Dyeing Properties of Net-Modified Cotton Fabric with Triazine Derivative Containing the Multireactive and Multicationic Groups

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ABSTRACT: Cotton fabric was modified with a 1,3,5-triazine derivative containing the multireactive and multicationic groups, 2,4,6-tri[(2-hydroxy-3-trimethyl-ammonium)-propyl]-1,3,5-triazine chloride (Tri-HTAC). Compared with unmodified cellulose, the net-modified cotton cellulose has different dyeing properties. The modified cotton was dyed with reactive dyes without the addition of salt. The color yield was higher than that on unmodified cotton, despite the addition of large amounts of salt in the latter case. After dyeing, compared with unmodified cellulose with reactive dyes, the reflectance spectrums of modified cotton did not change. The modified cotton got better wash fastness than the unmodified cotton. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 4388–4392, 2006

Key words: modification; dyes; dyeing

INTRODUCTION

The direct dyes and reactive dyes are widely used for dyeing cotton and its blends. Dyes of this type are anionic in character and in general owe their water solubility to the presence of sulfonate groups (SO_3^-). However, since cotton itself adopts an anionic surface charge in water, these dyes have low intrinsic affinity for the cellulose fiber. The repulsive charge between dyes and cotton can be overcome by adding an electrolyte such as sodium chloride or sodium sulfate, which has the effect of screaming the surface charge on the cellulose fiber. The large quantity of salt in the effluent, however, causes pollution of rivers and streams and upsets the biological equilibrium.[1–4] In addition, since dyebath exhaustion is low, environmental problems may also arise because of the strongly colored effluent.

To reduce the usage of salt and increase dyebath exhaustion, a number of attempts have been made to modify the cotton fiber using the compounds containing certain groups.[2–6] Previous studies have revealed that chemically modified cotton cellulose exhibits different behavior toward dyeing compared with that of unmodified cellulose. The modified celluloses examined were partially acetylated cellulose, carbamylethyl cellulose, and partially carboxymethylated cellulose, as well as cellulose grafted with polyacrylonitrile and polymethyl methacrylate using direct and reactive dyes. The cationic cotton, which has been chemically modified with Glytac A or epichlorohydrin derivatives, has been thoroughly investigated. Application of a fiber-reactive chitosan derivative, namely *O*-acrylamidomethyl-*N*-[(2-hydroxy-3-trimethyl-ammonium)-propyl] chitosan chloride (NMA-HTCC), to cotton fabric was reported.[4–6] These have been mainly compounds containing mono and bireactive groups; unfortunately, many of the chemicals used are not resistant to hydrolysis. The modified cotton with polymer, for example the NMA-HTCC, does not penetrate well into the individual fibers because of its molecular size. The reports of tridimension net-modified cotton with the multireactive and multicationic group derivatives are scarce. The net crosslinking cellulose may be more resistant to hydrolysis and improves elastic recovery of fabrics because of the inhibition of slippage between the molecules. The chemically net-modified cotton cellulose may impart different dyeing behavior.

In this study, the triazine derivative containing the multireactive and multicationic groups, 2,4,6-tri[(2-hydroxy-3-trimethyl-ammonium)propyl]-1,3,5-triazine chloride (Tri-HTAC), was applied to modify cotton cellulose. Because the triazine derivative could form net crosslinking with cellulose, there are many covalent bonds in modified cellulose molecules containing a lot of cationic groups. The dyeabilities of net-modified cotton cellulose are discussed. The fixing properties of modified cotton with reactive dyes were investigated.

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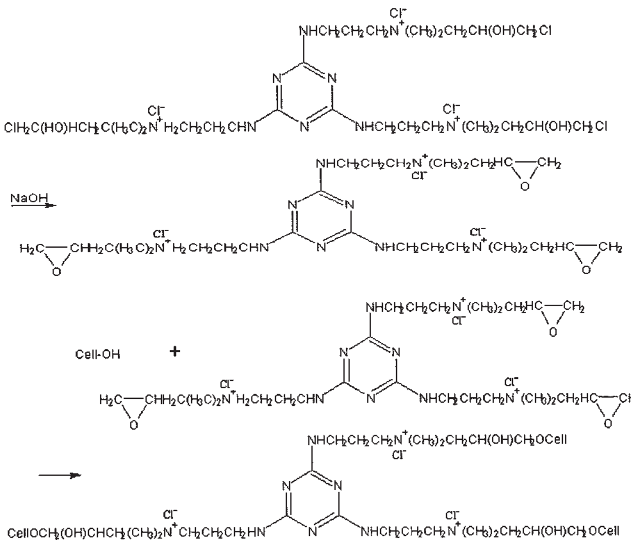

Scheme 1

EXPERIMENTAL

Materials

The reactive dyes, Yellow BF-RR, Red BF-3B, and Blue BF-RRN, were obtained from Shanghai Matex Chemical Company (Shanghai, China). Scoured and bleached cotton fabric was obtained from Beijing Textile Company (Beijing, China). Tri-HTAC was obtained from Shanghai Handa Chemical Company (Shanghai, China).

