

# Enhanced anti-microbial, anti-creasing and dye absorption properties of cotton fabric treated with Chitosan–Cyanuric Chloride hybrid

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**Abstract** In this study, cotton fabrics were chemically crosslinked with Chitosan–Cyanuric Chloride hybrid (Ch–Cy) in order to improve their physical–chemical properties. The effect of operational parameters (e.g., initial concentration of Ch–Cy, temperature, reaction time and pH) on the grafting process was evaluated. A high weight gain of the cotton fabrics (~ 4%) was obtained under optimum conditions at initial concentration [Ch–Cy] = 30% over weight of fabric (o.w.f.), at 50 °C, pH 4 after 3 h. The treated and untreated cotton samples were dyed with three natural dyes (i.e., cochineal, madder and weld). The dye absorption of the treated samples was improved noticeably and according to the grafted amount of Ch–Cy on the fabrics. Despite the dye adsorption enhancement, the fastness properties (washing, light,

rubbing) of the dyed samples remained at acceptable level. The wrinkle recovery angle of the treated samples increased minimum 60° showing the enhancement in the crease recovery of the fabrics. The treated cotton samples also showed promising antimicrobial behavior against gram negative and gram positive bacteria. This study shows that the dye adsorption, antimicrobial and anti-creasing properties of the treated samples are enhanced by this chemical treatment without any adverse effects on their tensile strength and color fastness properties.

**Keywords** Chitosan · Cotton fabric · Crosslinking · Anti-microbial · Anti-creasing · Natural dyeing

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## Introduction

Cotton is the most important natural fiber in textile industry. Despite its very good physical chemical and wearing properties, cotton has some shortcomings: (1) it has poor resistance against microbial growth and the most trouble-causing microorganisms (i.e., fungi and bacteria) can attack and spread over its surface, and (2) it wrinkles after washing and it is prone to shrinkage (Schindler and Hauser 2004). In order to overcome these shortcomings, researchers have developed a number of chemical finishes for antimicrobial protection and anti-creasing enhancement (Kim et al. 2010; Shahidi et al. 2007; Zhang et al. 2009). The

antimicrobial finishes are especially needed for fabrics directly in contact with skin such as underwear, socks, and fabrics used in public places such as hospitals, and hotels. Due to toxicity and negative impact on environment, many of formerly used antimicrobial products (e.g., phenolic compounds, mercury compounds, etc.) have been banned nowadays (Schindler and Hauser 2004; Kim et al. 2010). Therefore, the search for new formulations that are non-toxic, non-allergenic, and biodegradable continues (Abdel-Mohsen et al. 2012; Abdel-Halim et al. 2011; Frasc-Zemljčić et al. 2015; Annalisa et al. 2016; Zhou and Kan 2014; Zhao and Sun 2007; Hong and Sun 2011; Montazer et al. 2012; Son et al. 2006; El-Rafie et al. 2010; Fua et al. 2011; Periolatto et al. 2012).

Anti-crease finishes on cotton are normally applied to reduce its swelling and shrinkage, to enhance the smoothness, and to improve its wet and dry wrinkle recovery (Schindler and Hauser 2004; Kim et al. 2010). Since 1950, various formaldehyde-containing products have been used to give anti-crease treatments that have been popular in the market. Health and environmental concerns are the main reasons for development of new finishes (Hirsch et al. 1973; Liu et al. 2013; Latlief et al. 1951; Can et al. 2009; Aly et al. 2007; Li et al. 2008).

Several different approaches can be used for improving the antimicrobial properties of cotton such as plasma treatment, stabilization of metal based nanoparticles, and various chemical coatings. Many of these treatments are based on weak interactions of antimicrobial agents with cotton fabric and therefore not durable (Hong and Sun 2011; El-Rafie et al. 2010; Fua et al. 2011; Periolatto et al. 2012; Can et al. 2009; Aly et al. 2007). Adsorption of an antimicrobial agent such as chitosan on cotton fabric is one of the recent advancements in the field (Klaykruayat et al. 2010; Pillai et al. 2009; Martínez-Camacho et al. 2010). Chitosan, a linear polysaccharide composed of randomly distributed  $\beta$ -(1  $\rightarrow$  4)-linked D-glucosamine (deacetylated unit) and N-acetyl-D-glucosamine (acetylated unit), is a non-toxic, non-allergic, biodegradable biopolymer with interesting physical-chemical properties. This treatment enhances the absorption properties due to the presence of amine groups in its chemical structure (Mourya and Inamdar 2008; El-tahlawy et al. 2005). However, the adsorption of chitosan onto cotton is based on weak hydrogen bonds and van der-Waals interactions (Enescu 2008;

