

Article

Chemical Modification of Cotton Fabric Using Chitosan and Hydrolyzed Silk Fibroin

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Abstract. A cotton fabric modified with chitosan (CS) and hydrolyzed fibroin (HF) was prepared by using glyoxal as crosslinker. Fixation of CS and HF on cotton fabric was confirmed by Scanning electron microscopy (SEM) and Fourier transform infrared spectrometer (FTIR) and color depth (K/S) of finished fabrics which was dyed with acid dye. %Water absorption, tensile strength as well as %elongation and crease recovery angle were evaluated. Results of SEM micrograph and FTIR spectra clearly confirmed fixation of CS and HF on cotton fabric surface by using glyoxal as crosslinker. %Water absorption and %elongation of the finished fabrics increased with increased concentration of HF in finishing solution. However, decreases in tensile strength and %crease recovery were observed when increased concentration of HF was used. This work demonstrated that the surface properties of cotton fabrics was changed by HF modification, fixation of CS and HF placed onto cotton fabric changed the fabric surface properties, which facilitated more uptake of chemicals such as water and anionic acid dye. The cotton fabrics finished with HF exhibited antibacterial activity against the growth of *S.aureus* and *E.coli* which facilitated the finished cotton fabric as a functional materials, for example in a medical application.

Keywords: Cotton fabric, hydrolyzed fibroin, chitosan, acid dye, color depth.

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1. Introduction

Chemical modification has been in research attention as it can change the materials properties such as change in solvent stability [1] and antioxidant activity [2-3]. Cellulose has been modified by different oxidation and reduction reactions to enhance chemical process to enhance physical and mechanical properties of cellulose fibers and their sheets [4]. Low-pressure plasma process has been performed to improve deposition process on chemical physical activated cellulose fabric surfaces by pre-treated with O₂ plasma followed by acrylic acid. Being plasma treatment, acrylic acid as monomer reacted on cotton fabric surface and resulted in hydrophobic property of the fabric sample [5].

Cotton is a cellulosic fiber producing in the nature by a plant of genus *Gossypium*. It is highly used among textile fibers because of its sustainability, high availability, good mechanical properties and wear comfort [6]. However, cotton fiber is flat, hash and convoluted, it may cause irritation to wearers who have sensitive skin. To reduce the irritation by smoothen surface of cotton fabric; the cotton fabric surface was, thus modified by silk fibroin and CS, in this investigation. Surface modification techniques are attracted attention of many researchers as it is a tool to accomplish desired and improved properties such as wetting, adhesion, printing/dyeing ability and biocompatibility of material surface by introducing a variety of specific functional groups. Many innovative materials have been received from the techniques and used in the wide range of applications; those are biomedical materials, enzyme reactors, textiles and food industry [7]. Being modified by silk fibroin, cotton gains advantages, relating to improvement of reactivity and imparts various functions. Silk fibroin contains many types of amino acid; it is composed of hydroxyl, carbonyl and amino groups [8]. It provides luminosity, adaptation to skin, thermo-insulating and biodegradation, and used for many applications including enzyme immobilization, food, cosmetics, biomedical materials [9], composites [10–11], delivery of bioactive compound [12–13], tissue engineering [14–15] and functional fabric [16]. CS and fibroin molecules containing amino groups confer anti-bacterial activity, ecological safety and excellent biocompatibility [10, 17–18]. HF is of interest in this work to complex with CS, since high number of amino groups in HF facilitates more functional properties on the cotton surfaces. CS and HF are susceptible to be positive charge in acidic condition, they are used to modify cotton fabric surface in this work to alter properties of cotton fabrics. CS mixed with HF was used as modifying/finishing agents for cotton fabric using a crosslinker; glyoxal. Fixation of CS and HF was proved by FTIR and SEM. Changes in cotton fabric properties were assessed by dyeing with acid dye, %water absorption, specific tensile strength, %elongation and %crease recovery.

