

# Optimization of Cotton Crosslinking with Polycarboxylic Acids and Nano TiO<sub>2</sub> Using Central Composite Design

A. Nazari,<sup>1</sup> M. Montazer,<sup>2</sup> A. Rashidi,<sup>1</sup> M. Yazdanshenas,<sup>3</sup> M. B. Moghadam<sup>4</sup>

<sup>1</sup>Department of Textile Engineering (Center of Excellence in Textile), Science and Research Branch, Islamic Azad University, Tehran, Iran

<sup>2</sup>Department of Textile Engineering, Amirkabir University of Technology (Tehran Polytechnic), Tehran, Iran

<sup>3</sup>Department of Textile Engineering, Yazd Branch, Islamic Azad University, Yazd, Iran

<sup>4</sup>Department of Statistics, Allameh Tabataba'i University, Tehran, Iran

Received 6 May 2009; accepted 11 September 2009

DOI 10.1002/app.31470

Published online 27 April 2010 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** The cotton crosslinking with butane tetra carboxylic acid (BTCA) and citric acid (CA) in the presence of sodium hypophosphite (SHP) and nano TiO<sub>2</sub> (NTO) under different curing conditions were optimized using a statistical model. The central composite design (CCD) was used for variables based on Design of Expert software. The appropriate model to create optimum crease recovery angle was obtained for each condition. The X-ray

diffraction (XRD) and scanning electron microscopy (SEM) were also employed to indicate the NTO particles on the fabric surface with the size of nano particles and their crystallinity. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 2740–2748, 2010

**Key words:** crosslinking; polycarboxylic acid; nano TiO<sub>2</sub>; cotton fabric; UV irradiation; CCD

## INTRODUCTION

There is a growing demand for application of nanotechnology in textiles. The use of nano titanium dioxide for finishing textiles and producing new properties has been expanded recent years. This is because of their ability to absorb ultraviolet irradiation and act as photo catalyst. Furthermore, nano TiO<sub>2</sub> particles on the fabric surfaces will not affect their breathability or handle.<sup>1–9</sup> Various methods can be used to apply finishing materials on fabrics, including spraying, transfer printing, foaming, and padding among which padding is the most commonly used.<sup>10–17</sup>

At the same time, various poly-carboxylic acids were investigated as free-formaldehyde crosslinkers for durable press finishing of cotton.<sup>18–23</sup> The formation of ester linkages, free formaldehyde, improved tensile, and abrasion strength is the advantage of these compounds.<sup>24–27</sup> Polycarboxylic acids such as citric acid and 1,2,3,4-butane tetra carboxylic acid are cotton crosslinking agents that are environment friendly and can be suitable substitutes for methylols which contain crosslinkers.<sup>28–32</sup>

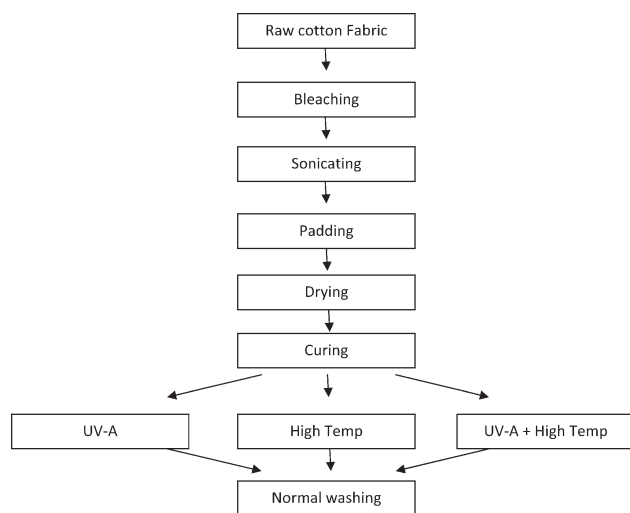
Using nano TiO<sub>2</sub> as photo catalyst to improve the crease recovery properties of the silk fabrics

was reported.<sup>33</sup> Chyung-chhyung wang and his colleagues used four different carboxylic acids, namely, butanetetracarboxylic acid (BTCA), maleic acid (MA), succinic acid (SUA), and citric acid (CA) as crosslinking agents to treat cotton fabrics in the presence of nanometer titanium dioxide as a catalyst under UV irradiation. They reported that the dry crease recovery angle (DCRA) and wet crease recovery angle (WCRA) values of the treated fabrics were decreased from BTCA to MA and CA and SUA, respectively, and the tensile strength retention values were increased from BTCA to MA and CA and SUA, respectively, at the same conditions. They also showed that the values of DCRA, WCRA for the various mixed catalysts were ZrO<sub>2</sub>/TiO<sub>2</sub> < SiO<sub>2</sub> < TiO<sub>2</sub> < Ag/TiO<sub>2</sub>.<sup>34</sup>

Cheng-chi Chen and his colleagues used succinic acid crosslinking agents in the presence of nanometer TiO<sub>2</sub> catalyst under the irradiation of UV to study the crosslinking reaction and the photo-reduction of succinic acid. They showed that a carboxylic acid group of succinic acid can be photoreduced to form the aldehyde group. They also suggested that the crosslinking reactions can occur between an aldehyde group of succinic acid and a hydroxyl group of cellulose. The same reaction can happen between free radicals of succinic acid and those of cellulose.<sup>35</sup>

Majid Montazer and colleagues suggested the results of the study on the subject of simultaneous X-linking and antimicrobial finishes on cotton fabrics. They used chitosan and *N*-(2-hydroxy) propyl-3-trimethyl ammonium chitosan chloride (HTCC)

Correspondence to: M. Montazer (tex5mm@aut.ac.ir).



