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Simultaneous crosslinking and cationization of cotton cellulose by using dialdehyde and choline chloride: comparison between the pad-dry-cure and microwave irradiation process

Ji Hwan Park · Hyung-Min Choi · Kyung Wha Oh

Abstract Simultaneous crosslinking and cationization of cotton cellulose were carried out by using two dialdehydes, glyoxal (GO) and glutaraldehyde (GA), along with choline chloride (ChCl). Two heating methods, conventional pad-dry-cure (PDC) and microwave irradiation, were investigated and compared. The results revealed that two aldehyde molecules reacted very differently in the presence of ChCl under two different heating methods. GO reacted predominantly with the cellulose molecule, stimulating the crosslinking reaction and consequently resulting in high wrinkle recovery angle (WRA) values regardless of the heating process. Contrarily, GA favored the reaction with ChCl, allowing high K/S values with acid dye under microwave irradiation. The crosslinked and cationized cotton cellulose was only obtained by treatment with GA and ChCl under the PDC process, resulting in high WRA and K/S values. Characteristics of the treated fabrics were also evaluated by Fourier transform infrared analysis, thermogravimetric analysis, scanning electron microscopy, water of imbibition, and tensile strength test. Additionally, the treatments with GA and ChCl also provided high antimicrobial properties of the cotton celluloses; thereby most bacteria reductions of the specimens were close or equal to 99.9 %. Therefore, economically viable yet ecofriendly crosslinking and cationization of cotton cellulose could be made by treatment with GA and ChCl.

Keywords Cotton cellulose · Crosslinking · Cationization · Pad-dry-cure process · Microwave irradiation · Ecofriendly

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Introduction

Cotton is the most important textile fiber and is mainly dyed with anionic dyes such as direct and reactive dyes. During dyeing of cotton, a large amount of salt (NaCl or Na_2SO_4), usually 30–150 g dm^{-3} (or up to 25 % on the weight of bath), is used to facilitate migration of dyes from the bath to the fiber surface and consequently enhances dye uptake and fixation (Zhang et al. 2007). The use of salt, however, causes a severe environmental problem in fresh water streams and must be removed before discharge to the effluent (Kim and Choi 2014).

Cationization of the cellulose molecule is mainly carried out to improve the affinity toward anionic

substances such as dyes in conventional textile processing and metal ions or unfixed dyes in effluent treatment (Yuan and Hauser 2014; Ma et al. 2012; Marshall and Wartelle 2004; Wartelle and Marshall 2005). Modifying cotton fibers with cationic charges prior to dyeing is an attractive route to promote negative dye-fiber affinity, thereby reducing the required amounts of salt (Yuan and Hauser 2014; Sharif et al. 2007; Kim and Choi 2014). Furthermore, various cationized cellulosic materials such as rice hulls, soybean hulls, and saw dust have been examined for controlling toxic heavy metals in effluent water (Ferrero and Periolatto 2012; Ma et al. 2012; Zhang et al. 2007).

Cellulose cationization is commonly carried out by several methods: first, a direct cationization of cellulose using a chemical compound with a reactive functional group. N-(3-chloro-2-hydroxypropyl) trimethylammonium chloride or a similar molecule could be a representative compound for this approach (Yuan and Hauser 2014). The second approach involves an indirect cationization by using a binding agent such as dimethyloldihydroxyethylene urea (DMDHEU) along with a cationic agent. The binding agent should react with both cellulose hydroxyl and a functional group of the cationic agent (Wartelle and Marshall 2005). This process has been mainly employed in textile applications since the common textile pad-dry-cure (PDC) process can be used. However, DMDHEU is a formaldehyde-releasing chemical and must be eliminated in the near future (Choi and Kim 1999). The third approach utilizes graft polymerization to introduce monomeric or polymeric cationizing agents within the cellulose, but it is not commercially applicable (Kim and Choi 2014). Each process has advantages and disadvantages in terms of efficiency, toxicity, and economy, but none of these processes has been commercially adapted yet. Therefore, a better process still needs to be developed for the cationization of cellulose.

Microwave-assisted organic synthesis has moved to the forefront of chemical research (Budimir et al. 2012; Cho et al. 2013; Guo et al. 2010; Katovic et al. 2008). Use of microwave (MW) irradiation provides a number of advantages over conventional heating, such as noncontact as well as instantaneous and rapid heating with high specificity (Budimir et al. 2012; Cho et al. 2013). Using MW irradiation in lieu of the common PDC textile process has great potential because it provides an even irradiation throughout the material, allowing more uniform and faster heating than conventional conduction or convection heating (Katovic et al. 2008). It is also known that MW irradiation is more energy efficient (Guo et al. 2010; Katovic et al. 2008).

Therefore, in this study we examined the feasibility of applying dialdehyde as a nonformaldehyde cross-linking agent and choline chloride (ChCl) as a cationic agent to simultaneously crosslink-cationize cotton cellulose. Especially ChCl is biodegradable and biocompatible. It is also being widely used as a feed additive for livestock and is an inexpensive commodity chemical (Kim and Choi 2014; Park et al. 2013). It also has been approved as a food additive by the US Food and Drug Administration. Thus, an investigation of the cationization of cotton using dialdehyde and ChCl is a reasonable step in the development of an ecofriendly yet economically viable process. Additional efforts were also made to examine the use of an energy saving, nonconventional method such as the MW irradiation process for drying-curing.

Experimental

Materials

A bleached and desized, plain weave cotton fabric (31×30 threads/cm^2) purchased from Korea Apparel Testing and Research Institute, Seoul, Korea, was used throughout the study. Two dialdehydes, such as glyoxal (GO, 40 % aqueous solution) and glutaraldehyde (GA, 25 % aqueous solution), ChCl (99 %) as a cationic agent, and ammonium sulfate (($Al_2(SO_4)_3$)-18H_2O, AS) as an acid catalyst were all obtained from Sigma-Aldrich, Inc., Korea. All the chemicals were reagent grade and used without any further purification. C.I. Acid Red 4 was also purchased from Aldrich.

Fabric treatments by PDC and pad-microwave irradiation

Cotton fabric (warp 21 cm $\times$ weft 30 cm, weight 4.5 g) was impregnated in the treatment bath containing appropriate amounts of dialdehyde, AS (4 % on the weight of dialdehyde), and ChCl (as needed). The concentration of the reagent was all on the weight of the bath in terms of the solid content of dialdehyde, unless otherwise noted. The fabric was then padded at

2 psi by using a padding mangle with wet pick-up of 100 ± 5 %, dried at 85 °C for 5 min in an oven (VOS-301SD Rikakikai Co., Ltd., Japan), and finally cured at 120 °C for 5 min in a curing oven (Werner Mathis AG, DHE 48989, Switzerland). Two dips and nips were used.

