Dyeing of Cotton Fibers Decrystallized by Alkali Swelling and Partial Substitution

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Synopsis

This report summarizes the observations made on the dyeing behavior of highly decrystallized cotton fibers obtained by partial acetylation and cyanoethylation of NaOH swollen fibers. The dyeing studies were also carried out after crosslinking these decrystallized samples. A purified direct dye, Chlorazol Sky-Blue FF, has been used for the studies. It is observed that partially cyanoethylated and acetylated celluloses show a dye uptake of more than twice that of the corresponding swollen controls even for low degrees of substitution such as about 5.0% acetyl content for the acetylated fibers and 1.0% nitrogen content for the cyanoethylated fibers. On crosslinking also the trend in the dye uptake pattern remained the same, though the actual amount of dye the fibers could adsorb was markedly reduced. The swollen, substituted, and crosslinked fibers showed a better uniformity of appearance than the swollen and crosslinked fibers.

INTRODUCTION

Some of the recent approaches[1-3] to produce highly decrystallized cotton employ substitution as a means to preserve the decrystallization produced by NaOH swelling even after washing and drying. The decrystallized fibers produced by partial substitution of NaOH swollen cottons can find extensive application in subsequent crosslinking treatments, where, as pointed out by Gagliardi and Wehner,[1] a better distribution of crosslinks can be expected. The extent of decrystallization so produced can be assessed from moisture regain, dye adsorption, or crystalline:amorphous ratio by x-ray or infrared methods, etc. Hebeish et al.[4] have recently studied the dyeing behavior of partially substituted cellulose films, including acetylated and cyanoethylated materials. However, these samples were not subjected to any preswelling treatments, and it was found that for the cyanoethylated samples the dye uptake was lower than for that of the control, while the acetylated and grafted samples showed a reverse trend. Apart from this, no other detailed study is available on the dyeing properties either of the substituted or of the decrystallized materials using direct dyes. A thorough investigation of the dye uptake of the decrystallized materials whereby it was also possible to show that this property could serve as an additional index in determining the efficacy of the decrystallization treatments was therefore undertaken.

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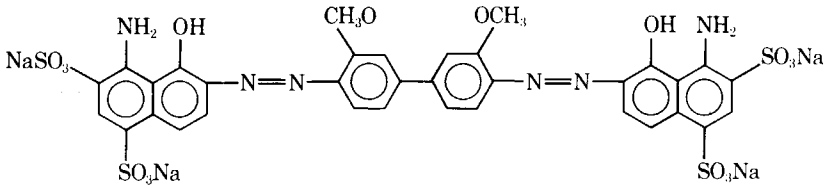
EXPERIMENTAL

Materials

Dewaxed and kier-boiled fibers from a fine variety (PSH) and a coarse variety (Digvijay) of cotton were used in the studies. Acrylonitrile used was of commercial quality while acetic anhydride was of "analar" grade. Commercial-grade Chlorazol Sky-Blue FF dye, having the structure shown here, was used after further purification.[5]



Preparation of Decrystallized Materials

Decrystallized samples were prepared by the procedure followed by Kulshreshtha and Dweltz[3] for partial acetylation and by Tsuji et al.[2] for partial cyanoethylation with slight modifications. Samples were swollen by using three different concentrations of NaOH [12, 15, and 21% (w/w)] prior to the partial substitution treatments. Benzene was used as a diluent while treating the fibers with the respective reagents. The reaction time and the concentration of the reactants were adjusted so that all the differently swollen materials had nearly the same acetyl content (6–8%) after partial acetylation and nearly the same nitrogen content (1.2–1.7%) after partial cyanoethylation. Limiting the substitution to such low levels was considered necessary to avoid any serious mechanical deterioration of the fibers. However, to see the effect of varying the substitution on the dye uptake, an additional set of cyanoethylated, as well as acetylated, samples were prepared by using a single preswelling concentration.

Dyeing of the Decrystallized Fibers

For dyeing the samples, a dye liquor which contained 0.3 g/l. dye and 5 g/l. sodium sulfate was used. Dyeing was carried out at 95°C for a period of 1 hr for all samples except those used for studying the variation of dye uptake with time, in which case the samples were dyed for periods of 5, 10, 20, and 40 min, and 1 hr. After the specified time, the samples were rinsed thoroughly with cold water and dried.

Estimation of Dye

Dye was extracted from the fiber with 25% aqueous pyridine and estimated spectrophotometrically by measuring the percent transmittance at 6200 A using a Spectronic-20 spectrophotometer and the usual procedure.

Preparation of Decrystallized and Crosslinked Materials, Dyeing and Dye Estimation

The decrystallized fibers of the finer variety of cotton were crosslinked along with the swollen controls using dimethylol dihydroxyethyleneurea (DMDHEU), with $MgCl_2$ as catalyst, following the conventional pad-dry-cure process. These were dyed as described and their dye content estimated as in the previous paragraph.

