

PREPARATION AND CHARACTERIZATION OF AMPHOTERIC COTTON BY N-CONTAINING REAGENT THROUGH POLYCARBOXYLIC ACID INTERCONNECTING LINKAGE

JU-YEONG MIN and HYUNG-MIN CHOI

*Department of Information Communication, Materials and Chemistry Convergence Technology,
Soongsil University, Seoul 156-743, Republic of Korea*

✉ *Corresponding author: Hyung-Min Choi, hchoi@ssu.ac.kr*

Cotton fabric was treated by N-containing reagent through polycarboxylic acid (PCA) interconnecting linkage. 1,2,3,4-Butanetetracarboxylic acid (BTCA) was selected as PCA due to its high reactivity. Triethanolamine hydrochloride (HTEA) was employed as N-containing reagent to treat cotton by using the pad-dry-cure method. Thus-treated fabric exhibited improved wrinkle resistance, dye affinity to conventional anionic dye, antimicrobial and amphoteric properties. The investigation of the wrinkle recovery angle, thermogravimetric analysis and Fourier transform infrared spectroscopy confirmed the fixation of HTEA through BTCA interconnecting linkage onto cotton. Elemental analysis and K/S value evaluation after dyeing with cationic or anionic dyes also affirmed HTEA fixation. X-ray diffraction analyses indicated that the reaction mainly occurred in the amorphous regions with little surface deposition, which was also substantiated by Scanning Electron Microscopy. The treated cotton exhibited 99.9% bacterial reduction and its amphoteric property was demonstrated by dyeing at various pHs.

Keywords: amphoteric cotton, 1,2,3,4-butanetetracarboxylic acid, triethanolamine hydrochloride, interconnecting linkage

INTRODUCTION

Cotton is one of the most important fibers due to its comfort, highly hydrophilic, minimal allergic to humans, less static and eco-friendly characteristics.^{1,2} Its market share in the clothing industry is still dominant, even with the development of various synthetic materials. On the other hand, low elastic recovery, low antibacterial property and high wrinkling are considered as drawbacks in cotton.^{3,4} Furthermore, its low dye affinity toward conventional anionic dyes requires the addition of large amounts of salts during the dyeing process. The presence of salt reduced surface negative charges, resulting in enhanced dye fixation and a reduction in the amounts of the dye needed to achieve the same color effect.⁵ However, the salt added, along with the unfixed dye, must be removed before effluent disposal into streams or lakes to minimize environmental problems.

Polycarboxylic acids (PCA) have been examined to replace conventional formaldehyde-containing crosslinking agents for cotton, such as dimethylol dihydroxy ethylene urea (DMDHEU),⁶ in increasing the resilience of cotton fiber. 1,2,3,4-

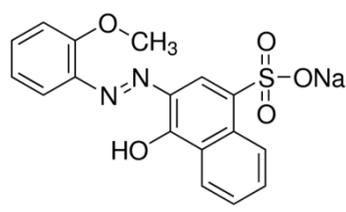
butanetetracarboxylic acid (BTCA) and citric acid (CA) have been mainly used among the various PCAs examined, but BTCA is especially regarded as the most efficient crosslinking agent.² Nevertheless, the presence of unreacted carboxylate groups considerably reduces the dyeability of PCA-treated cotton fabrics toward conventional anionic dyes. Cationic compounds have been added to reduce this problem.⁷ The addition of cationic compounds can block carboxylate anions, so repulsion is considerably reduced. Therefore, the previous studies revealed that the dyeability of cationized cotton is much greater than that of the pristine one for both direct and reactive dyes.⁵⁻⁸ Another advantage of cationized cotton could lie in its antibacterial characteristics.^{9,10} The cell walls of bacteria contain negative charges and thus cationized fiber can sorb bacteria and destroy them.¹⁰

Furthermore, the addition of a cationic compound onto PCA-treated cotton could produce amphoteric substrates. Aside from clothing applications, by reacting with both acid and base,

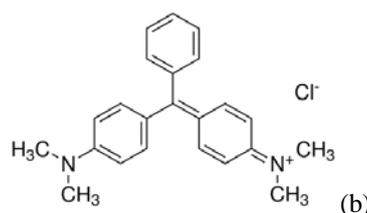
these substrates could be effectively employed in purifying industrial waste water or effluents. It has been proved that the efficiency of amphoteric substrates in removing contaminants is much better than that of cationized or hydrolyzed substrates.^{11,12} The removal of the used dye from the effluent is a critical process in considering the stability and toxicity of dyes containing aromatic groups.^{13,14} These amphoteric substrates could actively sorb both anionic and cationic dyes.¹¹ Furthermore, amphoteric cotton could generate different electrical properties at variable pHs and consequently, their applicability could be much broader than dyeing effluent treatment.

A literature survey performed in this study indicated that N-containing reagent has been added to crosslinking agent to improve the dyeability of treated cotton, mainly during DMDHEU treatment.^{15,16} Triethanolamine (TEA) has been used in PCAs treatment in the presence of the phosphorus compound to improve flame resistance characteristics.¹⁷ Other than the study of Blanchard and Reinhardt,¹⁸ who treated cotton by PCA and N-containing reagent, and examined it only in terms of dye affinity improvement, a little study has been carried out in order to investigate the additional characteristics of thus-treated cotton, such as related amphoteric and antimicrobial aspects.

Therefore, the current study investigated the effect of free amine (TEA) and amine hydrochloride (triethanolamine•hydrochloride (HTEA)) on cotton through PCA interconnecting linkage in terms of crosslinking effectiveness and dyeability. Among various PCAs, BTCA was selected as a crosslinker due to its high reactivity. Various instrumental methods, such as Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), thermogravimetric analysis (TGA) and X-ray diffraction (XRD), were used to investigate the chemical, topological, thermal and crystalline characteristics of the treated cotton fabrics, respectively.