Tayel et al. 2011; Strnad et al. 2000). For improving the binding and enhancement of the durability of the treatment, a cross-linking agent (e.g., polycarboxylic acids) can be used. The amine groups of chitosan and hydroxyl groups of cellulose can be chemically linked so as to permanently graft chitosan onto cellulose (Sadeghi-Kiakhani and Safapour 2015a; Kim et al. 2003; El-tahlawy et al. 2005; El-Shafei et al. 2008).

Easy care, wrinkle-resistant and antimicrobial cotton fabrics are highly demanded worldwide. Despite much advancement in the field, researchers are still searching for new environmentally friendly finishing methods to enhance anti-microbial, anti-creasing and dye absorption properties of cotton fabrics. In this research, chitosan is grafted on cotton fabrics using cyanuric chloride as a cross-linking agent. The effects of various finishing parameters (i.e., initial concentration of Ch-Cy, temperature, treatment time, and pH) on the weight gain %, dye adsorption, antimicrobial activity, and anti-crease properties are studied to shed more light on the topic. Moreover, design of experiments using response surface methodology (RSM) was employed for optimization.

## Experimental

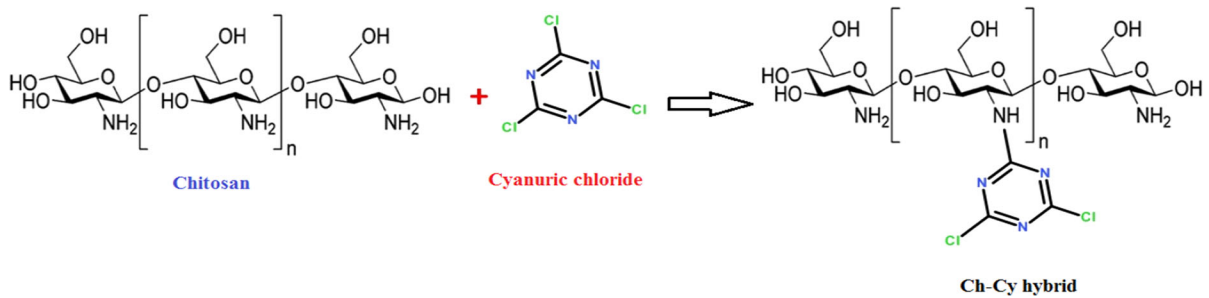
### Materials

Scoured and bleached plain woven cotton fabric (weft/cm: 36 and warp/cm: 32) was purchased from (Savalan Co., Iran). Chitosan (degree of deacetylation = 85%, M.W. = 1000 kDa) was provided by (Kitotak Co., Iran). Cyanuric chloride was purchased from Merck Company, and other chemicals used in this study were of analytical grade.

### Methods

#### *Synthesis of Ch-Cy hybrid*

Cyanuric chloride (0.15 mol, 2.7 g) was added slowly to Chitosan (4 g) in THF (100 mL) under stirring at 5 °C. The mixture was stirred for 24 h and the modified chitosan (Ch-Cy) was separated from the solvent by filtration, rinsed with methanol 3:1 tetrahydrofuran and dried at room temperature (Yield: 95%). The preparation of the Ch-Cy is provided in Fig. 1. The dried product was ground to a fine powder in a



**Fig. 1** Chemical reaction between chitosan and Cyanuric chloride. *Note:* the chemical structure of 100% deacetylated chitosan has been shown

Porcelain Mortar and sieved to a particle size between 0.2 and 0.4 mm. The synthesis method has been described in more detail elsewhere (Zargarkazemi et al. 2015).

