Dyeing Properties of PECH-Amine Cationized Cotton with Acid Dyes

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ABSTRACT: The dyeing properties of cationic cotton dyed with acid dyes are examined in this study. For comparison, nylon 6 and untreated cotton are dyed by the same acid dyes (Sandolan Red MF-2BL, Sandolan Golden Yellow MF-GL, and Sandolan Blue MF-GL). A cationic agent, polyepichlorohydrin-dimethylamine (PECH-amine), is used to modify cotton fabric. Significant increase in color yield is observed for cationic cotton over untreated cotton because of the introduced positively charged sites by cationic modification. Deeper shades are obtained in all cases with cationic cotton. All of the acid dyes used in this study show significant hooking behavior with both cationic cotton and nylon. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 3302–3306, 2006

Key words: PECH-amine; cationic cotton; acid dyes; *K/S* values

INTRODUCTION

Cotton fibers assume negative charges in water and these charges act to repel anionic dyes. To overcome the electrostatic repulsion, a large amount of electrolytes, such as Glauber's salt or sodium chloride, should be added to dyebath. Meanwhile, the high concentrations of electrolytes may reduce the solubility of anionic dyes. As a result, multiple rinses and after-washes should be carried on to remove unfixed dyes. Thus, dyeing cotton with direct and reactive dyes becomes a pollution-generating process.[1,2]

Increased awareness of environmental issues make researchers pay more attention to low-salt dyeing of cotton. One way is to modify the cotton fiber with cationic polymers. Therefore, the neutral substantivity of anionic dyes for cotton increase by introducing positively charged sites on the cotton.[3] Lewis and Mcilroy[4] have comprehensively reviewed a number of different cationic polymers for modification of cotton fibers that allow dyeing to be performed under neutral to slightly acidic conditions in the absence of electrolyte. All of these pretreatments introduced cationic agents in the form of quaternary, tertiary, or secondary amino residues, such as polyamide-epichlorohydrin or glycidyltrimethyl-ammonium chloride.[5,6] Several researchers have investigated the effect of cationic cotton dyed or printed with reactive and direct dyes. These literatures have reported that high dye fixation efficiencies could be obtained in dyeing or printing of cationized cotton with reactive and direct dyes.[7–14] Most acid dyes have very little affinity for cotton. But cationic cotton can be dyed readily with acid dyes. The ammonium groups act as dye sites. Therefore, with blended fabrics or mixed fabrics, using cationic cellulosic fiber and regular cotton, two-tone effects can be obtained in one-bath dyeing. Meanwhile, this phenomenon gives a possibility to one-bath dyeing for blended fabrics, using cationic cellulosic fiber and nylon.[15–17]

In this study, we use a cationic reactant, PECH-amine, to modify cotton fabric. Our goals were to examine the dyeing properties of cationic cotton, regular cotton, and nylon with acid dyes and to determine how cationic treatment affects the chroma, hue, lightness, and color fastness of the dyed fabrics.

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EXPERIMENTAL

Materials

We used a scoured, bleached, and mercerized, fluorescent whitening agents-free, 100% cotton weaving fabric with a density of 68 threads/in. in the warp and in the weft direction throughout this study. Scoured nylon weaving fabric was also prepared for comparison. The nylon was determined to be nylon 6 by DSC analysis. All chemicals are chemical pure grade.

The PECH-amine was synthesized and purified as follows: the first step was polymerization of epichlo-