For the MW irradiation process, the padded cotton fabric was directly placed flat in a commercial 700-W microwave oven (Daewoo Electronics, KR-V209Q, 20L, Korea) for an appropriate time (1, 2, and 5 min). No pre-drying step was used before the curing. The treated fabric was severely washed to remove unreacted chemicals and then dried again at 85 °C for 5 min. The specimen was then stored in the standardized chamber (21 ± 1 °C, 65 ± 2 % relative humidity) at least 24 h for further analyses.

Analyses for crosslinking and cationization

A level of crosslinking between the dialdehyde and cellulose molecule was estimated by conditioned wrinkle recovery angles (WRAs) of the pristine and treated cotton fabrics according to AATCC Technical Method 66-2008 (AATCC 2008). The fixation of cationic ChCl within the cotton fabric was analyzed in two ways: elemental analysis and anionic acid dye sorption. Elemental analysis (Euro Vector E, E/V RE2) was employed to determine the presence of nitrogen and other elements in cationized cotton. C.I. Acid Red 4 with λ_{max} at 520 nm was used to estimate the presence of cationic groups within the treated cotton cellulose. A dyeing solution contained acid dye (10 g/l), and sodium sulfate (6 g/l) was prepared. The pH of the dye bath was adjusted to 3–4 with acetic acid solution (0.1 mol/l) at a 20:1 liquor-to-fabric ratio. Dyeing was started at 40 °C; the temperature was increased to 98 °C for 25 min (increase rate 2.3 °C/min). Then the temperature was maintained for 35 min, and the bath was cooled to 60 °C for 15 min. Dyeing was carried out in a stainless tube in an IR dyeing machine (Daelim Starlet Co., Ltd., Korea). The reflectance of the acid-dyed fabric was measured by a Minolta Color Eye CM-512M3 (Japan), and the K/S value was calculated according to the Kubelka-Munk equation (Park et al. 2013):

$$K/S = (1 - R)^2/2R \qquad (1)$$

where R is the reflectance of the sample at λ_{max}.

Other characterizations of the treated cotton

Tensile strength was measured to evaluate the strengths of the pristine and treated cotton fabrics by using a Universal Testing Machine (H10KS Hounsfield, UK) according to ASTM D5035-11 (strip method) (ASTM 2013). At least three replications were used, and the average value was calculated. Hydrophilicity of the cotton fabrics after simultaneous crosslinking-cationization treatment was assessed by the water imbibition value. The samples were immersed in a distilled water bath for 3 h. The wetted sample was centrifuged for 30 min at 1,800 rpm and then weighed (W_w). The sample was then dried at 85 °C for an hour, and its dry weight (W_d) was determined. The water imbibition values were calculated by the following equation (Choi and Kim 1999):

$$\text{Water imbibition } (\%) = [(W_w - W_d)/W_d] \times 100 \qquad (2)$$

A Fourier transform infrared (FTIR) spectroscope with an attached ATR (Bruker, Vertex 70, USA) was used to analyze the dialdehyde-treated cotton fabrics in the spectral region of 4,000–600 cm^{-1} with 64 scans at 4 cm^{-1} resolution. UV absorbance of the dialdehyde solution was measured in a quartz cell (1 cm) by a UV-vis-NIR spectrophotometer (Shmadzu UV-3600, Japan). Thermal characteristics of pristine and treated cottons were appraised by thermogravimetric analysis (TGA, Mettler, USA). Scanning electron microscopy (SEM) (COXEM, CX-100S, Korea) was employed to study the effect of dialdehyde and ChCl treatment on the topological characteristics of the cotton fabrics.

Antimicrobial test

Antibacterial properties of the treated cotton fabrics were tested against *Staphylococcus aureus* (ATCC 6583P) and *Escherichia coli* (ATCC 8739) according to a modified testing method for antibacterial activity of the fabrics (JIS Z2801) (JIS 2000). The detailed procedure for the antibacterial test can be found in the previous study (Park et al. 2013). The reduction of bacteria was calculated as follows:
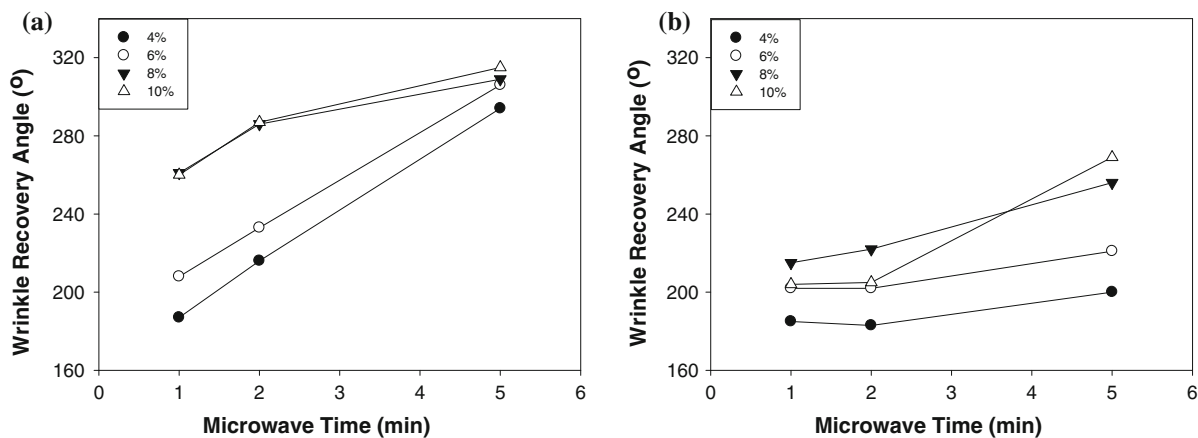
Fig. 1 WRAs of cotton fabrics treated with various concentrations of dialdehydes under MW irradiation. (AS: 4 % on the weight of dialdehyde). **a** GO; **b** GA

Antimicrobial activity $(S) = \log(\mathrm{M}_b/\mathrm{M}_a) - \log(\mathrm{M}_c/\mathrm{M}_a)$
$$= \log(\mathrm{M}_b/\mathrm{M}_c)$$
$$(3)$$

Reduction of bacteria $(\%) = [(\mathrm{M}_b - \mathrm{M}_c)/\mathrm{M}_b] \times 100$
$$(4)$$

where M_a is the average number of bacteria in a reference sample immediately after vaccination of the testing bacteria, M_b is the average number of bacteria in a reference sample after incubation for 24 h, and M_c is the average number of bacteria in an antimicrobial sample after incubation for 24 h. If the value of M_a is lower than that of M_b, the measurement of the sample is confirmed to have failed because of natural reduction due to the external environment.