#### Grafting cotton fabrics with the Ch–Cy hybrid

The cotton fabric specimens were washed in an aqueous solution containing 5 g/l of nonionic detergent (Lotensol, Hansa Co., India) at 60 °C for 30 min. The Ch–Cy powder was dissolved in an acetic acid solution (2%, pH = 4–5). The washed and dried cotton fabric was immersed in Ch–Cy solution at various temperatures and then was padded (using a laboratory padder at 90% wet pick up). The padded fabrics were dried at 80 °C for 15 min and cured at 120 °C for 5 min. In this study, the effects of initial Ch–Cy concentration 10, 15, 20, 30 and 40% over weight of fabric (o.w.f.), reaction temperature (25, 50 and 70 °C) and reaction time (1, 3 and 24 h) were evaluated on the grafting process efficiency. The treated fabrics were washed in distilled water, dried and stored in a desiccator. Weight gain (%) after the grafting process was determined using the following equation (Eq. 1):

$$\text{Weight gain (\%)} = \frac{W_{\text{final}} - W_{\text{initial}}}{W_{\text{initial}}} \times 100 \quad (1)$$

#### Mordanting cotton fabrics

Aluminum sulfate as a mordant was used for treatment of the untreated cotton fabrics. The scoured samples were mordanted in a neutral solution containing aluminum sulfate 5% o.w.f., a liquor to fabric ratio (L:R) 40:1, at boiling temperature for 60 min. After

mordanting, the samples were removed, thoroughly rinsed with water, squeezed and dried.

#### Dyeing method

The raw, mordanted and grafted cotton fabrics were dyed separately with three different natural dyes (cochineal 10% o.w.f., madder 40% o.w.f., and weld 30% o.w.f.) at neutral pH, and L:R of 40:1. The samples were soaked in the solution at 30 °C for 5 min before the addition of the dye powder. The temperature was raised to 100 °C within 20 min and kept constant at this temperature for 60 min. Finally, the samples were removed, rinsed with water, and dried in an oven at 40 °C.

The colorimetric data and reflectance ( $R$ ) of the dyed samples at various wavelengths were measured using GretagMacbeth Color-Eye 7000A reference spectrophotometer. The average of three measurements was used for further calculation of the color strength using the Kubelka–Munk equation (Eq. 2):

$$\frac{K}{S} = \frac{(1 - R)^2}{2R} \quad (2)$$

where  $K$  is the absorbance coefficient,  $S$  is the scattering coefficient,  $R$  is the reflectance value at  $\lambda_{\text{max}}$  (wavelength of maximum absorption).

#### Fastness properties

The wash fastness of the dried samples was evaluated according to the standard ISO 105 C06 C2S:1994 (E) method and the dyed samples were washed at 60 °C for 30 min. The light fastness test was performed under irradiation of the artificial light: Xenon arc fading lamp test for 100 h according to ISO 105

B02:1988 (E). Light fading was assessed using blue scale (1 = severe fading; 8 = no fading). The rub fastness test was performed according to ISO105-X12:1993 (E) standard using a crockmeter. The staining on the white test cloth was evaluated using the gray scale.

#### Antimicrobial test

The antimicrobial activity of the treated cotton fabrics was tested against gram negative bacteria (*E. coli*) and gram-positive bacteria (*S. aureus*) according to the ASTM E2149-01 method. In this method, a number of test tubes each containing 5.0 mL of Muller-Hinton broth (MHB, Difco, England) were autoclaved for 15 min at 121 °C. Circular fabric specimens (about 1.0 g) were challenged with  $1.0 \pm 0.1$  mL of bacterial inoculums. The test requires inoculation with microorganisms to a final concentration of  $10^6$ – $10^7$  CFU/mL (colony-forming units). Positive control tubes contained 5.0 mL of nutrient broth medium with tested bacterial concentrations of  $10^5$ – $10^6$  CFU/mL. Negative control tubes contained only inoculated broth. The tubes were incubated at 37 °C with shaking at 200 rpm for 24 h. The antimicrobial activity was expressed in terms of reduction (*R*%) of the organism after contact with the test specimen compared to the number of bacterial cells surviving after contact with the control. The percentage reduction was calculated using Eq. 3:

$$R(\%) = \frac{B - A}{B} \times 100 \quad (3)$$

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

#### Physical and mechanical properties

Surface morphology of the treated and untreated cotton fabrics was studied by an XL301 scanning electron microscope (SEM) (FEI-Philips). The wrinkle recovery angle (WRA) was measured according to AATCC test method 66-1989 and the tensile strength test was performed according to ASTM D1682-75 (1985). The bending length was measured using a bending length tester (Paramount Stiffness Tester) based on the cantilever principle.

#### Zeta potential

The treated and untreated fabric samples were cut into small pieces (approximately  $1 \times 2$  mm<sup>2</sup>). These samples were mixed in 0.001 M KCl at various pH, and stirred with a magnetic stirrer for 10 min. The zeta potential of the solutions was recorded using a Zeta sizer SZ100 Horiba instrument (Japan).