(a)



(b)

Scheme 1: Chemical structures of (a) C.I. Acid Red 4 and (b) C.I. Basic Green 4

EXPERIMENTAL

Materials

Scoured and bleached cotton fabric (KS K0905, warp 16.5 tex, weft 14 tex, warp and weft density 35 and 31 threads/cm, respectively) was purchased from KATRI. BTCA was received from Sigma-Adrich, Inc. (Korea) and TEA was obtained from Daejung Chemicals (Korea). These chemicals were all reagent grade and used without any purification. Sodium hypophosphite (SHP) and Triton X-100 (polyoxyethylene octylphenylether) from Ducksan Chemicals (Korea) were used as catalyst and wetting agent, respectively. Other chemicals, such as acetic acid, 37% hydrochloric acid (HCl) and sodium hydroxide (NaOH), were purchased from commercial sources. C.I. Acid Red 4 and C.I. Basic Green 4 (N,N,N',N',-tetramethyl-4,4'-diaminotriphenylcarbenium chloride, malachite green chloride) were purchased from Aldrich, Inc. and J.V. Company (Korea), respectively, and their chemical structures are shown in Scheme 1. HTEA was prepared by adding HCl to TEA in ice bath according to a previous study.¹⁶ The slurry was washed with ethanol, filtered and dried at 50 °C for 24 h in a vacuum oven.

Pad-dry-curing

Cotton fabric was impregnated in the treating solution containing 7% on the weight of bath (owb) of BTCA cationic agent at different mole ratios with BTCA (BTCA:cationic agent at 1:0, 0.3, 0.5, 1, 2 and 3), SHP at 4% on the weight of BTCA, and 0.1% owb of wetting agent. Approximately 5 g of cotton fabric (warp 20 cm × weft 15 cm) was immersed in the treating bath at 20:1 liquor-to-fabric ratio (LR) for 5 min and was padded by a laboratory padder (CH-8155, Werner Mathis AG, Switzerland) for two dips and nips. The fabric was then dried at 85 °C for 5 min in a drying oven (VOS-201SD, Eyela, Inc., Japan) and cured at 180 °C for 10 min in a curing oven (VOS-301SD, Eyela, Inc., Japan). The treated specimens were denoted as follows: B stands for BTCA, T is for TEA and HT is for HTEA, for example, BT0.5 is the specimen treated by BTCA with TEA at 1:0.5 mole ratio, and BHT2 is the specimen treated by BTCA with HTEA at 1:2 mole ratio.

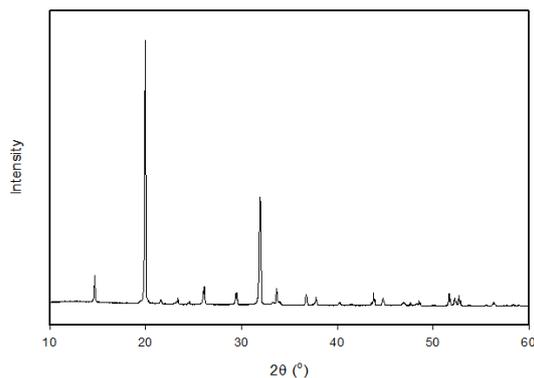


Figure 1: X-ray diffraction pattern for HTEA crystal

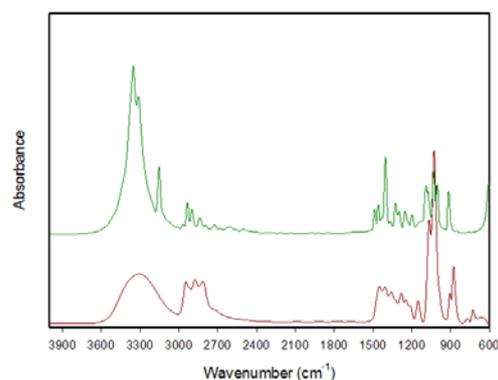


Figure 2: FT-IR absorbance spectra of reagents; (bottom) TEA and (top) HTEA

Instrumental analyses of treated cotton fabric

The specimen was analyzed by FTIR spectroscopy (Bruker, Vertex 70, Germany) with attenuated total reflectance attachment in the spectral region of 4000-600 cm^{-1} with 64 scans and 2 cm^{-1} resolution. SEM could be effectively used to study the surface morphology of the modified cotton. The specimen was coated twice with Au at 10 mA for 200 seconds by an ion coater and then analyzed at 2000x and 10,000x magnification by SEM (COXEM, CX-100S, Korea). The thermal characteristics of the modified cotton were assessed by TGA (Mettler, USA) in the 25~700 $^{\circ}\text{C}$ temperature range at 10 $^{\circ}\text{C}/\text{min}$ rate under nitrogen atmosphere. The presence of N-containing reagent was corroborated by using an elemental analyzer (OGP, USA) with a TCD detector for 200 mg of specimen.

The crystalline structure of cotton cellulose was evaluated by XRD (D2 PHASER, Bruker, Germany), employing a $\text{Co-K}\alpha$ ($\lambda = 0.1524$ nm) source, operating range at 30 kV and 10 mA. The sample was scanned at a speed of 1 $^{\circ}/\text{min}$ with 0.02 increment in the 2θ range from 55 $^{\circ}$ to 10 $^{\circ}$. The crystallinity index (CI) was calculated by the height of the crystalline peak at I002 and the height of the amorphous shoulder (I_{am}) by using the following equation:^{21,22,24}

$$\text{CI} = (I_{002} - I_{\text{am}}) / I_{002} \times 100 \quad (1)$$

I_{am} was a shoulder between two crystalline phases of (002) and (101).²² In addition, the crystallite size, L , of the reflection planes was calculated from the Scherrer equation as follows:

$$\text{Crystallite size, } L = (K \times \lambda) / (\beta \times \cos\theta) \quad (2)$$

where K is the Scherrer constant with the value of 0.94, λ is the X-ray wavelength (0.1542 nm), β is the half-height width of the diffraction band and θ is the Bragg angle corresponding to the planes. Furthermore, the surface chains occupied a layer approximately 0.57 nm thick, so the proportion of the crystallite interior chains was calculated as follows:²¹

$$\text{Crystallite interior chains, } X = (L - 2h)^2 / L^2 \quad (3)$$

where L is the crystallite size for the reflection plane, and h is the layer thickness of the surface chain (0.57 nm).