Net modifying to cotton fabric

Tri-HTAC was dissolved in distilled water to give different concentration solutions by weight. To each solution was added 1.5% sodium hydroxide as catalyst. Samples of cotton fabric were padded with the solutions to give 100% wet pick-up, placed in plastic sample bags and tightly sealed to prevent air penetration. The samples were kept at room temperature for a certain time. The modified fabrics were then washed with tap water until neutral and again washed in warm water using a domestic washing machine to remove unfixed Tri-HTAC. The fabric was air-dried at room temperature. Tri-HTAC was able to form covalent bonds with fibers under alkaline conditions (Scheme 1).

Dyeing of modified and unmodified cotton fabric

The unmodified and modified cotton fabrics were dyed (2% owf) in an IR dyeing machine (PYROTEC-2000); the liquor ratio being 1:15, sodium chloride (60 g/L), and sodium carbonate (10 g/L). Fabrics were immersed in the dyebath at room temperature, and the temperature was increased to 65°C at a rate of 1°C/min. Dyeing was carried out at this temperature for 60 min. After dyeing, all the dyed samples were rinsed in hot water and soaped in a solution of nonionic surfactants (OP-10, 1 g/L) at 90°C for 20 min at a liquor ratio of 1:15. The fabrics were removed, rinsed thoroughly in hot tap water until the rinsing water was clear and air-dried. In the latter case, the addition of electrolyte was omitted.

Measurement of dyes exhaustion and fixation

The exhaustion and fixation of the dyes on fabric were calculated by measuring the absorbance of the residual dyebath liquor. The percentages of dyebath exhaustion (E%) and fixation (F%) were calculated according to eqs. (1) and (2), respectively:

$$E(\%) = [1 - (C_2/C_1)] \times 100 \quad (1)$$

$$F(\%) = [(C_1 - C_2 - C_3)/C_1] \times 100 \quad (2)$$

where C_1 and C_2 are the concentrations of the dyes in the dyebath before and after dyeing, respectively, C_3 is the concentration of the dyes in a soaping solution of a nonionic surfactant (OP-10, 1 g/L).

Reflectance spectrums of the dyes were measured with Datacolor SP600$^+$ spectrophotometer.

Color yield analysis

The color yield (K/S) of the dyed fabric was determined by Datacolor SP600$^+$ spectrophotometer. The dye absorbance was measured in the visible region of the spectrum from 400 to 700 nm, and the reflectance at the wavelength of maximum absorption (λ_{max}) was used to calculate the color yield of dyed fabrics by the Kubelka–Munk Equation [eq. (3)].

$$K/S = \frac{(1-R)^2}{2R} \quad (3)$$

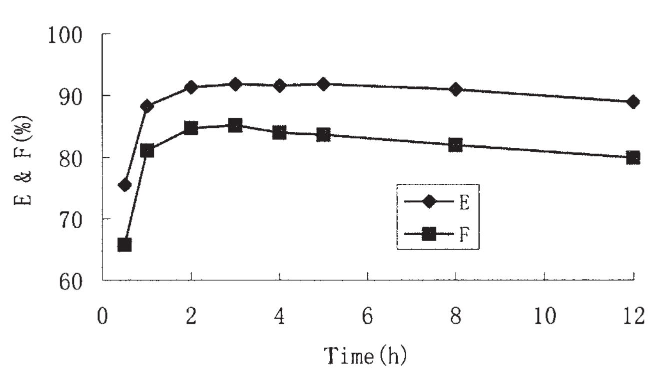

Figure 1 Exhaustion and fixation of the dyes on cotton with varying reacting time.

