

# Effect of Plasma Pretreatment on the Wrinkle-Resistance Properties of Cotton Fibers Treated with a 1,2,3,4-Butanetetracarboxylic Acid–Sodium Hypophosphite System with Titanium Dioxide as a Cocatalyst

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**ABSTRACT:** A 1,2,3,4-butanetetracarboxylic acid (BTCA)–sodium hypophosphite (SHP) wrinkle-resistance system played an important role in improving the wrinkle-resistance properties of cotton fibers. In this study, titanium dioxide ( $\text{TiO}_2$ ) was used as a cocatalyst to further enhance the wrinkle-resistance properties of BTCA–SHP-treated cotton fabrics, that is, those treated with (1) 5% BTCA and 10% SHP; (2) 5% BTCA, 10% SHP, and 0.1%  $\text{TiO}_2$ ; and (3) 5% BTCA, 10% SHP, and 0.2%  $\text{TiO}_2$ . In addition, the effect of plasma as a pretreatment process on the wrinkle-resistance properties of the three treatment systems was also studied. The experimental results reveal that the wrinkle-resistance properties of cotton fibers were improved after different wrinkle-resistance treatments. In addition, the plasma pretreatment further enhanced the wrinkle-resistance treatments to different extents, depending on the process parameters. Scanning electron microscopy images confirmed that such plasma pretreatment conditions imparted the best crosslinking effect on the cotton fibers. However, the wrin-

kle-resistance-treated cotton specimens had lower tensile strength and tearing strength values compared to the control sample, whereas the plasma pretreatment and cocatalyst may have compensated for the reduction in the mechanical strength caused by the wrinkle-resistance agents. In this article, the optimum conditions for the plasma pretreatment on the basis of the result of the wrinkle-recovery angle were analyzed with an  $L_9(3)^3$  orthogonal array testing strategy technique. The results showed that plasma treatment conditions with (1) a 10 mm/s speed, (2) a 0.1 L/min oxygen flow rate, and (3) a 4-mm jet-to-substrate distance together caused a significant improvement in the wrinkle-resistance properties of the cotton fibers treated with the three different BTCA treatments. Moreover, the treatment speed was the dominant factor, followed by jet-to-substrate distance and oxygen flow rate, in affecting the extent of improvement. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 1403–1410, 2011

**Key words:** coatings; crosslinking; surface modification

## INTRODUCTION

The crosslinking of cotton with 1,2,3,4-butanetetracarboxylic acid (BTCA) has provided an alternative route for the formaldehyde-free wrinkle-resistance treatment of cotton fabrics.<sup>1–5</sup> The crosslinking reaction is enhanced by catalysts, such as sodium hypophosphite (SHP) and titanium dioxide ( $\text{TiO}_2$ ).<sup>6–11</sup> To enhance the BTCA treatment with  $\text{TiO}_2$ , the surface modification of the cotton fiber is required. However, most of the surface modification processes involve the use of chemicals. Because of environmental consciousness, a dry treatment provides an

alternative for surface modification. Among various dry surface treatments, plasma is a promising surface-modification technique that can modify the material surface properties and composition without altering the bulk properties. In the past, plasma treatment has been conducted *in vacuo* and, thus, may not be a continuous process. However, in recent years, atmospheric pressure plasma jets have been developed and widely used in the textile industry to modify the fabric surface in an environmentally friendly way and resulting in a reduction of the wet chemical and energy consumption.<sup>12–14</sup> Plasma gas contains activated species that are able to initiate chemical and physical modifications at the fabric surface to cause an etching effect.<sup>13–17</sup> The process itself can improve the wrinkle-recovery ability of fabrics. Natural gas plays an important role in plasma treatment. One can vary the characteristics of the plasma by changing the gas used. In addition, the effectiveness of plasma treatment may also be affected by the plasma treatment conditions, such as treatment duration, gas flow rate, applied power,

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TABLE I  
Plasma Pretreatment Parameters for the Cotton Fabric

Output power (W)	Treatment speed (mm/s) <sup>a</sup>	Helium flow rate (L/min)	Oxygen flow rate (L/min)	Jet-to-substrate distance (mm)
80	2, 10, 50	15	0.1, 0.2, 0.3	2, 4, 6