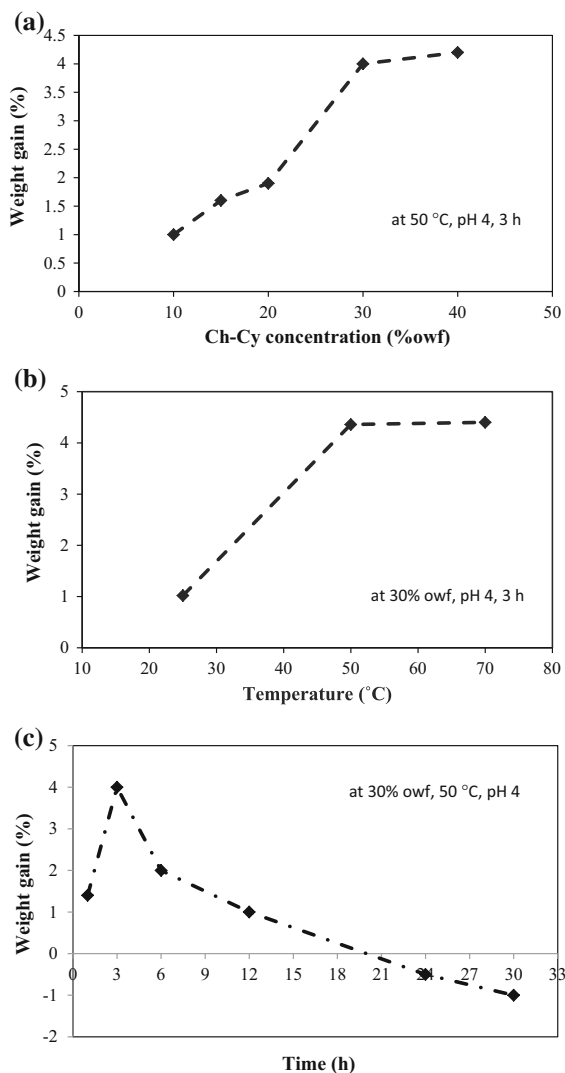
## Results and discussion

### Grafting of cotton fabric with chitosan

Cyanuric chloride is employed as a strong reactant for nucleophilic substitution of alcohols, carboxylic acids, and amines. The nitrogen atoms in the heterocyclic ring activate the system for nucleophilic attack. Therefore, cyanuric chloride can be used to crosslink chitosan molecules to cotton fabric via covalent bonds (Shore 1995). However, there are two unfavorable side reactions: (1) the Ch–Cy reacts with (–OH/–NH<sub>2</sub>) groups of another chitosan macromolecule; and (2) Ch–Cy will react with water molecules (i.e., hydrolyzes) which prevents it from further reaction. The produced HCl as a result of these reactions is removed by amino groups of chitosan in situ and the risk of cotton degradation will be minimized. The alternative solution is to add alkaline (e.g., NaOH) to the solution which increases the chance of Ch–Cy hydrolysis. Therefore, the effective parameters such as temperature, initial concentration of Ch–Cy, and the duration of reaction should be studied in order to find the optimum conditions.

### Initial concentration of Ch–Cy

The effect of Ch–Cy concentration on grafting process of cotton fabric is studied at pH 4 and 50 °C, for 3 h as shown in Fig. 2a. The results show that the weight gain of the treated fabric increases rapidly to above 4% and further increase in concentration of Ch–Cy does not increase the weight gain noticeably. This can be attributed to the surface saturation of cotton with Ch–Cy and similar behavior has been previously observed in other papers (Zargarkazemi et al. 2015; Aryabadie et al. 2015). So, the initial Ch–Cy concentration of 30% o.w.f. was considered as the optimum concentration for the grafting of cotton fabrics.



**Fig. 2** The effect of **a** Ch–Cy initial concentration, **b** temperature reaction, and **c** time reaction on grafting process of cotton fabric

#### The effect of temperature

The effect of temperature on the grafting process of cotton fabric is shown in Fig. 2b. The weight gain percentages of cotton at different temperatures 25, 50 and 70 °C were 1.02, 4.36 and 4.40%, respectively. The rate of grafting reaction increases sharply by increasing the temperature from 25 to 50 °C and remains almost constant afterwards. By increasing the temperature, the movement of polymeric chains increases and the required activation energy of the reactions is overcome. As a result, more effective

nucleophilic attacks of –OH groups of cellulose with Ch–Cy occurs. At the same time, the rate of hydrolysis or reaction of Ch–Cy with OH of water molecules increases. These two reactions compete with each other and it seems the maximum weight gain is achieved at 50 °C.