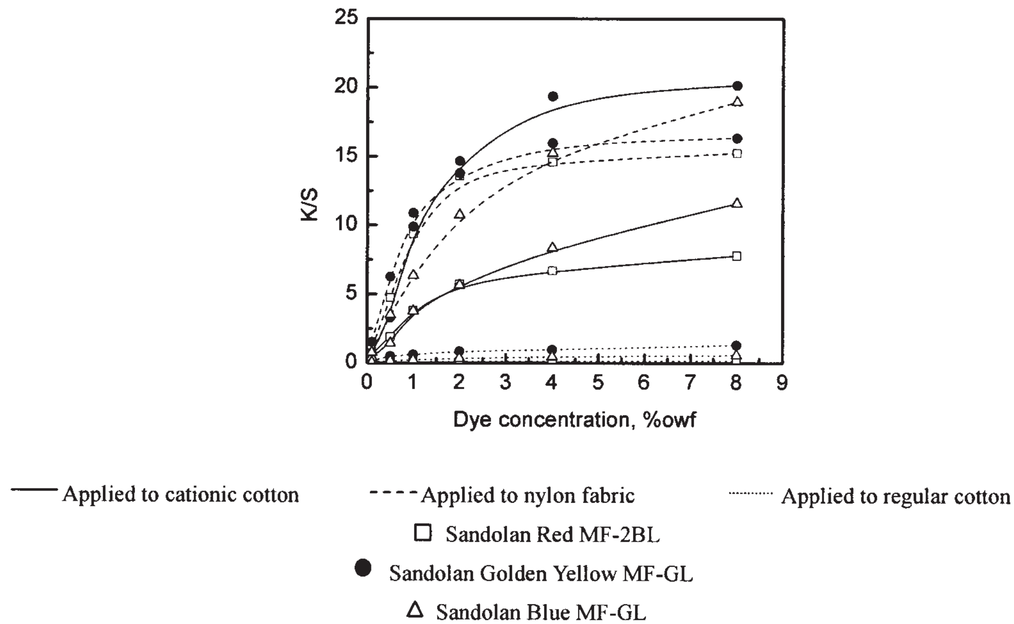

Figure 1 Relationship between K/S values of dyed samples and concentration.

rohydrin in CCl_4 with $BF_3O(C_2H_5)_2$ as a catalyst, to produce poly(epichlorohydrin) (PECH) to which 200 g epichlorohydrin was added at 29°C slowly over a period of 6 h and vacuum dried at 60°C. Then, the amine derivative was achieved by adding 60 g dimethylamine to 33 g PECH at 95°C slowly for 1 h and reacted further for 8 h. The molecular mass (Mn) of PECH is 1550 g/mol. The nitrogen content of PECH-amine is 2.10%.[18]

The dyes used were Sandolan Red MF-2BL, Sandolan Golden Yellow MF-GL, and Sandolan Blue MF-GL. All dyes were provided by Clariant Chemical Company and did not have C.I. numbers assigned. Other chemicals used in this study were NaOH and acetic acid.

Cationic treatment

The cotton fabrics were treated with 10% (owf) PECH-amine and 3 g/L NaOH at a liquid ratio of 50:1 from 40 to 80°C for an hour and then washed and dried. Unit "owf" means "on weight of fabric."

Dyeing procedure

The cationic cotton, regular cotton, and nylon samples were dyed at 0.1, 0.5, 1.0, 2.0, 4.0, and 8.0% (owf) using a 50:1 liquor ratio from 40 to 95°C. pH value was set to 5. The dyed samples were removed after 60 min. The samples were then rinsed in water, scoured at the boil for 20 min using 2 g/L of surfactant LR-2.

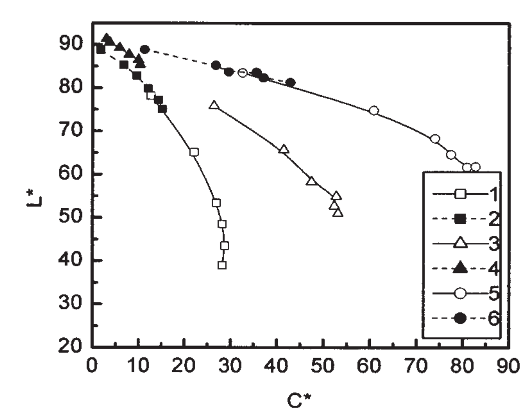

Figure 2 L^* versus C^* plots of cationic cotton and regular cotton for each dye (1 = cationic blue; 2 = regular blue; 3 = cationic red; 4 = regular red; 5 = cationic yellow; 6 = regular yellow).

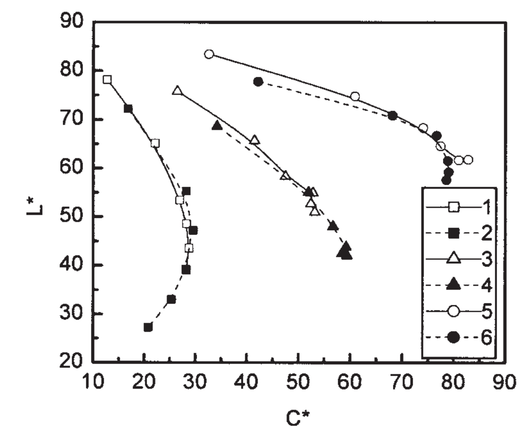

Figure 3 L^* versus C^* plots of cationic cotton and nylon for each dye (1 = cationic blue; 2 = nylon blue; 3 = cationic red; 4 = nylon red; 5 = cationic yellow; 6 = nylon yellow).