Performance evaluation and dyeing

The properties of the treated cotton fabric were determined by standard test methods. These methods included: JIS L1059-1, 1998, AATCC Test Method 66 for assessing the wrinkle recovery angles, for both warp and weft directions, ASTM 1682-64 (H10K-S UTM, Houns Field Co., USA) for evaluating the tensile strength by the raveled strip test, and ASTM D1925 for the whiteness index (D65 illuminant and observer 2 $^{\circ}$ angle).^{23,24}

Since the modified cotton fabric was expected to have amphoteric charges, its dyeing was carried out with both anionic (C.I. Acid Red 4) and cationic (C.I. Basic Green 4) dyes. Dyeing was performed at 0.3% on the weight of fiber at 20:1 LR in an Infrared Dyeing Machine (DL-6000, Daelim Starlet, Korea) at 40 rpm/min rotation speed. Acid dyeing (pH 3) was started at 40 $^{\circ}\text{C}$, the temperature was raised to 98 $^{\circ}\text{C}$ for 25 min with a rate of 23 $^{\circ}\text{C}/\text{min}$, was maintained for 35 min and then decreased to 60 $^{\circ}\text{C}$ for 15 min.⁶ Contrarily, basic dyeing (pH 8) was started at 25 $^{\circ}\text{C}$, raised to 98 $^{\circ}\text{C}$ during 73 min, maintained for 35 min, and then decreased to 60 $^{\circ}\text{C}$ in 15 min.^{11,24,25} Furthermore, the pH of the dyeing bath was controlled to pH 2, 4, 6, 8 and 10 by using HCl and NaOH to investigate the effect of pH during both dyeing processes. Surface reflectance of the treated and dyed cotton fabric was measured by Color Eye CM-512M3 (X-rite, USA). K/S values were calculated by the Kubelka-Munk equation as follows:

$$\text{K/S} = (1-R)^2 / 2R \quad (4)$$

where R = reflectance of the dyed materials at λ_{max} .

Antimicrobial test

The antimicrobial characteristics of the treated cotton (BHT1 and BHT 2) were evaluated by KS K 0693 with two microorganisms, namely, *Staphylococcus aureus* (ATCC 6538) and *Klebsiella pneumoniae* (ATCC 4352). The reduction of bacterial colonies was calculated as follows:

$$\text{Antimicrobial activity (S)} = \log (M_b / M_a) - \log (M_c / M_a) = \log (M_b / M_c) \quad (5)$$

$$\text{Reduction of bacteria (\%)} = [(M_b - M_c) / M_b] \times 100 \quad (6)$$

where M_a is the average number of bacteria in a reference sample immediately after inoculating 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 fail by natural reduction due to the external environment.⁶

RESULTS AND DISCUSSION

Comparison of cotton fabrics treated by TEA and HTEA

A comparison of TEA and HTEA with regard to their fixation onto cotton fabrics was made to select the optimal N-containing reagent. Before the treatment, the HTEA crystal prepared was analyzed by XRD¹⁹ and FTIR,²⁰ as shown in Figures 1 and 2. The XRD spectrum showed a typical HTEA crystal, as expressed in a previous study.¹⁹ Furthermore, Figure 2 reveals that, unlike TEA, HETA exhibited sharp hydroxyl absorptions at around 3300 cm^{-1} , suggesting a significant decrease in the amounts of hydrogen bonds in HTEA after quaternization with HCl. This was probably due to the presence of chloride ions, which could hinder the formation of hydrogen bonds between two hydroxyl groups. Sharp absorption bands at around 3300 cm^{-1} are commonly observed in the FTIR spectra of amine salts.²⁷

The K/S values of acid-dyed cotton treated by BTCA and TEA or HTEA are shown in Figure 3. The specimens with two different combinations, such as BT (B stands for BTCA and T stands for TEA), BHT (B stands for BTCA and HT stands for HTEA), were employed. B control was the

specimen treated only by BTCA in the absence of N-containing reagent. The numbers following the letter abbreviations represent the mole ratio between BTCA and TEA or HTEA, *i.e.* BHT2 indicates the specimen treated by BTCA and HTEA in a two-to-one mole ratio.

The results clearly indicate that the HTEA-treated cotton produced much greater K/S values than that treated by TEA. This substantiated that cationic nitrogen in HTEA could attenuate the repulsion between carboxylate and dye anions. HTEA was selected as N-containing reagent for the treatment with BTCA and it was hence used for further study.

Characterization of PCA-HTEA treated cotton fabrics

Scheme 2 illustrates a typical reaction mechanism of BTCA and HTEA with cotton. This scheme is based on the first reaction of BTCA and HTEA, followed by the reaction of BTCA and cellulose, but the reverse order, and/or the simultaneous reaction of BTCA, HTEA and cellulose could also be possible.

SHP, a latent catalyst, promoted two competing reactions of BTCA with the hydroxyl groups of cellulose and/or HTEA. Therefore, some disparity was expected in the rate of these competing reactions depending on the kind of PCAs. This information would help the selection of the proper PCA for specific end-use applications, *i.e.* improvement in resilience or in dye affinity toward anionic dyes. However, since BTCA was known to show very high reactivity, compared with other PCAs, such as citric acid, it was selected as a crosslinking agent in this study.^{23,28}