#### The effect of reaction time

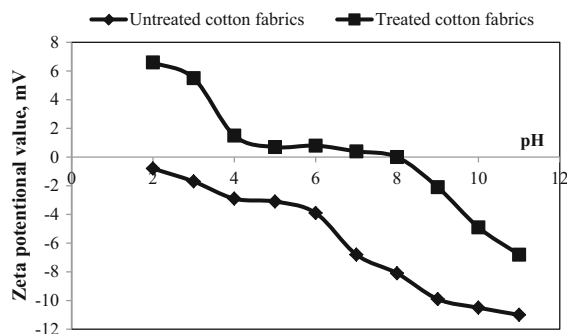
As can be seen in Fig. 2c, the maximum weight gain is achieved in 3 h of reaction at  $T = 50$  °C and  $C_{\text{Ch-Cy}} = 30\%$  o.w.f. The prolongation of reaction has an adverse effect on the grafting yield of the samples and even weight loss after 20 h. This is due to production of HCl during the grafting reaction and increased degradation of the cotton samples especially at elevated temperature of 50 °C (Shore 1995).

#### Response surface methodology (RSM) for optimization

RSM as a practical statistical method was also employed to optimize the weight gain % based on the aforementioned variables. A central composite design (CCD) was used to determine the optimum conditions for the grafting process of cotton by Ch–Cy. Four main parameters along with their levels investigated in this study are presented in Table S1 (Supporting information section). The statistical importance of the models was justified by the analysis of variances (ANOVA) for polynomial models with 95% confidence level (Table S2). The residual plots were utilized to study the suitability of the models' fit (Figure S1). The effect of operating variables (initial concentration of Ch–Cy, temperature, reaction time and pH) on the grafting process was studied in Figure S2. The optimized conditions were found to be: Concentration of Ch–Cy: 30% o.w.f., temperature: 50 °C, reaction time 3 h, and pH: 4. The experimental optimized conditions were in a good agreement with the predicted optimized conditions based on RSM analysis.

#### Zeta potential of the grafted cotton fabrics

The surface charge of the untreated and treated samples was studied using zeta potential measurement (Fig. 3). The untreated cotton fabrics have slightly negative surface charge over the whole studied pH



**Fig. 3** Zeta potential of the: *a* untreated cotton, *b* grafted cotton with Ch–Cy

range which increases to more negative values at elevated pH values ( $\text{pH} > 6$ ). The deprotonation of  $-\text{OH}$  groups at the surface of the treated and untreated cotton samples is most probably the reason for the negative surface charge of the samples. The surface charge of the grafted cotton fabric with chitosan is slightly negative in acidic pH (2–4) and the pH of zero charge is around 8. This positive surface charge of the treated cotton samples can be explained by the presence of  $-\text{NH}_2$  groups which are protonated in acidic condition. The negative surface charge increment is more pronounced at  $\text{pH} > 6$  for the untreated cotton sample and at  $\text{pH} > 8$  for the treated sample.

#### SEM analysis

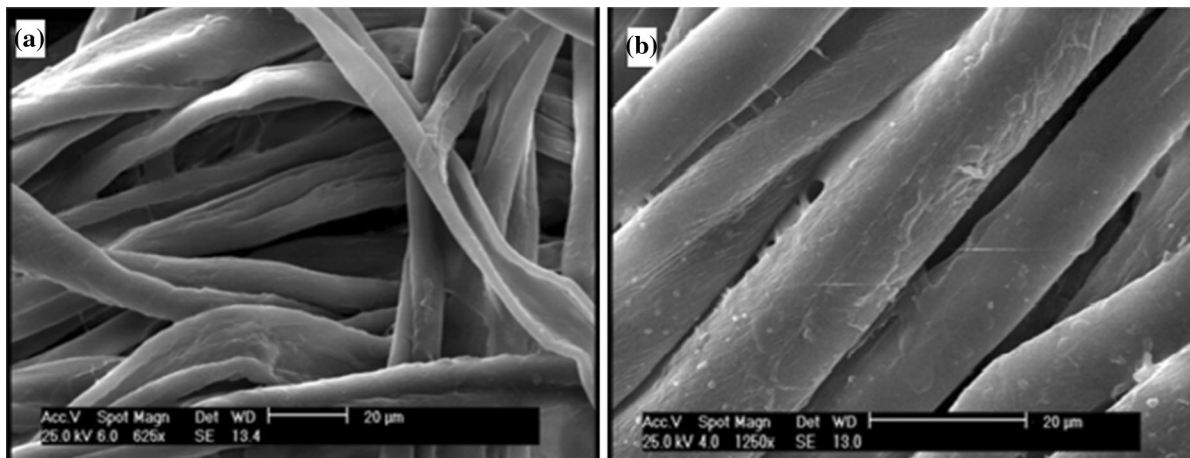
The surface morphology of the treated and untreated cotton fabrics was observed by SEM (Fig. 4). It seems the treated samples have been covered by another

