Behavior of Chemically Modified Cellulose towards Dyeing. XIV. Behavior of Cotton and Crosslinked Cottons before and after Mercerization towards Some Reactive Dyestuffs

A. T. EL-AREF, E. ALLAM, M. ABOU-AMER,* Z. EL-HILW and A. HEBEISH, *National Research Centre, Textile Research Division, Dokki, Cairo, Egypt*

Synopsis

Cotton fabric was crosslinked with DMDEU by applying the Form D-Process and Form W-Process. The cotton and crosslinked cotton were then treated with caustic soda solution of mercerizing strength. The ability of cotton and crosslinked cottons to dyeing with two reactive dyes, viz. Procion Blue MRB and Procion Red HB was examined. It was found that crosslinking reduces significantly the amenability of cotton to reactive dyes particularly when the Form D-Process was applied. Mercerization enhances dyeability of all substrates, but the enhancement was much greater in the case of noncrosslinked cotton. Based on dyeing and other properties such as tensile strength, elongation at break, and crease recovery, it was shown that crosslinking decreases considerably the affinity of cotton to caustic soda solution. It was further anticipated that different color designs with different patterns and properties can be conferred on a given cotton fabric by making use of local crosslinking and/or mercerizing followed by dyeing.

INTRODUCTION

The changes in the physical and chemical structure of cellulose brought about by esterification, etherification, crosslinking, and grafting have been reported to exert a considerable influence on the dyeability of cellulose.[1–15] This influence is dependent upon the type and degree of modification as well as on the nature of the dye used. In addition, the capability of poly(glycidyl methacrylate)-containing cotton to dyeing with different dyestuffs under different conditions was investigated.[16] Ring opening of the epoxide groups in this modified cotton under the influence of ionic species has been disclosed to be advantageous in permitting interchange of protons from the dye, thereby promoting dye fixation.

The present work is undertaken with a view of studying (a) the effect of dry and wet crosslinking of cotton on the ability of the latter to dyeing with reactive dyes and (b) the effect of mercerization of cotton and crosslinked cottons on their dyeability with reactive dyes.

* Helwan University, Faculty of Applied Arts, Textile Department, Cairo, Egypt.

Journal of Applied Polymer Science, Vol. 27, 871–878 (1982)
 CCC 0021-8995/82/030871-08$01.00

EXPERIMENTAL

Cotton Fabric

Mill-scoured, bleached cotton fabric (Provided by Misr Beida Dyers, Alexanderia, Egypt), which was not subjected to any type of finishing treatment was used. This fabric was further purified by treating it with a solution containing sodium carbonate (5 g/L) and soap (5 g/L) at the boil for 4 h. It was then thoroughly washed and dried at room temperature.

Reagents

Dimethyloldihydroxyethylene urea (DMDEU) was supplied under the name Arkofix NG by Höchst-Cassella, West Germany, and was employed as a reactant resin in the easy care finishing process.

Sodium hydroxide of reagent grade was used. Ammonium dihydrogen phosphate and magnesium chloride hexahydrate were of laboratory grade chemicals.

Procion Blue MRB and Procion Red HB were two reactive dyestuffs provided by I.C.I., England, and were employed without further purification.

Resin Finishing

Treatments of cotton samples with DMDEU were carried out using two different methods of application as described below.

Pad-Dry-Cure Method (Form D-Process)

This method involves padding of the substrate in a solution containing DMDEU (100 g/L) and ammonium dihydrogen phosphate (5 g/L) to ca. 80% wet pickup, followed by drying at 80°C for 5 min and curing at 140°C for 5 min. The resin-treated samples were then washed and dried.

Pad-Wet-Batch Method (Form W-Process)

In this process, cotton fabric is padded with a solution containing DMDEU (100 g/L), hydrochloric acid (100 g/L), and magnesium chloride hexahydrate (20 g/L), and then batched at room temperature overnight in a closed polyethylene cover. The treated samples are then unrolled, washed, neutralized, washed again, and left to dry in air.

Mercerization

The mercerization process was carried out by impregnation of cotton fabric in sodium hydroxide solution (240 g/L) for 30 s at 15°C, followed by squeezing to a wet pickup of ca. 100% and washing with running water. Mercerized cotton samples were then neutralized in dilute hydrochloric acid (1%) and then thoroughly washed and dried in air.

Dyeing

The untreated, the mercerized, and the DMDEU-treated cotton fabrics were dyed using two reactive dyestuffs, namely, Procion Blue MRB and Procion Red HB.