Results and discussion

Effect of the MW process on the dialdehyde reaction

In order to investigate the feasibility of MW irradiation in place of a conventional textile PDC process, screening experiments were carried out to initiate the reaction between dialdehyde and cotton cellulose. As shown in Fig. 1a, WRAs of the cotton fabrics treated with GO were elevated continuously with increasing MW irradiation time. In addition, at the same MW irradiation time an increase in the GO concentration also increased the WRAs, but this increase in WRAs

became smaller at high GO concentrations (10 %) and long MW irradiation time (5 min).

On the other hand, GA-treated cotton fabrics generally displayed lower WRAs than GO-treated cotton fabrics at the same conditions (Fig. 1b). This was most likely due to the lower actual mole of GA than mole of GO at the same % owb and greater penetration of GO into cotton cellulose (this will be discussed later in more detail). The WRAs close to or above 270° of cotton fabrics treated with both dialdehydes were exceptionally higher than those of pristine cotton (174°). These results therefore implied that the MW irradiation could be used in lieu of the PDC process in cotton crosslinking with dialdehyde. The process itself was very simple and did not require a pre-drying process.

Comparison of PDC and MW processes in the presence of ChCl

Based on the success of the reaction between cellulose and dialdehyde under the MW irradiation process, we now examined treatment of cotton fabrics in the presence of dialdehyde and ChCl. We expected that dialdehyde could act as a bridge between two unreactive molecules (cellulose and ChCl). The reaction among cellulose, dialdehyde, and $HOCH_2CH_2-$ in ChCl is believed to be an acetal formation as described in Scheme 1. The presence of an acid catalyst such as ammonium sulfate could facilitate the reaction. A high temperature curing is also needed to eliminate water molecules for completion of the reaction (Choi and

Scheme 1 Potential reaction mechanism among cellulose, dialdehyde (where $n = 0$ for GO and $n = 3$ for GA), and ChCl
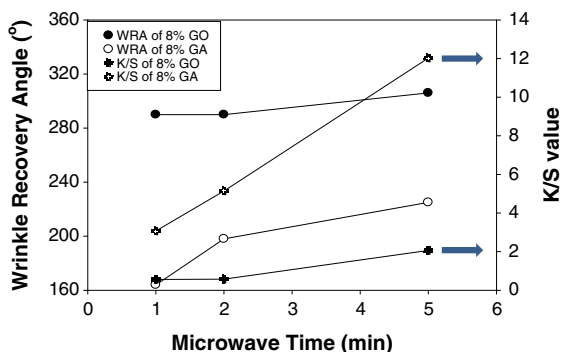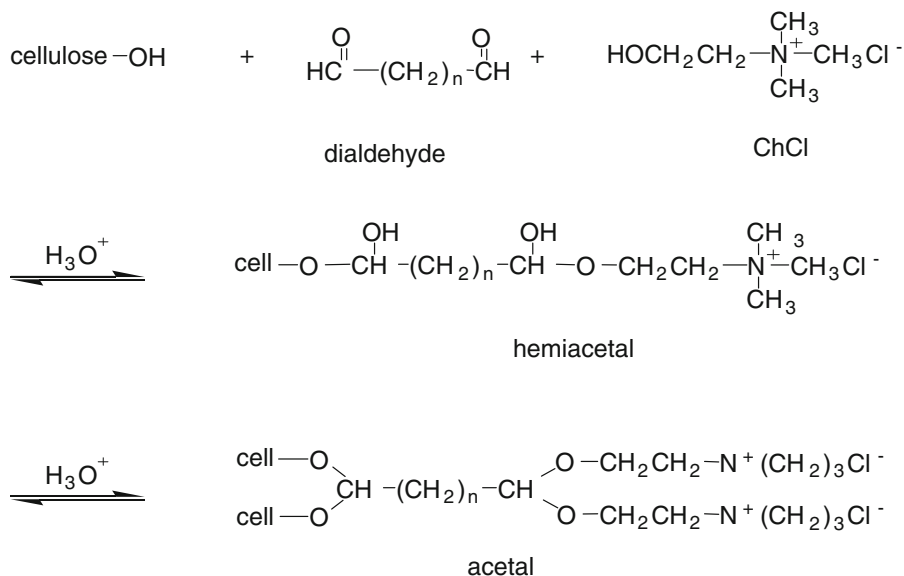

Fig. 2 WRAs and *K/S* values of cotton fabrics treated with dialdehyde and ChCl at different MW irradiation times (dialdehyde 8 %, AS 4 % of dialdehyde, and ChCl 4 %)

Kim 1999). The experimental results, however, showed that the reaction among the three components was not as simple as expected. Unexpected WRAs and *K/S* values were obtained from the experimental results, demonstrating a substantial difference in the reactivity of the two aldehydes in the presence of ChCl.

Results shown in Fig. 2 reveal that under MW irradiation the cotton fabrics treated with GO and ChCl exhibited high WRAs but very low *K/S* values. Contrarily, those treated with GA and ChCl at the same conditions showed the opposite results, i.e., low WRAs but very high *K/S* values. The specimens were directly exposed to MW irradiation after padding. In

addition, the cotton fabrics treated at the same reagent concentrations (8 % dialdehyde and 4 % ChCl) under the PDC process with GO demonstrated similar results as the MW irradiation process, i.e., a high WRA value (289°) and low *K/S* value (0.57). However, the cotton fabrics treated with GA and ChCl under the PDC process were very different from those treated under other conditions. Both the WRA and *K/S* values of these cotton fabrics were considerably high at 277° and 13.83, respectively.