<sup>a</sup> The treatment speeds of 2, 5, and 50 mm/s were related to treatment times of 0.5, 0.1, and 0.02 s/mm, respectively.

jet-to-substrate distance, and pore size or structure.<sup>12,15</sup> Detailed information concerning the effect of plasma pretreatment on the wrinkle-recovery properties of cotton imparted by BTCA treatment is still lacking. Moreover, the optimization of the effectiveness of the plasma treatment on the fabric is required. In this study, the optimum conditions of plasma pretreatment for wrinkle-resistance treatment under various amounts of BTCA were obtained through the  $L_9(3)^3$  orthogonal array testing strategy (OATS) technique with the process parameters of treatment speed (related to treatment time), oxygen flow rate, and jet-to-substrate distance. The surface morphology of cotton was investigated to find evidence of surface modification by plasma treatment and the presence of flame-retardant agents and ZnO/nano-ZnO on the fiber surface. Also, the mechanical strength was analyzed by a grab test and Elmendorf tearing test.

## EXPERIMENTAL

### Material

Plain weave 100% semibleached cotton fabric (58 picks/cm with a yarn count of 40 tex in the warp direction; 58 ends/cm with a yarn count of 38 tex in the weft direction) with a weight of 175 g/m<sup>2</sup> and a size of 25 × 25 cm<sup>2</sup> were used. The crosslinking agent was 1,2,3,4-butanetetracarboxylic acid (BTCA) supplied by the International Laboratory Ltd., (San Burno, USA) with 98% purity. The catalyst used was sodium hypophosphite (SHP) supplied by International Laboratory Ltd., San Burno, USA, also (guaranteed reagent grade). Titanium dioxide (TiO<sub>2</sub>, 2 μm diameter) obtained from the UniChem Ltd., (North Carolina, USA) in purity of 99.5+% All other chemicals used in the study were reagent grade.

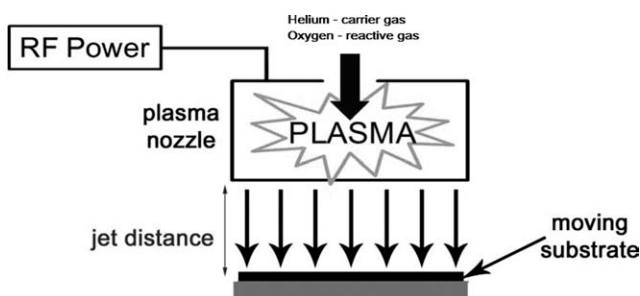


Figure 1 Schematic diagram of the plasma pretreatment.

### Plasma pretreatment and its optimization

The plasma treatment of the cotton fabrics was carried out by an atmospheric pressure plasma jet apparatus manufactured by SurfX Technologies (California, USA). The cotton fabric was moved according to a specified substrate moving speed, that is, the treatment speed. The machine produced a stable discharge at atmospheric pressure with a radio frequency (RF) of 13.56 MHz at 80 W. The treatment was carried out with a rectangular nozzle, which covered an active area of 25.4 × 1 mm<sup>2</sup> and was mounted vertically above the cotton fabric. Helium and oxygen were used as carrier and reactive gases, respectively. The plasma pretreatment of the cotton fabrics was conducted with different settings of treatment speed, oxygen flow rate, and jet-to-substrate distance according to Table I, and the setup for the plasma pretreatment is shown in Figure 1.

The optimum plasma pretreatment conditions were investigated with the  $L_9(3)^3$  OATS technique<sup>17,18</sup> on the basis of three parameters, namely, the (1) treatment speed (treatment time), (2) oxygen flow rate, and (3) jet-to-substrate distance, and three levels were set for each factor, whereas the decided levels were based on the conventional treatment, as shown in Table II. When one parameter changed, the other parameters were held constant. According to the rules of the OATS technique,<sup>18,19</sup> nine test runs were generated by the combination of the chosen parameters and the levels of each parameter, and the arrangement of the experimental trials is summarized in Table III. The cotton fabrics were pretreated by means of the plasma surface-modification process in accordance with the condition requirements stated in Table III, whereas the wrinkle-resistance treatment was based on three different conditions, that is, (1) 5% BTCA and 10% SHP; (2)