layer containing some small grains, which can be attributed to the presence of Ch–Cy on the cotton fabric. Similar observation has been previously reported in other relevant papers (Zargarkazemi et al. 2015; Aryabadie et al. 2015; Sadeghi-Kiakhani et al. 2013; Sadeghi-Kiakhani et al. 2015).

#### Antimicrobial activity

Antimicrobial activity was measured quantitatively to determine the efficiency of the grafting treatment to inhibit *E. coli* and *S. aureus* cells (Table 1). As can be seen, the untreated cotton fabric did not show any antimicrobial activity. The presence of chitosan on the surface of cotton even without any grafting shows minimum  $\sim 86\%$  microbial reduction. The grafted cotton samples showed even higher antimicrobial activities ( $\sim 98\%$ ) under the same conditions. This shows that the presence of chitosan on the fabric surfaces substantially enhances antimicrobial activity. Chitosan has a polycationic structure which can form a polymeric membrane around microorganisms, interact with their predominantly anionic components, or adsorb the oppositely charged nutrients and disturb their physiological activities (Aryabadie et al. 2015; Sadeghi-Kiakhani and Safapour 2015b; Sadeghi-Kiakhani et al. 2015).

The durability of applied Ch–Cy on the surface of cotton was evaluated according to ISO 6330-1984, through washing fastness test after 10 cycles of consecutive launderings. By increasing the number of washing cycles, the efficiency of Ch–Cy modified



**Fig. 4** SEM images of the: *a* untreated cotton, *b* treated cotton

**Table 1** Effect of number of washing on antimicrobial activity of cotton fabrics

Sample	Washing cycles	Surviving cells (CFU/mL)		Microbial reduction (%)	
		<i>E. Coli</i>	<i>S. aureus</i>	<i>E. Coli</i>	<i>S. aureus</i>
Raw cotton	–	$3.55 \times 10^5$	$3.75 \times 10^5$	Nothing	Nothing
Treated by chitosan	0	35,870	52,250	89.89	86.06
	2	52,400	61,545	85.20	83.58
	10	87,651	109,867	75.30	70.70
Treated by Ch–Cy	0	114	5205	99.96	98.61
	2	11,882	30,820	96.65	91.78
	10	31,426	53,953	91.14	85.61

fabric against microorganisms reduced relatively. The treatment durability against washing depends on the strength of bonds between Ch–Cy and the cotton fabric. The structural characteristics of Ch–Cy and cotton play a major role in providing enhanced washing durability of the antimicrobial agent on the fabrics. Reduction of the antimicrobial activity by increased number of washings can be attributed to release of weakly bonded chitosan molecules from the cotton surface. The antimicrobial activity of the treated samples after 10 washing cycles was 70–75 and 85–91% for the chitosan-treated and Ch–Cy treated samples, respectively. This clearly shows that the grafting process enhances the antimicrobial efficiency and durability of the treated cotton fabrics even after repeated washing cycles due to strong covalent bonds with cotton.

### Physical properties

Table 2 shows the results of tensile strength measurements of the treated and untreated cotton samples. It seems the treated samples are slightly stronger than the untreated cotton sample with lower values of elongation at break. The strength of the treated samples increases proportionally (from 1.8 to 9%) by

increasing the initial concentration of Ch–Cy (from 10 to 30%), respectively.

Cotton fabric has a poor wrinkle recovery as a result of its cellulosic chemical structure with a large number of hydroxyl groups. Wrinkles can be stabilized by intermolecular hydrogen bonds that easily break and reform in a creased configuration within the fiber during wetting/drying of the fabric. Therefore, easy care and wrinkle-resistant cotton fabrics are highly demanded worldwide (Can et al. 2009; Aly et al. 2007).