These results suggested that the reactivity of the two aldehyde molecules in the presence of ChCl was quite different under both the PDC process and MW irradiation. In the presence of ChCl, GO reacted mainly with cellulose molecules, stimulating cross-linking and consequently, resulting in high WRA values, regardless of the heating process. On the other hand, GA generally favored the reaction with ChCl, allowing high *K/S* values with acid dyes under MW irradiation. Only the cotton fabrics treated with GA under the PDC process produced simultaneous cross-linking and cationization, resulting in both high WRA and *K/S* values. With increasing MW irradiation time, the WRA and *K/S* values of the cotton fabrics treated with two aldehydes were improved, but the effects were only marginal, except the *K/S* value of GA. A further study is needed to develop an efficient MW radiation method for simultaneous crosslinking and cationization.
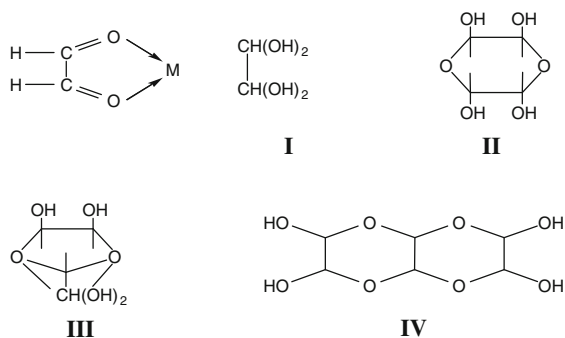
Scheme 2 Possible structures of GO in aqueous solutions (Choi and Kim 1999)

The reaction among cellulose hydroxyl, dialdehyde, and $HOCH_2CH_2-$ in ChCl is an acetal formation as described previously. An additional three $-CH_2$ group is the only structural disparity between GO and GA. Nevertheless, the reactivity of acetal formation in the two dialdehydes with cellulose and ChCl was not as simple as expected. It must be noted that the actual mole of GO used was ca. 1.73 times greater than that of GA at the same % owb, i.e., the concentrations of GO and GA at 4 % owb were 0.0465 and 0.0268 mol, respectively. This indicated that GO preferentially reacted with cellulose, not with ChCl, even at a higher concentration of GO than of GA. It is known that GO can readily form a pseudo-five-member chelate ring, as shown in Scheme 2 (Choi and Kim 1999). Because of this, the reaction mechanism of GO with cellulose and ChCl would be more complex than a simple acetal formation.

On the other hand, there are many different coexisting forms of GA in aqueous solutions, i.e., hemihydrate, dihydrate, and cis and trans isomers of cyclic hemiacetal, as well as dimers and acetal-like polymer structures, as illustrated in Scheme 3 (Migneault et al. 2004; Yoshioka and Goissis 2008; Wang and Hsieh 2010; Whipple and Ruta 1974; Wine et al. 2007). As many as 13 different forms of GA have been proposed in the literature; thus, the structure of GA in aqueous solutions has been the subject of much debate (Kawahara et al. 1992, Migneault et al. 2004). According to the previous studies, the major portion of GA takes a monomeric, predominantly cyclic hemiacetal form (structure IV) at pH 3–8 in dilute solution, and an α, β-unsaturated structure does not coexist in aqueous solution regardless of the GA

concentration (Kawahara et al. 1992; Yoshioka and Goissis 2008). However, in our study an absorption peak at 235 nm observed in the UV spectrum of the aqueous GA solution clearly demonstrated the presence of an α, β-unsaturated structure (V, VI in Scheme 3) at 25 °C, as shown in Fig. 3a.

An increase in the monomeric aldehyde forms of GA during heating was also investigated by UV absorbance. As shown in Fig. 3, GO did not show much difference in UV absorbance during heating. However, absorbance of GA at 280 nm for the carbonyl group (I, II in Scheme 3) increased substantially from 0.813 to 1.304 with 1 min of MW irradiation, whereas absorbance at 235 nm for the α, β-unsaturated double bond was decreased. This corroborated that cyclic hemiacetals and other non-aldehyde forms broke down to monomeric aldehyde GA after heating to enhance the reactivity of GA toward cellulose and ChCl.

Furthermore, substantial differences in boiling points and molecular weights of two aldehydes, 50 °C and 58.04 g/mol for GO and 187 °C and 100.12 g/mol for GA, could be another possible reason for the disparity in reactivity. At high temperature curing, GO molecules could be readily vaporized and transferred into the interior of the cotton fabric, consequently hindering the reaction with ChCl, which would more likely stay on the fabric surface because of its high boiling point and high molecular weight (302 °C and 139.62 g/mol). On the other hand, GA tended to remain on the fabric surface and react with ChCl. During less intensive heating, such as in the PDC process, the GA molecule could have a certain level of penetration within cellulose and consequently initiate the reaction with cellulose along with ChCl, resulting in an increase of both WRA and K/S values. For the following experiments, we thus only selected the PDC process to investigate simultaneous cross-linking and cationization of cotton cellulose with GA and ChCl.

Effect of ChCl concentrations

Figure 4 shows that the WRAs of cotton fabrics were enhanced with increasing concentrations of GA at the same amount of ChCl. However, the WRAs of cotton were reduced with increasing ChCl concentration at all GA concentrations. These results substantiated that

Scheme 3 Possible structures of GA in aqueous solution (Hardy et al. 1969; Migneault et al. 2004; Ruijgrok et al. 1990; Whipple and Ruta 1974; Wang and Hsieh 2010)
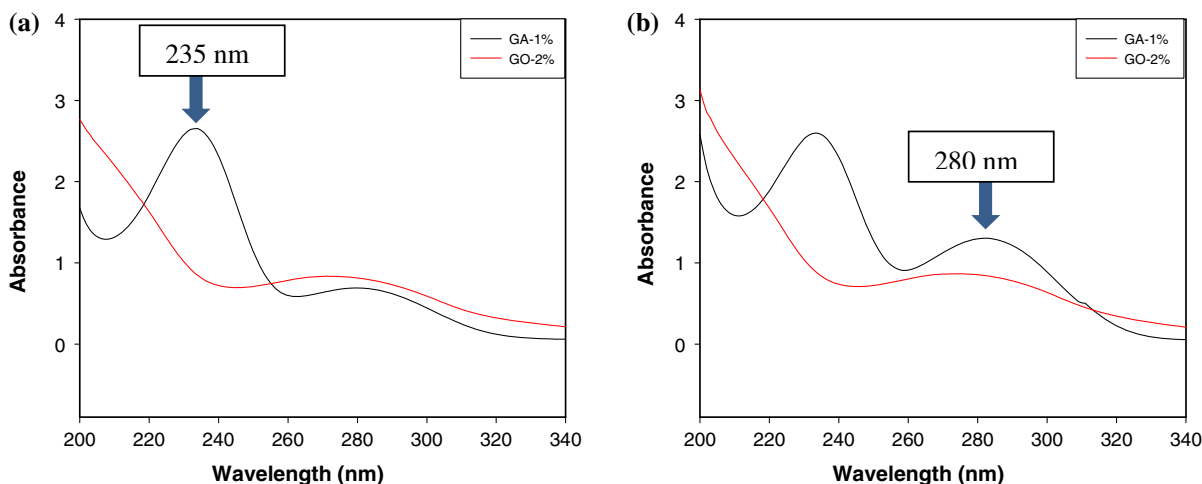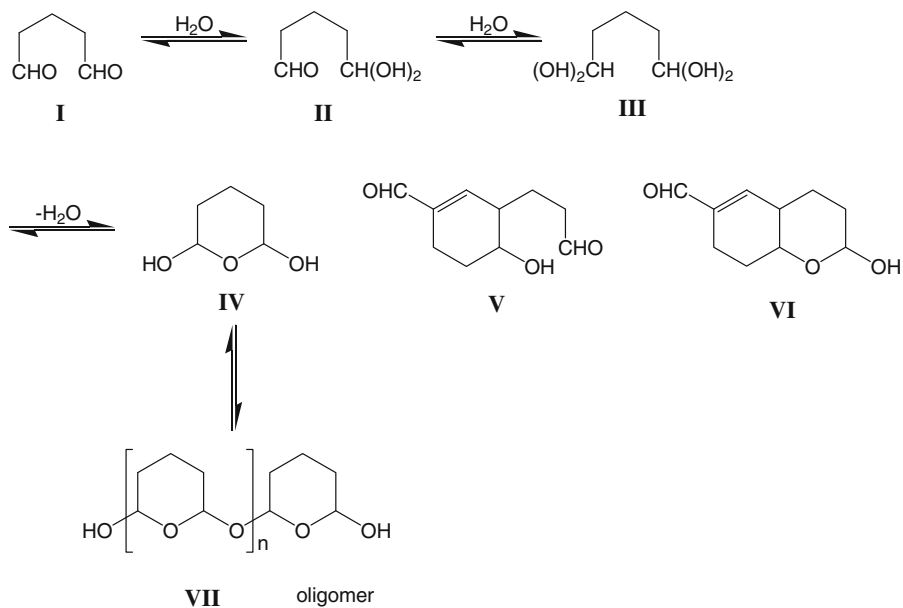

