

# Improvement of Anti-wrinkle Properties of Cotton Fabrics Treated with Additives of Neutral Salts

Huifang Xiao<sup>1</sup>, Kelu Yan<sup>1,2</sup>, and Bolin Ji<sup>1,2\*</sup>

<sup>1</sup>College of Chemistry, Chemical Engineering and Biotechnology, Donghua University, Shanghai 201620, PR China

<sup>2</sup>National Engineering Research Center for Dyeing and Finishing of Textiles, Donghua University, Shanghai 201620, PR China

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**Abstract:** By employing 1,2,3,4-butanetetracarboxylic acid (BTCA) as the finishing agent, SHP as the catalyst and neutral salts NaCl and Na<sub>2</sub>SO<sub>4</sub> as the additives, anti-wrinkle finish of cotton fabrics was carried out here. According to the Donnan equilibrium model and the actions of neutral salts in dyeing process of cellulosic fabrics, NaCl and Na<sub>2</sub>SO<sub>4</sub> should both promote the adsorption of BTCA anions onto the surface of fibers and diffusion into the interior of fibers. Consequently, BTCA would crosslink the interior molecular chains of cellulose, improving the anti-wrinkle properties of treated fabrics. In fact, experimental results confirmed the hypothesis that the two additives of neutral salts indeed both improved wrinkle recovery angle (WRA) of the treated fabrics and the optimal molar ratio of NaCl or Na<sub>2</sub>SO<sub>4</sub> to BTCA was 0.2:1 or 0.3:1, respectively. The neutral salts reduced the dosage of BTCA without decreasing WRA, reducing the manufacturing cost. Besides, the fabrics treated with neutral salts presented good durability. Furthermore, thermogravimetric analysis (TGA), X-ray diffraction (XRD) and Fourier transform infrared (FTIR) spectroscopy analyses revealed that neutral salts could catalyze the formation of BTCA anhydride by decreasing hydrogen-bond interactions between BTCA molecules.

**Keywords:** Anti-wrinkle finish, BTCA, Additives, Neutral salts, Adsorption

## Introduction

Cotton fabric with many excellent properties derives from natural cellulose fibers. Despite the numerous advantages, there are also some disadvantages, such as easy wrinkling of fabric in practical applications [1-3]. Because of its poor elasticity, it is essential to carry out anti-wrinkle finish of cotton fabric. At present, the finishing agents for cotton fabric are mainly formaldehyde-based chemicals, which exhibit good anti-wrinkle finish effects. But the released formaldehyde will cause great harm to human body [4,5]. Due to the problems of formaldehyde release in the treated fabrics during production, storage and consumer use, since the 1960s researchers have been dedicated to developing formaldehyde-free easy care agents [6-9]. Polycarboxylic acids, such as 1,2,3,4-butanetetracarboxylic acid (BTCA) and citric acid (CA), are tried to be used as formaldehyde-free cross-linking agents to replace DMDHEU [10,11]. BTCA is considered as the most promising compound of this kind of finishing agents, especially the development of catalyst sodium hypophosphite (SHP) makes BTCA more prominent for the anti-wrinkle finish of cotton fabrics [12]. Generally, the esterification reaction between BTCA and cellulose is known to proceed in two steps: formation of a five-membered cyclic anhydride intermediate through the dehydration of two adjacent carboxyl groups, and the formed acid anhydrides subsequently undergo an esterification reaction with the hydroxyl groups on the cellulosic macromolecules to form an ester bond [13-17]. However, BTCA cross-

linking efficiency is usually not enough and the unemployed BTCA would do harm to the environment as well as increase the manufacturing cost. Although CA is a kind of cheap compound and easily accessible, the yellowing issue is a main obstacle to its industrial application [10]. Therefore, the performance of adding neutral salts in the finishing system is being investigated in order to accelerate the esterification reaction between BTCA and cellulose, further improving the anti-wrinkle properties of treated fabrics.

The dyeing process of cellulose fabrics with dyes containing anionic soluble groups, usually carboxylate or sulfate groups, are divided into four steps. Firstly, dye anions get close to the interface between fibers and solution, and then they diffuse towards the fiber surface through the diffusion boundary layer on fiber surface. After that, the dye anions are adsorbed onto the surface of the fiber. Finally, the dye anions diffuse into the inner of fibers and are fixed on the cellulose macromolecules. In the dyeing process, neutral electrolytes such as sodium chloride (NaCl) and sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>) are usually required to be added, which can not only increase the dye uptake rate, but also improve the adsorption capacity. The previous studies reported when the cotton fabrics were dyed with direct dyes, it was necessary to add accelerants such as NaCl or Na<sub>2</sub>SO<sub>4</sub> [18,19]. Due to that the fiber surface was negatively charged, the added accelerants can reduce or overcome the Coulomb repulsion of negative charges of the fiber surface to dye anions in dyeing process, and consequently can promote the adsorption of dye anions onto the surface of fibers and diffusion to the interior of fibers. Therefore it could improve the utilization of dye finally. When BTCA is used for anti-wrinkle finish of

\*Corresponding author: jibolin19881015@163.com

cotton fabrics, some BTCA molecules would be ionized in aqueous solution [20,21]. The process of adsorption and diffusion of BTCA anions to the fibers is similar to the dyeing process of direct dyes. Therefore, the accelerants also can be used in the BTCA anti-wrinkle system.