TABLE I
Color Coordinates a^* and b^* of All Samples

Samples	Concentration (% owf)	Sandolan Blue MF-GL		Sandolan Red MF-2BL		Sandolan Go. Yellow MF-GL	
		a^*	b^*	a^*	b^*	a^*	b^*
Cationic cotton	0.1	−10.955	−6.448	75.802	26.346	5.202	32.173
	0.5	−16.431	−14.746	65.680	41.087	18.435	57.980
	1	−19.477	−18.600	58.230	46.629	25.532	69.481
	2	−21.236	−18.617	54.948	51.285	29.250	71.707
	4	−21.812	−18.737	52.722	50.083	35.149	72.923
	8	−22.251	−17.373	50.978	51.374	37.266	73.937
Regular cotton	0.1	−1.689	0.442	0.917	2.813	−0..393	11.318
	0.5	−6.260	−2.569	2.726	2.524	2.543	26.669
	1	−8.333	−4.681	5.477	2.120	4.782	29.058
	2	−10.422	−6.194	7.347	2.994	5.748	35.338
	4	−11.848	−8.065	9.768	2.001	6.815	36.492
	8	−12.392	−8.809	10.084	2.319	8.383	42.095
Nylon	0.1	−12.507	−11.210	34.093	−2.298	7.367	51.945
	0.5	−19.986	−19.903	51.559	6.335	21.906	64.456
	1	−19.917	−21.838	55.261	12.546	30.132	70.485
	2	−18.793	−20.901	56.282	18.011	37.504	69.339
	4	−16.642	−19.106	55.898	20.046	41.544	67.193
	8	−13.008	−16.217	55.304	18.681	44.051	65.085

Testing and measurements

The color properties of the dyed samples were measured by a GretagMacbeth Color-Eye 7000A spectrophotometer with Optiview software under illuminant D65 using 10° standard observer. The dyed fabrics were folded into four layers and placed in the large sample port. To obtain the average of its reflectance, three measurements in different surface positions were carried out for each sample. The reflectance data were recorded every 10 nm from 360 to 750 nm. K/S values and CIE (Commission Internationale de l'Eclairage) L^*, a^*, b^*, and C^* color coordinates were reported at the λ_{max} of each dyestuff. K/S value represents color yield. The dye solution was measured by a Unico-2102 PCS spectrophotometer.

Color fastness to washing was tested according to AATCC Test Method 61 (2A) and color fastness to crocking according to AATCC Crockmeter Method 8. Color change and staining were valuated with the AATCC color change and staining gray scale. All the samples prepared for color fastness testing were dyed samples following after-soaping.

The dyebath exhaustion percentage (%E) was calculated using eq. (1)[3]:

$$\%E = (A_0 - A_1)/A_0 \times 100 \quad (1)$$

where A_0 and A_1 are absorbance at the λ_{max} of dye originally in the dyebath and of residual dye after dyeing, respectively.

The percentage dye fixation of the adsorbed dye (%F) was calculated using eq. (2)[3]:

$$\%F = (K/S)_a/(K/S)_b \times 100 \quad (2)$$

where $(K/S)_b$ and $(K/S)_a$ are the color yields of samples measured before and after soaping, respectively.

The total fixation efficiency (%T) was calculated using eq. (3)[3]:

$$\%T = F \times E/100 \quad (3)$$

DSC analysis

The DSC measurement was performed on a Mettler Toledo instrument at a heating rate of 10°C/min before and after the dyeing process. Colored samples were dyed by 8% owf Sandolan Blue MF-GL.