TABLE II  
Parameters and Levels Used in OATS

Level	Treatment speed (mm/s)	Oxygen flow rate (L/min)	Jet-to-substrate distance (mm)
I	50	0.1	2
II	10	0.2	4
III	2	0.3	6

**TABLE III**  
**Experimental Arrangement**

Test run	Treatment speed (mm/s)	Oxygen flow rate (L/min)	Jet-to-substrate distance (mm)
1	50	0.1	2
2	50	0.2	4
3	50	0.3	6
4	10	0.1	4
5	10	0.2	6
6	10	0.3	2
7	2	0.1	6
8	2	0.2	2
9	2	0.3	4

5% BTCA, 10% SHP, and 0.1% TiO<sub>2</sub>; and (3) 5% BTCA, 10% SHP, and 0.2% TiO<sub>2</sub>.

#### BTCA two-bath pad-dry-cure treatment

The cotton fabrics were treated with crosslinking agents under three different conditions with various amount of BTCA, SHP, and TiO<sub>2</sub>, that is, (1) 5% BTCA and 10% SHP; (2) 5% BTCA, 10% SHP, and 0.1% TiO<sub>2</sub>; and (3) 5% BTCA, 10% SHP, and 0.2% TiO<sub>2</sub>. A two-bath method was used to apply the different BTCA treatment systems. In the first bath, the fabrics were dipped and padded with 5% BTCA in the presence of 10% SHP until a wet pickup of 80% was achieved at 25°C. The fabrics were then dried at 85°C for 5 min. In the second bath, the dipping and padding processes were performed again with a TiO<sub>2</sub> solution, which was dispersed in 10% Matexil DN-VL (dispersing agent). Subsequently, the second-bath padded fabrics were dried at 85°C for 5 min and were then cured at 170°C for 2 min. Finally, the fabrics were conditioned at 21 ± 1°C and 65 ± 5% RH for 24 h before any treatment.

#### Wrinkle-resistance properties

The wrinkle-recovery angle (WRA) was tested according to AATCC test method 66-2003 to evaluate the wrinkle-resistance properties of the cotton fabrics. WRA in both the warp and weft directions and for six specimens in each direction were tested. The average WRA value was calculated on the basis of the 12 readings within a tolerance of 5%.

#### Scanning electron microscopy (SEM)

The surface morphology of cotton fabrics was examined with a JEOL JSM-6490 scanning electron microscope (Tokyo, Japan) with an accelerating voltage of 20 kV and a current of 10 μA at a high magnification power up to 4000×.

#### Grab test

The tensile properties were measured in accordance with the ASTM D 5034-95 standard with a constant rate of extension Instron 4411 tensile testing machine (New Jersey, USA).

#### Elmendorf tearing test

The tearing strength was measured with an Elmendorf tearing tester manufactured by the Thwing-Albert Instrument Co. (New Jersey, USA), according to ASTM D 1424-96.

## RESULTS AND DISCUSSION

#### Optimum conditions for the plasma pretreatment on the wrinkle properties of the cotton fibers

The optimum plasma pretreatment conditions for each BTCA treatment were investigated with the L<sub>9</sub>(3)<sup>3</sup> OATS technique. On the basis of the technique, nine test runs were generated by the combination of the chosen parameters and the levels of each parameter, as shown in Tables II and III. Three variables, namely, the treatment speed, oxygen flow rate, and jet-to-substrate distance, were studied in the plasma pretreatment process, and three levels were set for each variable, as presented in Tables IV–VI, for optimization.

Table VII shows that the WRA results of the plasma-pretreated cotton fabrics continuously increased from 65.7 up to 70.0% compared to the untreated cotton fabric. However, the WRA results of samples without plasma pretreatment were only increased slightly, from 52.2 to 61.3% compared with the untreated cotton fabric. This was because the plasma pretreatment had some unique features that enhanced the wrinkle resistance of the cotton fibers. The plasma could remove organic contamination from the fiber surface and could, thus, prevent the interference of bonding between the fibers and BTCA. The formation of chemical functional groups by a plasma process led to acid–base interactions and covalent linkages with the crosslinking agent BTCA; this resulted in an improvement of the adhesion between the fiber and the crosslinking agent. The etching effect of plasma reduced weak boundary layers and increased the surface area to allow more chemicals to be attached. Moreover, the micro-roughness of the fiber surface increased friction forces, and thus, the wrinkle recovery increased obviously after the plasma pretreatment. The plasma pretreatment, which used helium as an inert gas, induce a higher cohesive strength by the formation of a thin crosslinking layer, which stabilized the surface mechanically and against the diffusion of low-molecular-weight species to the interface. Therefore,