Table 2 also shows the effect of grafting agent concentration (Ch–Cy) on the anti-crease properties of the cotton fabrics. The values of wrinkle recovery angle (WRA) for the Ch–Cy treated samples are much higher than those of the untreated fabric. Cross-linking reactions occur within the accessible regions with hydroxyl groups of cellulose resulting in a better resistance to deformation and improving elastic recovery from deformation (Montazer et al. 2012). Bending length (BL) is a measure of stiffness of the treated fabric samples. All the treated samples showed slightly higher BL values than that of the control sample indicating that the stiffness was not affected adversely by the treatment.

**Table 2** Physical properties of treated cotton fabric with Ch–Cy

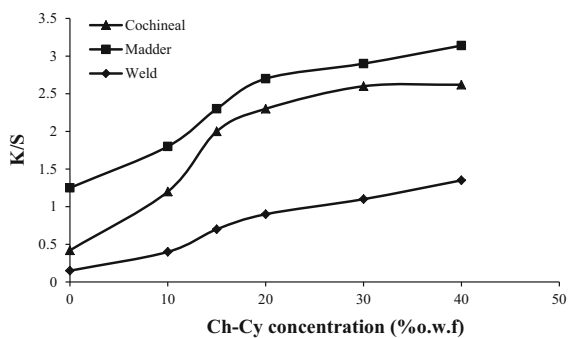
Ch–Cy (% o.w.f)	BL (cm)		WRA degree	Elongation at break (%)	Force at break (N)
	Warp	Weft			
0	2.13	1.64	65	23.7	15.6
10	2.22	1.66	125	20	12
15	2.24	1.67	125	20	12
20	2.27	1.66	130	20.4	13.5
30	2.29	1.68	135	21.4	13.5

WRA wrinkle recovery angle, BL bending length

## Dyeing and fastness properties

The adsorption properties of three natural dyes (i.e. cochineal, madder, and weld) on the treated samples improved to a large extent as can be seen from Fig. 5. As an example, the K/S value for the cochineal dyed untreated sample was only 0.4 which increased to 2.6 for the samples pre-treated with 30% Ch–Cy and remained almost constant at higher Ch–Cy initial concentrations. The dye adsorption enhancement is most probably due to the presence of more active sites (i.e., chitosan amino groups) at the surface of the treated cotton. The protonated amino groups can adsorb oppositely charged species (e.g., the dyes with –COOH substituents). The fact that the K/S versus Ch–Cy concentration reaches to a plateau can be explained by availability of the dye sites which obviously remains constant at higher initial concentration of Ch–Cy. The profile of K/S versus Ch–Cy initial concentration (Fig. 5) is quite similar to the profile of the weight gain (Fig. 2). This shows that: (1) the crosslinked chitosan is mainly responsible for the enhanced dye adsorption, and (2) the adsorption capacity of the treated samples are proportional to the initial Ch–Cy concentration.

Aluminum sulfate is sometimes used as a mordanting agent to enhance dyeing properties of natural dyes and the fastness properties of colored fabrics. The cotton fabrics were treated with 5% o.w.f mordant and the color strength of the mordanted cotton samples were investigated (Table 3). Although this treatment improves the color strength of the colored fabrics with these natural dyes, the K/S values are still relatively lower than those of the treated samples with Ch–Cy.





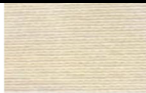


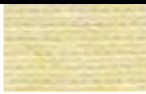

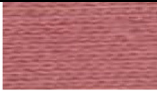
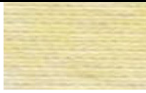
**Fig. 5** Effect of Ch–Cy concentration on the K/S values of the dyed samples. Three different natural dyes: Cochineal (10% o.w.f), madder (40% o.w.f), and weld (30% o.w.f)

This suggests that the treated cotton with Ch–Cy could be successfully dyed in more depth without addition of aluminum sulfate for mordanting which is also valuable from environmental point of view and reduces the load of contaminants in the discharged wastewater.