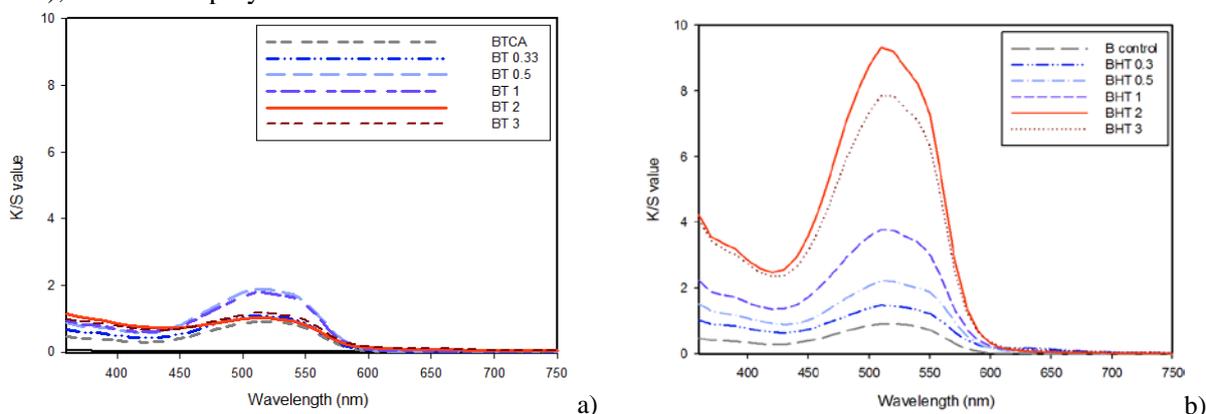
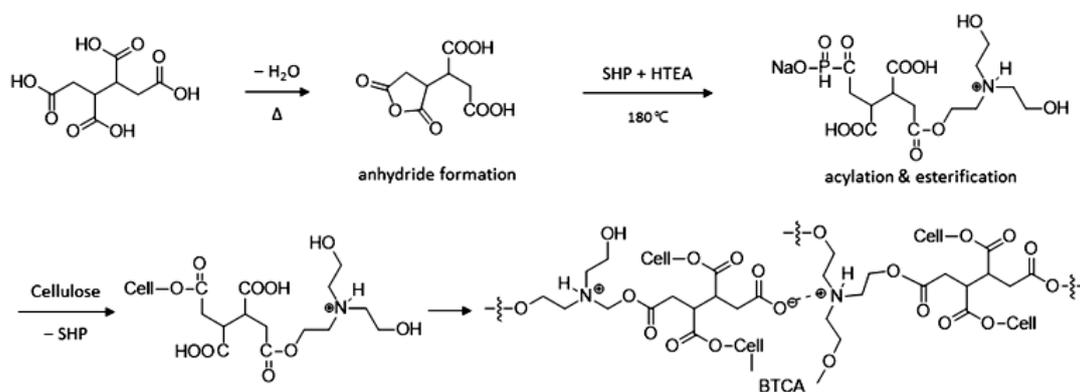


Figure 3: K/S values of cotton fabrics dyed with C.I. Acid Red 4 and treated with BTCA and N-containing agents; (a) BT and (b) BHT



Scheme 2: Potential mechanism of BHT samples treated by BTCA and HTEA

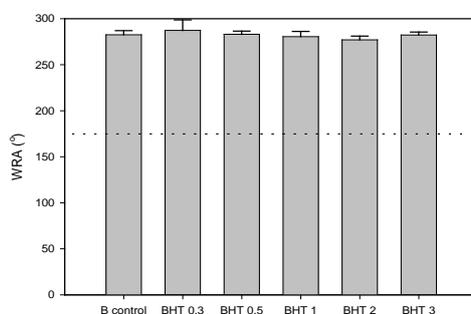
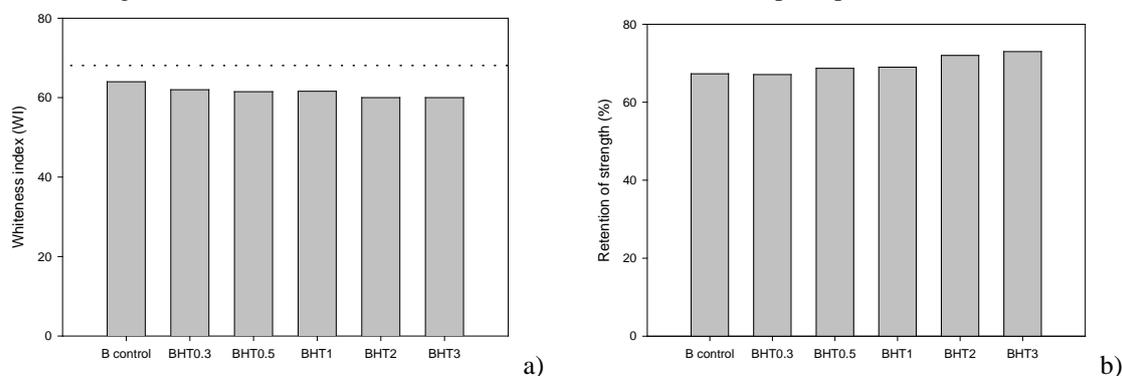
Figure 4: Effect of HTEA concentration on WRAs of BHT samples (pristine: $174 \pm 4.7^\circ$)

Figure 5: Effect of HTEA concentration on WI (a) and retention of strength (b) of BHT samples (WI of pristine: 68.1)

Assessing the wrinkle recovery angle (WRA) is an indirect way to measure the level of crosslinks within treated cotton.³² This is because an improvement of WRA occurred by the replacement of secondary hydrogen attractions by primary covalent crosslinks obtained by the reaction between BTCA and cellulose chains.²⁸ As shown in Figure 4, the WRA of the BTCA-treated cotton was considerably greater than that of the pristine one. In

addition, WRAs tended to decrease with an increase in HTEA concentration. This decrease was expected since the reactions of BTCA toward cellulose and HTEA were two competing reactions, as described above.

Whiteness indices (WI) of the treated BHT cotton fabrics were also evaluated. As shown in Figure 5(a), the results demonstrated that the BTCA treatment slightly decreased the WI of the treated

fabric, and the decrease was greater with HTEA probably because of the presence of nitrogen. It is known that the crosslinking treatment at high temperature generally reduces the WI of treated fabrics, regardless of the crosslinking type.^{16,23} Since the curing conditions in this study included 180 °C for 10 min, a certain reduction of WI was expected. Such a reduction, however, could be minimized by the presence of additives, such as polyethylene glycol.²³

Moreover, the retention of tensile strength also decreased upon BTCA and/or HTEA treatment, as shown in Figure 5(b). These reductions were typical behaviors of crosslinked cotton fabrics due to the introduction of rigid, durable covalent bonds between two cellulose chains.²³ Unlike WI, the presence of HTEA was beneficial in maintaining the strength of the treated cotton fabrics. This was because HTEA could reduce a direct crosslinking reaction between BTCA and cellulose.