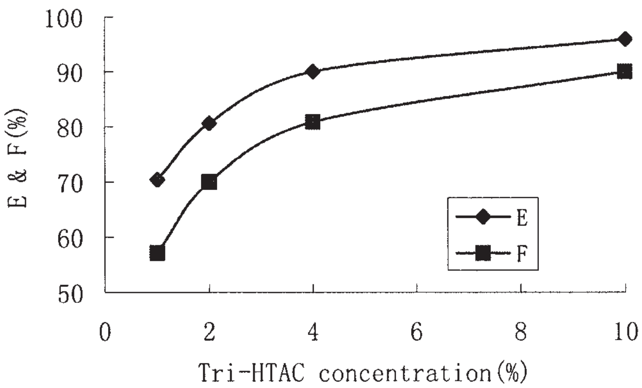

Figure 2 Exhaustion and fixation of the dyes on cotton with varying Tri-HTAC concentration.

where *K* is the absorption coefficient of the substrate, *S* is the scattering coefficient of the substrate, and R is the reflectance of the dyed fabric at λ_{max}.

Measurements

Color fastness was evaluated according to the respective international standards: fastness to washing, ISO 105-C04 (1989) and fastness to rubbing, ISO 105-X12 (1993).

RESULTS AND DISCUSSION

Determination of the modifying conditions for cotton

Reacting time

The effect of varying reacting time was studied to find the length of time required. The modified cotton samples were dyed with Red BR-3B to assess the rate of reaction. The results shown in Figure 1 indicate that the exhaustion and fixation of dyes on modified cotton increases rapidly over the first 3 h. After this, the exhaustion and fixation of dye increases only slightly. It shows that the reaction was almost complete within

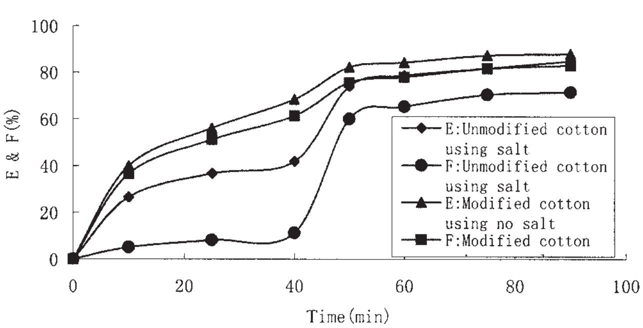

Figure 3 Exhaustion and fixation of the dyes at varying dyeing time.

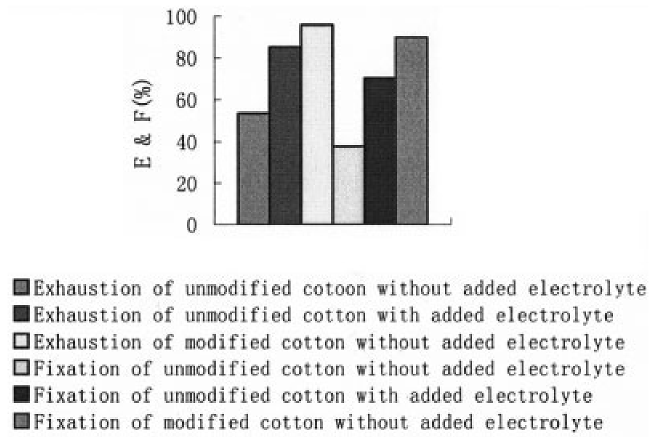

Figure 4 The dyeing properties on unmodified and modified cotton with Red BF-3B.

3 h. To ensure complete reaction, the reaction time of 5 h was used in subsequent experiments.

Tri-HTAC concentration

Tri-HTAC concentration was varied from 1 to 10% using access alkaline. The results in Figure 2 show that the exhaustion and fixation of dye were low at Tri-HTAC concentration of below 2%. Above this concentration, the exhaustion and fixation of the dyed samples increased sharply, after which the exhaustion and fixation increased more slowly. The 95.92% exhaustion and 90% fixation were achieved at 10% Tri-HTAC.

Dyeing properties of the modified cotton

Effect of dyeing time

The effect of dyeing time was investigated on cotton that had been modified with 10% Tri-HTAC (reaction time, 5 h). The results in Figure 3 show that the dyeing

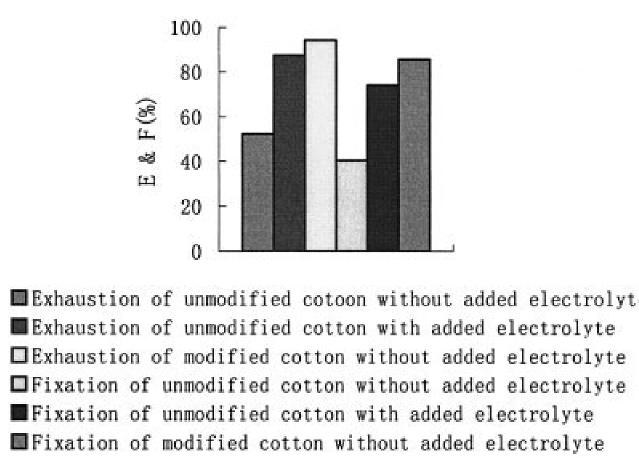

Figure 5 The dyeing properties on unmodified and modified cotton with Yellow BF-RR.

