

Use of Chitosan to Improve Dyeability of DP-Finished Cotton (II)

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ABSTRACT: Chitosan was used to improve the dyeability of DP-finished cotton. Cotton fabric was treated with a mixture of chitosan, 4,5-dihydroxy-1,3-dimethyl-2-imidazolidinone (DHDMI), and catalyst in a one-step process. To investigate the effect of molecular weight of chitosan on the dyeability of treated fabrics, six chitosan samples of different molecular weights were prepared by depolymerization with sodium nitrite; 185,300, 73,200, 59,000, 21,000, 14,000, and 3,800, respectively. Chitosan improves dye uptake of direct and acid dyes considerably, and the dye uptake increases with the increase of the molecular weight of chitosan. Reactive dye uptake increases slightly in alkaline condition as the molecular weight of chitosan decreases. Higher dye uptake is obtained in acidic condition than in alkaline condition. Chitosan treatment has no discernable effect on the colorfastness to washing, but decreases the colorfastness to wet crocking by about half a point. And chitosan affects other properties of treated fabric; lower wrinkle recovery, stiffer handle, and higher breaking strength as the molecular weight of chitosan increases. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 1515–1521, 1998

Key words: chitosan; DHDMI; sodium nitrite; depolymerization; dyeability

INTRODUCTION

It is well known that durable press (DP)-finished cotton is less dyeable because the fiber crosslinked by the conventional DP finishing agent is not able to swell sufficiently in aqueous dyeing solution. To improve the dyeability of crosslinked cotton, reactive cationic additives such as glycidyl-trimethyl ammonium chloride, epoxides, hydroxyalkyl nitrogenous agents, and hydroxyalkyl amines were included in the finishing formulation.^{1–4} Cotton crosslinked with DHDMI, a non-formaldehyde DP finishing agent, is dyeable to some extent with some direct and reactive dyes.^{5–7}

Chitosan, the acetylated derivative of chitin, has been applied on wool fabric to improve shrink

resistance and dyeability.^{8,9} It was reported that chitosan pretreatment effectively eliminates the differences of dyeing behavior between damaged and undamaged wool fibers with the increase of the dyeing rate and exhaustion of acid dyes. Rippon improved the dye coverage of immature cotton fibers by treating with chitosan.¹⁰ Burkinshaw and Karim pretreated leather with chitosan and found that the addition of chitosan increased both the rate and uptake of some acid dyes and improved color fastness properties.^{11,12}

In this study, chitosan was added in the DP finishing bath formulated with DHDMI and a catalyst to improve the dyeability of crosslinked cotton. Cotton fabric was treated by the pad-dry-cure method in a one-step process. Six chitosans of different molecular weight were used to evaluate the effect of molecular weight on dye uptake of direct, acid, and reactive dyes. Colorfastness and performance properties were also assessed.

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EXPERIMENTAL

Scoured and bleached cotton poplin ($43 \times 29/\text{cm}^2$) weighing 113 g/m^2 was used. DHDMI (Arkofix V) of a 45% solution and catalyst (Catalyst V) were supplied by Hoechst Ltd. Chitosan was obtained from Protan Inc., and its degree of deacetylation was 86%. Dyes used were CI Direct Blue 212, CI Direct Green 27, CI Direct Red 81, CI Acid Blue 277:1 (leveling type), CI Acid Yellow 79, and CI Acid Red 246 (milling type), CI Reactive Red 183, and CI Reactive Blue 184. Other reagents used were of laboratory grade.

Chitosan (M.W. 185,300) was depolymerized by using sodium nitrite, and six chitosans of different molecular weights were prepared: 185,300 (A), 73,200 (B), 59,000 (C), 21,000 (D), 14,000 (E), and 3,800 (F). The molecular weight of depolymerized chitosans was determined by the viscometric method.¹³ All the infrared spectra of depolymerized chitosans were collected with a Nicolet FTIR spectrometer using the KBr pellet method.

Fabric samples were padded with the mixture including 3% chitosan, 5% owf DHDMI, and 3% owr catalyst to give 90–100% pickup. The padded samples were dried at 110°C for 3 min, cured at 150°C for 5 min, and rinsed in distilled water. For comparison, DP finished samples were prepared by treating with the solution including 5% owf DHDMI or 1,3-dimethylol 4,5-dihydroxyethyleneurea (DMDHEU) and 3% owr catalyst by pad-dry-cure method described earlier.