No detailed information about the characteristics of neutral salts acting as additives in a BTCA anti-wrinkle finish system is noticed. In this research, new experimental conditions were designed by using neutral salts as additives for BTCA reaction with cellulose. In virtue of the mechanism of neutral salts in dyeing and the theoretical analysis of the Donnan equilibrium, the influences of both NaCl and Na<sub>2</sub>SO<sub>4</sub> on anti-wrinkle effects of cotton fabric treated with BTCA were studied. Besides, the optimum dosages of additives and durability of the treated fabrics were studied in detail. Thermogravimetric analysis (TGA), X-ray diffraction (XRD) and Fourier transform infrared (FTIR) spectroscopy were employed to characterize the actions of the neutral salts in the BTCA reaction with cellulose. This study would provide a new direction for developing additives for BTCA finishing of cotton fabrics.

## Experimental

### Materials

Desized, scoured, bleached and mercerized 40 s×40 s plain-woven pure cotton fabric (weighing 117 g/m<sup>2</sup>) was purchased from Hualun printing and dyeing Co., Ltd. (Shanghai, China). 1,2,3,4-Butanetetracarboxylic acid (BTCA), sodium hypophosphite (SHP) monohydrate, sodium chloride (NaCl) and sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>) were analytical grade and purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Sodium hydroxide (NaOH) was obtained from Lingfeng Chemical Reagent Co., Ltd. (Shanghai, China). All reagents were used as received.

### Fabric Treatments

Cotton fabric was dipped and nipped two times with an average pick-up of 90 % in a 6.4 wt% BTCA and a catalyst SHP aqueous solution with or without neutral salts. The amount of the catalyst was adopted at a 0.5 molar ratio to BTCA, and the amount of the neutral salts were adopted at a different molar ratio to BTCA. And then the fabric was dried at 90 °C for 2 min, and cured at 160 °C for 3 min in a curing oven (Werner Mathis Ltd., Switzerland). The treated fabrics were washed by tap water for 10 min and then immersed in a 0.1 M NaOH solution for 5 min at room temperature, and finally dried at 80 °C for 5 min before FTIR measurements.

### Donnan Equilibrium Analysis

When two coexistent phases are subject to the restriction that one or several of the ionic components cannot pass from one phase into the other, a particular equilibrium is set up, called the Donnan equilibrium [22,23]. The classical

Donnan equilibrium is based on the Boltzmann equation [24]. The ions of Na<sup>+</sup> and Cl<sup>-</sup> ionized by NaCl were analyzed in the BTCA anti-wrinkle system.

### Fabric Performance Measurement

Samples were conditioned for 4 h at (65±2) % relative humidity and (20±1) °C conditions before measurements. The wrinkle recovery angle (WRA) was tested according to the American Association of Textile Chemists and Colorists (AATCC) Testing Method 66-2008 on a SDL Atlas M003A tester in order to evaluate the wrinkle-resistant performance of the specimens. The WRA obtained for the conditioned fabrics was the average of two tests.

Tearing strength was measured according to the American Society of Testing Materials (ASTM) Testing Method D1424-1996 by a Thwing-Albert Elmendorf tearing machine, and tearing strength retention (TSR) was calculated as following:

$$TSR(\%) = \frac{T_t}{T_u} \times 100\% \quad (1)$$

where  $T_t$  is tearing strength (cN) of the treated sample,  $T_u$  is tearing strength (cN) of the untreated sample. All measurements of mechanical properties were carried out on the warp and weft direction.

### Fourier Transform Infrared (FTIR) Spectroscopy

FTIR was used to determine the degree of cross-linking between polycarboxylic acid and cellulose [25]. Fabric samples were dried under vacuum at the temperature of 50 °C for 2 h and were grounded into powders. Sample powders were mixed with KBr and prepared by pressed-disk technique before FTIR test, and sample mass and KBr mass were accurately weighed at 2.0 mg and 200.0 mg, respectively. FTIR spectra were collected by a Nicolet 380 FTIR spectrometer (Nicolet Analytical Instruments, USA) with a scan range of 4000-400 cm<sup>-1</sup> and a resolution of 4 cm<sup>-1</sup>.

### Thermogravimetric Analysis (TGA)

TGA of sample was performed by using a TG209 F1 TGA system following such procedures: Sample was first heated up to 120 °C from room temperature in a heating rate of 10 °C/min in a nitrogen atmosphere to eliminate the water in samples. After being cooled down to room temperature, the sample was then heated again to 600 °C and weight losses were recorded. The sample mass used was about 3.0-5.0 mg.

### X-ray Diffraction (XRD)

The analytical application of X-ray diffraction gives information on the molecular structure of the sample by measuring the degree of crystallinity and crystallite size of the samples. The composition and structure of the test specimen were examined by the D/max-2550 VB+/PC X-ray Diffractometer manufactured by Rigaku Ltd. The testing specimen mounted on the machine was rotated relative to

the X-ray source at a rate of 0.025°/second from 5° to 90°. Diffracted radiation intensity that came from the sample was detected by the detector which rotated simultaneously at 0.02°/second. The specimen was prepared by dissolving BTCA and neutral salts in distilled water, and then were heated at 50°C to constant weights.