Fig. 3 Effect of heating on UV absorbance of dialdehydes: **a** before heating; **b** after 1 min of MW irradiation

GA can react with both cellulose molecules and the HOCH$_2$CH$_2$– group in ChCl.

Evidence of ChCl fixation within cotton cellulose was substantiated by two methods: elemental analysis and negative dye sorption. As shown in Table 1, the nitrogen contents of the cotton fabrics were considerably increased by treatment with GA and ChCl. However, the nitrogen content reached a maximum at 4 % ChCl. This higher nitrogen content revealed fixation of ChCl within cotton.

The presence of cationic ChCl within cotton cellulose was further confirmed by sorption of acid dye. Cationic cellulose treated with ChCl would have an outstanding capacity to sorb an anionic dye through an ionic bonding between cationized cellulose (Cell-R-N$^+$(CH$_3$)$_3$Cl$^-$) and acid dye (Dye-SO$_3^-$) (Sharif et al. 2007; Yuan and Hauser 2014). Thus, the greater K/S values could indicate the reaction between GA and ChCl. Results in Figs. 5 and 6 demonstrate that the acid dye sorption measured by the K/S value increased very significantly with the addition of ChCl. However, the increase in K/S values was not linearly proportional to the increase in ChCl concentrations. Instead, the K/S values were the highest in the cotton fabric
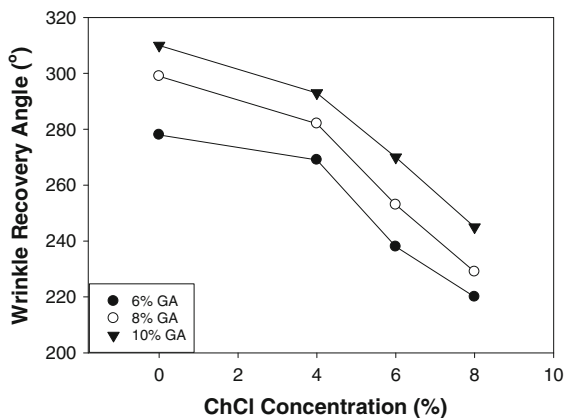
Fig. 4 Effect of ChCl concentrations on WRAs of cotton fabrics treated with GA

Table 1 Elemental analyses of cotton fabrics treated with 10 % GA with ChCl

Specimen	Element			
	N (%)	C (%)	H (%)	O (%)
Pristine	0.031	40.851	6.139	47.945
ChCl 0 %	0.029	40.987	6.243	47.821
ChCl 4 %	0.556	40.764	6.058	47.981
ChCl 6 %	0.447	40.835	6.045	47.822
ChCl 8 %	0.499	40.785	6.113	48.135

treated with 4 % ChCl, regardless of the GA concentration. A similar trend was also observed in the elemental analysis data (Table 1). These suggested
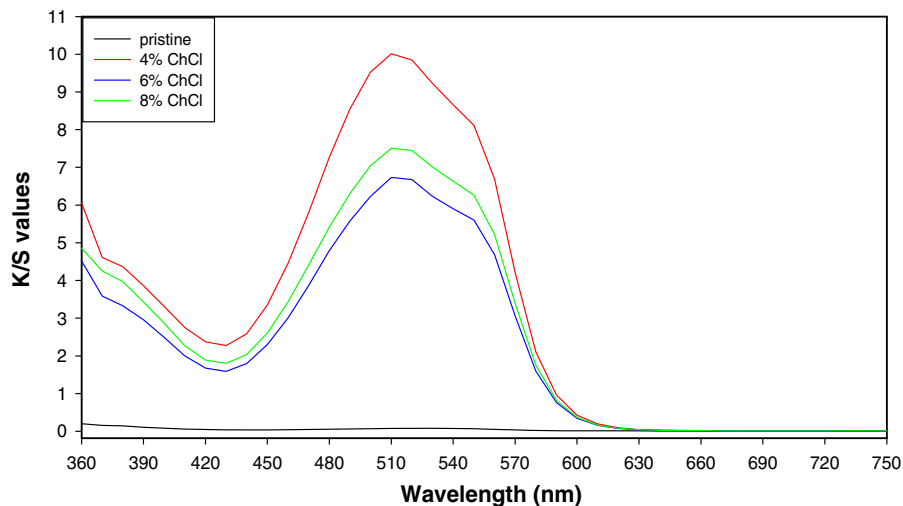

Fig. 6 Effect of ChCl concentrations on K/S values of cotton fabrics treated with GA

that at 6 and 8 % concentrations, GA reacted more easily with cellulose than $HOCH_2CH_2$- in ChCl. Thus, the concentration of ChCl should be optimized for each GA concentration to obtain a maximum efficiency at a minimum reagent concentration in cross-linking and cationization.