**Figure 1** The process of cotton treatment with BTCA and CA under different curing methods.

with three crosslinking agents including CA, BTCA, and glutaraldehyde (GA). They reported that the durability of the HTCC-treated fabric improved by adding any of the three crosslinking agents. They also indicated that crosslinking agents GA, BTCA, and CA enhance the crease resistance properties of cotton fabrics. This leads to producing a durable antimicrobial fabric using chitosan and HTCC and also a permanent crease resistant on the cotton fabric.<sup>36</sup>

Jaewoong Lee and colleagues used *m*-amino-phenyl hydantoin (*m*-APH) and acid crosslinking agents for durable press and antimicrobial finishes on cotton fabrics. They indicated that in a single finishing process, the BTCA/*m*-APH treatment produced cotton fabrics with crease resistance as well as antimicrobial properties.<sup>37</sup>

Recently, Montazer et al.<sup>38</sup> reported the use of central composite design for experimental plan to opti-

**TABLE I**  
Range of Variables

Variable	Lower limit	Upper limit
CA concentration (g/L)	50.96	99.04
BTCA concentration (g/L)	50.96	99.04
Nano TiO <sub>2</sub> (%)	0.12	5.02
Curing method	UV, High temp, UV-Temp	

mize dyeing of wool with madder and liposomes, and also modification of wool surface by liposomes in dyeing with weld.<sup>39</sup>

In this study, the resistance of bleached cotton fabric against creasing was optimized by using nano TiO<sub>2</sub>, sodium hypophosphite and two different polycarboxylic acids, namely, CA and BTCA. To this end, three various conditions including UV, High temp, and UV-Temp were used. The best treatment conditions for X-linking of CA and BTCA agents will be subsequently discussed.

## EXPERIMENTAL

### Material

BTCA and CA, sodium hydroxide and sodium hypophosphite (SHP) were supplied by Merck Chemical Co., Germany. Nonionic detergent (Rucogen DEN) composed of fatty alcohol ethoxylate from Rudolf Chemie Co., (Tehran, Iran). Nano titanium dioxide was employed as the photo catalyst with the anatase crystalline structure and average particle size of 21 nm from Degussa Chemie Co., Duisburg, Germany. The desized, scoured, and bleached plain weave 100% cotton fabric was used with wrap density 32 yarn/cm, weft density 30 yarn/cm, and fabric weight of 118 g/m<sup>2</sup>.

**TABLE II**  
Central Composite Design for Crosslinking Cotton Fabric with CA- and BTCA-Cured with UV

Run number	A: CA (g/L)	B: Nano TiO <sub>2</sub> (%)	X: CRA (W + F)	Run number	D: BTCA (g/L)	E: Nano TiO <sub>2</sub> (%)	Y: CRA (W + F)
1-CA	58	4.3	209	1-BTCA	75	2.57	225
2-CA	75	2.57	192.5	2-BTCA	92	0.84	198
3-CA	99.04	2.57	213	3-BTCA	75	2.57	227.5
4-CA	75	2.57	197.5	4-BTCA	75	2.57	215
5-CA	75	5.02	178	5-BTCA	50.96	2.57	213
6-CA	75	0.12	188	6-BTCA	75	5.02	202.5
7-CA	92	0.84	206	7-BTCA	75	2.57	222
8-CA	75	2.57	176	8-BTCA	92	4.3	234
9-CA	75	2.57	215	9-BTCA	75	0.12	220
10-CA	75	2.57	182	10-BTCA	58	0.84	219.5
11-CA	50.96	2.57	185	11-BTCA	75	2.57	225.5
12-CA	58	0.84	189	12-BTCA	58	4.3	233.5
13-CA	92	4.3	210	13-BTCA	99.04	2.57	238

**TABLE III**  
**Central Composite Design for Crosslinking Cotton Fabric with CA- and BTCA-Cured at High Temperature**

Run number	A: CA (g/L)	B: Nano TiO <sub>2</sub> (%)	X: CRA (W + F)	Run number	D: BTCA (g/L)	E: Nano TiO <sub>2</sub> (%)	Y: CRA (W + F)
14-CA	75	2.57	210	14-BTCA	58	4.3	196
15-CA	75	2.57	189	15-BTCA	99.04	2.57	234
16-CA	75	0.12	193	16-BTCA	50.96	2.57	214.5
17-CA	92	4.3	171	17-BTCA	75	0.12	222
18-CA	58	4.3	184	18-BTCA	92	4.3	221.5
19-CA	92	0.84	210	19-BTCA	75	2.57	217
20-CA	58	0.84	206	20-BTCA	75	2.57	217
21-CA	75	2.57	205.5	21-BTCA	58	0.84	217
22-CA	75	2.57	195.5	22-BTCA	75	2.57	250.5
23-CA	75	5.02	192	23-BTCA	92	0.84	233
24-CA	50.96	2.57	194	24-BTCA	75	2.57	220.5
25-CA	75	2.57	196	25-BTCA	75	2.57	219
26-CA	99.04	2.57	207	26-BTCA	75	5.02	220.5

### Instrument

Finishing compounds were prepared and dispersed using an ultrasonic bath (200 V, 50 W, 40 KHz). Thermal oven was used to dry and cure the samples. Some treated samples were exposed to the UV irradiation of an HPA 400S lamp (400W, Philips, Belgium). Scanning electron microscopic (SEM) observations on specimens of treated fabrics was carried out using an LEO 440i electron microscope (UK). An X-ray diffractometer Type 3003 PTS, SEIFERT, Germany ( $\lambda = 1.54060 \text{ \AA}$ , at 40 kV, and 30 mA) with Cu K $\alpha$  irradiation was used to identify the crystalline phase and also crystal size, using the Scherrer method.<sup>3</sup> The angular domain was 0–70° (2 $\theta$ ). The Scherrer equation is as follows:

$$D = \frac{K \lambda}{B \cos \theta} \quad (1)$$

where  $K$  was taken as 0.9 and  $B$  is the full width of the diffraction line at half of the maximum intensity.