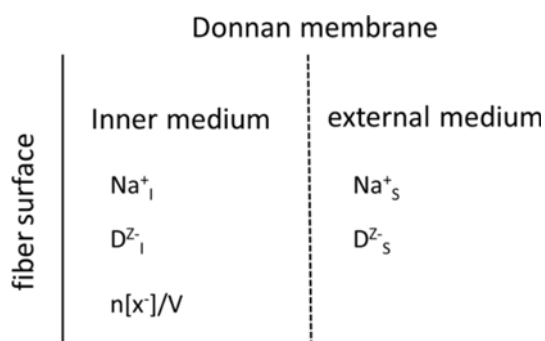
## Results and Discussion

### Donnan Equilibrium Analysis of Anti-wrinkle Finishing System

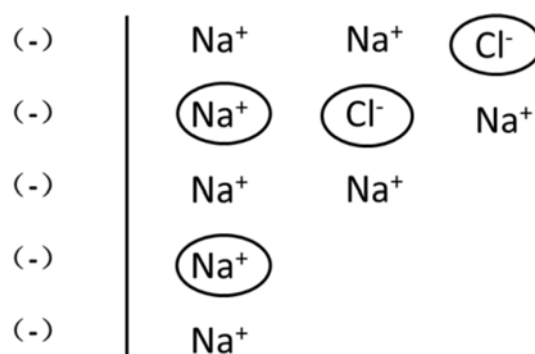
According to the Donnan equilibrium model, the fiber surface could be regarded as the double layers of electronic potential and the junction line between fiber surface and finishing liquid could be used as a semipermeable membrane. All ions in finishing liquid could get through the membrane. However, the fiber surface charge was fixed. As shown in Figure 1, the inner part of the fiber was regarded as an inner membrane system and the external solution was regarded as an outer membrane system. In addition, when the balance was electrically neutral, the net charge of inside or outside of the membrane should be zero:

$$[Na^+] = Z[D^{Z-}] + \frac{n(X^-)}{V} \quad (2)$$

Take sodium chloride (NaCl) as an example to further explain the Donnan equilibrium (Figure 2). When NaCl was added, the system contained cellulose anion (Cell-O<sup>-</sup>), Na<sup>+</sup>, H<sup>+</sup>, Cl<sup>-</sup>, H<sub>2</sub>PO<sub>2</sub><sup>-</sup> and BTCA anions. The Cell-O<sup>-</sup> could only stay in the inner membrane, not to spread to the outer membrane, but other ions were mobile and could establish the balance according to the charge balance conditions in the inner and outer membrane. Assuming that the volume of the internal and external membrane was equal and unchanged during the balance process, the net charge in the membrane and the outer membrane should be kept neutral. The equation (2) showed that after NaCl was added into the finishing bath, the concentration of Na<sup>+</sup> in the outer membrane



**Figure 1.** Distribution of ions in and out of the membrane. Note: [D<sup>Z-</sup>] is the concentration of BTCA anions, n is the unit quality fiber with x<sup>-</sup> charge, and V is the Donnan membrane volume of the unit quality fiber.



**Figure 2.** Schematic diagram of salt effect: (Na<sup>+</sup>) and (Cl<sup>-</sup>) are ions for NaCl salt.

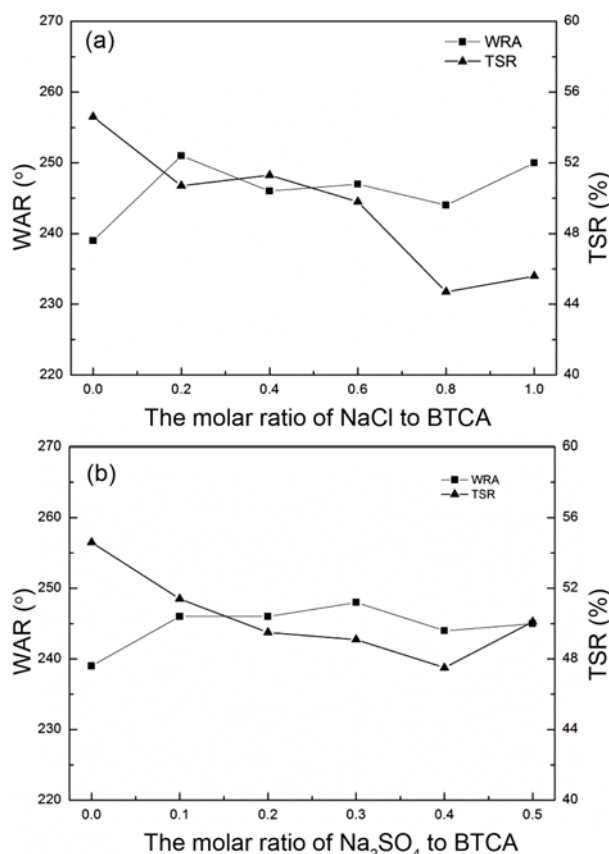
system would increase. Because Na<sup>+</sup> had an advantage of small volume, it was easy for it to move into the inner membrane from the outer membrane. Since the inner membrane and the outer membrane were electrically neutral when it was balanced, the concentration of [D<sup>Z-</sup>] of the inner membrane would increase. According to the experimental results, the pH value of BTCA and SHP (in a molar ratio 0.5 to BTCA) finishing solution was about 2.3, and the relative concentration of BTCA anion was about 7% [21]. Absolute value of electric layer potential on the fiber surface was decreased as a result that the partial negative charges on the fiber surface were offset by the added Na<sup>+</sup> from the salts. Therefore, the repulsion action of the adsorption of the BTCA anions onto the fiber surface was reduced. The adsorption rate was increased to some extent and BTCA anions diffused into the fiber inner easily.

