55	78.5	0.49	70
0.9	0.85	94.4	0.72	80	0.63	70
1.2	1.1	91.6	0.96	80	0.88	73.3
1.4	1.3	92.8	1.2	85.7	1	71.4

[Chitosan MW 6×10^5 Da], Pad-dry-cure method.

It is observed that the amount of fixed chitosan % increases by increasing the chitosan concentration from 0.5 to 1%. This is rather a direct consequence of the relatively greater availability of chitosan molecules at 1% chitosan concentration in the vicinity of the fabric structure. This situation provides more proper environment for interaction of chitosan with cotton cellulose thereby counterbalancing the loss in fixed chitosan % after washing. Stated in other words, the fixation % of chitosan on the fabric using 1% chitosan concentration is characterized by strong bonding in particular, crosslinking as a result of easier accessibility of chitosan molecules in the proximity of cellulose hydroxyls which allows full interactions with these hydroxyl groups of cotton cellulose through BTCA. Once this is the case, there would not be a chance for unreacted and/or loosely adhered chitosan on the fabric surface. The amount of fixed chitosan % at chitosan concentrations higher than 1% increases marginally by using higher amounts (concentrations) of chitosan. This may be due to high viscosity of chitosan solutions at higher concentrations which may cause lower interaction efficiency.

3.4. Curing temperature and time

The effect of curing temperature on the amount of fixed chitosan add-on cotton, when the latter were treated with a multifinishing formulation consists of chitosan (1%), BTCA (8×10^{-4} mole/g sample), and 0.6 mole of sodium acetate trihydrate to 1 mole BTCA is studied. Evidently, raising the curing temperature up to 160 °C is to bring about substantial increment in the amount of fixed chitosan on the treated fabrics. As expected, increasing the curing temperature improves the extent of crosslinking of BTCA within the cellulose while also increasing the linked chitosan. Curing temperature higher than 160 °C causes a decrement in the amount of fixed chitosan most probably due to breaking down crosslinks under the effect of higher temperature and the highly acidic condition used.

Also, the effect of curing time on the amount of fixed chitosan add-on cotton is investigation. Prolonging the curing time improves the crosslinking process and increases the amount of fixed chitosan onto cotton fabrics but curing at 5 min gives results near to that for 4 min. So, considering these effects as a whole, it is concluded that a temperature of 160 °C and curing time of 4 minutes constitute the most appropriate condition for curing.

3.5. Effect of chitosan MW on chemical, physical and mechanical

3.5.1. Properties of treated fabrics

Table 2 shows the effect of chitosan molecular weight on major technical properties of the multifinished fabric. It can be realized from the results that performance properties display significant improvement when measured by crease recovery of the fabrics after multifinishing treatment in general, but by increasing the MW of chitosan crease recovery values increases probably because HMWC itself is very cohesive and thus enhance the reinforcement of the fabric. This is reflected on the tensile strength of the multifinished fabrics where the latter shows significant drop in tensile strength when compared with the untreated fabric. The multifinished fabrics also acquire slightly increased roughness, but did not reach the level which affects their smoothness and, therefore, comfort. And this increase in roughness of treated fabrics reach zero with LMWC. In addition the stiffness of the treated fabric show significant increase with HMWC but this undesirable property is not observed with LMWC. Considering the effect of chitosan MW on physical and mechanical properties of treated fabric (Table 2) as a whole, it is clear that decreasing the MW of chitosan acts in favour of the preparation of easy care cotton fabric with acceptable performance. On the other hand, increasing the MW of chitosan is accompanied by a decrease in the amount of fixed chitosan on the cotton fabrics. This is related to the decrement in the crosslinking efficiency (El-Tahlawy et al., 2005) as a result of lower penetration of high molecular weight chitosan into the molecular structure of cotton.

Table 5
Effect of washing cycles on the antimicrobial activity of fabrics containing 1% chitosan.

Number of washing cycles	Antimicrobial activity expressed as inhibition zone (mm)						
	Tested organisms						
	Bacteria				Yeast		
	Gram negative	Gram positive			*Saccharomyces cerevisiaea*	*Candida albicans*	*Saccharomyces cerles*
	E. coli	*Staphylococcus aureus*	*Bacillus subtilis*	*Bacillus cereus*			
Before W	30	29	26	29	27	28	29
After 5 W	25	23	23	26	26	21	23
After 10 W	23	20	22	24	23	20	22
After 15 W	21	20	21	23	20	19	21
Control	0	0	0	0	0	0	0

Reaction conditions: [Chitosan], 1% (in 1% acetic acid) with MW; 6×10^5 Da W: washing.