### Method

The aqueous finishing dispersion was prepared by the mixtures of carboxylic acid crosslinking agents CA and BTCA and SHP with the amount of 60% CA or BTCA and nano TiO<sub>2</sub> (based on O.W.B) and required percentage of distilled water in ultrasonic bath for 15 min.

The cotton fabrics were padded with 90% wet pick up by freshly prepared aqueous solutions. Padded fabrics were dried at 60°C for 3 min to remove mobile water. The treated samples were cured with different conditions: UV (15 min UVA irradiation), High temp (150°C, 5 min for CA, and 180°C, 2 min for BTCA) and UV-Temp (UVA irradiation and high temperature). Then, the finished

**TABLE IV**  
**Central Composite Design for Crosslinking Cotton Fabric with CA- and BTCA-Cured at High Temperature and UV**

Run number	A: CA (g/L)	B: Nano TiO <sub>2</sub> (%)	X: CRA (W + F)	Run number	D: BTCA (g/L)	E: Nano TiO <sub>2</sub> (%)	Y: CRA (W + F)
27-CA	58	0.84	218.5	27-BTCA	75	2.57	240
28-CA	58	4.3	184.5	28-BTCA	75	2.57	244.5
29-CA	99.04	2.57	218	29-BTCA	92	0.84	250
30-CA	75	2.57	210	30-BTCA	75	2.57	229.5
31-CA	75	0.12	205	31-BTCA	75	2.57	245
32-CA	75	2.57	208.5	32-BTCA	75	5.02	207
33-CA	92	0.84	180	33-BTCA	99.04	2.57	245
34-CA	75	2.57	216.5	34-BTCA	75	2.57	234
35-CA	50.96	2.57	201	35-BTCA	75	0.12	232
36-CA	75	5.02	182	36-BTCA	50.96	2.57	216
37-CA	75	2.57	205	37-BTCA	92	4.3	237
38-CA	92	4.3	195.5	38-BTCA	58	4.3	221.5
39-CA	75	2.57	210	39-BTCA	58	0.84	213.5

TABLE V  
ANOVA for Response Surface Quadratic Model with CA

Source	Sum of squares	Df	Mean square	F Value	P-value Prob > F
Model	2350.27	11	213.66	1.43	0.2158
A[CA]	168.14	1	168.14	1.13	0.2980
B[Nano TiO <sub>2</sub> ]	447.06	1	447.06	2.99	0.0950
C[Curing]	398.17	2	199.08	1.33	0.2804
AB	22.69	1	22.69	0.15	0.6997
AC	259.06	2	129.53	0.87	0.4313
BC	377.49	2	188.75	1.26	0.2986
A <sup>2</sup>	38.39	1	38.39	0.26	0.6162
B <sup>2</sup>	588.53	1	588.53	3.94	0.0573
Residual	4030.90	27	149.29		
Lack of fit	2763.40	15	184.23	1.74	0.1684
Pure error	1267.50	12	105.63		
Cor total	6381.17	38			

samples were washed at 70°C for 30 min using a solution containing 2 g/L Na<sub>2</sub>CO<sub>3</sub> and 1 g/L non-ionic detergent (Rucogen DEN), and finally dried at ambient conditions. The process of treatment on cotton samples are shown in Figure 1.

Dry crease recovery angle (DCRA) of warp (w) plus filling (f) of the treated-cotton fabrics was evaluated using the AATCC test method 66–2003. Specimens were prepared in 40 × 15 mm swatches and 500 ± 5 g of weight was loaded on the folded specimens for 5 min ± 5 s. The recorded vertical angle guidelines were aligned and the recovery angles were measured.

### The experimental design

The central composite design used for experimental plan with four variables is shown in Table I. Four variables including the amounts of BTCA, CA, nano titanium dioxide, and different curing methods were studied. Theranges of these variables are shown in Table I. Details of the central composite design for crosslinking the bleached cotton fabric with CA and BTCA in the presence of nano TiO<sub>2</sub> are presented in Tables II–IV.

Also, the influence of the variable on the results Y (CRA) was adjusted using the following second order polynominal function:

$$Y = b_0 + \sum b_i X_i + \sum b_{ij} X_i X_j + \sum c_i X_i^2 \quad i \geq j$$

$$i, j = 1, 2, 3$$

In this equation,  $b_0$  is an independent term according to the mean value of the experimental plan,  $b_i$  are regression coefficients that explain the influence of the variables in their linear form,  $b_{ij}$  are regression coefficients of the interaction terms between variables, and  $c_i$  are the coefficients of quadratic form of variables.