Therefore, the NaCl added into the BTCA finishing bath might promote the adsorption of BTCA anions onto the fiber surface and further diffusion into the inner of the fiber. In addition, more fiber molecular chains would take part in esterification reactions with BTCA, so as to improve the anti-wrinkle effect of the treated fabrics.

### Anti-wrinkle Properties of Fabrics Treated with Neutral Salts

To study the effect of neutral salts on the anti-wrinkle properties of BTCA-treated fabrics from the analysis of Donnan equilibrium, NaCl was selected as the additive to treat cotton fabrics firstly. For the 6.4 wt% BTCA and 1.5 wt% SHP one-bath pad-dry-cure treatment, the average of wrinkle recovery angle (WRA) of fabrics treated with different contents of NaCl or Na<sub>2</sub>SO<sub>4</sub> is illustrated in Figure 3.

The data in Figure 3(a) evidenced that overall WRA of the specimens treated with NaCl additive increased about 12° and reached to the highest value of 251° at a 0.2 molar ratio. Sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>) added in the BTCA treatment also can improve the treated cotton fabric WRA and the WRA reached to the maximum 248° at a 0.3 molar ratio of Na<sub>2</sub>SO<sub>4</sub>



**Figure 3.** Effects of (a) NaCl and (b) Na<sub>2</sub>SO<sub>4</sub> on anti-wrinkle properties of BTCA-treated fabrics.

to BTCA as shown in Figure 3(b). Generally speaking, during the curing process, BTCA reacted with the cellulose molecules of the cotton fabrics most probably through the formation of cyclic anhydrides as reactive intermediates [13-17]. In the presence of neutral salts, which can reduce the repulsion of negative fiber surface to BTCA anions, BTCA molecules were able to crosslink the hydroxyl groups of the cellulosic macromolecules easily, contributing to a higher WRA.

The tearing strength retention (TSR) values of fabrics treated with neutral salts in the BTCA-SHP solutions are also presented in Figure 3. The results obviously showed that the TSR of treated fabrics in the presence of neutral salts, dropped to a lower value as the molar ratio of neutral salts to BTCA was increased to 1.0. The TSR reduced with increasing of the WRA and the magnitude of strength loss was enhanced with the increase in cross-linking degree of the cellulose molecules through BTCA molecules [26]. According to the discussion of Donnan equilibrium, the introduction of Na<sup>+</sup> could reduce the repulsion of negative charges on the surface of cellulose fibers to the BTCA anions, so that BTCA anions were more likely to be adsorbed onto the fiber surface and then diffuse into the fiber

**Table 1.** Effects of NaCl or Na<sub>2</sub>SO<sub>4</sub> on anti-wrinkle properties of fabrics treated with different BTCA contents

BTCA concentration (wt%)	NaCl/Na <sub>2</sub> SO <sub>4</sub> concentration (wt%)	WRA (°)	TSR (%)	
			Warp	Weft
4.7	0.3 / 1.2	228 / 220	61.9 / 63.8	49.4 / 54.6
5.1	0.3 / 1.2	229 / 225	58.6 / 59.1	56.7 / 54.8
5.6	0.3 / 1.2	234 / 227	54.8 / 55.3	51.2 / 52.2
6.0	0.3 / 1.2	237 / 236	53.4 / 53.2	48.1 / 49.7
6.4	0.3 / 1.2	247 / 244	54.6 / 54.8	49.8 / 51.9
6.4	0	232	61.9	57.7

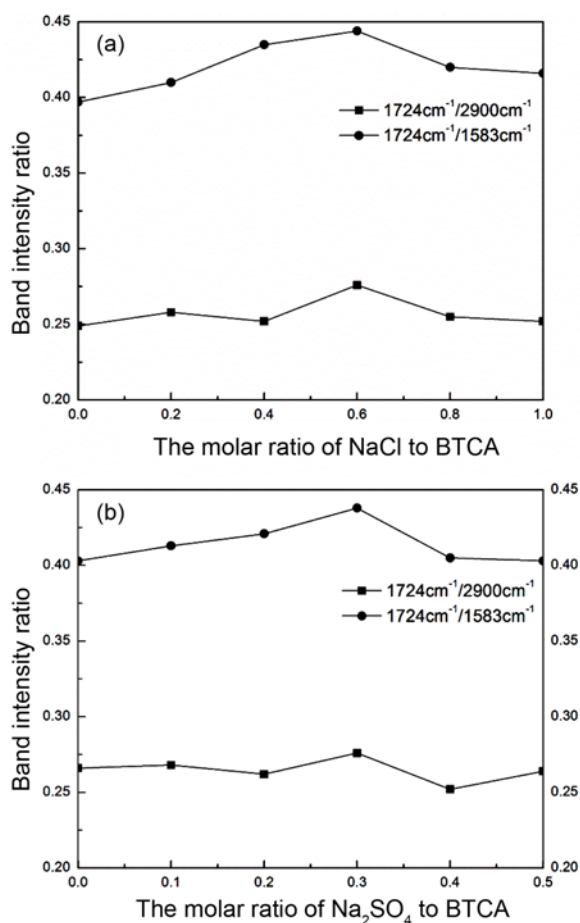
Note: The date in front of or behind the slash were the results of the fabrics treated with NaCl additives and Na<sub>2</sub>SO<sub>4</sub> additives, respectively.

inner, increasing cross-linking between BTCA and internal cellulose chains.