2. Materials and Methods

2.1. Materials

Chitosan (CS) of 99% DD supplied by Seafresh Chitosan of (Chompon, Thailand) was dissolved in 1 %v/v acetic acid (Merck) to receive 1.5 %w/v CS solution.

Gum-free fibroin was received by degumming of silk wastes (supplied from Jul Mai Thai Co.,Ltd. (Phetchaboon, Thailand)) in 0.2 %w/v Na₂CO₃ (Fisher Scientific) at 60 °C for 30 min and rinsed with 250 mL of distilled hot water, rinsing procedure was repeated ten times to remove remaining sericin. After drying, 2.5 g of fibroin was added into 1 M NaOH (Ajax Fine Chem), the mixture was stirred at room temperature for 24 h, solution of hydrolyzed fibroin (HF) was subsequently received. 50% acetic acid (Merck) was added to neutralize HF solution. A volume of 250 mL solution was made up with distilled water. HF solution of 1% w/v was obtained for further investigation.

Volumes of 20, 40, 60, 80 and 100 mL of HF solution was added into 100 mL of 1.5 %w/v of CS solution. The mixed solution was stirred for 30 min, after that 100 mL of 0.025 % w/v glyoxal (Acros Organics) was added, the mixed solution was stirred for 1 h at room temperature.

2.2. Finishing of Cotton Fabrics with Chitosan Combined with Hydrolyzed Fibroin

Five recipes of finishing solution of cotton fabrics were prepared. Finishing solution of 250 mL of each recipe contained 2 %w/v glyoxal, 2 %w/v CS, 0.48 %w/v magnesium chloride hexahydrate (Ajax Fine Chem), 0.24 %w/v acetic acid and 100 mL of solution of CS combined with silk fibroin of various volumes (20, 40, 60, 80 and 100 ml). Bleached 100% cotton fabrics (30x40 cm, 310 g/m²) were padded through finishing solution of each recipe using a laboratory padder (Union LST, MU504A), the padded fabrics were dried in a laboratory dryer (Union LST, MD) at 105 °C for 2 min and subsequently cured at 105 °C for another 2 min. The labels G, was marked for the sample finished with sole glyoxal. The labels G_CF 0.08, G_CF 0.16, G_CF 0.24, G_CF 0.32 and G_CF 0.40 were marked for the samples finished with glyoxal plus CS mixed with 20, 40, 60, 80 and 100 mL HF solution, associated to 0.08 to 0.40 %w/v, respectively. For labels G_HF and G_CS, they were marked for samples finished with glyoxal plus 100 mL HF solution and glyoxal plus 100 mL CS solution, respectively. The finished fabrics were rinsed with distilled water at 60 °C for 30 min and air-dried to remove un-reacted finishing agents, prior to further analyses and testing.

2.3. Analyses of Finished Cotton Fabrics

Functional groups in finished cotton and unfinished cotton fabrics were analyzed by Fourier transform infrared spectrometer. Samples were cut into small pieces and mixed with KBr powder, then press into pellet. The pellets of samples were analyzed using Fourier transform infrared spectrometer (Perkin Elmer, Spectrum RXI) over 400–4000 cm^{-1} with 8 solution of 64 scan numbers. Morphology of the fabrics were examined under an electron microscope (JEOL, 5410LV) at a working potential of 5 kV. Dyeing to proof fixation of finishing agents on fabric cotton surface was conducted as follows: washed fabrics were cut into 10 x 10 cm size, and dyed with 0.05% acid dye (Telon Red 51) at 60 °C at a liquor ratio of 1:20 for 40 min with addition of acetic acid. The dyed fabrics were rinsed and dried in air. %Reflectance of dyed–finished cotton and dyed–unfinished cotton fabrics was determined using a reflectance spectrophotometer (MiniScan XE PLUS) over the range of 400–700 nm. Color strength of dyed fabrics were further calculated using Kubelka-Munk equation.