Figure 6 presents the TGA curves of cotton fabrics treated by BTCA and HTEA. The residues

at 700 °C for all the BHT specimens were about 10% greater than that for the pristine one. It was reported that crosslinking of cotton generally increased the % residue at high temperature.⁶ In addition, the % residue tended to increase with an increase in HTEA concentration. The water loss at low temperature noted on the TGA curves was more prominent for the pristine than for the treated cotton fabrics, thereby suggesting that the ionic groups in the treated cotton could hold water molecules more tightly.

The 1st derivative curves revealed that the peak decomposition temperatures (inflection point) of the cotton treated by BTCA and HETA decreased. It is known that the peak temperatures for treated cotton are generally lower than for the pristine one because of the acidic and thermal degradation occurring during the treatment.⁶ However, this temperature tended to increase with the increase in HTEA concentration, suggesting enhanced thermal stability in the presence of N-containing reagent, HTEA.¹⁷

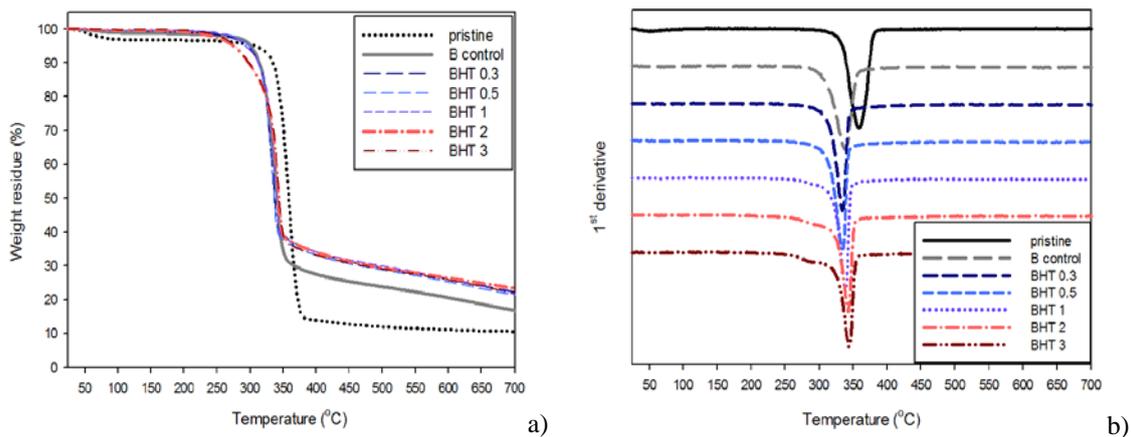


Figure 6: TGA data for BHT samples; (a) TGA curves and (b) 1st derivative curves

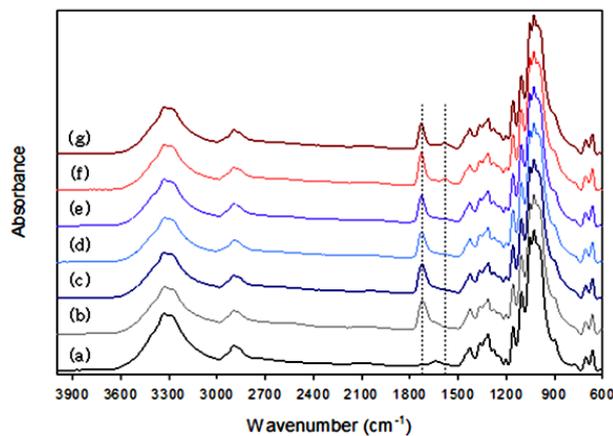


Figure 7: FT-IR spectra of BHT samples; (a) pristine, (b) B control, (c) BHT 0.3, (d) BHT 0.5, (e) BHT 1, (f) BHT 2, and (g) BHT 3

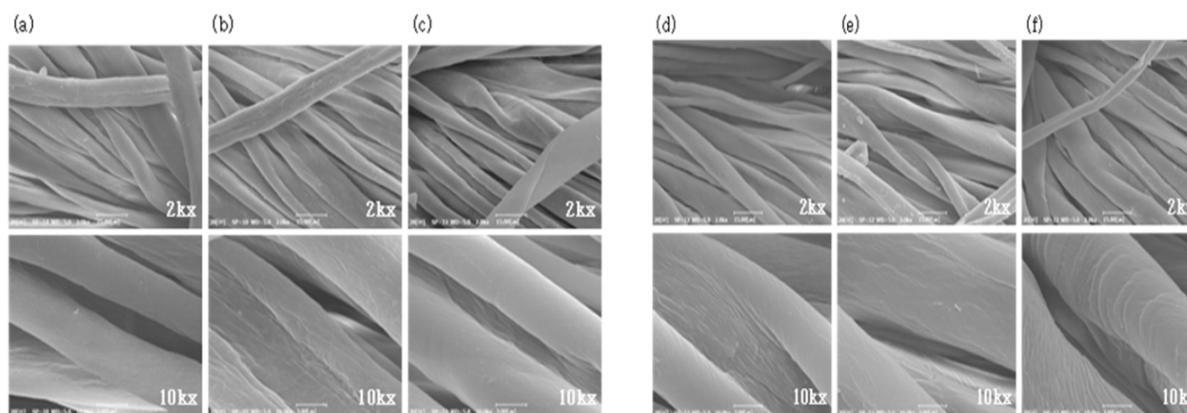


Figure 8: SEM micrographs of BHT samples; (a) B control, (b) BHT 0.3, (c) BHT 0.5, (d) BHT 1, (e) BHT 2, and (f) BHT 3