To sum up, NaCl and Na<sub>2</sub>SO<sub>4</sub> can be used as the additives to improve the resilience of fabrics treated with BTCA. However, high cost of BTCA is one of the factors limiting its application in large-scale industrialization. Due to the beneficial effects of neutral salts, it is practicable that the amount of BTCA may be reduced by adding neutral salts, consequently reducing the cost. Therefore NaCl or Na<sub>2</sub>SO<sub>4</sub> was added into BTCA solutions with different contents to study the anti-wrinkle properties of the treated fabrics. As shown in Table 1, when the amount of BTCA was reduced from 6.4 wt% to about 5.6 wt%, WRA of the treated fabric was not decreased as NaCl was added, and TSR of the treated fabrics now was still acceptable. The similar results were obtained for the fabrics treated with Na<sub>2</sub>SO<sub>4</sub> additives (Table 1). The results showed that the addition of neutral salts could reduce the dosage of BTCA without decreasing the anti-wrinkle properties of treated fabrics.

First of all, the alkaline washing of the fabric was carried out as the method in experimental section before FTIR evaluation to convert the acid anhydrides and carboxyl groups which did not participate in the esterification reaction to carboxylates. The 1724 cm<sup>-1</sup> peak now was completely attributed to the ester carbonyl formed by BTCA and hydroxyl groups of cellulose. The ratio of the absorption at 1724 cm<sup>-1</sup> to the absorption at 2900 cm<sup>-1</sup> (1724 cm<sup>-1</sup>/2900 cm<sup>-1</sup>) could evaluate the degree of esterification and cross-linking between BTCA and cellulose. The higher the ratio value was, the higher the degree of covalent cross-linking of esterification was [2,21].

As demonstrated in Figure 4(a), the ester band ratio (1724 cm<sup>-1</sup>/2900 cm<sup>-1</sup>) reached to the maximum value of 0.276 when the molar ratio of NaCl to BTCA was 0.6. However, it decreased with molar ratio further increasing. In addition, the average of carboxyl groups (1724 cm<sup>-1</sup>/1583 cm<sup>-1</sup>) of each BTCA molecule involved in esterification also showed the same change trend and it reached to the maximum value

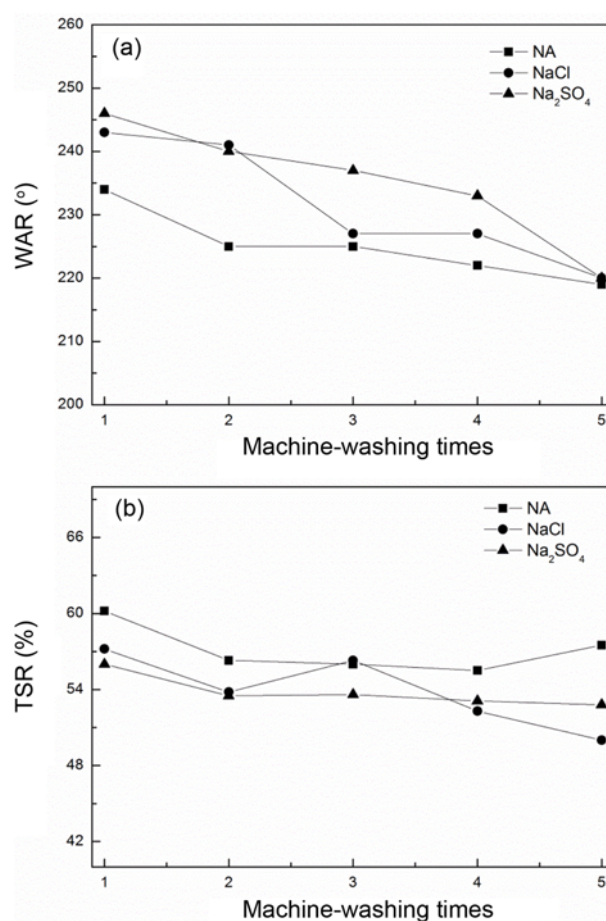


**Figure 4.** Effects of (a) NaCl and (b)  $\text{Na}_2\text{SO}_4$  additives on the cross-linking of BTCA with cotton fabrics.

of 0.444 at the molar ratio of 0.6. It was proved that the cross-linking between BTCA and fibers was promoted when NaCl was used as the additive. The optimum molar ratio of NaCl to BTCA should be 0.2:1 on the basis of the highest WRA value now. As shown in Figure 4(b), with the molar ratio of  $\text{Na}_2\text{SO}_4$  to BTCA increasing to 0.3, the ester bond ratios ( $1724\text{ cm}^{-1}/2900\text{ cm}^{-1}$ ) reached to the maximum value of 0.276 and then decreased with the molar ratio increasing. The value of  $1724\text{ cm}^{-1}/1583\text{ cm}^{-1}$  showed the same trend, reaching to the maximum value of 0.438 at the molar ratio of 0.3. Therefore the optimum molar ratio of  $\text{Na}_2\text{SO}_4$  to BTCA should be 0.3:1, which corresponded to the results of Figure 3(b).