Dyeing with Procion Blue MRB

Cotton fabric was padded in a dyebath containing the dyestuff (2%), common salt (3%), and soda ash solution (5%) to a wet pickup of ca. 100%. The padded samples were batched for 45 min, washed, and then treated in a solution containing 5 g/L soap for 15 min at 60°C, followed by rinsing and drying.

Dyeing with Procion Red HB

Cotton fabric was padded in a dyebath containing the dyestuff (2%), common salt (3%) to a wet pickup of ca. 100%, and batched for 45 min and then padded in soda ash solution (5%) and further batched for another 45 min then cured at 100°C for 5 min. The dyed fabric was washed and treated with a solution containing 5 g/L soap at 60°C for 15 min, followed by rinsing with hot and cold water, and finally dried at ambient conditions.

Crease Recovery

A Wrinkle Recovery Tester, T. J. Edwards, Inc., Boston, MA, was used for crease recovery measurements throughout the present study.[17]

Tensile Strength

The tensile strength and elongation at break were measured on the tensile strength testing machine type FMGW 500 (Veb Thuringer Industriewerk Rauenstein) at 25°C and 65% relative humidity. The results quoted are the mean of 10 breaks for the warp direction with a test length of 20 cm at a constant breaking time of 20 s.

Color Strength

Color strength, expressed as K/S, was calculated from the reflectance measurements and Kubelka–Munk equation.[18] Beckman Spectrophotometer, Model 26, integrating sphere system, UV-visible analytical system (produced by Beckman Instruments International S.A., Switzerland) was used. Color strength values were calculated as follows:

$$K/S = (1 - R)^2/2R$$

where R is the reflectance (measured at wavelength 700 μ) and K and S are the absorption and scattering coefficients, respectively.

RESULTS AND DISCUSSION

Crosslinking of Cotton

Table I shows that treatment of cotton fabric with DMDEU in presence of $NH_4H_2PO_4$ according to the pad-dry-cure method resulted in crosslinked cotton. This is evidenced by the outstanding increase in crease recovery as well as the substantial loss in tensile strength and elongation at break. A similar situation is encountered when the fabric was treated with DMDEU in presence of HCl and $MgCl_2 \cdot 6H_2O$, using the pad-wet-batch method. However, the retained tensile strength and elongation at break for the pad-wet-batch method are much greater than those obtained with the pad-dry-cure method. Meanwhile the dry crease recovery obtained with the latter is significantly higher than that of the pad-wet-batch method, and the opposite holds true for wet crease recovery.

The great loss in both tensile strength and elongation at break when the pad-dry-cure method was applied could be ascribed to embrittlement confined on cotton cellulose by crosslinking together with cellulose degradation under the influence of the acid catalyst at the high temperature of curing.[19,20] This is not the case with respect to the pad-wet-batch method, where neither high temperature is involved nor a possibility for cellulose to collapse exists. That is why the cotton fabric did not lose much of its tensile strength and elongation at break after crosslinking treatment by the pad-wet-batch method.

Mercerization of Cotton and Crosslinked Cottons

The three aforementioned substrates, viz., untreated cotton fabric, cotton fabric treated with DMDEU according to the pad-dry-cure method, and cotton fabric treated with DMDEU as per the pad-wet-batch method, were treated with

TABLE I
Effect of Mercerization on Some Properties of Cotton and Crosslinked Cottons

Substrate	Crease recovery (°) ($W + F$)		Tensile strength (warp) (kg)	Elongation at break (%)
	Dry	Wet		
I. Untreated cotton fabric	145	165	58	11
II. Cotton fabric after DMDEU treatment as per the pad-dry-cure method	280	265	32	4
III. Cotton fabric after DMDEU treatment as per the pad-wet-batch method	265	285	50.7	9
IV. Mercerized cotton fabric	150	158	55.1	18
V. Cotton fabric treated with DMDEU as per the pad-dry cure followed by mercerization	250	245	34	4.5
VI. Cotton fabric treated with DMDEU as per the pad-wet batch followed by mercerization	260	268	52	14

caustic soda of mercerizing strength. The effects of this treatment on crease recovery, tensile strength, and elongation at break of these substrates are shown in Table I.