Water of imbibition of the cotton fabrics treated with GA and ChCl was also investigated to study the effect of ChCl addition on hydrophilicity. The results in Fig. 7 reveal that the cotton fabrics treated with GA in the presence of ChCl generally showed higher water of imbibition compared with those of the pristine and of the cotton fabric treated with GA only. This substantiated that the cationization of cotton increased not only the sorption of anionic dyes, but also the
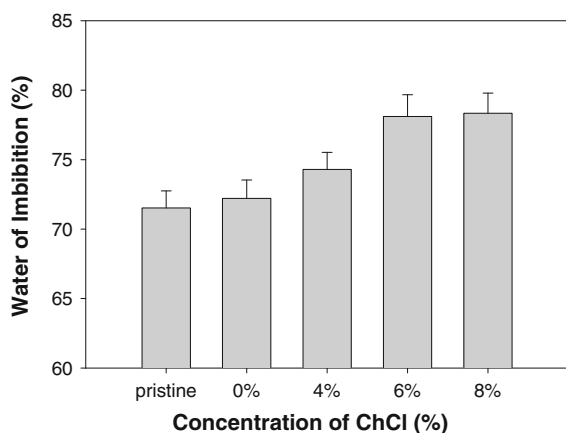
Fig. 5 Representative K/S values of cotton fabrics treated with GA at different ChCl concentrations (λ_{max} of the specific dye was 520 nm)

Fig. 7 Effect of ChCl concentrations on water of imbibition of cotton fabrics treated with 10 % GA
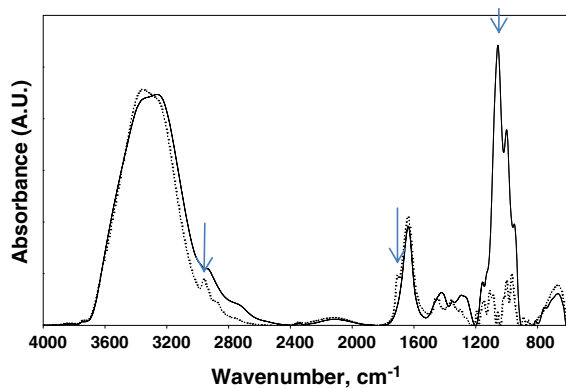

Fig. 8 FTIR spectra of GO (*solid line*) and GA (*dotted line*)

sorption of water because of the presence of the hydrophilic ionic compound.

FTIR analysis

FTIR spectra of two dialdehydes in aqueous solution were almost identical except for a few areas of disparities: GO showed a more prominent peak at $1,058$ cm^{-1} for C–O stretching, and GA exhibited sharp peaks at $1,710$ cm^{-1} for aldehyde –C=O stretching and at $2,960$ cm^{-1} for sp^3 C–H stretching (Fig. 8). These spectra again confirmed that GO was in a more hydrated form or any other dimeric or polymeric form than GA, as described previously.

As shown in Fig. 9a, no aldehyde carbonyl peak was found in the cotton fabrics treated with GA and ChCl before drying. However, the small peaks at $1,713$ cm^{-1} for the aldehyde carbonyl stretching

vibration were observed in the GA-treated cotton fabrics after an extensive drying of the specimen at 100 °C for 12 h (Fig. 9b). The peak heights at $1,713$ cm^{-1} decreased with increasing ChCl concentrations, i.e., 0.107, 0.105, 0.095, and 0.083 for the specimens treated with GA with 0, 4, 6, and 8 % ChCl, respectively. This again corroborated that the presence of ChCl reduced the reactivity of GA, resulting in smaller amounts of aldehyde groups in the FTIR spectra. The evidence for ChCl attached to the treated cotton cellulose through the reaction via GA could not be confirmed by FTIR analyses showing no C–N$^+$ bond in ChCl, presumably because of the overlap with peaks in the cellulose molecule.

Thermal analyses and strength retention of the GA-treated cotton fabrics

Figure 10 represents the TGA curves of the cotton fabrics at different concentrations of GA and ChCl. All of the samples demonstrated similar behaviors with two main steps of weight loss. The first one, observed at up to ca. 120 °C, was related to the loss of absorbed water. The second major weight loss, which was much more significant, began at temperatures between 290 and 320 °C. This was mainly attributed to the thermal decomposition of cellulose along with GA and ChCl (Guo et al. 2010).

All % residues at 700 °C of cotton fabrics were substantially higher than those of pristine cotton regardless of the concentrations of reactants, presumably because of ash from GA and ChCl and the introduction of crosslinking within the cellulose molecules (Fig. 11). Moreover, % residues decreased initially at 4 % ChCl and then started to increase with further addition of ChCl.

The temperatures at the maximum decomposition rate from first derivative curves were shifted from 380 °C for the pristine cotton to around 360–365 °C for the specimens treated with GA only, indicating a reduction of thermal stability due to the treatment in the presence of an acid catalyst (Fig. 12). Additionally, the presence of ChCl tended to reduce these temperatures even further to 350–360 °C. Similar results, i.e., a higher % residue in the TGA curve and shift to lower temperature for the maximum decomposition rate in the first derivative curve for the treated cotton fabrics, were observed in the previous studies (Choi and Kim 1999; Kim and Choi 2014).
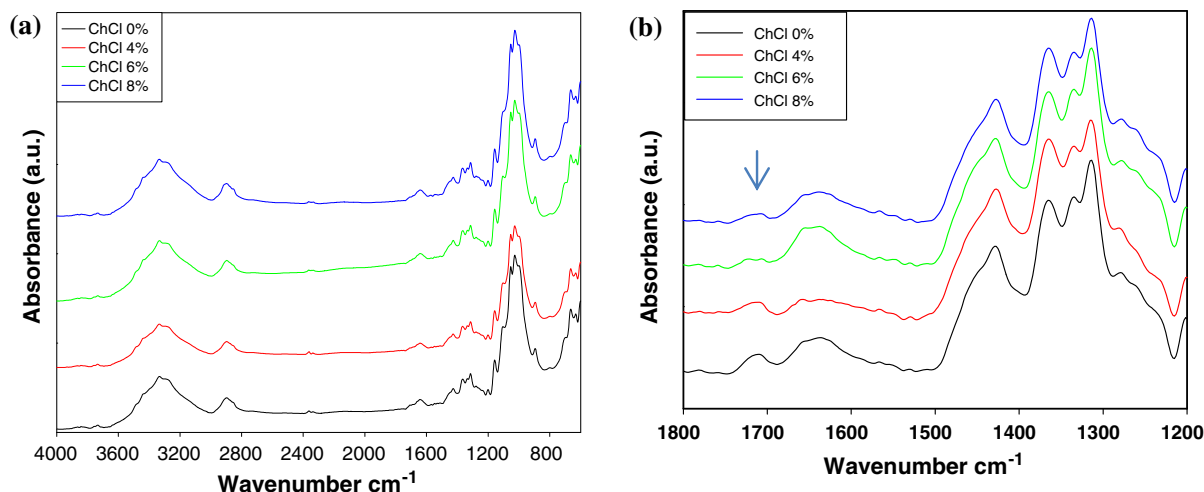
Fig. 9 FTIR spectra of cotton fabrics treated with GA (10 %) and ChCl: **a** before drying; **b** dried for 12 h at 100 °C
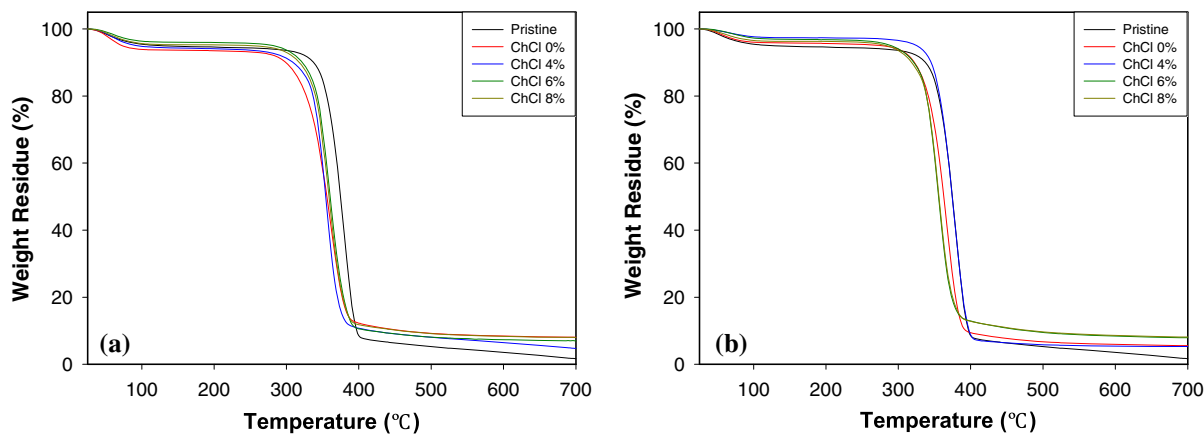