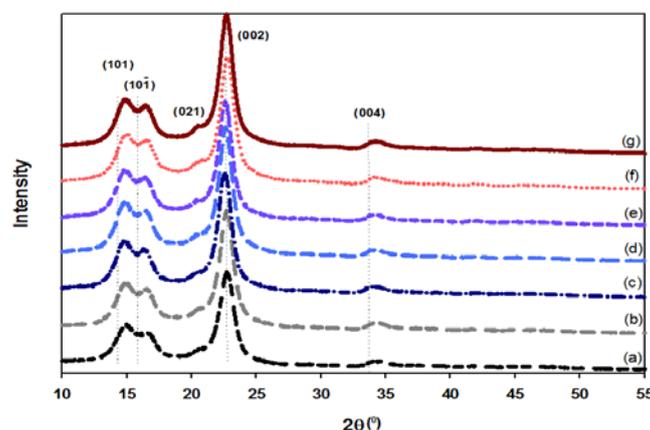


Figure 9: XRD spectra of BHT samples; (a) pristine, (b) B control, (c) BHT 0.3, (d) BHT 0.5, (e) BHT 1, (f) BHT 2, and (g) BHT 3

Evidence of HTEA fixation in cotton through the BTCA interconnecting linkage was already shown in Figure 3 by using indirect K/S value evaluation. In addition, ionic bonding formation could be possible between $-\text{COO}^-$ in BTCA and $-\text{N}^+$ in HTEA. Figure 7 illustrates the FTIR spectra of HTEA-treated cotton in the presence of BTCA. Ester carboxyl peaks at 1730 cm^{-1} for the BTCA-treated cotton substantiated the reaction between BTCA and HTEA and/or cellulose.^{17,26-28} The C-N stretching peak at $1000\sim 890\text{ cm}^{-1}$ also corroborated the attachment of HTEA to cellulose through the BTCA interconnecting linkage. Furthermore, the peak at 1580 cm^{-1} for carboxylate suggests the presence of a potential ionic linkage between $-\text{COO}^-$ in BTCA and $-\text{N}^+$ in HTEA.²⁸ The presence of nitrogen in specimen BHT2 ($0.84\pm 0.013\%$) proven by elemental analysis also confirmed the fixation of HTEA onto cotton through the BTCA interconnecting linkage.

Morphological and crystalline characteristics

The effect of BTCA and HTEA treatment on the surface morphology of cotton was investigated by SEM, as shown in Figure 8. Even with high concentration of HTEA, no significant change was observed in the morphology of cotton, indicating little surface deposition of BTCA and HTEA. This reaction mainly occurred in the amorphous area of the HETA-BTCA-treated cotton fabrics, which was substantiated by XRD analyses, as shown in Figure 9 for BHT. This spectrum confirmed that the crystalline structure of the treated cotton did not change and hence, the cellulose I structure was preserved.^{21,22} Moreover, the calculated values of CI, L and X were all in a similar range: of $84\sim 85$, 6 ± 0.5 , $0.65\sim 0.69$, respectively, regardless of HTEA concentration. These results clearly verified that the treatment mainly occurred in the amorphous region of cellulose, as stated above.

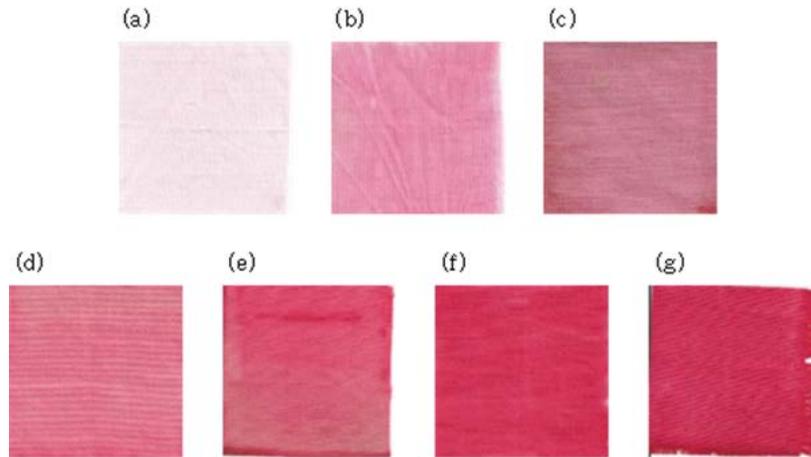


Figure 10: Color of BHT samples dyed with C.I. Acid Red 4; (a) pristine, (b) B control, (c) BHT 0.3, (d) BHT 0.5, (e) BHT 1, (f) BHT 2, and (g) BHT 3

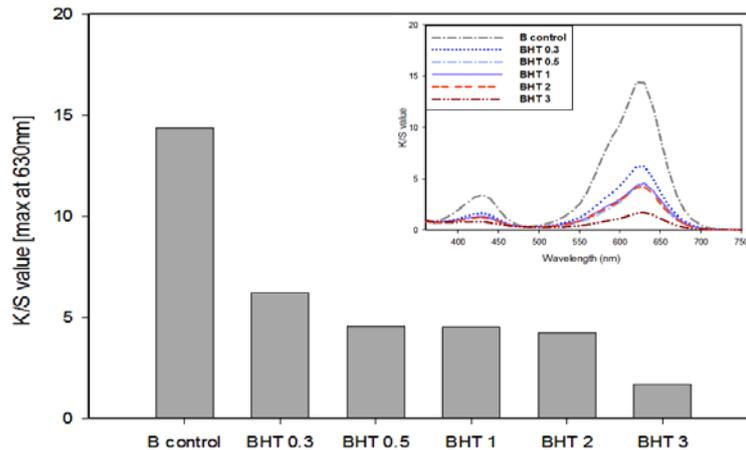


Figure 11: K/S values of BHT fabrics dyed with C.I. Basic Green 4

Affinity toward anionic dye

Acid dye usually contains at least one sulfonate group and thus, it could be conveniently used to evaluate the cationic characteristics of the HTEA-treated cotton.⁷⁻⁹ The K/S values of the cotton fabrics treated with HTEA-BTCA and subsequently dyed with acid dye were previously illustrated in Figure 3 and dyed specimens were shown in Figure 10 for visual evaluation. Both K/S values and visual evaluations revealed that acid dye sorption continuously increased with the increase in HTEA concentration. Unlike visual specimens, however, the increase in the K/S value was up to the one-to-two mole of BTCA-HTEA specimen, and then started to decrease. This suggested that a too high level of HTEA could diminish the reaction efficiency of BTCA with cellulose and HTEA,

probably by increasing the bath pH. The dyed specimen BHT3 tended to be slightly darker than BHT2, and this difference in visual evaluation and the K/S value of the dyed specimens were probably due to the yellowing effect that the dyed specimens presented at high HTEA concentrations.¹ In general, the K/S values of BHT specimens dyed by acid dyes were generally lower than expected, probably because of the ionic repulsion between the unreacted carboxylate groups in BTCA and the sulfonate groups in acid dye.