2.4. Testing of Finished Cotton Fabrics

%Water absorption of rinsed fabrics was measured to observe change in hydrophilicity property of cotton fabrics. The finished cotton and unfinished cotton fabrics of 4 x 4 cm were weighed and immersed into distilled water. After 4 hr, the fabrics were removed from the water and excessive water was wiped off, the fabrics were then weighed, 3 replicates of sample were used. %Water absorption of the cotton fabrics was calculated by

$$\% \text{Water absorption} = \frac{\text{Wt. of wet fabric} - \text{Wt. of oven dried fabric}}{\text{Wt. of oven dried fabric}} \times 100$$

Tensile strength and %elongation at break of threads in warp direction from finished cotton and unfinished cotton fabrics were tested on tensile testing machine (Lloyd Testing machines) with a 50 mm gauge length at a 50 mm/min rate of extension. Specific tensile strength of the threads was calculated by breaking force/linear density, 3 replicates of sample were used. Crease recovery angles of the fabrics were evaluated according to AATCC 128 (James H. Heal & Co., Ltd.). Briefly, the fabric was cut into 4 x 1.5 cm in size, and folded in half (portrait orientation). After that, a weight of 500 g was put on the folded specimen for 5 min, after that the 500 g weight was removed and the recovery angle of the folded end was read at 5 min recovery. Antimicrobial activity of cotton finished fabrics was assessed using disc diffusion assay for *Staphylococcus aureus* (gram positive) and *Escherichia coli* (gram negative). The sterilized fabrics were placed on the cultured bacteria growth in agar plate and incubated for 24 hr at 37 °C. Antibacterial activity was assessed by measuring diameter of clear zone.

3. Results and Discussion

3.1. %Wet Pick Up of Finished Fabric

%Wet pick up of finished fabrics was shown in Fig. 1, fabric finished with glyoxal plus HF (G_HF) shows higher value of %wet pick up (73.85%) than that of fabric finished with glyoxal plus CS (G_CS) (68.45%). While the value of fabric finished with the sole glyoxal is lowest as 64.03% and fabrics finished with glyoxal plus CS and HF (G_CF 0.08 to G_CF 0.40) show tendency of increased %wet pick up at increasing concentration of HF. This associates with an increase in concentration of HF in the finishing solution, increasing the hydrophilic amino and carboxylic groups in the complex, and thus resulting in a higher affinity of hydrophilic groups to cotton fabric surfaces.

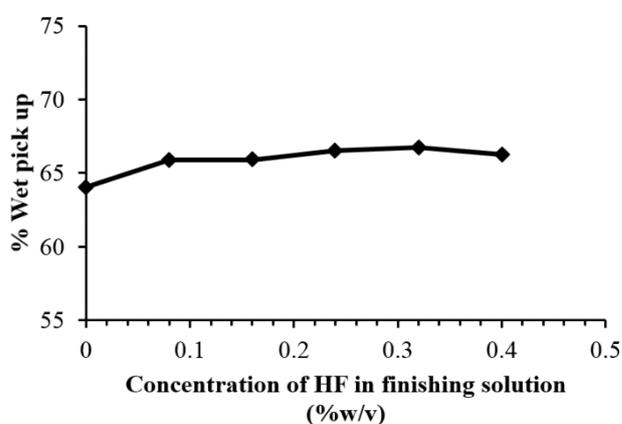


Fig. 1. % Wet pick up of samples finished with glyoxal and CS mixed with various concentration of HF.

3.2. Proof of Modification of Cotton Fabric Surface

FTIR spectra in the range of 400–4000 cm^{-1} of unfinished cotton fabric and finishing agents including HF, CS and glyoxal were present in Fig. 2. FTIR spectrum of unfinished cotton fabric (Fig. 2(a)) shows O-H stretching, C-H stretching, H-O-H bending and C-O stretching at 3800–3000, 2850–2950, 1652 and 1050 cm^{-1} , respectively, while the spectrum of HF (Fig. 2(b)) shows absorption bands of C=O stretching at 1657 cm^{-1} and 1644 cm^{-1} , also N-H bending at 1441 cm^{-1} . For the spectrum of CS (Fig. 2(c)), absorption band at 1657 cm^{-1} corresponding to C=O stretching are present. The band at 1638 cm^{-1} associated with C=O stretching of glyoxal is shown in Fig. 2(d).