## RESULTS AND DISCUSSION

### Physical properties

Tables II–IV lists the dry crease recovery angle (DCRA) of cotton fabrics treated with BTCA and CA under different conditions. Tables II–IV show the increase values of DCRA with increasing the concentration of the crosslinking agent. However, the increase of nano TiO<sub>2</sub> concentration increases the value of DCRA and further increase of the nano TiO<sub>2</sub> decreases the DCRA. This may be caused by the agglomeration on nano TiO<sub>2</sub> in the solution bath or on the fabric and/or inhibiting the action of the crosslinking agent on cotton under higher concentrations of nano TiO<sub>2</sub>. The results of Table II show that by using the given concentration of the crosslinking agent, nano TiO<sub>2</sub>, sodium hypophosphite, and curing condition, the values of DCRA with BTCA will be more than CA. This can be attributed to one

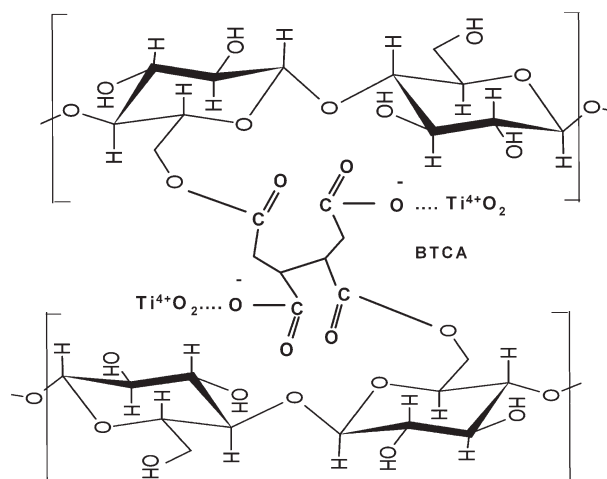


Figure 2 Formation of ester linkages between BTCA and cellulosic chains and electrostatic linkages between BTCA and NTO.

**TABLE VI**  
Different Models Obtained Using Various Curing Conditions on CA-Treated Fabric

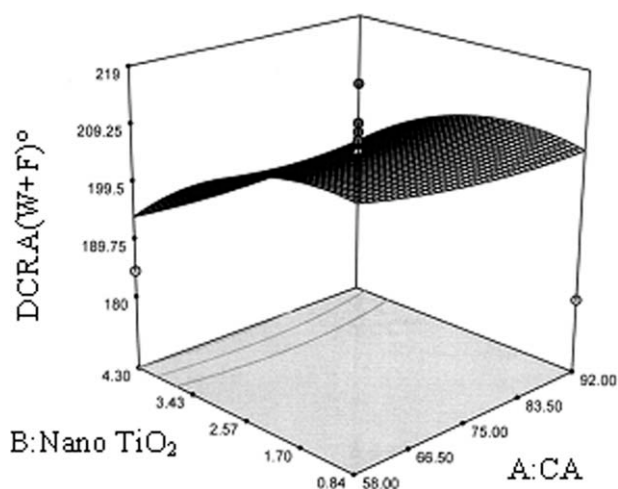
Curing	Model
UV	DCRA = +187.99061 -0.40058 × CA + 6.32591 × NTO + 0.046753 × CA × NTO + 4.69291E -003 × CA <sup>2</sup> -1.77434 × NTO <sup>2</sup>
High temp	DCRA = +228.92232 -0.75508 × CA + 1.10394 × NTO + 0.046753 × CA × NTO + 4.69291E -003 × CA <sup>2</sup> -1.77434 × NTO <sup>2</sup>
UV-Temp	DCRA = +240.15962 -0.84952 × CA + 1.92672 × NTO + 0.046753 × CA × NTO + 4.69291E -003 × CA <sup>2</sup> -1.77434 × NTO <sup>2</sup>

more carboxylic acid group of BTCA when compared with CA.

Three curing methods including UV irradiation (UV), high temperature (Temp), and the combination of these two methods (UV-Temp) have been used in this study. As shown in Tables II–IV, the order of decrease in DCRA for these three methods is as follows: UV-Temp > High temp > UV.

However, for high concentrations of both CA and BTCA (99.04 g/L), the order of decrease in DCRA is as follows: UV-Temp > UV > High temp.

It appears that in the UV-Temp curing method, both crosslinking mechanisms of cotton fabric based on UV and Temp occurred. As suggested by Welch using high temperature leads to the formation of intermediate anhydride cycles and ester linkages.<sup>18</sup> Furthermore, the crosslinking of cotton fabric through nano TiO<sub>2</sub> and UV irradiation were suggested by formation of aldehyde groups.<sup>35</sup> Therefore, compared with UV-Temp curing method, fabrics treated based on UV or High temp methods show lower DCRA. At the concentration of 99.04 g/L of both polycarboxylic acids, there is higher increase of the value of treated fabrics DCRA based on the UV method when compared with the high temp method. This can be due to the higher availability of polycarboxylic acids to react with particle sizes of nano TiO<sub>2</sub> and pairs of electrons and holes formed



**Figure 3** Design of expert plot for treated cotton with CA.

through UV irradiation. As shown in Tables II–IV, the increase of nano TiO<sub>2</sub> concentration helps improve the DCRA due to higher possibility of the crosslinking of cotton cellulose. However, the higher concentration of nano TiO<sub>2</sub> causes decrease of DCRA. This can be considered as a result of particles agglomeration of nano TiO<sub>2</sub> that is caused by the preventive effect for producing cross bonds via BTCA and CA in cellulose chains.

As shown in Table V, in similar conditions, samples treated with BTCA have higher DCRA when compared to those with CA. This is because BTCA with four carboxylic groups could form two cyclic anhydride intermediates at the same time. As a result, it was supposed that four carboxylic groups on BTCA allowed ester bonds more readily.<sup>37</sup>

Furthermore, crosslinking of cotton fabrics with 1,2,3,4-butanetetracarboxylic acid (BTCA) are effectively promoted by nano TiO<sub>2</sub> and sodium hypophosphite, BTCA can maintain NTO particles (Fig. 2). There is ionic interaction between carboxylate anionic groups related to polycarboxylic acid and NTO cation. This kind of interactions has been previously reported.<sup>40</sup>