For direct and acid dyes, dyebath was formulated with 1% owf dyestuff and additives; 3% sodium carbonate for direct dyes, acetic acid to adjust pH 2–3 for acid leveling dye, 2% owf acetic ammonium for acid milling dyes. The temperature was raised from room temperature to the boil and held for 60 min. For reactive dyes, the dyebath containing 1% owf dyestuff and 2% sodium sulfate was held for 30 min, then subsequently 8% sodium carbonate was added and held for 50 min at room temperature. In other procedure for reactive dye, the pH of dyebath was adjusted to 5.5–6.0 with acetic acid. All dyeing procedures were carried out at a liquor ratio of 50 : 1.

Dye uptake was assessed by measuring K/S value on a Macbeth colorimeter. Colorfastness to washing and crocking was evaluated according to the AATCC Test Method 61-1985 and AATCC Test Method 8-1989, respectively. Performance properties were evaluated by standard procedures including breaking strength, ASTM D-1682-64; bending stiffness, ASTM D-1388-55; wrinkle re-

Table I Molecular Weight of Depolymerized Chitosans

Sample	Concentration of NaNO_2 (g/dL)	$[\eta]$	M.W.
A	—	1.435	185,300
B	0.0208	0.605	73,200
C	0.0415	0.495	59,000
D	0.1073	0.190	21,000
E	0.2145	0.130	14,000
F	0.4290	0.039	3,800

covery angle, ASTM D-1295-67. All the tests except wrinkle recovery angle were conducted in the warp direction.

RESULTS AND DISCUSSION

Depolymerization of Chitosan

In the process of depolymerization reaction with sodium nitrite, amino groups of chitosan are attacked and subsequently β -glucosidic linkages are cleaved to form aldehyde groups at the site of chain cleavage and nitrogen gas. The chain scission induced by this reaction results in one unmodified chain of lower molecular weight and one chain, also of lower molecular weight, in which terminal unit is a 2,5-anhydro-D-mannose unit.^{14,15}

The molecular weight of depolymerized chitosan was determined by the Mark-Houwink equation and the results are shown in Table I. Viscosity measurement of chitosan samples was carried out by using 0.1M acetic acid/0.2M NaCl as a solvent at 25°C and the viscometric constants of k and a are $1.81 \times 10^{-3} \text{ cm}^3/\text{g}$ and 0.93, respectively.¹⁶

Figure 1 shows IR spectra of depolymerized chitosans. In the spectrum of chitosan A, $-\text{NH}_2$ deformation band at 1580 cm^{-1} predominates over $\text{C}=\text{O}$ stretching (amide I) band at 1650 cm^{-1} . This phenomenon is shown in the spectra of chitosan B, C, and D. As the molecular weight of chitosan decreases, $\text{C}=\text{O}$ stretching band at 1650 cm^{-1} appears more distinctly and it predominates over $-\text{NH}_2$ deformation band at 1580 cm^{-1} in the spectrum of chitosan F. This is due to the decrease in amino groups, which is transformed into nitrogen gas during depolymerization.

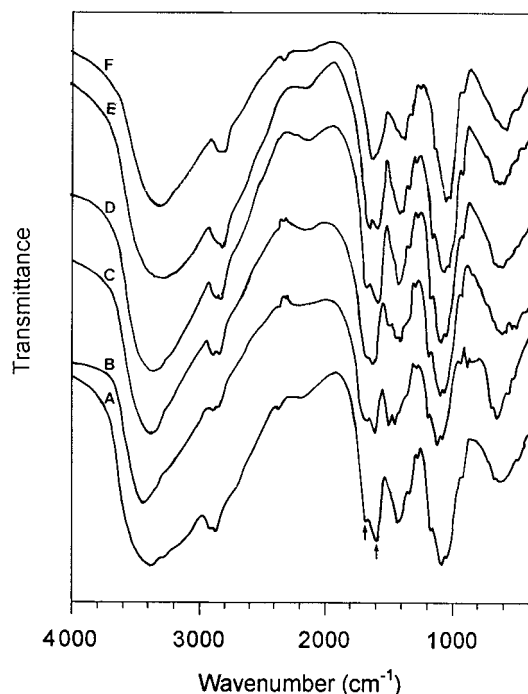


Figure 1 IR spectra of depolymerized chitosans.