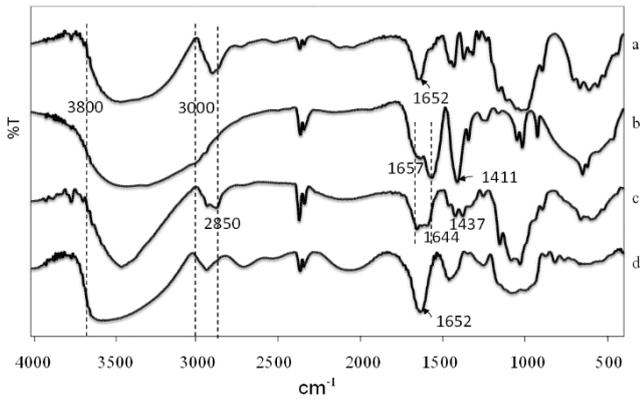


Fig. 2. FT-IR spectra of (a) unfinished cotton fabric (b) HF (c) CS and (d) glyoxal in the range of 400–4000 cm^{-1} .

Figure 3 shows FTIR patterns of unfinished fabric and the fabric finished with the sole glyoxal whereas those of the fabrics finished with glyoxal plus CS and glyoxal plus HF are similar. The absorption bands were observed at 1632 and 1657 cm^{-1} as shown in Fig. 3(b) and (c) corresponding to C=N stretching due to the crosslinking between glyoxal and HF and also CS via Schiff base reaction as suggested in other literatures [19–20]. In addition, N-H bending absorption bands in HF and CS present at 1451 and 1550 cm^{-1} . These results prove that cotton fiber surfaces are chemically modified by CS and HF in curing process due to crosslinking reaction of cellulose, CS and HF by glyoxal at 105 °C for 2 min.

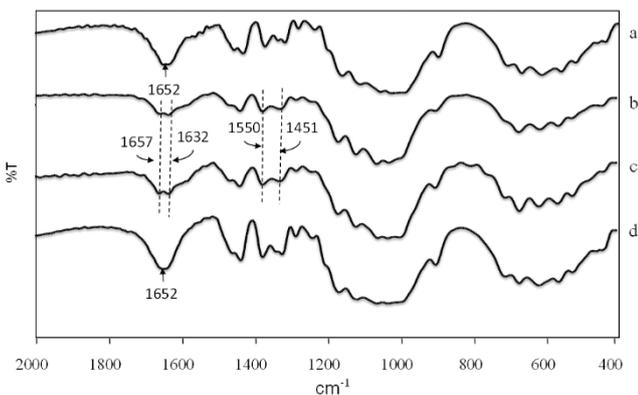


Fig. 3. FTIR spectra of cotton fabrics (a) unfinished (b) finished with glyoxal plus HF (c) finished with glyoxal plus CS and (d) finished with sole glyoxal in the range of 400–2000 cm^{-1} .