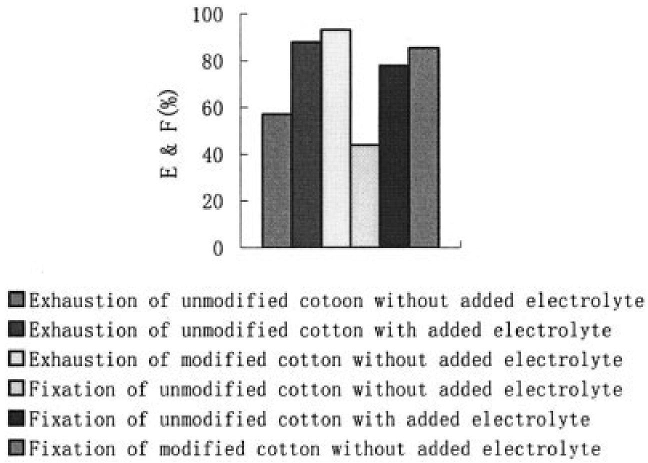

Figure 6 The dyeing properties on unmodified and modified cotton with blue BF-RRN.

took place rapidly during the first 15 min of the process. Compared with unmodified cotton, the dyes exhaustions were markedly improved due to the formation of ionic bonds. The fixation on modified cotton was higher than that on unmodified cotton. The rate then slowed down and exhaustions and fixations rose slowly after that. The results show that the dyeing had reached the equilibrium after 60 min.

Effect of different dyes

The dyeing properties of cotton treated with Tri-HTAC were evaluated using the reactive dyes. To investigate the fixing properties of different reactive dyes, Yellow BF-RR, Red BF-3B, and Blue BF-RRN were used for cotton. Exhaustions and fixations of the dyes on unmodified cotton without and with added electrolytes and on modified cotton without added electrolytes were compared.

The results, shown in Figures 4–6, indicate that exhaustion and fixation of all dyes on net-modified cotton were higher than those on unmodified cotton.

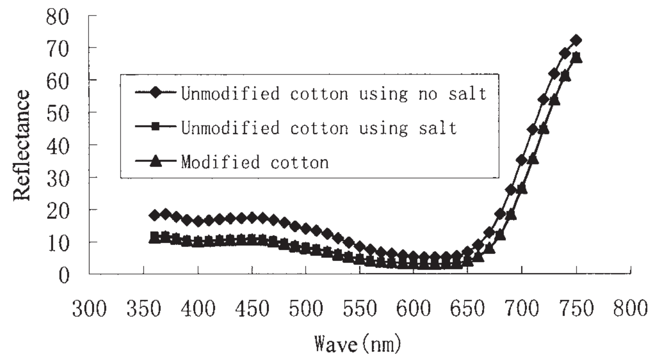

Figure 8 The reflectance spectrums on unmodified and modified cotton with Blue BF-RRN.

The higher exhaustions and fixations obtained for the fabrics modified with Tri-HTAC without added electrolyte may be due to the presence of a lot of quaternary ammonium groups on net-modified cotton. The high dyebath exhaustion of cotton modified with Tri-HTAC in the absence of added salt is of great benefit in avoiding the large volumes of salt frequently present in dyehouse effluent.

After dyeing with reactive dyes, the reflectance spectrums of modified cotton and unmodified cotton showed that the reflectance spectrums of modified cotton do not change (seen in Figs. 7–9).