**TABLE VII**  
ANOVA for Response Surface Quadratic Model with BTCA

Source	Sum of squares	Df	Mean square	F Value	P-value Prob > F
Model	2365.85	4	591.46	4.55	0.0047
D[BTCA]	1297.20	1	1297.20	9.99	0.0033
E[Nano TiO <sub>2</sub> ]	103.03	1	103.03	0.79	0.3794
F[curing]	965.63	2	482.81	3.72	0.0347
Residual	4416.24	34	129.89		
Lack of fit	3304.74	22	150.22	1.62	0.1941
Pure error	1111.50	12	92.62		
Cor total	6782.09	38			

TABLE VIII  
Different Models Obtained Using Various Curing  
Conditions on BTCA-Treated Fabric

Curing	Model
UV	DCRA = +191.68167 + 0.43246 × BTCA - 1.19763 × NTO
High temp	DCRA = +192.37398 + 0.43246 × BTCA - 1.19763 × NTO
UV-Temp	DCRA = +202.56629 + 0.43246 × BTCA - 1.19763 × NTO

### Statistical analysis

For treated samples with CA, the analysis of variance (ANOVA) is given in Table V. According to the ANOVA results, the fitted models of crease recovery angle by using CA are shown in Table VI.

Figure 3 shows the response surface of the model. By using the Design of Expert software, the optimum design point with desirability of 0.815 is for CA with concentration of 58(g/L), nano TiO<sub>2</sub> 1.31(%), and curing method of UV-Temp.

The analysis of variance (ANOVA) of treated cotton with BTCA is given in Table VII. According to the ANOVA results, the fitted models of DCRA using BTCA are shown in Table VIII.

Besides, Figure 4 shows the response surface of the model. By using the Design of Expert software, the optimum design point with desirability of 0.832 is about the BTCA concentration of 92(g/L), the nano TiO<sub>2</sub> concentration of 0.84(%), and the curing method of UV-Temp.

### Mechanism of crosslinking reaction in the presence of nano TiO<sub>2</sub>

From the predominant parameters on the experimental results shown in this article, the crosslinking

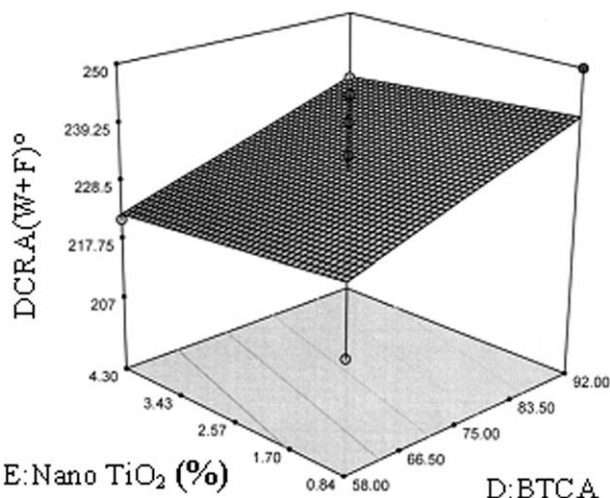


Figure 4 Design of expert plot for treated cotton with BTCA.

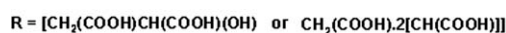
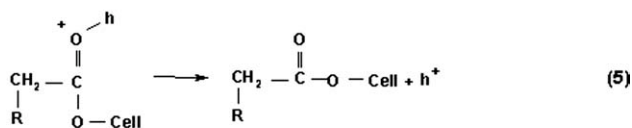
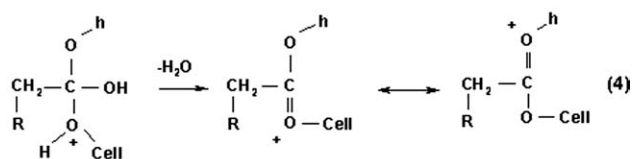
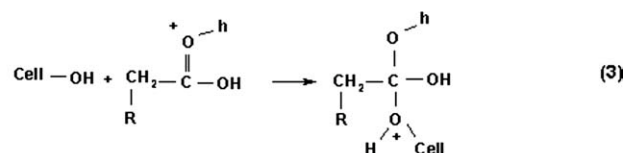
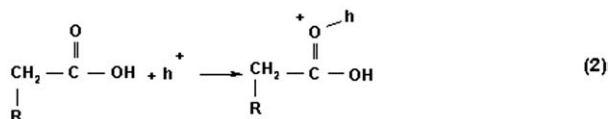


Figure 5 Mechanism of cellulose crosslinking with polycarboxylic acids using nano TiO<sub>2</sub> through proton attraction.

reactions of cotton fabric by CA and BTCA in the presence of nano TiO<sub>2</sub> under UV irradiation are indicated in Figures 5 and 6. The crosslinking mechanism of cellulose with polycarboxylic acids can be followed in the presence of proton and/or electron. The crosslinking mechanism of cotton through proton attraction is more likely. This is because of the

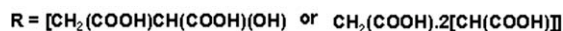
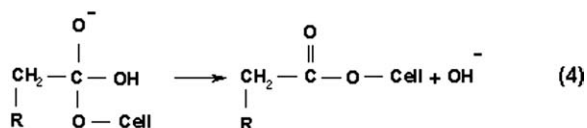
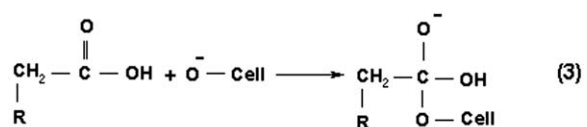
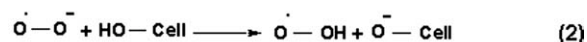


Figure 6 Mechanism of cellulose crosslinking with polycarboxylic acids using nano TiO<sub>2</sub> photo catalyst through electron attacks.