**TABLE IV**  
**Orthogonal Table for Optimization of the Plasma Pretreatment Followed by Treatment with 5% BTCA and 10% SHP**

Test run	Parameter				WRA (°)
	Treatment speed (mm/s)	Oxygen flow rate (L/min)	Jet-to-substrate distance (mm)		
1	50	0.1	2		106.4
2	50	0.2	4		107.1
3	50	0.3	6		104.2
4	10	0.1	4		112.4
5	10	0.2	6		110.5
6	10	0.3	2		111.4
7	2	0.1	6		106.8
8	2	0.2	2		107.6
9	2	0.3	4		106.3
$\sum$ WRA (°)					
$\sum$ I	317.7	<b>325.6</b>	325.4		
$\sum$ II	<b>334.3</b>	325.2	<b>325.8</b>		
$\sum$ III	320.7	321.9	321.5		
Difference <sup>a</sup>	16.6	3.7	4.3		

<sup>a</sup> The dominant factors were in the following order: Treatment speed > Jet-to-substrate distance > Oxygen flow rate.

Numbers in bold exhibit the greatest value among all of the values shown in the levels of the different factors used, and numbers in italic show the level of importance of each factor.

plasma pretreatment improved the wrinkle resistance of the cotton fabrics.

When only 5% BTCA and 10% SHP were used, WRA increased significantly to 52.2%. This was because the catalyst SHP accelerated the formation of anhydride intermediates, which in turn, esterified cotton cellulose. However, there were several disadvantages of the use of SHP as catalyst. It had a high possibility of causing shade changes in the dyed fab-

rics. In addition, the use of phosphorus compounds in textile finishing raises environmental concerns. When phosphorous compounds are discharged into streams and lakes, they may serve as nutrients and accelerate the growth of algae. To reduce the disadvantages of using a phosphorous compound, some researches have carried out studies to investigate the probability of decreasing the amount of SHP by using TiO<sub>2</sub> as a cocatalyst.

**TABLE V**  
**Orthogonal Table for the Optimization of the Plasma Pretreatment Followed by Treatment with 5% BTCA, 10% SHP, and 0.1% TiO<sub>2</sub>**

Test run	Parameter				WRA (°)
	Treatment speed (mm/s)	Oxygen flow rate (L/min)	Jet-to-substrate distance (mm)		
1	50	0.1	2		107.6
2	50	0.2	4		108.3
3	50	0.3	6		105.4
4	10	0.1	4		113.7
5	10	0.2	6		111.8
6	10	0.3	2		112.7
7	2	0.1	6		108.0
8	2	0.2	2		108.8
9	2	0.3	4		107.5
$\sum$ WRA (°)					
$\sum$ I	321.3	<b>329.3</b>	329.0		
$\sum$ II	<b>338.2</b>	328.9	<b>329.5</b>		
$\sum$ III	324.3	325.6	325.3		
Difference <sup>a</sup>	16.9	3.7	4.2		

<sup>a</sup> The dominant factors were in the following order: Treatment speed > Jet-to-substrate distance > Oxygen flow rate.

Numbers in bold exhibit the greatest value among all of the values shown in the levels of the different factors used, and numbers in italic show the level of importance of each factor.

**TABLE VI**  
**Orthogonal Table for the Optimization of the Plasma Pretreatment Followed by Treatment with 5% BTCA, 10% SHP, and 0.2% TiO<sub>2</sub> Treatment**

Test run	Parameter			WRA (°)
	Treatment speed (mm/s)	Oxygen flow rate (L/min)	Jet-to-substrate distance (mm)	
1	50	0.1	2	109.1
2	50	0.2	4	109.8
3	50	0.3	6	106.9
4	10	0.1	4	115.3
5	10	0.2	6	113.4
6	10	0.3	2	114.3
7	2	0.1	6	109.5
8	2	0.2	2	110.3
9	2	0.3	4	109.0
∑ WRA (°)				
∑ I	325.8	<b>333.9</b>	333.7	
∑ II	<b>343.0</b>	333.5	<b>334.1</b>	
∑ III	328.8	330.2	329.8	
Difference <sup>a</sup>	17.2	3.7	4.3	

<sup>a</sup> The dominant factors were in the following order: Treatment speed > Jet-to-substrate distance > Oxygen flow rate.