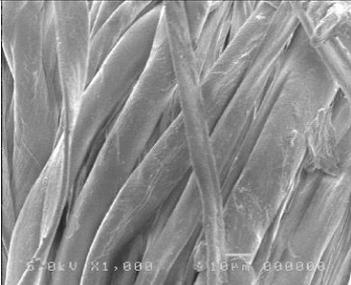
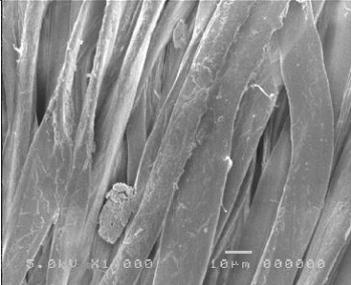
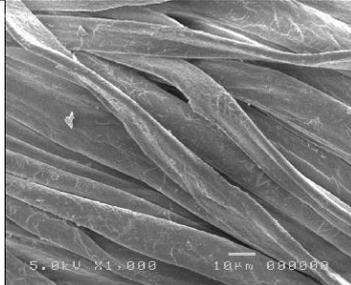
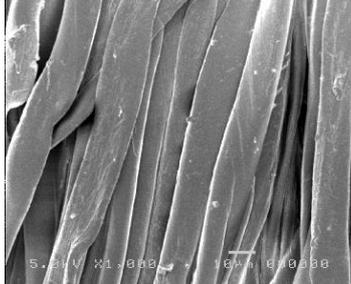
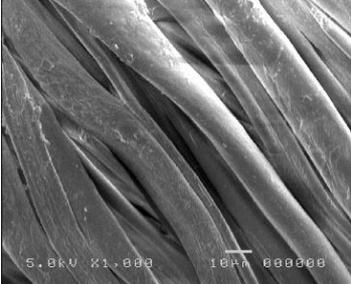
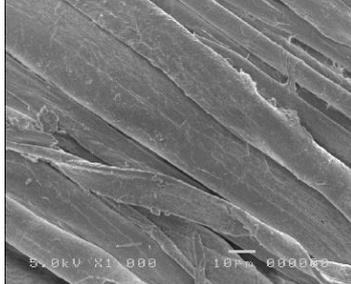
SEM images in Table 1 present surface morphology of cotton fiber of unfinished and finished fabrics. As seen in unfinished fabric (UF), cotton fiber is flat and

convoluted, its surface is rather smooth. In the case of fabric finished with glyoxal (G), the fiber is coarse as the presence of particles on the surface. In fabrics finished with glyoxal plus HF, and glyoxal plus CS (G_HF and G_CS), more particle is deposited on the fabric surface, round fibers are observed. SEM images indicate penetration of CS and HF through the fiber before crosslinking by glyoxal using pad-dry-cure technique. For fabrics finished with glyoxal plus CS and with HF of varied concentrations (G_CF 0.08 to G_CF 0.40), fiber surface is completely covered with continuous film of CS and HF.

3.3. Color Depth of Unfinished and Finished Cotton Fabrics

Relationship of color depth (K/S) of finished cotton fabrics and wavelength in the range of 400–700 nm is shown on Fig. 4, the fabrics show maximum color depth at wavelengths of 530 and 570 nm. Unfinished and fabric cotton finished with the sole glyoxal, glyoxal plus HF gave the similar K/S over the range of 400–700 nm whereas the fabric finished with glyoxal plus CS gave much higher value. This could be explained that CS on cotton fabric surface enhances color depth because much more molecules of acid dye bind by amino groups containing in CS. Figure 5 shows K/S values at 530 nm of the fabrics finished with glyoxal plus HF of varied concentrations compared with that finished with the sole glyoxal (0 %w/v HF). When 0.08 %w/v HF plus glyoxal was used, K/S of the fabric is much higher than that of the sole glyoxal. Further increase in HF concentrations from 0.08 to 0.24 %w/v, K/S values seems to be constant and then substantial decrease when 0.24 and 0.40 %w/v HF were used. That means concentrations of 0.08 to 0.24 %w/v HF yield appropriate number of amino groups on cotton fabric surface, more molecules of acid dye were adsorbed, K/S was increased as results. The results demonstrated that property of cotton fabric surface was changed after treatment. Introduction of amino group in CS and HF in cotton fabric resulted in increased positive charge on cotton fabric surface under acidic dyeing condition, therefore increase in anionic acid dye uptake. However, further increase in volumes of HF solution from 0.24 to 0.40 %w/v might lead to over crosslinking which reduce dye accessibility as found in cellulosic fabrics crosslinked with methylol resin [21]. With the dyeing of anionic acid dye, greater values of color depth were found in the samples treated by CS and HF.

Table 1. SEM images of finished fabrics of 1000 magnification.

Samples	SEM Image	Samples	SEM Image
UF		G_CF 0.08	
G		G_CF 0.24	
G_HF		G_CF 0.32	
G_CS		G_CF 0.40	

Note: UF is unfinished, HF is hydrolyzed fibroin, CS is chitosan, G is glyoxal and CF is CS mixed with HF.