Performance Properties

Table II shows the performance properties of untreated DHDMI, DMDHEU, and DHDMI/chitosan (A–F)-treated cotton fabrics. All the DHDMI/chitosan-treated samples are more hydrophilic than the DP finished samples. This result is attributed to the reactive sites such as hydroxyl and amino groups in chitosan structure. Fabrics treated with DHDMI/chitosan of higher molecular weight (A, B, and C) have low wrinkle recovery angle compared with DHDMI-treated fabric, indicating that very little crosslinking has

occurred between DHDMI and cellulose. This suggests that chitosan of high molecular weight prevents DHDMI from crosslinking with cellulose. Chitosan contributes to the increase of breaking strength retention, which is detrimentally affected by DP finishing. This is due to the adhesion of fabric structure by chitosan. And for this reason, the handle of fabric treated with DHDMI/chitosan is stiffer than that of untreated and DP finished fabrics.

Uptake of Direct Dyes

Table III shows direct dye uptake on untreated, DP finished, DHDMI/chitosan-treated samples. Dye uptake on DMDHEU and DHDMI-treated samples is almost negligible except the uptake of CI Direct Red 81 on the DHDMI-treated sample. DHDMI-treated cotton is substantially more receptive to CI Direct Red 81 than DMDHEU-treated one, as shown in Table III. DMDHEU is reported to have mainly interlamella crosslinks, whereas DHDMI induces intralamellar crosslinks rather than interlamellar ones, resulting in the fact that DHDMI crosslinked cotton still keeps its pores available for small direct dye such as CI Direct Red 81.^{6,7} Blanchard and Reinhardt⁷ reported that dye sorption of large direct dyes, such as CI Direct Red 79 and CI Direct Red 80, on DHDMI-treated cotton does decrease considerably. This is partially because large dye molecules do not have enough space for coplanary sorption on DHDMI-treated cotton.

The direct dye sorption of DHDMI/chitosan-treated samples exceeds the dye sorption of untreated one. Obviously, the amino and hydroxyl groups of chitosan enhance the substantivity of

Table II Characteristics of Treated Fabrics

Treated Sample	Add-On (%)	Moisture Regain (%)	WRA (°, w + f)	B.S. Rtn ^a (%)	Stiffness (cm)
Untreated	—	6.89	176	100 ^b	1.5
DMDHEU	4.4	4.10	294	56	1.5
DHDMI	4.8	4.31	271	76	1.5
DHDMI/Chitosan(A)	7.4	5.93	207	91	1.5
DHDMI/Chitosan(B)	7.2	5.74	219	101	4.6
DHDMI/Chitosan(C)	8.1	5.67	215	97	3.2
DHDMI/Chitosan(D)	8.2	5.84	252	89	3.0
DHDMI/Chitosan(E)	7.4	5.86	269	94	2.2
DHDMI/Chitosan(F)	6.7	5.59	264	82	2.0

^a Breaking strength retention.

^b 19.75 kg.

Table III Direct Dye Uptake (K/S) of DHDMI/Chitosan-Treated Samples

Treated Sample	Add-On (%)	Direct Blue 212	Direct Green 27	Direct Red 81
Untreated	—	1.209	2.718	4.110
DMDHEU	4.4	0.085	0.134	0.266
DHDMI	4.8	0.314	0.225	3.272
DHDMI/Chitosan(A)	7.4	4.778	9.376	11.157
DHDMI/Chitosan(B)	7.2	6.334	10.024	13.242
DHDMI/Chitosan(C)	8.1	4.601	6.760	10.997
DHDMI/Chitosan(D)	8.2	5.587	6.875	10.788
DHDMI/Chitosan(E)	7.4	3.145	3.669	8.975
DHDMI/Chitosan(F)	6.7	1.640	2.092	5.817

anionic dyes. As shown in Figure 2, direct dye uptake on DHDMI/chitosan-treated samples tends to increase as molecular weight of chitosan increases and then slightly decreases at the highest molecular weight used in this study, 185,300. Chitosan of high molecular weight provides more easily accessible dye sites on the fiber surface because it is too big to penetrate inside the fiber, thus inducing deposition on the fiber surface. Chitosan of low molecular weight creates less dyeing sites because the amount of amino group in chitosan is decreased during depolymerization reaction. In addition, chitosan of low molecular weight is expected to have greater penetrating power.