Numbers in bold exhibit the greatest value among all of the values shown in the levels of the different factors used, and numbers in italic show the level of importance of each factor.

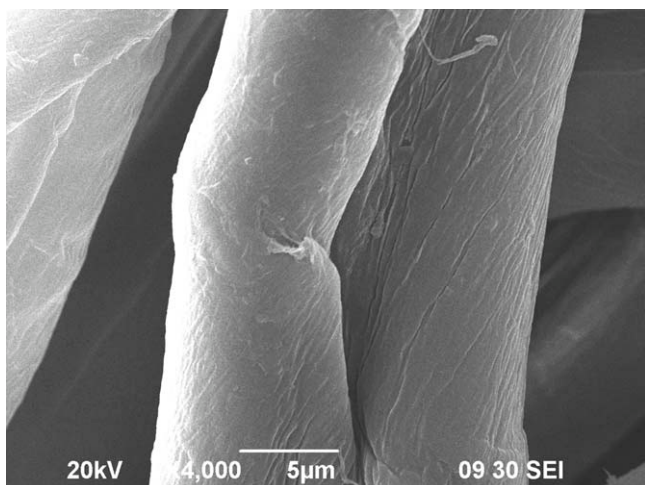
As shown in Table VII, 5% BTCA in the presence of 10% SHP and 0.1% TiO<sub>2</sub> (as a cocatalyst) was used, and the addition of TiO<sub>2</sub> as a cocatalyst further increased WRA by 58.5%. This was because both TiO<sub>2</sub> and SHP accelerated the catalytic reaction through the formation of ester bonds between the cyclic anhydride ring and the hydroxyl group of cellulose. The improvement of WRA by the addition of TiO<sub>2</sub> in the BTCA treatment was probably due to the unique photocatalytic properties of TiO<sub>2</sub>, which is a kind of N-type semiconductor. The hydroxyl radical ( $\cdot\text{OH}$ ) and superoxide anion ( $\cdot\text{O}_2^-$ ) formed may have acted as catalysts to accelerate the formation of anhydrides from poly(carboxylic acid)s. Furthermore, the effect of hydroxyl radical ( $\cdot\text{OH}$ ) and superoxide anion ( $\cdot\text{O}_2^-$ ) on the increase of the charge localization of the solid cellulose medium in which the esterification and crosslinking occurred may have also been significant. Therefore, the WRA results of the cotton fiber treated with 5% BTCA, 10% SHP, and 0.2% TiO<sub>2</sub> further increased 61.3%

compared with those of the untreated cotton fabric. The increment was proportional to the increased amount of TiO<sub>2</sub> from 0.1 to 0.2% in the BTCA treatment bath.

As shown in Table VII, there was an increasing trend after BTCA treatment in the presence of SHP (catalyst) and TiO<sub>2</sub> (cocatalyst). The WRA results of the plasma-pretreated fabrics further improved compared with those of the untreated fabrics. This confirmed that the plasma treatment with a 10 mm/s speed, a 0.1 L/min oxygen flow rate, and a 4-mm jet-to-substrate distance was the most effective method for improving the wrinkle-resistance properties of the BTCA-treated fabric in the presence of SHP. Moreover, the results shown in Table VII demonstrate clearly that cotton fabrics with plasma pretreatment in the optimum conditions followed by BTCA treatments had the largest WRA values when compared with those shown in Tables IV, V, and VI, respectively. Therefore, we concluded that the plasma pretreatment was an effective pretreatment