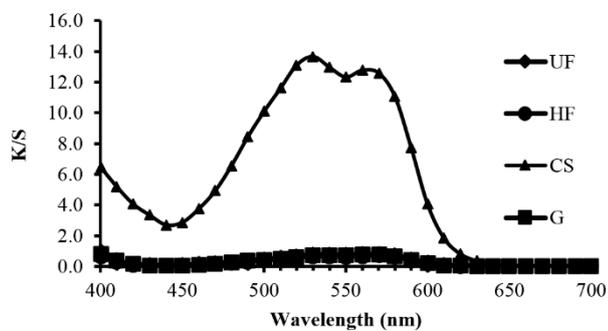


Fig. 4. Relationship of color depth of finished fabrics and wavelength.

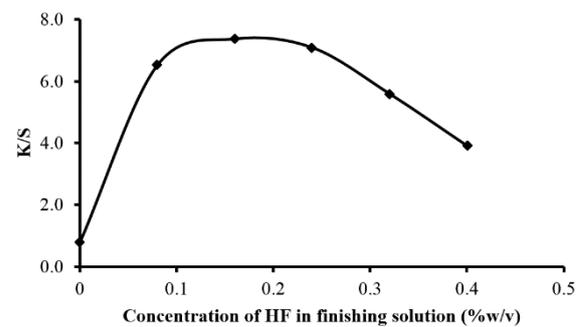


Fig. 5. Relationship of color depth of finished fabrics at 530 nm and concentration of HF in finishing solution.

3.4. %Water Absorption of Finished Cotton Fabrics

%Water absorption values of cotton finished fabrics are varied. The value of unfinished (UF) is lowest (157 ± 0.16 %) while the values for the fabric finished with sole glyoxal (G), glyoxal plus CS (G_CS) and glyoxal plus HF (G_CF) are 164 ± 0.17 , 155 ± 0.16 and 176 ± 0.18 %, respectively. Slight increase in water absorption values are found for the fabrics finished with glyoxal plus CS and HF of 0.08, 0.16 and 0.24 %w/v HF (G_CF 0.08, G_CF 0.16, G_CF 0.24) (see Fig. 6). Further increase in concentrations of HF to 0.32 and 0.40 %w/v, the values of the finished cotton fabrics (G_CF 0.32 and G_CF 0.40) are increased, the highest value is observed when 0.40 %w/v HF was used. Increase in %water absorption clearly correlates with change in fabric surface properties, hydrophilic groups from HF retained water molecules, hydrogel film was subsequently generated during the measurement, thereby great values were observed as was found in sericin silk protein finished on cotton and polyester fabrics [22-25].

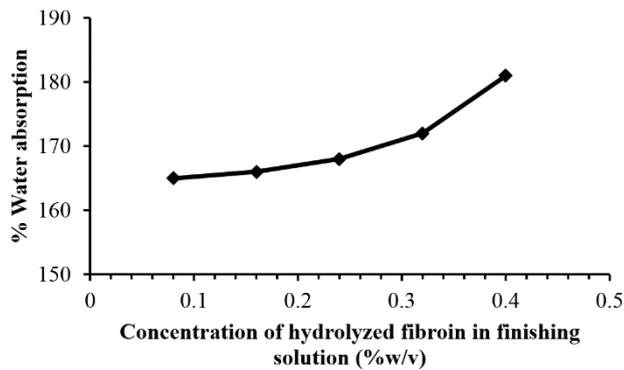


Fig. 6. Relationship of %water absorption of finished fabrics and concentration of HF in finishing solution.