Fig. 10 TGA thermograms of cotton fabrics treated with GA in the presence of ChCl. **a** 8 % GA; **b** 10 % GA

Degradation of cotton fabrics caused by cross-linking-cationization treatment was further confirmed by the tensile strength data, as shown in Fig. 13. The treatment of cotton by using GA reduced the tensile strength of the fabric. These reductions occurred at all GA concentrations, and the range for the strength reduction was between 20 and 35 % from that of the pristine cotton. In the absence of ChCl, the strength retentions were gradually decreased with increasing GA concentrations. The presence of ChCl however tended to improve the strength retention of cotton at the same GA concentration. It should be noted that no fabric softener was used in this study; therefore, in practical applications, the addition of a softener could minimize the strength loss of the treated fabrics.

Nevertheless, the surface characteristics of the cross-linked and cationized cotton fabrics did not change much, and residues of ChCl were not observed on the treated fiber surface, regardless of the ChCl concentrations, as revealed in the SEM micrographs (Fig. 14).

Antimicrobial characteristics of the cotton treated with GA and ChCl

Antimicrobial characteristics could be an additional benefit obtained by the crosslinking and cationization of cotton with GA and ChCl. As shown in Table 2, the antimicrobial properties of the treated cotton fabrics in the presence of ChCl were enhanced considerably, and the reduction of bacteria reached almost 100 % against
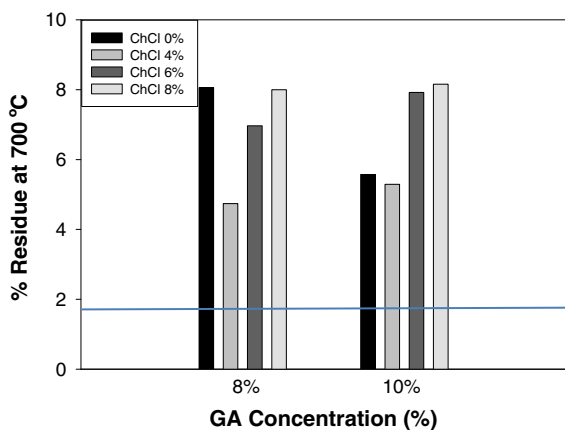
Fig. 11 Effect of ChCl concentrations on the % residue of cotton fabrics treated with various GAs (the *solid line* at 1.68 indicates % residue of pristine cotton)
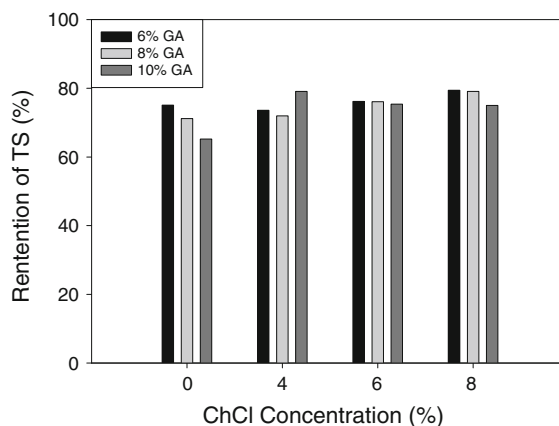

Fig. 13 Effect of ChCl concentrations on retentions of the tensile strength of cotton fabrics treated with various GAs
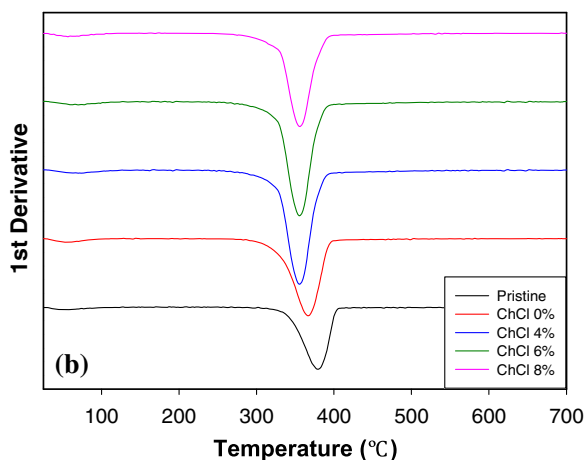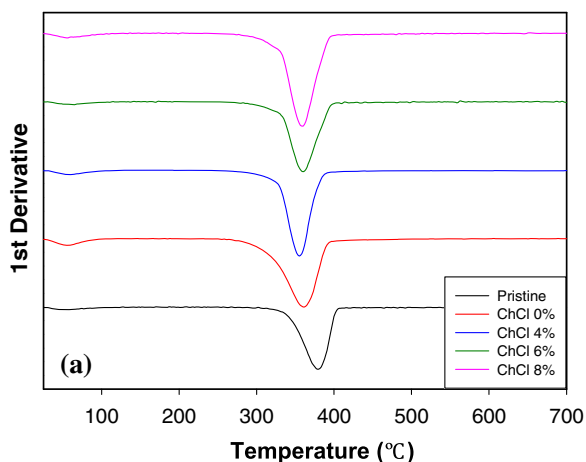