**TABLE VII**  
**Optimized Plasma Pretreatment Conditions Subjected to Different BTCA Treatment Systems**

BTCA treatment system	Treatment speed (mm/s)	Oxygen flow rate (L/min)	Jet-to-substrate distance (mm)	Dominating factor	WRA of the untreated fabric (°)	WRA of plasma-pretreated fabric (°)
0% BTCA	–	–	–	–	67.8	–
0% BTCA	10	0.1	4	–	–	71.9
5% BTCA and 10% SHP	10	0.1	4	Treatment speed	103.2	112.4
5% BTCA, 10% SHP, and 0.1% TiO <sub>2</sub>	10	0.1	4	Treatment speed	107.5	113.7
5% BTCA, 10% SHP, and 0.2% TiO <sub>2</sub>	10	0.1	4	Treatment speed	109.4	115.3

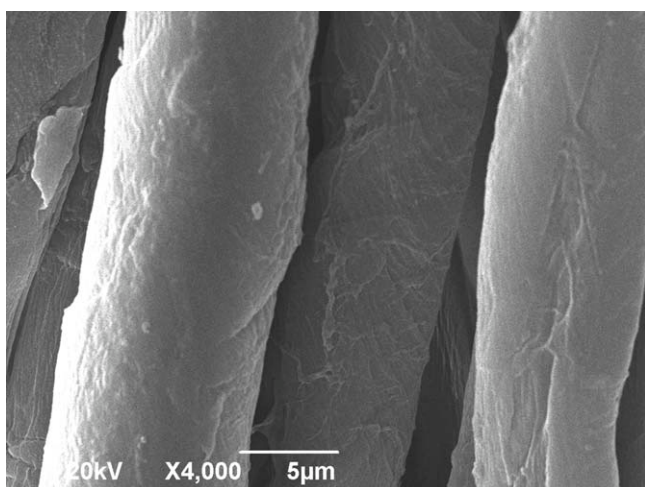


**Figure 2** Control cotton fiber.

for enhancing wrinkle-resistance properties of the cotton fibers treated with different BTCA treatments.

#### Effect of the plasma pretreatment parameters

The treatment speed controlled the extent of material surface modification, and the optimum conditions prevented damage to the materials. The slow treatment speed might have provided sufficient time for the high concentration of active species generated from the plasma jet to accumulate on the fabric surface and cause an etching effect to alter the material surface or interior characteristics. Tables IV–VI show that a speed of 10 mm/s was the best treatment speed and provided enough time for the substrate to be bombarded by the concentrated active species produced in plasma gases, which enhanced WRA and minimized fiber damage. A high oxygen flow rate carried a high concentration of active species in the plasma jet and caused a relatively severe etching effect to alter the material surface characteristics.