On basis of the results of Figure 4, the neutral salts NaCl and  $\text{Na}_2\text{SO}_4$  would improve the WRA of the treated fabrics. Due to the improvement of BTCA diffusion into the fiber, the durability of the finished fabric should be improved theoretically.

Figure 5 represents that fabric WRA decreased with the increase of machine-washing times. However, the WRA of fabrics treated with neutral salts was still higher compared



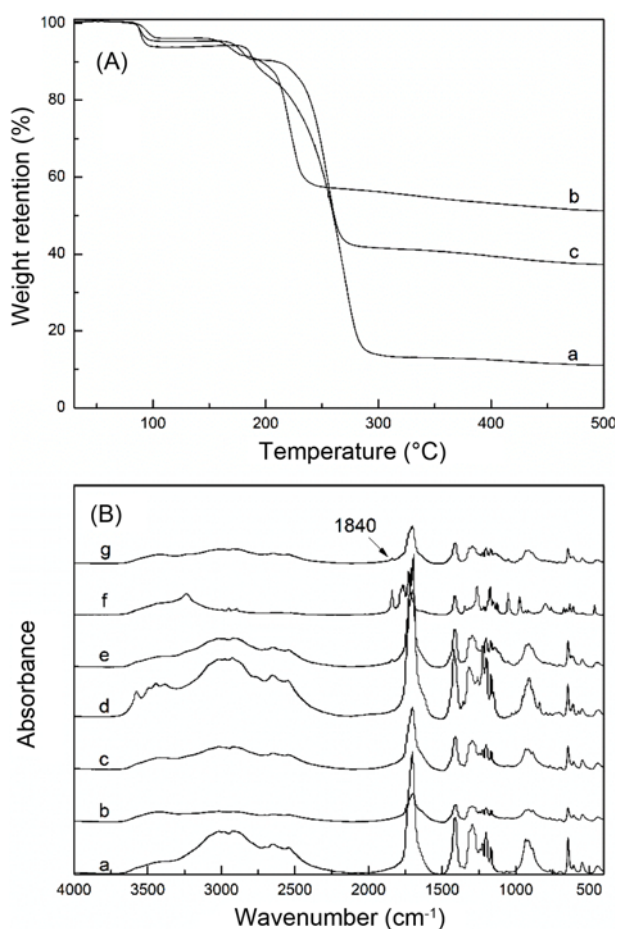
**Figure 5.** Effects of machine washing times on (a) WRA and (b) TSR of the treated fabrics. Note: The data here was the average results of the two tests. NA meant that no sodium chloride or sodium sulfate was added.

with that without additives. From the view of strength, the weft TSR of treated fabrics was decreased a little but still satisfactory in presence of the neutral salts additives. To sum up, according to the analysis of the Donnan equilibrium, the neutral salts can promote the diffusion of BTCA into the cellulose fibers, and as a result more BTCA reacted with cellulose, which was also proved by the higher ester absorbance of the fabrics treated with neutral salts in Figure 4, and consequently the durability of treated fabrics was improved.

#### Characterization of the Actions of Neutral Salts in Anhydride Formation

Regardless of the constant amount of catalyst SHP in the study, ester absorbance of the treated fabrics was strengthened after neutral salts were added into the finishing bath, thus there should be some other actions from the salts. In order to further clarify the effects of neutral salts, BTCA compounds with different neutral salts were heated up in a thermo-





**Figure 6.** (A) TGA curves of BTCA chemicals with different neutral salts: (a) BTCA, (b) BTCA-NaCl, (c) BTCA-Na<sub>2</sub>SO<sub>4</sub>. (B) FTIR spectra of different chemicals heated at different temperatures for 2 min: (a) BTCA, 150 °C, (b) BTCA, 170 °C, (c) BTCA, 180 °C, (d) BTCA-NaCl, 150 °C, (e) BTCA-Na<sub>2</sub>SO<sub>4</sub>, 170 °C, (f) BTCA-NaCl, 180 °C, and (g) BTCA-Na<sub>2</sub>SO<sub>4</sub>, 180 °C.

gravimetric analysis (TGA) furnace under nitrogen atmosphere. The samples were prepared by dissolving BTCA and neutral salts in distilled water and then were heated at 50 °C to constant weights.

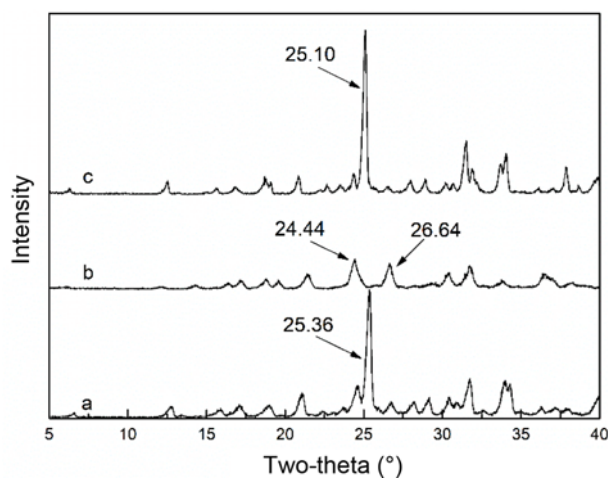
The weight losses of BTCA with different neutral salts under increased temperatures are shown in Figure 6(A). Pure BTCA (Figure 6(A-a)) started losing weight at 180 °C by forming anhydride and continued with further weight loss corresponding to degradation of the compound [27]. However, the two salts of both NaCl and Na<sub>2</sub>SO<sub>4</sub> lowered the temperature of initial weight loss of BTCA to about 146 °C (Figure 6(A-b)) and 167 °C (Figure 6(A-c)), respectively. In order to investigate whether the weight loss was due to the formation of BTCA anhydride by dehydration, FTIR was employed to obtain the spectra of different compounds. All samples were firstly heated at specific temperatures for 2 min under the nitrogen atmosphere before FTIR test. Figure 6(B) indicates