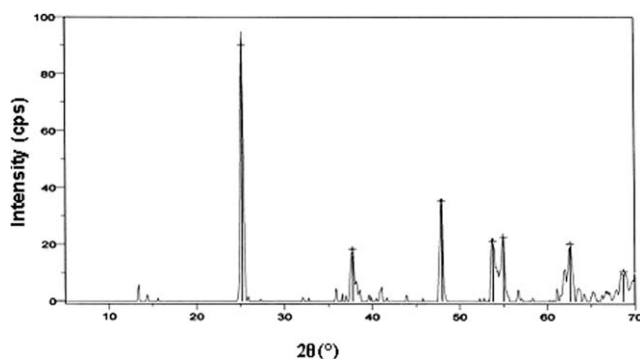


Figure 7 XRD pattern of pure nano TiO<sub>2</sub> powders.

inclination of oxygen in the carbonyl group to attract protons (h<sup>+</sup>). Polycarboxylic acid molecules absorbed on the surface of the nano TiO<sub>2</sub> particles are subjected to the reaction of photoreduction under UV irradiation. Therefore, as shown in Figure 5, first, the nano TiO<sub>2</sub> under ( $\lambda < 385$  nm) irradiation forms the pair of electron (e<sup>-</sup>) and hole (h<sup>+</sup>) [eq. (1)]. The hole has positive charge but polycarboxylic acids are electron donors; so, the h<sup>+</sup> activates the oxygen of the carbonyl group. This stage is eq. (2). In the next stage, the nucleophilic reaction occurs. Oxygen as a nucleophile portion of cellulose is attached to carbon with positive charge [eq. (3)]. The next stage is elimination. Here, the produced intermediate loses one water molecule. The resulting compound has two resonance forms [eq. (4)]. In the last stage, hole (h<sup>+</sup>) will separate from the product and lead to the ester linkage among carboxyl group and cellulose [eq. (5)] and the crosslinking of cellulose polymer chains is carried out.

The mechanism through electron attack can be suggested (Fig. 6) by the oxygen radical attack to hydroxyl groups of cellulose. This provides the nucleophilic need for reaction with carbonyl groups of polycarboxylic acids. The esterification of cellulose occurs and can be followed with other hydroxyl groups of cellulose and carbonyl groups of polycarboxylic acids.

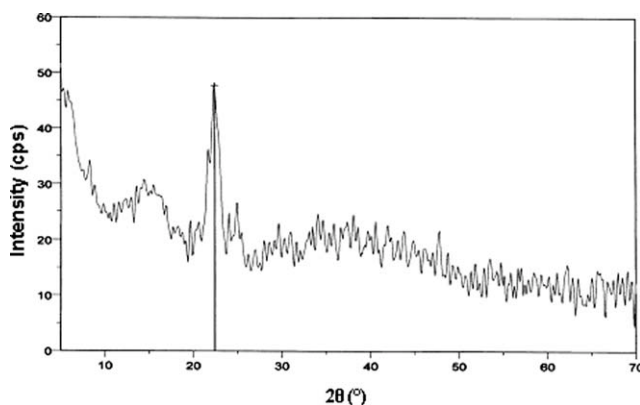


Figure 8 XRD pattern of bleached cotton fabric (2.57% nano TiO<sub>2</sub>, UV-Temp).

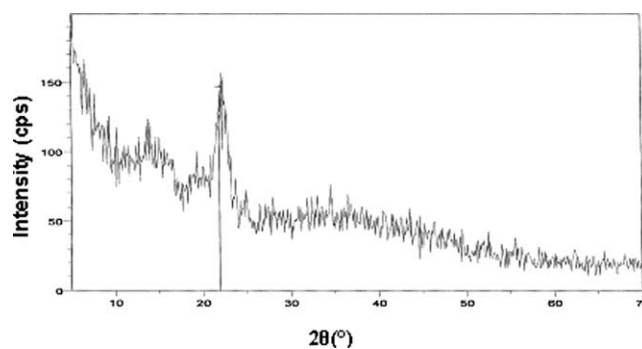


Figure 9 XRD pattern of sample 29-CA (50.96 g/L CA, 2.57% nano TiO<sub>2</sub>, UV-Temp).

### Characterization techniques

#### X-ray diffraction (XRD) analysis

The XRD patterns of pure nano TiO<sub>2</sub> (Fig. 7), TiO<sub>2</sub>-coated fabric (Fig. 8), and treated-cotton fabrics with polycarboxylic acids cured with UV-Temp condition (Figs. 9 and 10) are reported. It can be observed that the major peak of all spectrums is anatase ( $2\theta = 25.2^\circ$ ), whereas the peak related to rutile phase ( $2\theta = 27.5^\circ$ ) cannot be observed in XRD spectrums.<sup>4</sup> Therefore, the coated fabrics with nano TiO<sub>2</sub> particles have anatase crystallite phase and can effectively operate under UV irradiation. From full width at half maximum (FWHM) of the peak at  $25.2^\circ$  (0.3971) and using Scherrer's equation, the average crystal size of about 38.55 nm can be calculated.