RESULTS AND DISCUSSION

K/S values of dyed samples

The build-up of increasing depths of shade is an important commercial consideration; therefore, the effect of cationization in affecting color yield in comparison to regular cotton and nylon was examined. It can be seen from Figure 1 that the nylon fabric has the highest K/S value when it was dyed by Sandolan Red MF-2BL and Sandolan Blue MF-GL. But for Sandolan Golden Yellow MF-GL, the cationic cotton has the highest K/S value, when the concentration is up to 4% (owf). The K/S values of regular cotton are all under 1.4, most of them are less than 0.5, which means very little acid dye exhausted onto the untreated cotton

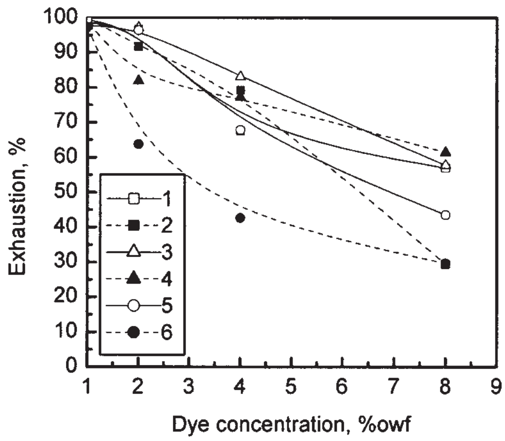

Figure 4 Effect of dye concentration on exhaustion at the isotherm adsorption equilibrium (1 = nylon red; 2 = cationic red; 3 = nylon yellow; 4 = cationic yellow; 5 = nylon blue; 6 = cationic blue).

fabric. There is a large increase in K/S value from regular cotton to cationic cotton.

Color assessment of dyed samples

It can be seen from Figure 2 that each of the dyes has lower lightness value for the cationic samples than for the conventional samples, which means the observed darkening color in the case of cationic samples. These kinds of phenomena could be compared with those shown in K/S values. The K/S values of conventional samples are much lower than those of cationic samples on the occasion of the same dye concentration. As the shade depth increases, the chroma increases and the lightness decreases in strength for both the regular and cationic samples. As shown in Figures 2 and 3, the lightness value of nylon samples is the highest of all three kinds of fabrics, which correlates with the observed most darkening color of nylon samples. Overall, chroma increases with the increasing of the concentration, which means the color saturation increases. For the blue samples, after the 2% dyeing, the chroma is constant for the cationic sample and a downward curve can be observed in the plot. The same thing happens in the case of cationic red samples after the 4% dyeing. All of the three dyes show significant hooking behavior with both cationic cotton and nylon, indicating that predicting shades on cationic cotton requires caution. Much more attention must be paid to recipe prediction when using dyes prone to hooking.[11] For regular cotton, linear color behaviors appear.

a^* is redness/greenness coordinate and b^* is yellowness/blueness coordinate. It can be seen from Table I that all of the three kinds of dyes show significant hooking behavior with nylon. As far as cationic cotton is concerned, only blue and red dyes show hooking behavior.

Dyebath exhaustion, dye fixation, and total fixation efficiency of samples

Figure 4 shows that, at low concentrations of applied dye, the dye is almost completely exhausted, but there is a limited degree of adsorption at high concentrations, which appears to be the saturation adsorption of the treated fiber.

Exhaustion, fixation, and fixation efficiency are decreased as the dye concentration increases in solution (Table II). And fixation efficiency of nylon fabric is larger than that of cationic cotton on the occasion of the same dye and the same dye concentration.

Color fastness to crocking and washing

To compare the fastness properties of similarly colored fabrics, cationic cotton and nylon fabric of all dye concentrations were used. It can be seen from Table III that crock fastness of all three dyes on nylon is excellent with ratings of 4–5 or 5. Ratings of dry crock fastness on cationic cotton vary from dye to dye but are between 3 and 4 and 5, and worse than nylon. Ratings of wet crock fastness of Sandolan Golden Yellow MF-GL on cationic cotton are <3 when the concentration exceeds 2% owf. With the PECH-amine treatment, the modification happens mainly on the surface of cotton fibers because high-molecular mass of PECH-amine blocks it from penetrating into the

TABLE II
Exhaustion, Fixation, and Fixation Efficiency of Cationic Cotton and Nylon