Fig. 12 First derivatives of cotton fabrics treated with GA in the presence of ChCl. **a** 8 % GA; **b** 10 % GA

two microorganisms, *S. aureus* and *E. coli*. Interestingly, the cotton fabric treated with GA in the absence of ChCl also provided high antibacterial characteristics equal to those of the fabrics treated with GA and ChCl. Observing such a phenomenon is not very surprising because GA has been used as a disinfectant and sterilizer to reduce or inhibit the growth of microorganisms in industries such as pulp, industrial cleaning, petroleum, and water treatment (Gorman et al. 1980).

Conclusions

To initiate the reaction between two unreactive molecules, cellulose and ChCl, two dialdehydes were examined under different heating systems, MW irradiation and the PDC process. The results indicated that under MW irradiation the cotton fabrics treated with GO or GA and ChCl did not show simultaneous crosslinking and cationization. GO reacted predominantly with the cellulose molecule, stimulating the crosslinking reaction, whereas GA favored the reaction with ChCl, allowing high K/S values with acid dye under MW irradiation. GA-treated cotton fabrics with ChCl under the PDC process only resulted in both high WRA and K/S values. These disparities were presumably due to substantial differences in the boiling point and molecular weight of the components. GO with a low boiling point and molecular weight was easily vaporized and penetrated within the fiber, making it

Fig. 14 Scanning electron micrographs of the pristine and cotton fabrics treated with 10 % GA with various ChCl concentrations. **a** pristine; **b** ChCl 4 %; **c** ChCl 6 %; **d** ChCl 8 %
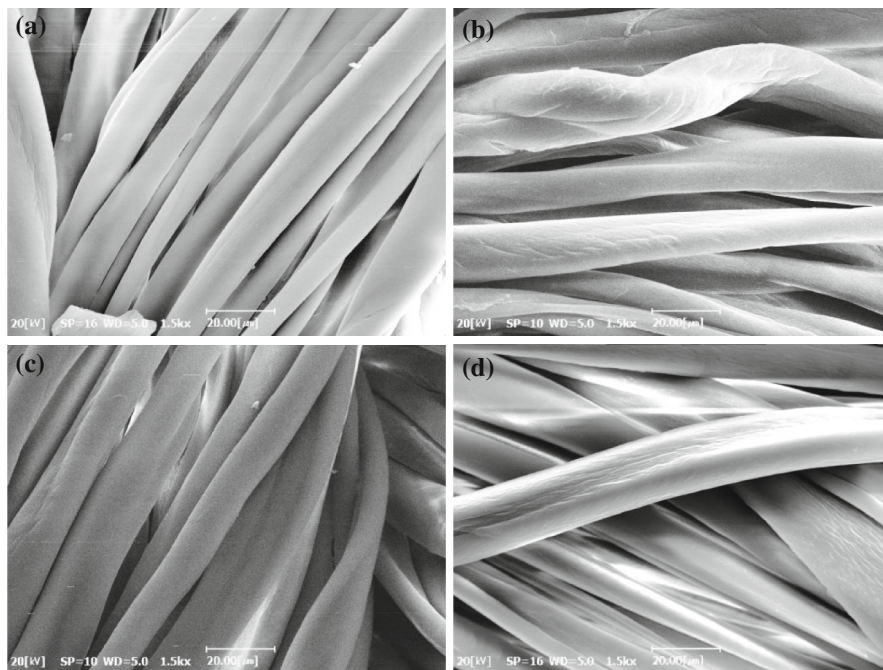

Table 2 Antimicrobial characteristics of cotton fabrics treated with 10 % GA with ChCl

Specimen	Bacteria reduction (%)	
	Staphylococcus aureus	*Escherichia coli*
Pristine cotton	32.6	37.8
ChCl 0 %	99.9	99.5
ChCl 4 %	99.9	99.7
ChCl 6 %	99.9	99.4
ChCl 8 %	99.9	99.6

difficult to react with ChCl, which would stay on the fiber surface because of the high boiling point along with the high molecular weight. The PDC process with GA was only used in the following study.

WRAs of cotton fabrics were enhanced with increasing GA concentrations at the same amount of ChCl. However, WRAs of cotton were reduced with increasing ChCl concentrations at all GA concentrations. These results validated that GA reacted with both cellulose molecules and ChCl. Evidence of ChCl fixation within cotton cellulose was confirmed by elemental analysis and the anionic dye sorption method. Both nitrogen content and acid dye sorption of the cotton fabrics were considerably increased by adding ChCl, but reached the maximum at 4 % ChCl.

The cationization of cotton also increased the water sorption because of the presence of the hydrophilic ionic compound.

With extensive drying at 100 °C/12 h, small peaks at $1,713 \text{ cm}^{-1}$ for aldehyde carbonyl stretching were observed in the GA-treated cotton fabrics. The peak heights decreased with increasing ChCl concentrations, verifying the smaller amounts of aldehyde groups due to the reduced reactivity of GA in the presence of ChCl.

All of the samples demonstrated similar behaviors in the TGA curves with two main steps of weight loss related to the water loss and thermal decomposition of cellulose, GA, and ChCl. All % residues of cotton fabrics at 700 °C were considerably higher than those of pristine cotton regardless of the concentrations of reactants. However, the temperatures at the maximum decomposition rate from the first derivative curves were shifted to lower regions because of GA and ChCl treatments. These data confirmed the general reduction of thermal stability due to the treatment with the acid catalyst. Degradation of cotton was further confirmed by the 20–35 % reduction in tensile strength in the pristine cotton. However, the surface characteristics of the crosslinked and cationized cotton fabrics did not change much.

An additional benefit of crosslinking and cationization with GA and ChCl was the substantial

improvement in the antimicrobial characteristics of the treated cotton. Almost 100 % of bacterial reductions were obtained by the fabrics treated with GA alone and with GA and ChCl. Therefore, the cotton fabrics treated with GA and ChCl could have the following characteristics after treatment: high wrinkle resistance properties, improvement of anionic dye sorption consequently decreasing the use of salts during the dyeing process, and antimicrobial characteristics.

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