Affinity toward cationic dye

Since the cotton treated by HTEA through BTCA interconnecting linkage exhibited amphoteric property, cationic dye was also used to examine its anionic characteristics. The results

demonstrated that control fabric B, *i.e.* BTCA-treated cotton in the absence of HTEA, produced a higher K/S value than those treated with HTEA, as shown in Figure 11. The fabric treated without HTEA obviously contained greater negative charges than those with HTEA due to the unesterified, free carboxyl groups within BTCA. Since the reaction between BTCA and cellulose generally requires anhydride formation of carboxylic groups in BTCA as precursor, at least two carboxylic groups in each BTCA molecule would be in a free state without crosslinking.²⁸ Therefore, these free carboxylic groups could act as sites for ionic attraction between the BTCA-treated cotton and cationic dye.

Furthermore, with the increase in HTEA concentration, the K/S values with cationic dye continuously decreased. Two reasons could be considered here: firstly, the increase in quaternary nitrogen ion ($-N^+$) increased the repulsion of cationic dye, and secondly, the enhanced possibility of ionic bonding formation between the unreacted carboxylate ion within BTCA and N^+ , consequently, reducing the affinity toward cationic dye.

Characterization of amphoteric property

The amphoteric characteristics of the BTCA-treated cotton were also evaluated by dyeing with cationic dye at various pH values, as shown in Figure 12. The HTEA-treated cotton in the presence of BTCA showed the lowest affinity toward cationic dye at pH 2, regardless of the mole ratio between BTCA and HTEA. Generally, the pKa values for carboxylic acid are around pH 3~5 and most of the carboxylic acid groups could be

present in a non-ionized state ($-COOH$) at pH 2 and thus, the charge for the HTEA-treated cotton could be mainly cationic. This consequently increased the repulsion against cationic dye. With the increase in pH to 4 and 6, the K/S values of the cationic dyed specimens improved. At these pH values, the ratio of ionized and non-ionized carboxylic acid would be close to one. Since a large portion of the ionized carboxyl groups could form ionic bonding with quaternary nitrogen, the increase in the K/S value was less than expected. The specimen with the greater amount of HTEA, *i.e.* BHT2, resulted in a lower K/S value than that of BHT1. HTEA could not directly bind to cotton cellulose without the BTCA interconnecting linkage. Therefore, too high amounts of HTEA would provide greater amounts of positive charge to the treated cotton, but also reduced the reactivity of BTCA toward cotton, because of the presence of two competing reactions. The highest K/S values were obtained at pH 8, regardless of HTEA concentration. This was due to the reduced number of cationic quaternary nitrogen and the increased number of ionized carboxylic groups at this pH, allowing ready ionic bonding against cationic dye. However, further increase in pH to 10 considerably decreased the K/S value of cationic dye, suggesting possible hydrolysis of esterified interconnecting linkage among cellulose, BTCA and HTEA. Therefore, the results clearly indicated that HTEA treatment of cotton through BTCA interconnecting linkage provided amphoteric cotton, and its utilization in the dye removal process must be carried out with careful pH control.^{30,33}

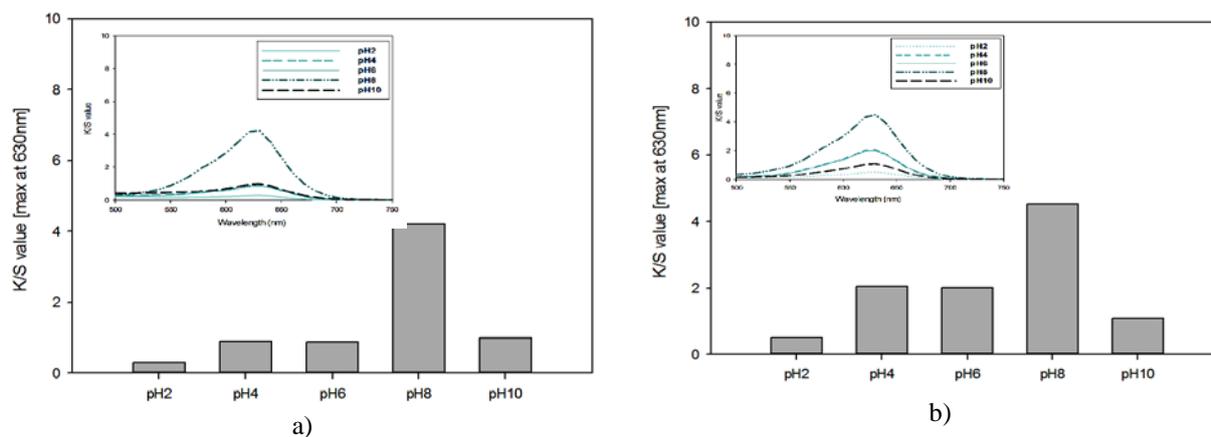


Figure 12: K/S values of BHT samples dyed with C.I. Basic Green 4 at different pH; (a) BHT1 and (b) BHT2

Antimicrobial characteristics

The antimicrobial characteristics of specimen BHT2 revealed that its bacterial reduction was of 99.9% against *S. aureus* and *K. pneumoniae*, whereas for the pristine one, it was of 33% and 38%, respectively. The results clearly implied that the addition of HTEA to cellulose through BTCA

could significantly increase the antibacterial property of the treated fabric. This was due to the synergistic effect of the quaternary ion of HTEA and the presence of BTCA. A previous study noted that PCA-treated cotton also inhibited bacterial growth.⁹

Table 1
Antimicrobial characteristics of cotton fabrics

Specimen	Bacterial reduction (%)	
	<i>S. aureus</i>	<i>K. pneumoniae</i>
Pristine	33.0	38.0
BHT1	99.9	99.9
BHT2	99.9	99.9

CONCLUSION

Amphoteric cotton fabric was produced using N-containing reagent through BTCA interconnecting linkages. BTCA was able to connect cellulose and N-containing reagent *via* esterification. The results clearly indicated that the HTEA-treated cotton produced much higher K/S values than those treated by TEA. Thus, HTEA was mainly used as N-containing reagent for further study.