Samples	Concentration (% owf)	Sandolan Blue MF-GL			Sandolan Red MF-2BL			Sandolan Go. Yellow MF-GL		
		%*E*	%*F*	%*T*	%*E*	%*F*	%*T*	%*E*	%*F*	%*T*
Cationic cotton	2	63.73	71.21	45.38	91.71	49.68	45.54	81.90	88.42	72.42
	4	42.64	72.12	30.75	79.25	52.15	41.33	77.25	89.20	68.91
	8	29.62	88.64	26.27	29.40	52.70	15.50	61.40	91.50	56.18
Nylon	2	96.43	69.59	67.10	96.62	89.60	86.58	97.16	85.40	82.97
	4	67.81	84.70	57.43	67.49	93.06	65.81	83.04	96.74	80.34
	8	43.50	95.49	41.54	56.91	91.43	53.74	57.69	97.30	56.13

TABLE III
Color Fastness to Crocking and Washing of Dyed Cationic Cotton and Nylon Samples

		Sandolan Red MF-2BL					Sandolan Golden Yellow MF-GL					Sandolan Blue MF-GL				
		Wash shade change	Cross staining		Crock		Wash shade change	Cross staining		Crock		Wash shade change	Cross staining		Crock	
Samples	Concentration (% owf)		C/N	W	Dry	Wet		C/N	W	Dry	Wet		C/N	W	Dry	Wet
Cationic cotton	0.1	2–3	4–5	4–5	5	4–5	2–3	4–5	4–5	5	4–5	2–3	4–5	4–5	5	4–5
	0.5	2–3	4–5	4	5	4	2–3	4–5	4–5	4–5	3–4	2–3	4–5	4–5	5	4–5
	1	2–3	4–5	3–4	5	4	2	4	3–4	4–5	3	2–3	4–5	3–4	4–5	4–5
	2	2	4–5	3	4–5	3–4	2	4	3	4	2–3	2–3	4–5	3	4–5	4
	4	2	4	3	4–5	3–4	2	3–4	2–3	3–4	2–3	2	4–5	2–3	4	3–4
	8	2	4	3	4–5	3–4	2	3–4	2–3	3–4	2–3	2	4	2–3	4	3
Nylon	0.1	3	4–5	4–5	5	4–5	3–4	4–5	4–5	5	4–5	3	4–5	4–5	5	4–5
	0.5	3	4–5	4–5	5	4–5	3	4	4–5	5	4–5	3	4–5	4–5	5	4–5
	1	3	3–4	4	5	4–5	3	4	4–5	5	4–5	2–3	4–5	4–5	5	4–5
	2	2–3	3	3–4	5	4–5	3	3–4	4	5	4–5	2–3	3–4	4	5	4–5
	4	2–3	2–3	3	5	4–5	2–3	2–3	3–4	5	4–5	2–3	3	3	5	4–5
	8	2–3	2–3	3	5	4–5	2–3	2	3	5	4–5	2	2–3	3	5	4–5

C, cotton staining; W, wool staining; N, nylon staining.

fibers.[7–9,13] Positively charged sites introduced by PECH-amine are concentrated on the surface of the fibers and therefore surface dyeing happens. The color fastness to washing of dyed cationic cotton and nylon is not satisfactory, especially in the case of shade change, and that of cationic cotton is worse. Positively charged sites can be occupied by OH^- with increase in the pH value, and a large amount of dye molecules desorbs into soap solution, which makes shade change rating lower than expected. Cationic cotton exhibits excellent cotton cross staining rating, because acid dyes have very little affinity for regular cotton.

DSC analysis

It can be seen from Table IV that dyeing process hardly affects the final thermal process of nylon fiber. But for regular cotton and cationic cotton, dyeing process affects the final thermal process and decreases the decomposition temperature of those two kinds of fibers. Table IV also shows that cationic treatment decreases the decomposition temperature of regular cotton.

CONCLUSIONS

The cationic modification of cotton with PECH-amine is dyed successfully with acid dyes because of the introduction of positively charged sites. A large increase in K/S values for the cationic cotton over regular cotton is observed. All of the three dyes show significant hooking behavior with both cationic cotton and nylon. Much more attention must be paid to recipe prediction when using dyes prone to hooking. Fastness to washing and rock for cationic cotton is somewhat lower than the values for nylon. Surface dyeing happens to cationic cotton for PECH-amine blocking the dye molecules' from penetrating into the fibers.

TABLE IV
DSC Analysis Results (Colored Samples Were Dyed by 8% owf Sandolan Blue MF-GL)

	Temperature (°C)		
	Cationic cotton	Regular cotton	Nylon
Before dyeing	365.56	375.57	225.65
After dyeing	334.38	358.57	221.12

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