Color yield (*K*/*S*) values of dyed fabric

Table I shows the colorimetric data for unmodified and net-modified cotton. The modified cotton was more dull and yellowish than the unmodified cotton. Cotton net-modified with Tri-HTAC produced higher color yield without salt than did unmodified cotton dyed in the presence of a large quantity of salt. This is of great benefit as it enables a reduction in the salt presence in dyehouse effluent. In this case, cotton net-modified with Tri-HTAC showed complete dyebath exhaustion, in fact gave higher color yield than

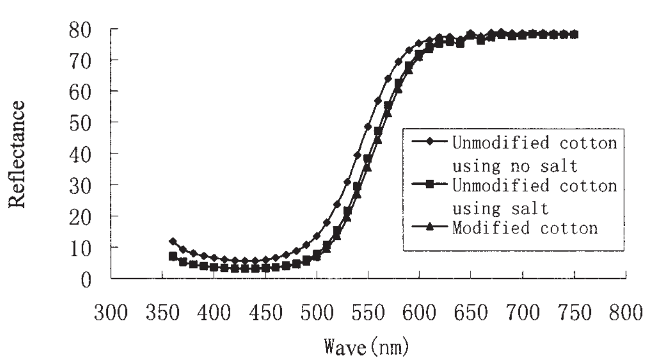

Figure 7 The reflectance spectrums on unmodified and modified cotton with Yellow BF-RR.

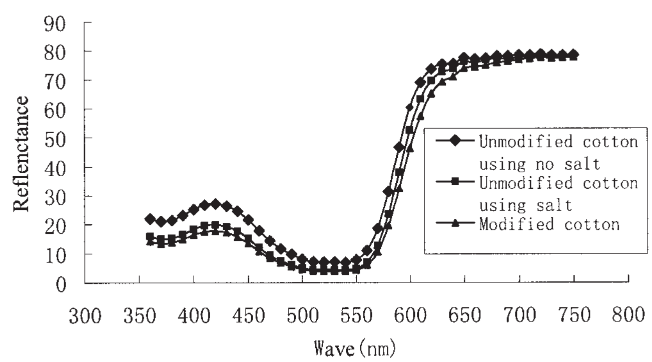

Figure 9 The reflectance spectrums on unmodified and modified cotton with Red BF-3B.

TABLE I
Colorimetric Data of Modified and Unmodified Cotton Fabric

		K/S	ΔE	L	a	b	ΔL	Δa	Δb
BF-3B	Unmodified	10.29		51.84	61.27	12.48			
	Modified	13.59	3.43	48.56	61.51	13.42	−3.29	0.24	0.95
BF-RR	Unmodified	11.9		70.47	31.34	76.59			
	Modified	13.58	3.04	68.72	33.82	76.83	−1.74	2.48	0.24
BF-RRN	Unmodified	16.21		27.33	−3.32	−18.3			
	Modified	17.02	1.80	26.15	−1.97	−18.4	−1.19	1.35	−0.13

unmodified dyed cotton. The higher color yield on modified cotton is considered to result from the formation of ionic bonds between the cationic group of fabrics and the anionic groups on the dyes.

When they were compared visually, the shades of the dyed fabrics of the cotton modified with Tri-HTAC showed a noticeable shade difference compared to its unmodified counterpart. To express the shade differences between modified and unmodified cotton, the color difference (ΔE) was calculated using the measured values of CIELAB. The shade differences observed between the modified and unmodified cotton fabrics may be due to a different arrangement of dyes molecules on the fiber caused by the Tri-HTAC.

Fastnesses properties

The fastness properties of dyed cotton are summarized in Table II. From Table II, it can be seen that wet rubbing fastness and washing fastness of dyed modified samples with Tri-HTAC were better than those of unmodified cotton. The higher fastness obtained for the fabric modified with Tri-HTAC maybe not only due to the formation of covalent bonds between the dyes and the cotton but also the formation of more ionic bonds between the quaternary ammonium groups on cotton and the anionic sites on the reactive dyes.

TABLE II
Fastness Properties of Dyes on Cotton

		Fastness to rubbing		Fastness to washing	
Samples	Dyes	Dry	Wet	SC	SW
Modified	Red BF-3B	4–5	4	4	4
	Yellow BF-RR	4–5	4	4	4
	Blue BF-RRN	4–5	4	4	4
Unmodified	Red BF-3B	4–5	3–4	3	3
	Yellow BF-RR	4–5	3–4	3	3
	Blue BF-RRN	4–5	3–4	3	3–4

SC, staining on cotton; SW, staining on wool.

CONCLUSIONS

Cotton fabric was modified with a triazine derivative containing multireactive and multicationic groups, Tri-HTAC. The net-modified cotton exhibited different behavior towards dyeing compared with that of unmodified cotton. The modified cotton was dyed with reactive dyes without the addition of salt. The exhaustion, fixation, and color yield on net-modified cotton were higher than those on unmodified cotton, despite the addition of a large amount of salt in the latter case. In comparison with unmodified cotton, the washing fastness and wet rubbing fastness of dyed net-modified cotton fabrics were better. This will be of great benefit, as it will enable a reduction in the salt present in dyehouse effluent.

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