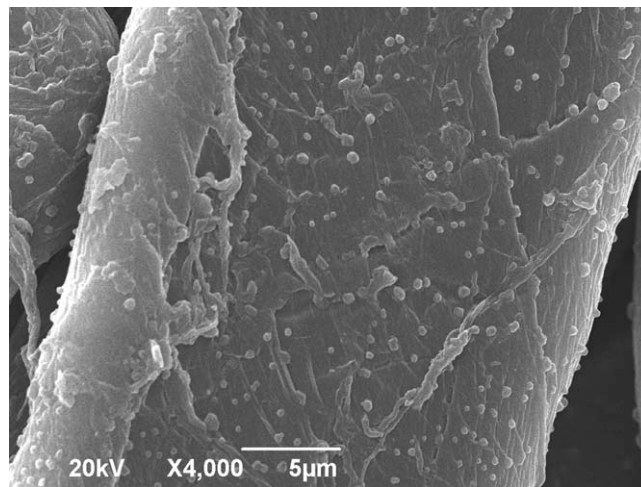


**Figure 3** Plasma-pretreated cotton fiber.

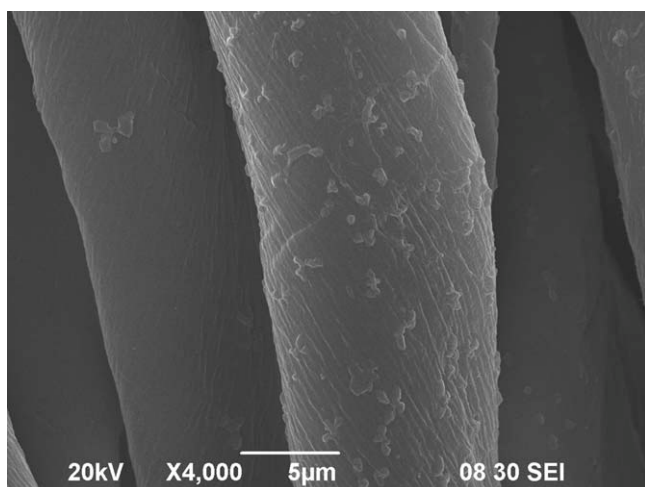
When the plasma-treated fabrics were subjected to the 5% BTCA treatment in the presence of 10% SHP, the treatment required a 0.1 L/min oxygen flow rate to maximize the potency of the treatment to contribute a better WRA. When the cocatalyst  $\text{TiO}_2$  was added in the treatment, a 0.1 L/min oxygen flow rate was sufficient to roughen the fabric surface and allow  $\text{TiO}_2$  particles to fill up the etched surface. The particles probably restricted the molecular movement of cellulose. In addition, the optimum jet-to-substrate distances for the different BTCA treatments were dissimilar. From the OATS technique results, we concluded that distance was another dominant factor in addition to treatment speed. When the distance between the plasma jet nozzle and fabric surface was too small, the flow of the gas from the nozzle was almost blocked by the fabric, and the gas could only be bounced off the surface and fly out in more parallel to the fabric surface direction, which greatly reduced the effectiveness of the treatment. However, when the distance reached 6 mm, the velocity and activity of the active species in the plasma greatly decreased when it reached the fabric surface, and thus, no effective plasma pretreatment occurred. Therefore, 4 mm was an acceptable range for the plasma gas flow on the fabric surface in this study.

#### Surface morphology

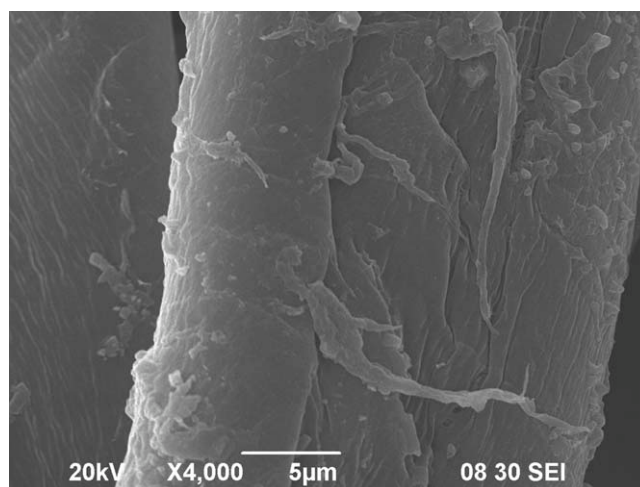
Figures 2 and 3 show the SEM images of untreated and plasma-pretreated cotton fibers, respectively. Cracks and voids were formed on the fiber surfaces. Surface roughness changes induced by etching were evident after the plasma pretreatment. The influence of the crosslinking of different BTCA treatments on the cotton surface was also investigated with SEM, and the results are shown in Figures 4–6. Carboxylic acid groups in BTCA possibly acted as functional



**Figure 4** Plasma-pretreated cotton fabric with 5% BTCA and 10% SHP.



**Figure 5** Plasma-pretreated cotton fabric with 5% BTCA, 10% SHP, and 0.1% TiO<sub>2</sub>.



**Figure 6** Plasma-pretreated cotton fabric with 5% BTCA, 10% SHP, and 0.2% TiO<sub>2</sub>.

groups of the crosslinking reaction in the presence of a catalyst (SHP) and cocatalyst (TiO<sub>2</sub>), and the crosslinking reaction for the various acids in the presence of a catalyst may particularly have been a condensation reaction that caused the deposition of the crosslinking agent in or on the treated fibers. Figures 4–6 show that crosslinking might have played an important role in improving the wrinkle-resistance properties of the cotton fiber. The surface of the fibers treated with the highest concentration of BTCA, SHP, and TiO<sub>2</sub> had a greater crosslinked area and a higher deposition of crosslinking agent. As shown in Figure 6, the cotton fibers were coated with the resin matrix with a cylindrical fiber and faceted fiber adjacent, whereas the surface of the untreated fiber (Fig. 2) was clean and did not have a crosslinked area or deposition of the crosslinking agent. As a result, the plasma pretreatment with a 10 mm/s speed, a 0.1 L/min oxygen flow rate, and a 4-mm jet-to-substrate was the most effective method for improving the wrinkle-resistance properties of the BTCA-treated fabric in the presence of SHP. The plasma pretreatment created not only microroughness on the surface of the cotton fabrics,

which resulted in better mechanical interlocking of the fiber surface to BTCA, but also functional groups, which led to chemical interfacial bonding between the fiber and crosslinking agent.