It is seen (Table I) that mercerization does not exert a significant influence on the crease recovery of the cotton fabric. The increase in dry crease recovery or the decrease in wet crease recovery brought about by mercerization of this substrate cannot by looked upon as significant difference if compared with unmercerized cotton. This is also the case with crosslinked cotton prepared according to the pad-wet-batch method. Mercerization has practially no effect on the dry crease recovery while decreasing marginally wet crease recovery of this crosslinked cotton. Different situation is encountered with crosslinked cotton prepared according to the pad-dry-cure method. A significant decrease in both dry and wet crease recovery is observed after mercerization.

When application of DMDEU is carried out by the pad-dry-cure method (known in practice as Form D-Process), the cellulosic material is in the collapsed or unswollen state during curing. As a result, the crosslinks take place in highly disordered regions. On the other hand, the crosslinks are located largely in regions of relatively some lateral order when application is carried out by the pad-wet-batch method (known in practice as Form W-Process).[19] With this in mind, together with the short time (30 s) allowed for mercerization in the present work, one would expect higher magnitude of crosslink scission with cotton cellulose treated as per the Form D-Process than per the Form W-Process. Stated in other words, breaking down of crosslinks in cotton cellulose treated with DMDEU according to the pad-dry-cure method would be much greater than its mate obtained with the pad-wet-batch method by virtue of availability of larger amounts of crosslinks on the surface and/or nearly in case of the Form D-Process as compared with the Form W-Process. This would account for the substantial decrease in both dry and wet crease recovery of cotton crosslinked by the pad-dry-cure method under the alkali hydrolysis during mercerization.

Table I shows the effect of mercerization on the tensile strength and elongation at break of cotton fabric before and after the latter has been crosslinked by application of the Form D-Process and the Form W-Process. It is clear that mercerization is accompanied by a marginal decrease in the tensile strength and considerable increase in elongation at break in case of the cotton fabric. This is rather logical since no tension is applied during mercerization. It is well established that mercerization brings about a profound change in the fine physical structure of cotton cellulose such as decreased crystallite size and crystallinity without necessarily improving molecular orientation.[21,22] As a consequence of this, a decrease in tensile strength and an increase in elongation at break would be expected.

Mercerization leaves the tensile strength and elongation at break of crosslinked cotton practically unaltered provided that crosslinking is carried out by the Form D-Process. The same holds true for the Form W-Process, but the elongation at break of the crosslinked cotton is enhanced considerably after mercerization (Table I). This suggests that mercerization of wet crosslinked cotton cellulose is accompanied by a relief of stress on some of the cellulose chains via breaking down some of the crosslinks, thereby favoring elongation at break. Indeed, the substantial decrease in wet crease recovery observed with wet crosslinked cotton after mercerization supports this.

Dyeing with Procion Blue MRB

The said cotton and crosslinked cottons before and after mercerization were dyed with Procion Blue MRB under similar conditions. For simplicity, untreated cotton fabric will be referred to as substrate I, crosslinked cotton prepared by the Form D-Process as substrate II, crosslinked cotton prepared by the Form W-Process as substrate III, whereas substrates IV, V, and VI will represent these substrates after mercerization. Table II shows the effect of dyeing with Procion Blue MRB on these substrates.

It is clear (Table II) that crosslinking of cotton cellulose prior to dyeing decreases significantly the ability of cotton cellulose to dye with the reactive dye in question. This is observed regardless of the crosslinking methods. However, crosslinking according to the pad-dry-cure method brings about crosslinked cotton with much lower reactivity to the dye than the pad-wet-batch method.

The dyeing of cotton cellulose with reactive dyes can be considered to occur in the following steps: (a) diffusion of the dye molecules from the solution phase to the cellulose/solution interface, (b) absorption of the dye molecules from the interface on the cellulose surface, (c) diffusion of the dye molecules into the microstructure of cellulose, (d) reaction between dye molecules and cellulose hydroxyls in the alkali medium, and (e) reaction between dye molecules and water in alkaline medium. Introduction of crosslinks in the molecular structure of cotton cellulose would certainly have adverse effects on a, b, c, and d. Crosslinking not only decreases the accessibility of cotton to the dye, but also results in blocking of some of the cellulose hydroxyls which are sites for dye absorption and reaction. This would account for the serious drop in color strength by crosslinking of cotton cellulose prior to dyeing.

Differences in color strength between crosslinked cottons (substrates II and III) could be attributed to difference in location, number, and distribution of crosslinks in the molecular structure of cotton cellulose, which seems to be determined by the state of the cotton during crosslinking. However, differences in the products of DMDEU and their interaction with cotton cellulose during the crosslinking treatment cannot be ruled out.