3.6. Antimicrobial activities of cotton fabrics containing chitosan

Chitosan is now attracting more and more scientific and industrial interest from diversified fields such as chemistry, biochemistry, pharmacology, biotechnology, and food and textile sciences. Properties such as biodegradability, biocompatibility, non-toxicity, wound healing and antimicrobial activity have generated much research work. Many unique products have been developed for various applications such as surgical sutures, artificial skin, cosmetics and dietary foods (Öktem, 2003).

For all the above advantages, we have used chitosan having different molecular weights along with BTCA as a crosslinking agent to produce multifinished cotton fabrics as detailed in the forgoing sections. In this section, the antimicrobial activity of these multifinished fabrics is studied under different conditions. Results obtained and their discussion is given below.

3.6.1. Effect of molecular weight of chitosan on the antimicrobial activity of treated cotton fabrics

Treatment of cotton fabrics with a multifinishing formulation consisting of chitosan (1%), BTCA (8×10^{-4} mole/g sample), and 0.6 mole of sodium acetate trihydrate to 1 mole anchor was conducted as per the pad-dry-cure method. The antimicrobial activity of fabrics treated with different MWs of chitosan was evaluated and the results obtained are set out in Table 3. It is obvious that the maximum antimicrobial activity against bacteria (Gram positive and negative) and yeast is exhibited by cotton fabrics treated with chitosan having the lowest MW within the range studied. On the other hand, all the treated fabric samples have no antimicrobial activity against the tested fungi. This may be due to the lower antifungal activity of the treated fabrics against fungi with a chitin or chitosan component in their cell wall (Allan & Hardwiger, 1979).

3.6.2. Effect of fixed amount of chitosan on the antimicrobial activity of treated cotton fabrics

The effect of the different amounts of chitosan fixed on antimicrobial activity of the multifinished fabrics is studied. The results indicate that the antimicrobial activity is strengthened as the amount of fixed chitosan increases. On the contrary, it was observed that all treated fabrics displayed no antimicrobial activity against tested fungi; in accordance with the above results and could be explained on similar basis.

Enhancement in antimicrobial activities of the treated fabrics containing larger amounts of fixed chitosan is in conformation with previous reports (Fouda, El Shafei et al., 2009; Helander, Nurmiaho-Lassila, Ahvenainen, Rhoades, & Roller, 2001; Lim & Hudson, 2003; Tsai & Su, 1999). The interaction of the positively charged chitosan with the negatively charged residues at the cell surface of bacteria and yeast is anticipated to be greater at higher amounts of chitosan. The effect of such interaction is to cause extensive cell surface alterations and alters cell permeability. This brings about the leakage of intracellular substances, such as, electrolytes, uv-absorbing materials, proteins, amino acids, glucose, and lactate dehydrogenase. As a rewet, chitosan inhibits the normal metabolism of microorganisms and finally leads to the death of these cells.

3.6.3. Effect of washing on different amounts of fixed chitosan add-on cotton

Cotton fabrics containing different amounts of fixed chitosan were subjected to several washing cycle (5, 10 and 15 washes) with a view to examine the durability of chitosan as antimicrobial finish. Results of amounts of fixed chitosan before and after washing are summarized in Table 4.

It is seen (Table 4) that the amount of fixed chitosan decreases substantially after washing. This is the case regardless of the magnitude of the fixed chitosan onto the fabric. The multifinished cotton fabric under investigation seems to contain certain amount of unfixed chitosan which are loosely adhered to the fabric surface and, therefore, are liable to washing. Liability to washing of chitosan depends, according to current results, on the number of washes which, in turn, reflects the severity of washing. It is likely that some of the intimately associated chitosan within the cotton fabric is also removed during severe washing; such chitosan removal accounts for the decrement in chitosan content even with the fabric containing the highest amount of fixed chitosan.

3.6.4. Effect of washing cycles of cotton fabrics-containing 1% chitosan on their antimicrobial activity

Antimicrobial activities of cotton fabrics containing 1% of chitosan after 5, 10 and 15 washing cycles are shown in Table 5. It was observed that, the antimicrobial activity of cotton fabrics containing 1% chitosan decreased by increasing the washing cycles

On the other hand, it was found that the treated fabrics in question display no antimicrobial activity with respect to tested fungi.

4. Conclusion

Multifinishing formulations for green synthesis of finished cotton fabrics that enjoy ease of care characteristics and antimicrobial activity were established. The green synthesis is based on the use of chitosan having different molecular weights along with the nontoxic 1,2,3,4-butane tetracarboxylic acid (BTCA). Variations in molecular weight could be achieved by subjecting high molecular weight chitosan to enzymatic hydrolysis. The finishing treatment was carried out according to the conventional pad-dry-cure method. BTCA performs dual functions: as a crosslinking agent and also as anchor molecules for chitosan fixation on the cotton fabrics. The so obtained fabrics display anticrease and easy care properties in addition to antimicrobial properties even after 15 washes. The fabrics retain much of their strength properties and comfort after the multifinishing treatment in question.

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