### Mechanical strength

Table VIII shows the tensile strength and tearing strength of the untreated and plasma-pretreated cotton fabrics subjected to different wrinkle-resistance formulations. The results show that the tensile and tearing strengths of the control sample were 315.01 N and 917.6 gf, respectively. Once the fabrics were treated by atmospheric plasma gas (optimum conditions of 10 mm/s speed, 0.1 L/min oxygen flow rate, and 4 mm jet-to-substrate distance), the mechanical strength of the specimens increased slightly, that is, 5.84% for the tensile strength and 4.25% for the tearing strength, as shown in Table VIII. The enhancement of the mechanical strength was attributed to the fact that the plasma treatment roughened the fabric surface and resulted in the enhancement of interyarn and interfiber friction; this led to the development of a larger cohesive force during the

**TABLE VIII**  
Tensile and Tearing Strengths of the Plasma-Pretreated Cotton Subjected to Different BTCA Treatment Systems

BTCA treatment system	Plasma treatment			Tensile strength (N)		Tearing strength (gf)	
	Treatment speed (mm/s)	Oxygen flow rate (L/min)	Jet-to-substrate distance (mm)	Untreated fabric	Plasma-pretreated fabric	Untreated fabric	Plasma-pretreated fabric
0% BTCA	10	0.1	4	315.013	333.413	917.6	956.6
5% BTCA and 10% SHP	10	0.1	4	196.750	194.000	453.8	483.1
5% BTCA, 10% SHP, and 0.1% TiO <sub>2</sub>	10	0.1	4	190.988	197.838	540.6	561.3
5% BTCA, 10% SHP, and 0.2% TiO <sub>2</sub>	10	0.1	4	185.550	199.375	529.1	561.1

application of tensile stress and tearing force. Hence, a larger amount of energy was required to extend and tear the fabrics.

Table VIII shows obviously that the tensile and tearing strengths of the cotton specimens treated with BTCA in the presence of SHP dropped to a great extent. This was due to the fact that BTCA depolymerized cellulose and increased the brittleness of the cotton fibers at high temperatures curing with low pH, that is, pH 1–2. The addition of TiO<sub>2</sub> had no significant effect on the tensile strength of the test specimens; however, the cocatalyst slightly increased the tearing strength of the test specimens. This was due to the resulting increased yarn friction, which helped increase the yarn slippage resistance. In comparison with the samples treated with wrinkle-resistance agents, the tensile and tearing strengths of the plasma-treated fabrics subjected to the wrinkle-resistance treatment increased slightly, as shown in Table VIII. The reduction of the mechanical strength was attributed to the strong acidity of the finishing bath, which tendered the fabric strength. However, the negative effect was compensated by the plasma treatment.

### CONCLUSIONS

The wrinkle-resistance process is very important and inevitable for cotton fabrics because of their high wrinkling tendency. Moreover, plasma pretreatment for the modification of cotton fabrics has obvious high industrial application potential, as it is an environmentally friendly dry process that does not involve any of the solvents and reagents for the wet chemical process. The process itself improved the wrinkle-recovery ability of the fabric slightly. In this study, the optimization of the plasma pretreatment was investigated with OATS. The results show that the plasma pretreatment with a 10 mm/s speed, a 0.1 L/min oxygen flow rate, and a 4 mm jet-to-substrate distance was the most effective method for

improving the wrinkle-resistance properties of the BTCA-treated fabric, in which treatment speed was the dominant factor followed by the jet-to-substrate distance and the oxygen flow rate. SEM images confirmed that such plasma pretreatment conditions imparted the best crosslinking effects on the cotton fibers. In addition, the wrinkle-resistance-treated cotton specimens had a lower tensile strength and tearing strength compared to the control sample; this resulted from side effects of the crosslinking agent used, whereas the plasma pretreatment and cocatalyst may have compensated for the reduction in the mechanical strength caused by the wrinkle-resistance agents.

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