that pure BTCA did not show the anhydride absorbance at about 1840 cm<sup>-1</sup> under 150 °C (Figure 6(B-a)) or 170 °C (Figure 6(B-b)). Pure BTCA under 180 °C (Figure 6(B-c)) and BTCA-NaCl under 150 °C (Figure 6(B-d)) started to show the anhydride absorbance but not clear, and BTCA-Na<sub>2</sub>SO<sub>4</sub> under 170 °C (Figure 6(B-e)) showed a noticeable absorbance. However, a very strong peak at 1840 cm<sup>-1</sup> was generated for BTCA-NaCl with temperature increasing to 180 °C (Figure 6(B-f)), and the absorbance almost kept no change for BTCA-Na<sub>2</sub>SO<sub>4</sub> (Figure 6(B-g)). Anyway, they were both stronger than that of pure BTCA under the same temperature, serving as a solid evidence to the neutral salts promoting the formation of anhydride. This may also explain the increasing WRA values (Figure 3) and ester absorbance (Figure 5) of fabrics treated with NaCl or Na<sub>2</sub>SO<sub>4</sub>, because anhydride is considered to be the active intermediate for the reaction of BTCA with cellulose [13-17,28].

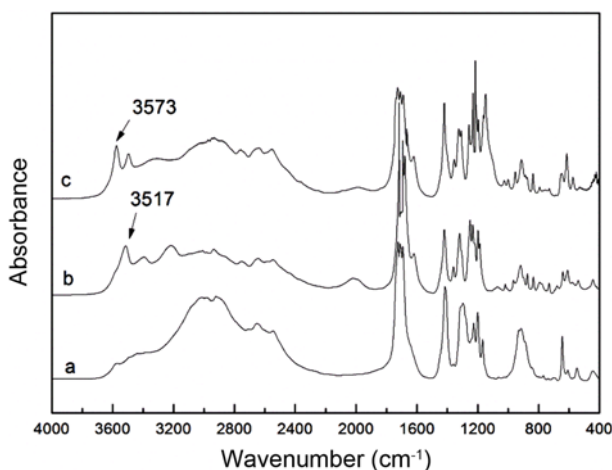
When the X-ray entered a crystal from a certain direction, the coherent waves produced by the extra nuclear electron of each atom would interfere with each other. Strong X-ray diffraction in some special directions, the spatial distribution of the diffracted rays in the direction and intensity were closely related to the crystal structure. Specific crystal material has its own unique diffraction pattern.

Figure 7 illustrates the X-ray diffraction (XRD) diagrams of BTCA, BTCA-NaCl and BTCA-Na<sub>2</sub>SO<sub>4</sub>, respectively. The diffraction intensity of BTCA was different from that of BTCA-NaCl or BTCA-Na<sub>2</sub>SO<sub>4</sub>, which might be caused by the breaking up of hydrogen-bonds between BTCA molecules in the presence of neutral salts.

The pure BTCA sample had the strongest peak at two-theta angle of 25.36 °, which can be regarded as the XRD characteristic peak of BTCA. The strongest peak of BTCA-NaCl sample moved to 24.44 ° and 26.64 °, which suggested that the crystal structure of BTCA changed. The possible



**Figure 7.** XRD spectra of BTCA chemicals with different neutral salts; (a) BTCA, (b) BTCA-NaCl, and (c) BTCA-Na<sub>2</sub>SO<sub>4</sub>.



**Figure 8.** FTIR spectra of different chemicals; (a) BTCA, (b) BTCA-NaCl, and (c) BTCA-Na<sub>2</sub>SO<sub>4</sub>.

reason was that NaCl among BTCA carboxyl broke the hydrogen-bonds, thus affecting the crystal structure. In the mixed sample of BTCA and Na<sub>2</sub>SO<sub>4</sub>, the strongest peak moved to 25.1°, which further confirmed that intermolecular hydrogen-bonds between BTCA molecules were affected by the neutral salts.

To further prove the hypothesis that neutral salts can weaken the hydrogen-bonds interactions between BTCA molecules, Fourier transform infrared (FTIR) measurements were carried out. The samples were prepared in the same method as that before XRD test. Presented in Figure 8 are FTIR spectra of different chemicals. BTCA carboxyls have strong association, forming hydrogen-bonds, so the vibration frequency of the hydroxyl group was low and appeared at about 3000 cm<sup>-1</sup> [29]. The absorbance peak of the mixtures of BTCA-NaCl and BTCA-Na<sub>2</sub>SO<sub>4</sub> appeared at 3517 cm<sup>-1</sup> and 3573 cm<sup>-1</sup>, respectively. This was probably due to that the hydroxyl groups formed hydrogen-bonds and neutral salts broke the inter- and intramolecular hydrogen-bonds of BTCA molecules. As a result, the absorption peak shifted to the higher wavenumbers. The reactivity of BTCA molecules would be improved when the inter- or intramolecular hydrogen-bonds were weakened. It was easier for BTCA to form anhydride, which would esterify with cellulose fibers. In addition, there were more splitted peaks of BTCA-NaCl and BTCA-Na<sub>2</sub>SO<sub>4</sub> at about 1730 cm<sup>-1</sup>, also confirming that the hydrogen-bonds were weakened by the neutral salts.