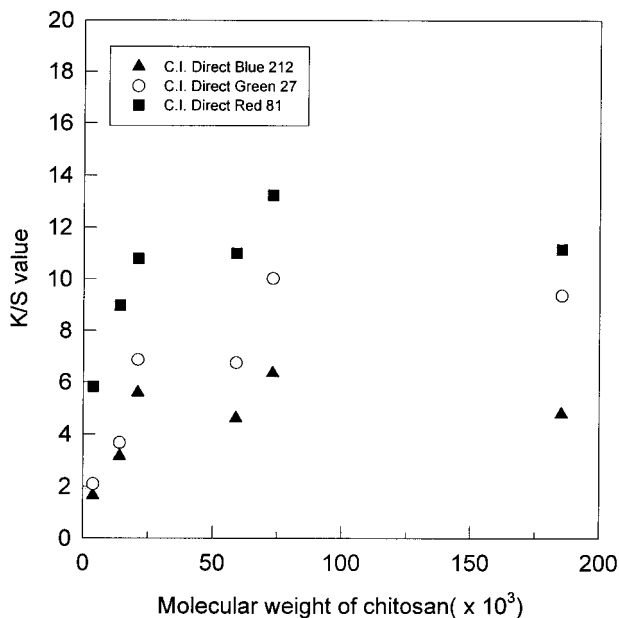
**Figure 2** Plots of direct dye uptake vs. molecular weight of chitosan for DHDMI/chitosan treated samples.

Figure 3 shows the effect of chitosan on the rate of dye uptake. DHDMI/chitosan-treated samples were found to take up dye faster than untreated one, resulting in higher exhaustion. The exhaustion increases with the increase in the molecular weight of chitosan. After 40 min of dyeing, DHDMI/chitosan (A) sample shows 99% exhaustion compared to 25% exhaustion for the untreated sample.

Uptake of Acid Dyes

Table IV shows acid dye uptake on untreated, DP-finished, DHDMI/chitosan-treated samples. Acid dye uptake on untreated and DP-finished samples

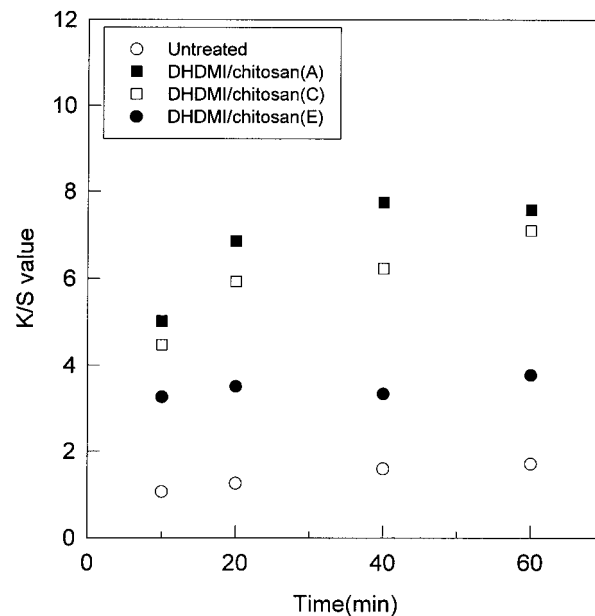
**Figure 3** Rate of dye uptake (C.I. Direct Green 27) on untreated and DHDMI/chitosan treated samples.

Table IV Acid Dye Uptake (K/S) of DHDMI/Chitosan-Treated Samples

Treated Sample	Add-On (%)	Acid Blue 277 : 1	Acid Yellow 79	Acid Red 246
Untreated	—	0.208	0.306	0.237
DMDHEU	4.4	0.142	0.207	0.262
DHDMI	4.8	0.208	0.318	0.380
DHDMI/Chitosan(A)	7.4	5.275	3.218	7.405
DHDMI/Chitosan(B)	7.2	4.540	2.424	5.722
DHDMI/Chitosan(C)	8.1	4.420	2.538	5.587
DHDMI/Chitosan(D)	8.2	3.389	1.663	4.040
DHDMI/Chitosan(E)	7.4	1.188	0.857	2.328
DHDMI/Chitosan(F)	6.7	0.314	0.555	0.767

is not significant, as shown in Table IV. Uptake of acid dyes onto untreated and DP-finished cotton fabrics is enhanced by treatment with chitosan. This result is due to the amino groups of chitosan creating additional dye sites for acid dye anion. Adsorption of acid dyes is attributed to electrostatic attraction between amino groups and dye anions, and van der Waals forces. As shown in Figure 3, acid dye uptake increases as the molecular weight of chitosan increases. This indicates that chitosan of high molecular weight provides amino groups more easily accessible to dye molecules. Lower uptake of acid dyes on DHDMI/chitosan samples treated with chitosan of low molecular weight is partially due to the reduction of amino groups in the process of depolymerization