RESULTS AND DISCUSSION

Table I gives the details of the swollen and decrystallized materials used for dyeing studies as well as their dye uptake. Figure 1 shows variation in dye uptake with preswelling concentrations for the differently swollen and decrystallized fibers belonging to the two varieties of cotton. No appreciable difference was observed in the dye uptake of the two varieties studied. It may be observed that even a 12% NaOH treatment improves considerably the dye uptake over that of the kiered controls, while decrystallization by partial substitution enhances the dye uptake considerably. With 15% NaOH, the swelling is almost complete, and raising the alkali concentration to 21% had little effect on increasing the dye uptake of either the controls or the decrystallized materials. Both cyanoethylation and acetylation produced a dye absorption which was more than double that of the corresponding NaOH swollen controls. It can also be noted that cyanoethylation has a higher decrystallizing effect than acetylation as shown by the increased dye uptake for the former. This is in line with the observations made by x-ray and infrared crystallinity measurements[6] on these samples, where it was found that cyanoethylation produces a higher decrystallization than acetylation for a very limited substitution. These results could be attributed

TABLE I
Treatments, Extent of Substitution Given as Percent N or Percent Acetyl, and Dye Uptake for Two Different Varieties of Cotton

	PSH			Digvijay		
Treatment	Acetyl, %	Nitrogen, %	Dye uptake, g/kg of fiber	Acetyl, %	Nitrogen, %	Dye uptake, g/kg of fiber
Dewaxed and kier-boiled	—	—	8.60	—	—	8.90
12% NaOH swollen	—	—	13.07	—	—	12.70
12% NaOH swollen and acetylated	7.60	—	29.06	7.20	—	29.74
12% NaOH swollen and cyanoethylated	—	1.39	36.06	—	1.35	36.16
15% NaOH swollen	—	—	16.88	—	—	17.10
15% NaOH swollen and acetylated	6.53	—	35.75	6.97	—	38.00
15% NaOH swollen and cyanoethylated	—	1.53	47.22	—	1.72	48.50
21% NaOH swollen	—	—	18.60	—	—	18.10
21% NaOH swollen and acetylated	8.05	—	37.39	8.18	—	38.50
21% NaOH swollen and cyanoethylated	—	1.40	43.33	—	1.50	44.75

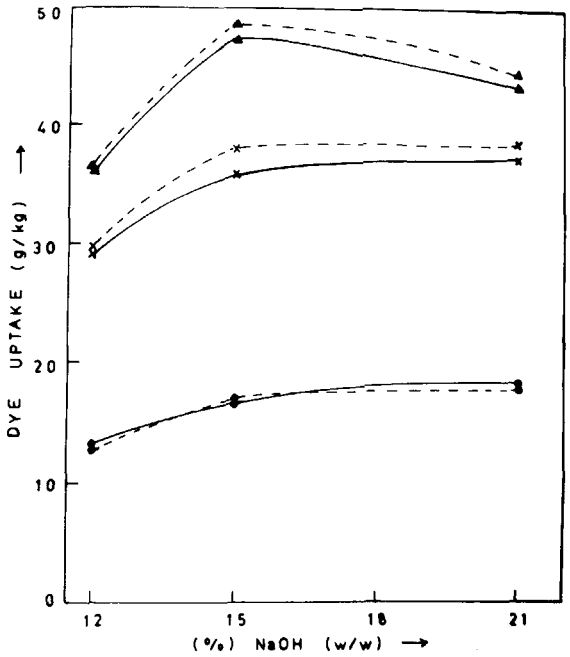


Fig. 1. Variation of dye uptake with preswelling NaOH concentration. (—) PSH; (- - -) Digvijay; (●—●) controls; (x—x) partially acetylated; (▲—▲) partially cyanoethylated.

to the larger volume of the cyanoethyl group than the acetyl group, by virtue of which the former is able to bring about more severe distension of molecular bundles.

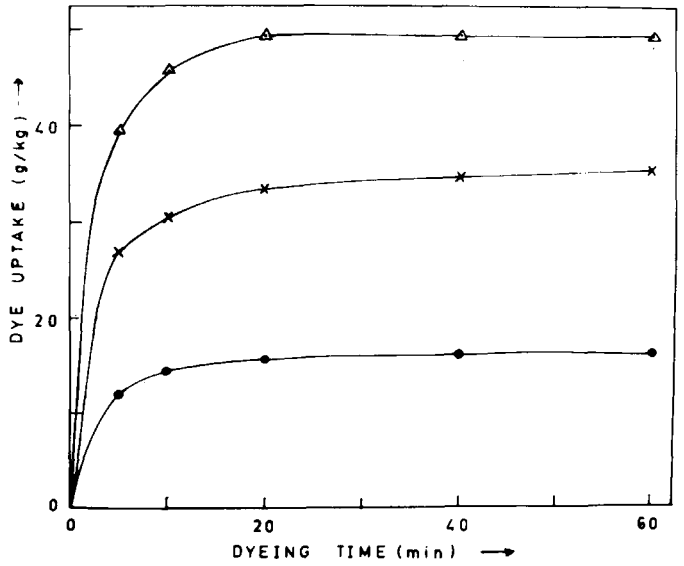


Fig. 2. Variation of dye uptake with time for PSH cotton. (●—●) 15% NaOH swollen; (x—x) 15% NaOH swollen and partially acetylated; (△—△) 15% NaOH swollen and partially cyanoethylated.