#### SEM

Figure 11(a–f) illustrates the SEM of nano TiO<sub>2</sub> powder (a) (magnification = 1500 $\times$ ) and untreated cotton fabric (b), CA-treated fabric (c and d), BTCA-treated fabric (e and f) (magnification = 500 $\times$ ). Figure 11(b) shows the morphology of cotton fiber with smooth surface. The morphological changes in the appearance of cotton fibers treated with CA and

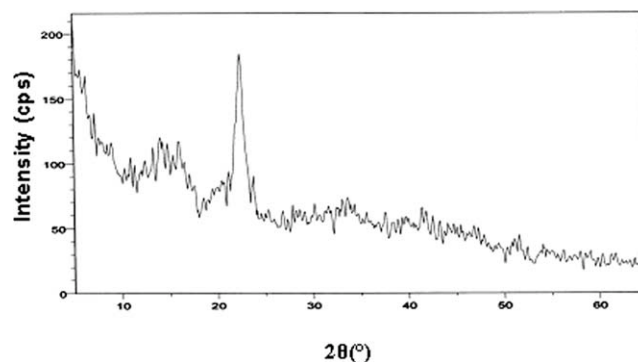
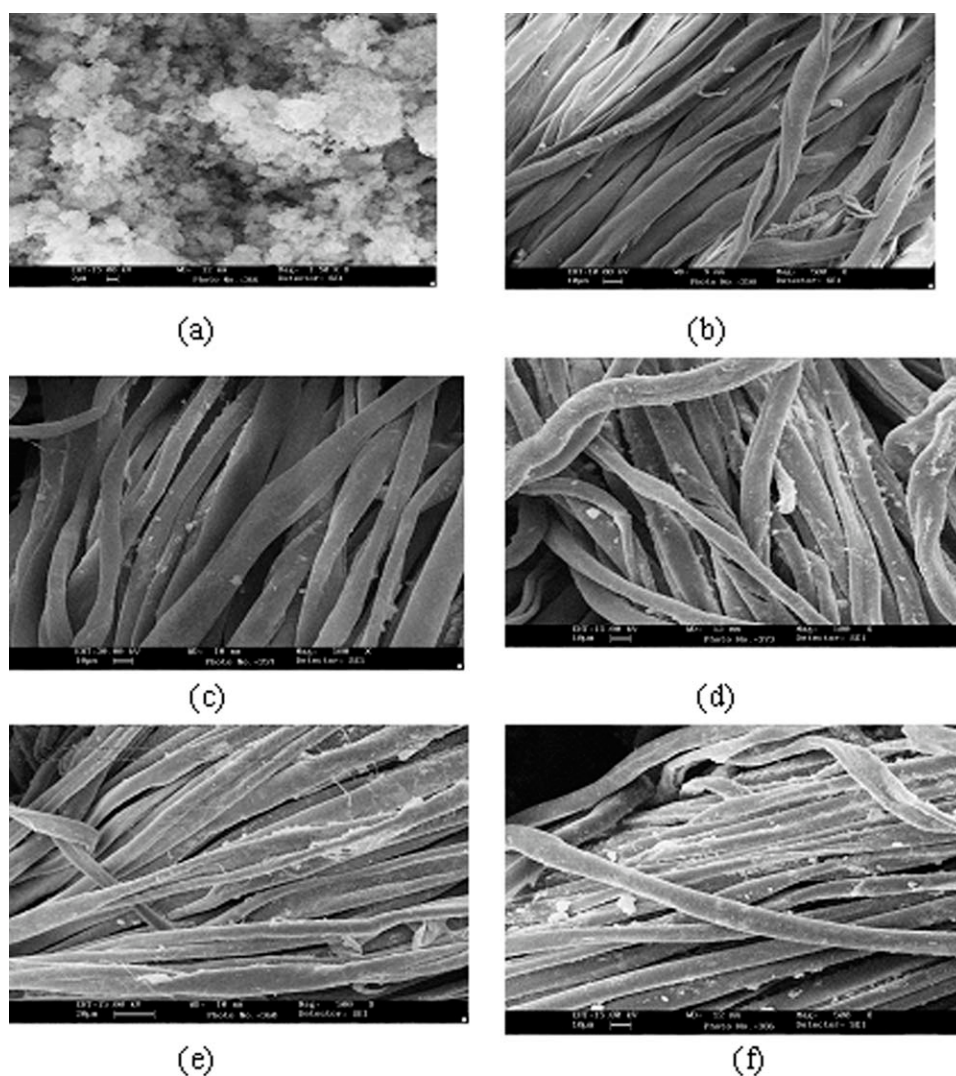


Figure 10 XRD pattern of sample 24-BTCA (50.96 g/L BTCA, 2.57% nano TiO<sub>2</sub>, UV-Temp).



**Figure 11** SEM images of the (a) nano  $\text{TiO}_2$  powder, (b) untreated cotton fabric, and (c) 50.96 g/L CA, (d) 99.04 g/L CA, (e) 50.96 g/L BTCA, (f) 99.04 g/L BTCA, treated-cotton fabrics in the presence of 2.57(%) nano  $\text{TiO}_2$  and UV-Temp curing method.

BTCA in the presence of nano  $\text{TiO}_2$  are shown after padding and UV-Temp curing [Fig. 11(c–f)]. These pictures show that, in the same condition, the surface of the treated BTCA has a higher number of nano  $\text{TiO}_2$  particles than CA. This may be because higher carboxylic acid groups of BTCA can maintain more particles of nano  $\text{TiO}_2$ . However, these images are proof of the fact that nano  $\text{TiO}_2$  particles were applied on cotton fabric by the padding process, but their distribution on fiber surface was not quite even, which has become possible because of the aggregation of some nano  $\text{TiO}_2$  particles.