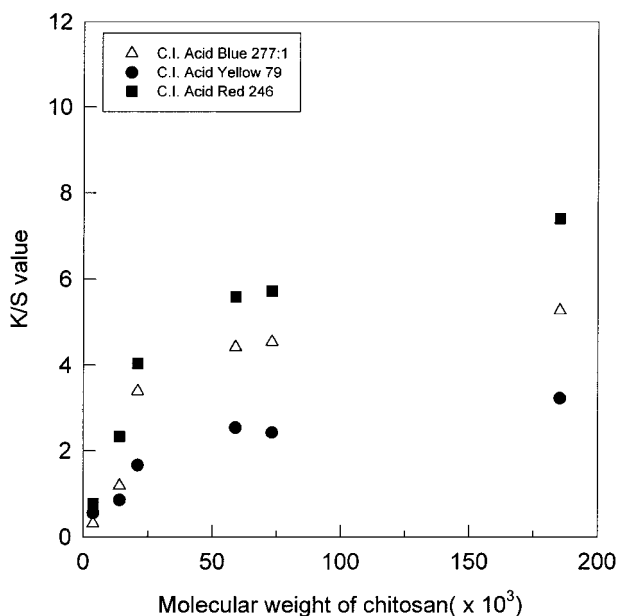


Figure 4 Plots of acid dye uptake vs. molecular weight of chitosan for DHDMI/chitosan-treated samples.

reaction, as described earlier. This is substantiated by the infrared spectra showing that —NH_2 deformation band at 1580 cm^{-1} becomes weaker gradually as the molecular weight of chitosan decreases and finally C=O stretching band at 1650 cm^{-1} predominates over —NH_2 deformation band at 1580 cm^{-1} in the spectrum of chitosan F.

Uptake of Reactive Dyes

Table V shows reactive dye uptake on untreated, DP-finished, DHDMI/chitosan-treated samples. The uptake of reactive dyes on DP-finished cotton is decreased remarkably. Reactive dyes form covalent linkages with hydroxyl groups of cellulose. Crosslinks between hydroxyl groups of cellulose and *N*-methylol groups of DMDHEU or hydroxyl groups of DHDMI are expected to reduce dye sites in cellulose for reactive dyes. However, DHDMI/chitosan-treated samples give higher dye uptake than DHDMI-treated sample. This indicates that hydroxyl groups of chitosan provide additional dye sites to form covalent linkages with reactive dyes in alkaline condition. Uptake of reactive dyes increases slightly with the decrease in molecular weight of chitosan in alkaline condition. It is thought because hydroxyl end groups in chitosan of low molecular weight are formed by the depolymerization,¹⁴ and they provide more open dye sites on the samples treated with chitosan of low molecular weight.

In acidic condition, the dyeing mechanism of reactive dyes on DHDMI/chitosan-treated samples is similar to that of reactive dyes on protein fibers because amino groups on these samples provide dye sites. Because both CI Reactive Blue 184 and CI Reactive Red 183 are the nucleophilic substitution reaction type, they form salt linkages with amino groups in the acidic condition. As shown in Table V, the uptake of CI Reactive Red

Table V Reactive Dye Uptake (K/S) of DHDMI/Chitosan-Treated Samples

Treated Sample	Add-On (%)	Reactive Blue 184	Reactive Red 183 ^a
Untreated	—	11.678	6.508 (1.086)
DMDHEU	4.4	0.625	0.368 (0.253)
DHDMI	4.8	1.715	2.246 (2.970)
DHDMI/Chitosan(A)	7.4	4.386	5.172 (9.085)
DHDMI/Chitosan(B)	7.2	4.607	4.817 (8.956)
DHDMI/Chitosan(C)	8.1	4.472	4.877 (10.386)
DHDMI/Chitosan(D)	8.2	4.457	5.341 (12.423)
DHDMI/Chitosan(E)	7.4	5.263	5.413 (9.684)
DHDMI/Chitosan(F)	6.7	6.626	6.281 (5.244)

^a Values in parenthesis are obtained in acidic condition (pH 5.5–6.0).