For assessment of wash fastness properties of the dyed cotton samples, they are normally sandwiched between two other fabrics (1-standard white cotton fabric and 2-standard natural woolen fabric). The color change of the dyed sample (CC), staining on the adjacent cotton fabric (SC), and staining on the adjacent woolen fabric (SW) are then evaluated visually using a standard gray scale. The color fastness properties of the untreated and treated cotton fabrics are summarized in Table 4. The results show that the wash fastness, light fastness, and rub fastness properties are generally very good. The treated cotton samples by Ch–Cy or aluminum sulfate (mordanted) showed somewhat better results. This shows that the fixation of the dye molecules at the surface of the cotton fabrics by the grafting process/mordanting can slightly improve the fastness properties. It should be emphasized here that the higher wash fastness of the treated sample has been achieved despite its higher color depth.

Cochineal and Madder have both anthraquinone structure with some ionizable groups such as –OH/–COOH (Mihalick and Donnelly 2006). At elevated pH, these groups are partially ionized and increase the solubility of the dye molecule in water. Therefore, in the absence of mordanting agent or strong electrostatic interaction between the fabric and the dye molecule, the dyed samples has a relatively low wash and rub fastnesses as can be seen from Table 4 (especially in case of using madder). Aluminium and other metal ions with vacant orbitals can create complexes between –OH groups of the cotton fabric and –OH/–COOH groups of the dye molecules. This enhances the bonding interaction and the wash/rub fastnesses of the dyed samples accordingly. The presence of chitosan on the surface of cotton fabrics can also enhance the bonding with the dye molecules. The amino groups of chitosan are most probably responsible for better interactions with dye molecules (e.g. via hydrogen bonding). They can also be protonated at low pH and enhance the electrostatic interactions between the cotton fabric and the dye molecules.

**Table 3** The ratio of the absorbance coefficient to the scattering coefficient (K/S) for samples dyed with 10% o.w.f. cochineal, 40% o.w.f. madder, and 30% o.w.f. weld

Sample	Cochineal		Madder		Weld	
	K/S	Image	K/S	Image	K/S	Image
Dyed cotton	0.42		1.25		0.12	
Treated cotton	2.67		3.14		1.35	
Mordanted cotton	0.51		2.88		1.16	

**Table 4** Color fastness of the dyed cotton fabrics

Dye	Sample	Wash fastness			Light fastness	Rub fastness	
		CC	SC	SW		Dry	Wet
Cochineal	Untreated/raw cotton	4	4–5	5	6–7	4–5	4–5
	Treated cotton	5	5	5	7	4–5	4
	Mordanted cotton	5	5	5	7	4–5	4
Madder	Untreated/raw cotton	2–3	2	2–3	3–4	3	3
	Treated cotton	4–5	4–5	4–5	5	4	4
	Mordanted cotton	4–5	4–5	4–5	5	4	4
Weld	Untreated/raw cotton	a	a	a	a	a	a
	Treated cotton	3–4	4	3–4	4–5	4	4
	Mordanted cotton	4	4	3–4	4–5	4	4

CC Color change, SC staining on cotton, and SW staining on wool

<sup>a</sup>Not measurable due to very low absorption of dye on cotton fabrics

The rate of light fastness of the dyed cotton sample was 6–7 (Good–Very good) and it was improved to 7 for the treated cotton samples. Cochineal natural dye has an anthraquinone chemical structure and that should be the main reason for its high light fastness properties of the dyed samples.

The evaluated rub fastness of the dyed samples under dry condition was very good (4–5) which was reduced to 4 under the wet conditions. Considering the higher concentration of cochineal dye at the surface of the treated samples compared with that of the untreated cotton, the rub fastness results are quite promising.

## Conclusions

The cotton fabrics were successfully grafted by chitosan biopolymer via formation of strong covalent bonds. The maximum weight gain of the cotton samples was achieved at pH 4–5, initial Ch–Cy concentration of 30% o.w.f. at 50 °C, pH 4 for 3h. The surface positive charge of the treated cotton fabric in acidic condition, measured by zeta potential, was a clear indication of the grafted chitosan at its surface. The grafted fabrics showed very good antibacterial activity and noticeable resistance against *E. coli* and *S.*

*aureus* microorganisms even after 10 washing and drying cycles. The treatment slightly improved the strength of the fabrics and reduced their elongation at break. Additionally, the wrinkle recovery and dye absorption of the treated cotton was remarkably enhanced with no adverse impact on its fastness properties. This treatment can be applied as a potential antimicrobial and anti-crease pretreatment which will also enhance the dye adsorption properties of the treated sample without any adverse effect on tensile strength and color fastness properties.

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