Figure 2 shows the increase in dye uptake with time for 15% NaOH swollen and decrystallized fibers. Initially the dye uptake increases very fast. The variation with time follows nearly the same pattern for the control as for the decrystallized fibers, and at all times the decrystallized fibers show a dye uptake which is much more than that of the control.

Figure 3 shows the variation in the dye uptake with acetyl content and nitrogen content (for a limited range of substitution) for the partially substituted materials. In both cases, there is initially a sudden increase in the dye uptake with substitution, after which time it tends to level off. Higher substitution can lead to two mutually opposing effects, viz., 1) an increase in distension, which can cause an increase in the dye uptake, and 2) blocking of more and more OH groups, resulting in fewer hydroxyls available for binding with the dye which ultimately can lead to a reduction in the dye uptake. The latter may be the reason for the absence of any remarkable increase in the dye uptake beyond about 6% acetyl content and 2% N content.

Figure 4 shows the effect of DMDHEU crosslinking on the dye uptake of decrystallized fibers along with the controls for the fine variety of cotton (PSH). It is found that here, too, the dye uptake of the decrystallized and crosslinked sample is much higher than that of the swollen and crosslinked fibers with nearly the same nitrogen content. Decrystallized and crosslinked fibers showed a better uniformity of shade on dyeing than the swollen and crosslinked fibers. It would appear that the difficulties encountered in dyeing crosslinked fibers can be overcome, at least in part, if the material is decrystallized prior to crosslinking.

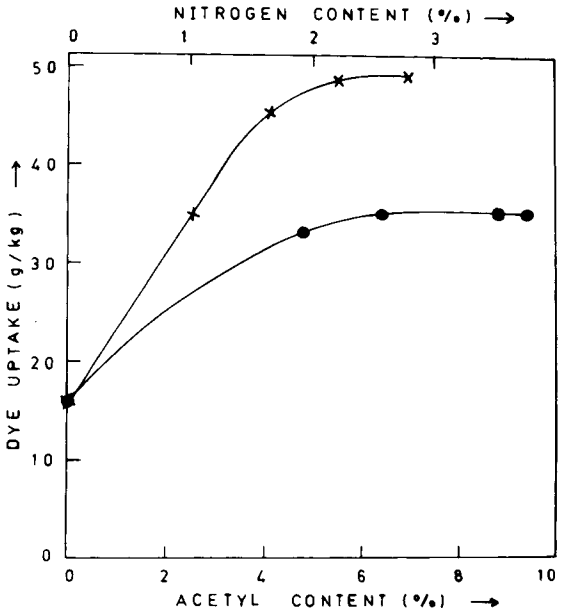


Fig. 3. Variation of dye uptake with percent acetyl and percent N for PSH cotton fibers preswollen in 15% NaOH; (●—●) partially acetylated; (x—x) partially cyanoethylated.

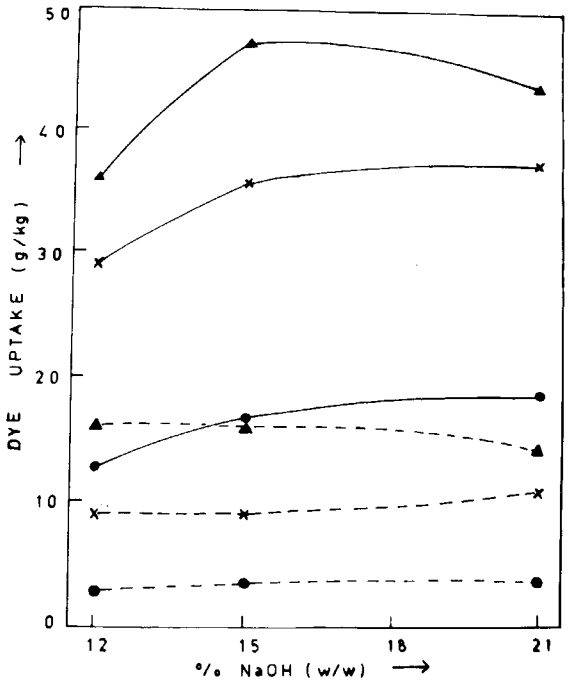


Fig. 4. Variation of dye uptake with preswelling NaOH concentration for swollen decrystallized and crosslinked PSH cotton fibers: (—) before crosslinking; (- - -) after crosslinking; (●—●) control; (x—x) partially acetylated; (▲—▲) partially cyanoethylated.

CONCLUSIONS

The uptake of direct dyes of cotton fibers is a function of the physical state of the fiber at the time of dyeing. Thus, samples swollen in NaOH and subjected to partial cyanoethylation showed a higher dye uptake than the control (NaOH swollen), while cellulose films cyanoethylated without any prior swelling treatment showed a reverse trend.[4]

At low levels of substitution, which have been preceded by swelling, a small variation in the actual degree of substitution did not affect the dye uptake in any significant manner. This was especially true when substitution was greater than a certain minimum.

Under identical preswelling conditions, partial cyanoethylation produced a higher decrystallization than partial acetylation.

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