3.5. Mechanical Properties of Finished Cotton Fabrics

Specific tensile strength of unfinished and finished cotton fabrics shows inversed tendency as compared with %water absorption. The values slightly increased in the order of cotton fabric finished with glyoxal plus HF (G_HF) (0.148 ± 0.026 N.tex⁻¹) < the fabric finished with sole glyoxal (G) (0.150 ± 0.015 N.tex⁻¹) < unfinished fabric (UF) (0.157 ± 0.006 N.tex⁻¹) < the fabric finished with glyoxal plus CS (G_CS) (0.163 ± 0.016 N.tex⁻¹). Figure 7 shows specific tensile strength of the fabrics finished with the sole glyoxal (G), with glyoxal plus CS and HF (G_CF 0.08, G_CF 0.16, G_CF 0.24, G_CF 0.32 and G_CF 0.40). Significant increase in the value is found in cotton fabric finished with glyoxal plus CS and HF. Slightly decreased values are observed when concentrations of HF were increased (from 0.08 to 0.40 %w/v). Similarly, decrements in specific tensile strength value of cellulosic fibers like cotton and rayon

due to increase in finishing agent concentration were also found in other types of finishing agent such as BTCA and methylol resin; Arcofix NEC [26-28].

%Elongations of unfinished fabric (UF), fabric finished with sole glyoxal (G), glyoxal plus HF (G_HF) and glyoxal plus CS (G_CS) were 20.33 ± 3.88 , 17.93 ± 2.19 , 16.13 ± 4.35 and 18.08 ± 3.84 %, respectively. The value of fabric finished with the CS and 0.32 % w/v HF (G_CF 0.32) is lowest. Insignificantly increase values are found in fabrics finished with glyoxal plus CS and HF (G_CF 0.08, G_CF 0.16, G_CF 0.24, G_CF 0.32 and G_CF 0.40) as shown in Fig. 8.

From the results of specific tensile strength and %elongation, HF crosslinked with CS on cotton fabric surface could maintain both values. It seems to have no effect on molecular movement of cotton fiber when tension was applied. This is because of its low penetration due to large molecules, thus, it deposited on the fabric surface. In contrast, CS and HF caused lower tensile strength and %elongation as they moved into the fiber during padding process and then was crosslinked in curing process. It is clearly confirmed by SEM images that round fibers were observed in fabrics finished with glyoxal plus CS and HF.

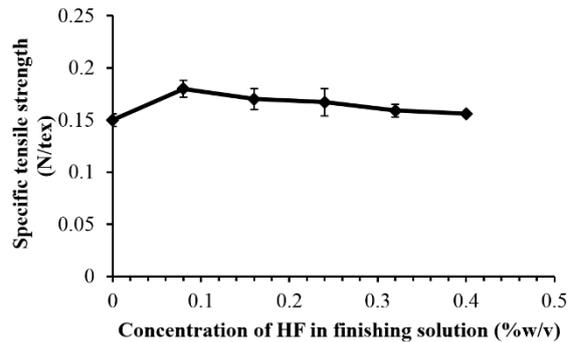


Fig. 7. Relationship of specific tensile strength of finished fabrics and concentration of HF in finishing solution.

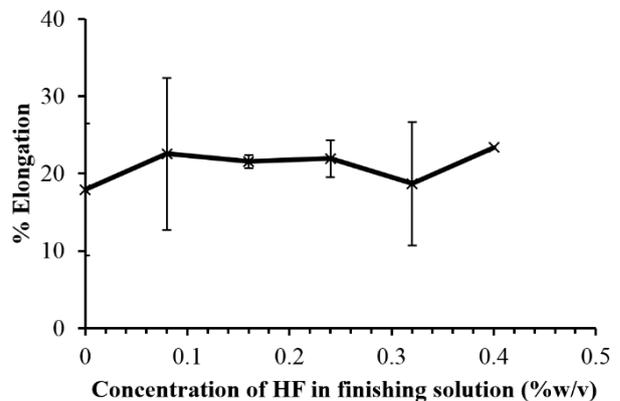


Fig. 8. Relationship of %elongation of finished fabrics and concentration of HF in finishing solution.