TABLE II
Behavior of Cotton and Crosslinked Cottons before and after Mercerization towards Dyeing with Procion Blue MRB

Substrate	Crease recovery (°) ($W+F$) Dry	Wet	Tensile strength (warp)(kg)	Elongation at break (%)	Color strength (K/S)
I. Untreated cotton fabric	140	154	60	11.5	3.30
II. Cotton fabric after DMDEU treatment as per the pad-dry-cure method	270	250	31	4	0.27
III. Cotton fabric after DMDEU treatment as per the pad-wet-batch method	250	281	53	9.5	1.14
IV. Mercerized cotton fabric	152	163	56.9	17.5	6.05
V. Cotton fabric treated with DMDEU as per the pad-dry cure followed by mercerization	244	250	30.4	4.5	1.15
VI. Cotton fabric treated with DMDEU as per the pad-wet batch followed by mercerization	270	281	50	13.4	1.75

It is also seen (Table II) that the color strength (expressed as K/S) of substrate I is roughly half of that of substrate IV. This implies that mercerization of cotton cellulose enhances significantly its reactivity to the reactive dye used (Procion Blue MRB). The enhanced reactivity of cotton by mercerization could be associated mainly with decreased crystallite size and crystallinity of cotton cellulose.[21,22] Mercerization does also increase the color strength of crosslinked cotton but not as much as in case of noncrosslinked cotton (substrate I). Crosslinked cottons (substrates II and III) acquire K/S of 0.27 and 1.14, respectively, before mercerization. This contrasts with K/S of 1.15 and 1.75 for these substrates after mercerization, i.e., substrates V and VI. The implication of this is that crosslinking of cotton cellulose reduces significantly its affinity to caustic soda, particularly when the crosslinking treatment is carried out as per the Form D-Process.

A comparison between Tables I and II would reveal that dyeing with Procion Blue MRB has no serious effect on crease recovery, tensile strength, and elongation at break of all substrates examined.

Dyeing with Procion Red HB

The six substrates in question were dyed with Procion Red HB according to a procedure described in the experimental section. Results of color strength (expressed as K/S) together with other properties are set out in Table III. It is clear that: (a) The color strengths of substrates II and III are significantly lower than that of substrate I, indicating that crosslinking diminishes the ability of the dye to react with cotton cellulose; (b) the dyeability of substrate I enhances markedly by mercerizing it prior to dyeing since the color strength of substrate II is much higher than that of substrate I; (c) mercerization of crosslinked cottons prior to dyeing brings about crosslinked cottons with improved dyeability (substrates V and VI), but the magnitude of this improvement is much lower as compared with that observed with noncrosslinked cotton; (d) the dyeability of

TABLE III
Behavior of Cotton and Crosslinked Cottons before and after Mercerization towards Dyeing with Procion Red HB

Substrate	Crease recovery (°) ($W+F$) Dry	Crease recovery (°) ($W+F$) Wet	Tensile strength (warp)(kg)	Elongation at break (%)	Color strength (K/S)
I. Untreated cotton fabric	142	163	59	12.5	2.49
II. Cotton fabric after DMDEU treatment as per the pad-dry-cure method	270	265	32.2	4	0.38
III. Cotton fabric after DMDEU treatment as per the pad-wet-batch method	271	282	50	8.5	1.31
IV. Mercerized cotton fabric	159	152	57	15	6.05
V. Cotton fabric treated with DMDEU as per the pad-dry cure followed by mercerization	249	245	34.9	4.5	1.24
VI. Cotton fabric treated with DMDEU as per the pad-wet batch followed by mercerization	264	270	48	12.5	2.25

crosslinked cotton prepared as per the Form W-Process before (substrate III) and after (substrate V) mercerization is higher than their mates prepared by the Form-D-Process (substrates II and VI); and (e) a comparison between results of tensile strength, elongation at break, and crease recovery of the dyed substrates and the undyed substrates given in Table I would imply that dyeing with Procion Red HB also has a striking effect on these properties.

The above findings are tallied with those obtained with Procion Blue MRB. Hence they can be explained on similar basis as shown above.

Practical Significance

It has been shown above that the ability of crosslinked cottons to reactive dyes differs much from the noncrosslinked cotton. It has also been shown that the crosslinking of cotton reduces significantly the affinity of cotton to caustic soda of mercerizing strength. Hence it is anticipated that different color designs together with different patterns and properties may be imparted to a given cotton fabric by making use of local crosslinking and/or mercerization followed by dyeing.

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Received April 9, 1981
Accepted June 29, 1981
Corrected proofs received December 21, 1981