### Conclusion

Sodium chloride (NaCl) or sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>) salts would reduce the negative charges on the surface of cellulose fibers according to the Donnon equilibrium model, promoting the adsorption of BTCA anions onto the surface and diffusion into the interior of fibers, which further

improved the wrinkle recovery angle (WRA) of BTCA-treated fabrics. The optimum molar ratio of NaCl and Na<sub>2</sub>SO<sub>4</sub> to BTCA was 0.2:1 and 0.3:1, respectively. With the addition of neutral salts, the amount of BTCA can be reduced from 6.4 wt% to 5.6 wt% without affecting the anti-wrinkle properties of treated fabrics. The added neutral sodium salts increased the esterification and cross-linking reaction between BTCA and cellulose. Consequently, the absorbance of ester bonds between BTCA and cellulose increased. The WRA of fabrics treated with neutral salts increased by about 12° and TSR was still satisfactory. Furthermore, neutral salts as the additives improved the durable properties of the treated fabrics. Based on the results of TGA, XRD and FTIR, neutral salts may catalyze the formation of BTCA anhydride by decreasing the hydrogen-bond interactions of BTCA molecules.

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### References

1. V. A. Dehabadi, H. J. Buschmann, and J. S. Gutmann, *Text. Res. J.*, **83**, 1974 (2013).
2. C. Zhao and G. Sun, *Ind. Eng. Chem. Res.*, **54**, 10553 (2015).
3. Y. K. Lam, C. W. Kan, and C. W. M. Yuen, *Fiber. Polym.*, **11**, 551 (2010).
4. U. Sewekow, *Text. Chem. Color.*, **28**, 21 (1996).
5. W. Wei and C. Q. Yang, *Text. Chem. Color.*, **32**, 53 (2000).
6. Jr. J. G. Frick and Jr. R. J. Harper, *Text. Res. J.*, **52**, 141 (1982).
7. K. J. Yoon, J. H. Woo, and Y. S. Seo, *Fiber. Polym.*, **4**, 182 (2003).
8. Y. H. Yu, E. S. Lee, and E. S. Bang, *Fiber. Polym.*, **9**, 715 (2008).
9. E. S. Lee and S. I. Kim, *Fiber. Polym.*, **5**, 230 (2004).
10. P. Tang, B. Ji, and G. Sun, *Carbohydr. Polym.*, **147**, 139 (2016).
11. W. Sricharussin, W. Ryo-Aree, W. Intasen, and S. Pongraksakirt, *Text. Res. J.*, **74**, 75 (2004).
12. B. K. Andrews, N. M. Morris, D. J. Donaldson, and C. M. Welch, *U. S. Patents*, 5221285 (1993).
13. C. Q. Yang and X. L. Wang, *Text. Res. J.*, **66**, 595 (1996).
14. B. H. Kim, J. Jang, and S. W. Ko, *Fiber. Polym.*, **1**, 116 (2000).
15. K. J. Yoon, J. H. Woo, and Y. S. Seo, *Fiber. Polym.*, **4**, 182 (2003).

16. N. Bhattacharyya, B. A. Doshi, and A. S. Sahasrabudhe, *Text. Chem. Color.*, **31**, 33 (1999).
17. W. Sricharussin, W. Ryo-Aree, W. Intasen, and S. Poungraksakirt, *Text. Res. J.*, **74**, 475 (2004).
18. A. Johnson, "The Theory of Coloration of Textiles", 2nd ed., pp.223-224, Society of Dyes and Colourists, Bradford, 1989.
19. B. Yu, W. Wang, and Z. Cai, *J. Text. Inst.*, **105**, 321 (2014).
20. C. Q. Yang, *Text. Res. J.*, **63**, 420 (1993).
21. B. Ji, P. Tang, K. Yan, and G. Sun, *Carbohydr. Polym.*, **132**, 228 (2015).
22. P. J. Bassler and A. J. Grodzinsky, *Biophys. Chem.*, **46**, 57 (1993).
23. J. T. Overbeek, *Prog. Biophys. Biophys. Chem.*, **6**, 57 (1956).
24. R. Zhao, O. Satpradit, H. H. M. Rijnaarts, P. M. Biesheuvel, and A. van der Wal, *Water Res.*, **47**, 1941 (2013).
25. N. M. Morris, E. A. Catalano, and B. A. K. Andrews, *Cellulose*, **2**, 31 (1995).
26. I. S. Kang, C. Q. Yang, W. S. Wei, and G. C. Lickfield, *Text. Res. J.*, **68**, 865 (1998).
27. C. E. Morris, N. M. Morris, and B. J. Trask-Morrell, *Ind. Eng. Chem. Res.*, **35**, 950 (1996).
28. C. Q. Yang, *Text. Res. J.*, **61**, 433 (1991).
29. Y. Ning, "Structural Identification of Organic Compounds and Organic Spectroscopy", 2nd ed., pp.490-494, Science Press, Beijing, 2000.