Crease recovery angle (CRA) of unfinished (UF), fabrics finished with glyoxal (G), glyoxal plus CS (G_CS) and glyoxal plus HF (G_HF) were 115 ± 5 , 101 ± 3.61 , 94.67 ± 0.58 and 96.33 ± 1.16 . The values for fabrics finished with the sole glyoxal (G), with glyoxal plus CS and HF (G_CF 0.08 to G_CF 0.40) are shown in Fig. 9. When CS and HF were added into finishing agent, CRA of fabric is substantial increased. However, increased in HF concentration to 0.16 %w/v the value is remarkably decreased. Further increases in HF concentration up to 0.40 %w/v, CRA values are insignificantly decreased. The same effect of increase in silk fibroin concentration on lowering CRA has been found in silk sericin as a finishing agent for cotton fabric [22].

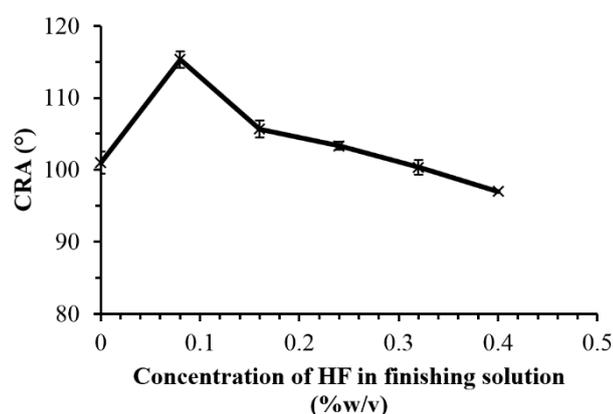


Fig. 9. Relationship of crease recovery angle of finished fabrics and concentration of HF in finishing solution.

Results of antibacterial activity of cotton finished fabrics are shown in Table 2. Cotton fabric finished with glyoxal plus CS (G_CS) shows no activity against *S.aureus* and *E.coli* as none of clear zone was observed on the sample. The result is different from another investigation of cotton finished with CS and other crosslinkers i.e. butanetetracarboxylic acid and Arkofix NEC (low formaldehyde content dimethylol urea resin) [26], likewise, silk fabric modified by CS [29]. However, those finished fabrics with glyoxal plus CS and HF of varied concentrations (G_CF 0.08, G_CF 0.16, G_CF 0.24, G_CF 0.32 and G_CF 0.40) show the activity against both *S.aureus* and *E.coli*, they are able to inhibit *S.aureus* more than *E.coli*. This associates with amino acids from HF, they may play a role on antibacterial activity as has been supported by another literature [30]. Besides, both the fabrics finished with glyoxal and CS for antibacterial activity. However, the fabric with the combination of CS and HF demonstrates clear zone against *E.coli*. It can be explained that CS and HF might have a synergistic effect against *E.coli* as the activity increased, in turn, with increasing HF concentration. Nevertheless, no increased tendency of the activity with increased HF concentration, as well as no clear zone against *E.coli* of G_HF and G_CF 0.40 are observed, which might be affected by uneven and low % wet pick up of finished samples.

Table 2. Antibacterial activity of cotton finished fabrics.

Samples	Clear zone against <i>S.aureus</i> (mm)	Clear zone against <i>E.coli</i> (mm)
G_CS	0	0
G_HF	4	0
G_CF 0.16	11	6
G_CF 0.24	12	6
G_CF 0.32	8	8
G_CF 0.40	7	0

4. Conclusion

Chemical modification of cotton fabric surface using CS and HF was achieved by using glyoxal as crosslinker. FTIR spectrum and SEM images proved that cotton fabric surface was modified by glyoxal, CS and HF associated with C=O absorption band was observed at $\sim 1650\text{ cm}^{-1}$ and images of polymer film covered on the cotton fabric surface. The modified cotton surface was expected to be softer and smoother which is suitable for reducing skin irritation of the wearer. The change in surface properties of cotton fabric affected to %water absorption, tensile strength and crease recovery angle values due to more positive charges of amino groups from CS and HF presented on finished cotton fabric surface led to greater dye uptake and improved antibacterial activities. High % water absorption and antibacterial property facilitated the finished cotton fabric as a health care material which can also be used in medical applications.

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