183 on DHDMI/chitosan-treated samples in acidic condition increases with the decrease in the molecular weight of chitosan and reaches to the maximum at M.W. 21,000 (sample D), and decreases thereafter. The range of M.W. 21,000 is considered to be the optimum condition forming linkages between dye molecules and amino groups. The uptake of CI Reactive Red 183 is higher in the acidic than in the alkaline condition, except the sample F. This indicates that amino groups are more accessible than hydroxyl groups on the surface of the DHDMI/chitosan (A–E)-treated samples.

Colorfastness to Washing and Crocking

Tables VI–VII show the colorfastness to washing and crocking of the dyed samples. Chitosan does not adversely affect the colorfastness to washing, but decreases the colorfastness to wet crocking of DHDMI/chitosan-treated samples by half a point. The results indicate that bindings between cellulose and chitosan and between chitosan and dyes

are not weak. The binding of chitosan to cellulose is attributed to both van der Waals forces and ionic interactions between amino groups of chitosan and hydroxyl groups of cellulose. It was reported that application of chitosan on fibers with hydroxyl and/or carboxyl acid groups, such as cellulosic fibers, cellulose acetate, protein fibers, etc., permits coatings tightly adhered to the fiber due to ionic interactions.¹⁷ Rippon¹⁰ suggested another binding mechanism involves in insolubilization of chitosan, which is the removal of amino groups by dehydration during the drying step, with the subsequent formation of imido crosslinks.

The covalent bonding between chitosan and cellulose would be expected to the DHDMI/chitosan-treated sample because DHDMI could make a two-point attachment as a crosslinker; one to amino groups in chitosan, and the other to hydroxyl groups in cellulose. Masri et al.⁸ used DMDHEU as a crosslinker to make chitosan grafting and covalent attachment to the wool and obtained improved resistance to laundering shrinkage.

Table VI Colorfastness to Washing of the Dyed Samples

Treated Sample	Direct Green 27		Acid Blue 277 : 1		Reactive Red 183	
	Color Change	Cotton Stain	Color Change	Cotton Stain	Color Change	Cotton Stain
Untreated	5	5	—	—	4/5	4
DHDMI	—	—	4	5	—	—
DHDMI/Chitosan(A)	5	5	4	5	5	5
DHDMI/Chitosan(B)	5	5	4	5	5	5
DHDMI/Chitosan(C)	5	5	4/5	5	5	5
DHDMI/Chitosan(D)	5	5	4	5	5	5
DHDMI/Chitosan(E)	5	5	4	5	5	5
DHDMI/Chitosan(F)	5	5	4	5	5	5

Table VII Colorfastness to Crocking of Dyed Samples

Treated Sample	Direct Green 27		Acid Blue 277 : 1		Reactive Red 183	
	Dry	Wet	Dry	Wet	Dry	Wet
Untreated	5	4	—	—	4/5	4
DHDMI	—	—	4/5	4/5	—	—
DHDMI/Chitosan(A)	4/5	3/4	4/5	3/4	4/5	4
DHDMI/Chitosan(B)	4/5	3/4	4/5	3/4	4/5	3/4
DHDMI/Chitosan(C)	4/5	4	4/5	3/4	4/5	3/4
DHDMI/Chitosan(D)	4/5	3/4	4/5	4/5	4/5	3/4
DHDMI/Chitosan(E)	4/5	4	4/5	4/5	4/5	3/4
DHDMI/Chitosan(F)	4/5	4/5	4/5	4/5	4/5	3/4

CONCLUSIONS

Chitosan improves uptake of direct and acid dyes on untreated as well as DP finished cotton. The uptake of direct and acid dyes increases as the molecular weight of chitosan increases. However, the uptake of reactive dyes slightly increases with the decrease in molecular weight of chitosan in alkaline condition. The uptake of reactive dyes on DHDMI/chitosan-treated samples is higher in the acidic condition than in the alkaline condition, except the F sample. Chitosan treatment has no discernable effects on the colorfastness to washing, but decreases the colorfastness to wet crocking by about half a point. Chitosan affects the other properties of treated fabric; less wrinkle recovery angle, stiffer handle, and higher breaking strength as the molecular weight of chitosan increases.

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