### CONCLUSIONS

The purpose of this study was to optimize the cross-linking of cotton cellulose with polycarboxylic acids using a photocatalyst (nano  $\text{TiO}_2$ ) along with

conventional catalyst (sodium hypophosphite) by using a statistical model. As polycarboxylic acid CA and BTCA was employed that are environment friendly compounds without formaldehyde. Also three different curing methods (UV, High temp, and UV-Temp) are applied to compare the crosslinking behavior of cellulose. It can be concluded that at a given polycarboxylic acid concentration, catalyst concentration, and curing method, the DCRA for BTCA is higher than CA, and the yellowness index for BTCA is lower than CA. The statistical analysis by Design of Expert indicated that the sample treated with 58 g/L CA, 1.31% nano  $\text{TiO}_2$  and 34.8 g/L SHP and cured with UV-Temp show the optimum DCRA (209.76) with a desirability of 0.815. The optimum conditions for BTCA with a desirability of 0.832 gave DCRA 241 with 92 g/L BTCA, 0.84% nano  $\text{TiO}_2$ , and 55.2 g/L SHP cured with UV-Temp.



According to the statistical analysis, for the fabric samples treated with CA, the nano TiO<sub>2</sub> concentration was more influential on DCRA. However, the concentration of BTCA was more effective for the samples treated with BTCA.

## References

1. Uddin, M. J.; Cesano, F.; Bonino, F.; Bordiga, S.; Spoto, G.; Scarano, D.; Zecchina, A. *J Photochem Photobiol A Chem* 2007, 189, 286.
2. Cassaignon, S.; Koelsch, M.; Jolivet, J. P. *J Mater Sci* 2007, 42, 6689.
3. Wang, H.; Wu, Y.; Xu, B. Q. *Appl Catal B* 2005, 59, 139.
4. Jung, K. Y.; Park, S. B. *J Photochem Photobiol A Chem* 1999, 127, 117.
5. Watson, S. S.; Beydoun, D.; Scott, J. A.; Amal, R. *Chem Eng J* 2003, 95, 213.
6. Lu, C. H.; Wu, W. H.; Kale, R. B. *J Hazard Mater* 2008, 154, 649.
7. Bozzi, A.; Yuranova, T.; Kiwi, J. *J Photochem Photobiol A Chem* 2005, 172, 27.
8. Hsieh, S.; Zhang, F. R.; Sili, H. *J Appl Polym Sci* 2006, 100, 4311.
9. Ding, Z.; Hu, X.; Yue, P. L.; Lu, G. Q.; Greenfield, P. F. *Catal Today* 2001, 68, 173.
10. Dong, Y.; Bai, Z.; Liu, R.; Zhu, T. *Atmos Environ* 2007, 41, 3182.
11. Russell, E. *Text Horiz* 2002, 9, 7.
12. Xin, J. H.; Daoud, W. A.; Kong, Y. Y. *Text Res J* 2004, 74, 97.
13. Yeo, S. Y.; Lee, H. J.; Jeong, S. H. *J Mater Sci* 2003, 38, 2143.
14. Kathiervelu, S. S. *Synth Fibres* 2003, 32, 20.
15. Zhang, J.; France, P.; Radomyselskiy, A.; Datta, S.; Zhao, J.; Ooij, W. V. *J Appl Polym Sci* 2003, 88, 1473.
16. Yang, H. Y.; Zhu, S. K.; Pan, N. *J Appl Polym Sci* 2003, 92, 3201.
17. Wu, Y.; Chi, Y. B.; Nie, J. X.; Yu, A. P.; Chen, X. H.; Gu, H. C. *J Funct Polym* 2002, 15, 43.
18. Welch, C. M. *Text Res J* 1988, 58, 480.
19. Gagliardi, D. D.; Shippee, F. B. *Text Res J* 1959, 29, 54.
20. Yang, C. Q. *Text Res J* 1991, 61, 433.
21. Yang, C. Q.; Wang, X. *Text Res J* 1996, 66, 595.
22. Yang, C. Q.; Wang, X.; Kang, I. *Text Res J* 1998, 68, 457.
23. Yang, C. Q.; Wang, X.; Kang, I. *Text Res J* 1997, 67, 334.
24. Lu, Y.; Yang, C. Q. *Text Res J* 1990, 69, 685.
25. Shao, H.; Sun, J. Y.; Meng, W. D. *Text Res J* 2004, 74, 851.
26. Mao, Z.; Yang, C. Q. *J Appl Polym Sci* 2001, 81, 2142.
27. Sricharussin, W.; Ryo-Aree, W.; Intasen, W.; Poungraksakirt, S. *Text Res J* 2004, 74, 475.
28. Welch, C. M. *Text Chem Colorist* 1997, 29, 21.
29. Hebeish, A.; Hashem, M.; Abdel-Rahman, A.; El-Hilw, Z. H. *J Appl Polym Sci* 2006, 100, 2697.
30. Lee, E. S.; Kim, H. J. *J Appl Polym Sci* 2001, 81, 654.
31. Li, Z. R.; Jiang, W. C.; Wang, L. J.; Meng, W. D.; Qing, F. L. *Text Res J* 2007, 77, 227.
32. Hauser, P. J.; Smith, C. B.; Hashem, M. M. *Autex Res J* 2004, 4, 95.
33. Wang, C. C.; Chen, C. C. *Appl Catal A Gen* 2005, 293, 171.
34. Wang, C. C.; Chen, C. C. *J Appl Polym Sci* 2005, 97, 2450.
35. Chen, C. C.; Wang, C. C. *J Sol Gel Sci Technol* 2006, 40, 31.
36. Montazer, M.; Afjeh, M. G. *J Appl Polym Sci* 2007, 103, 178.
37. Lee, J.; Broughton, R. M. *Text Res J* 2007, 77, 604.
38. Montazer, M.; Taghavi, F. A.; Toliyat, T.; Bameni Moghadam, M. *J Appl Polym Sci* 2007, 106, 1614.
39. Montazer, M.; Zolfaghari, A.; Toliyat, T.; Moghadam, M. B. *J Liposome Res* 2009, 19, 173.
40. Yuranova, T.; Laub, D.; Kiwi, J. *Catal Today* 2007, 122, 109.