The presence of crosslinking was confirmed by WRA and TGA analysis, and the fixation of HTEA in cotton was substantiated by elemental analysis and anionic dye affinity. The higher the amount of HTEA, the lower the WRA was. FTIR analysis indicated esterified cotton, along with the presence of HTEA. While the resilience of the BTCA-HTEA treated cotton fabrics measured by WRAs was increased, their WIs and retention of strength decreased. The presence HTEA tended to facilitate the reduction of WIs, but the opposite was observed for the retention of strength. SEM and X-ray diffraction substantiated that the reaction mainly occurred in the amorphous region of cotton with little surface deposition.

The BTCA-HTEA treated cotton produced amphoteric cotton that can be used to treat effluents containing both negative and positive dyes. In these systems, however, the pH must be optimized for each dye, for example, pH 8 for cationic dye. In addition, the modified cotton showed antimicrobial properties with 99.9% bacterial reduction.

ACKNOWLEDGMENT: This work was supported by the BK21 Plus Program through NRF grant funded by the Ministry of Education (No.

31Z20150313339) in the Republic of Korea.

REFERENCES

- R. Shamey and T. Hussein, *Text. Prog.*, **37**, 15 (2005).
- V. A. Dehabadi, H. J. Buschmann and J. S. Gutmann, *Text. Res. J.*, **83**, 1974 (2013).
- S. H. Lim and S. M. Hudson, *Carbohydr. Res.*, **339**, 313 (2004).
- M. Montazar and M. G. Afjeh, *J. Appl. Polym. Sci.*, **103**, 178 (2007).
- A. K. R. Choudhury, *AATCC J. Res.*, **1**, 11 (2014).
- J. H. Park, H. M. Choi and K. W. Oh, *Cellulose*, **21**, 3107 (2014).
- M. F. Shahin, *Int. J. Eng. Res. Appl.*, **5**, 62 (2015).
- P. J. Hauser and A. H. Tabba, *Color. Technol.*, **117**, 282 (2001).
- S. K. A. Mohammad, E. Y. Mohammad and R. N. Mohammad, *Cellulose*, **16**, 1147 (2009).
- K. F. El-Tahlawy, M. A. El-Bendary, A. G. El-Hendawy and S. M. Hudson, *Carbohydr. Polym.*, **60**, 421 (2005).
- S. Xu, J. Wang, R. Wu, F. Wang and H. Li, *Chem. Eng. J.*, **117**, 161 (2006).
- H. Song, D. Wu, R. Q. Zhang, L. Y. Qiao, S. H. Zhang *et al.*, *Carbohydr. Polym.*, **78**, 253 (2009).
- B. R. Babu, A. K. Parande, S. Raghu and T. P. Kumar, *J. Cotton. Sci.*, **11**, 141 (2007).
- A. Pala and E. Tokat, *Water Res.*, **36**, 2920 (2002).
- I. Cerkez, H. B. Kocer, S. D. Worley, R. M. Broughton and T. S. Huang, *J. Appl. Polym. Sci.*, **124**, 4230 (2012).
- E. J. Blanchard and R. M. Reinhardt, *Ind. Eng. Chem. Res.*, **28**, 490 (1989).
- H. Yang and C. Q. Yang, *J. Fire Sci.*, **25**, 425 (2007).
- E. J. Blanchard, R. M. Reinhardt and B. A. K. Andrews, *Textile Chem. Color.*, **23**, 25 (1991).
- Y. Zhang and Z. Li, *J. Chem. Eng. Data*, **55**, 4434 (2010).
- D. G. Brannon, R. H. Morrison, J. L. Hall, G. L. Humphrey and D. N. Zimmerman, *J. Inorg. Nucl. Chem.*,

33, 981 (1971).

²¹ Q. Chen, Q. Wang, N. Mitsumura and H. Niida, *Mater. Sci. Appl.*, **4**, 839 (2013).

²² S. K. Park, J. O. Baker, M. E. Himmel, P. A. Parilla and D. K. Johnson, *Biotechnol. Biofuels*, **3**, 1 (2010).

²³ K. W. Oh and H. Choi, *Cellulose Chem. Technol.*, **36**, 69 (2002).

²⁴ S. Park and H. Choi, *Cellulose Chem. Technol.*, **52**, 311 (2018).

²⁵ R. Gong, Y. Jin, F. Chen, J. Chen and Z. Liu, *J. Hazard. Mater.*, **137**, 865 (2006).

²⁶ K. Porkodi and K. V. Kumar, *J. Hazard. Mater.*, **143**, 311 (2007).

²⁷ R. A. Heacock and L. Marion, *Can. J. Chem.*, **34**, 1782 (1956).

²⁸ W. Xu and Y. Li, *Text. Res. J.*, **70**, 588 (2000).

²⁹ C. Chung, M. H. Lee and E. K. Choe, *Carbohydr. Polym.*, **58**, 417 (2004).

³⁰ F. X. Perrin, V. Nguyen and J. L. Vernet, *J. Sol-Gel. Sci. Technol.*, **28**, 205 (2003).

³¹ H. Kono, *Gels*, **1**, 94 (2015).

³² V. Popescu, E. Vasluianu and G. Popescu, *Carbohydr. Polym.*, **111**, 870 (2014).

³³ S. F. Azha, L. Sellaoui, M. Sh. Shamsudin, S. Ismail, A. Bonilla-Petriciolet *et al.*, *Chem. Eng. J.*, **351**, 221 (2018).