Comparative Study of the Properties of Differently Decrystallized and Crosslinked Cotton Fibers

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Synopsis

The physical, structural, and mechanical properties of decrystallized cotton fibers prepared by preswelling in different concentrations of alkali followed by partial substitution—to nearly the same extent irrespective of the preswelling alkali concentration—by acetylation or cyanoethylation have been compared. The decrystallized fibers have been crosslinked with dimethylol dihydroxy ethylene urea (DMDHEU), along with the swollen controls, and the mechanical properties have been measured on these samples. It was found that preswelling in NaOH solution of lower concentration (12–15%) prior to cyanoethylation results in better decrystallized fibers which also possess better strength uniformity, whereas a higher concentration of NaOH (15% or above) is necessary for acetylation to obtain fibers with nearly similar characteristics. On crosslinking, the swollen and substituted fibers show a better strength retention and a higher strength uniformity than the swollen control, for the same degree of crosslinking.

INTRODUCTION

In recent years, considerable interest has been shown by research workers in the production of decrystallized cotton by alkali swelling followed by partial substitution. Tsuji and coworkers[1,2] prepared partially cyanoethylated (PC) samples after various preswelling treatments and studied the physical and structural properties of these samples. In a recent publication on decrystallization and acetylation of different cellulosic materials, Kulshreshtha and Dweltz[3] have reported the effect of varying the concentration of preswelling alkali on the structure and properties of partially acetylated (PA) cotton. The role of bulky substituents in minimizing the adverse effects of subsequent crosslinking reactions has been highlighted by Gagliardi and Wehner.[4] It has also been reported that cellulosic materials acetylated[5] by conventional methods could not be crosslinked because of an insufficient number of OH groups, while partial cyanoethylation[6] by conventional procedures led to considerable strength losses. The choice of reagent, the extent of swelling before substitution, and the degree of substitution all seem to be very important in getting materials with good strength retention after crosslinking. Published data on the physical and structural properties of the decrystallized fibers produced by partial substitution, however, are too meager to permit a reasonably accurate forecast of conditions suitable for the good mechanical performance of cotton fibers after crosslinking.

The present study aims at identifying such conditions of decrystallization, produced by partial esterification and etherification of NaOH swollen cotton fibers by critically examining their various fiber properties, so that the decrystallized fibers can be used to advantage in subsequent crosslinking treatments.

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The acetyl content was chosen to be substantially the same in all acetylated samples while the nitrogen content was kept nearly equal in the case of cyanoethylated samples.

EXPERIMENTAL

Materials

Dewaxed and kier-boiled cotton fibers belonging to two different varieties—one coarse (Digvijay) and another fine (PSH)—have been used in the studies.

Decrystallization by Partial Acetylation

Fiber samples in sliver form were swollen in NaOH of specified concentration (12, 15, or 21% w/w) at room temperature for 10 min and centrifuged such that the alkali pickup never exceeded 200%. The centrifuged samples were then treated with acetic anhydride diluted with benzene. The reaction time and concentration of acetic anhydride in benzene were suitably adjusted so as to get a uniformly treated sample with nearly the same acetyl content irrespective of the preswelling NaOH concentration. With 21% alkali, a 10-min treatment in 30% acetic anhydride was sufficient to give an acetyl content of 7–8%, while with 12% alkali, 40% acetic anhydride and about a 35-min treatment were required to give nearly the same acetyl content. After the specified time of treatment, the sample was washed thoroughly and air dried.

Decrystallization by Partial Cyanoethylation

After swelling and centrifuging the fiber samples as in the previous case, they were treated with a solution of 35% commercial grade acrylonitrile in benzene for about 12 min at room temperature. The treated fibers were then washed in running water, soured in 2% acetic acid for 15 min washed again, and dried. Samples so prepared had a nitrogen content of about 1.5%. Samples with higher nitrogen contents could be obtained by extending the time of treatment in acrylonitrile.

The respective controls were similarly obtained by treating the centrifuged sample with benzene only.

Crosslinking of Decrystallized Fibers

Crosslinking of the fibers was carried out with 4% DMDHEU using $MgCl_2 \cdot 6H_2O$ as catalyst and polyethylene as softener. Samples were immersed in the crosslinking bath for 15 min and were padded to get a wet pickup of about 80%. They were later kept at about 80°C in a stoppered bottle for 15 min and then cured at 150–160°C for about 3 min. A few hours after curing, the samples were washed thoroughly with a mild detergent and air dried. The degree of crosslinking (% N) was estimated from the absorbance of the carbonyl band in the infrared spectrum with the aid of a suitable calibration graph, for the crosslinked controls and cyanoethylated samples, while for crosslinked acetylated samples % N were determined chemically.

MEASUREMENT OF FIBER PROPERTIES

Strength Tests

The samples were pre-dried over $CaCl_2$ and conditioned at 65% RH before the strength tests. Bundle tenacity was determined at 0 and $\frac{1}{8}$ in. gauge lengths using a Stelometer. Single-fiber tests of about 100 for each sample were carried out at 1-cm gauge length using an Instron tensile tester.

Acetyl and Nitrogen Contents

The relative intensity of the carbonyl peak and the nitrile peak in the infrared absorption spectra of PA and PC samples, respectively, can be directly correlated with acetyl or nitrogen contents for low degrees of substitution (DS less than 0.5). By measuring the absorbance ratio

$$\frac{a_{C=O}}{a_{C-H}}$$

or

$$\frac{a_{C\equiv N}}{a_{C-H}}$$

as the case may be, the acetyl and nitrogen contents could be estimated with the help of calibration graphs.

Moisture Regain

Duplicate samples of about 0.5 g each were predried over $CaCl_2$ and then conditioned at 65% RH until constant weight was reached. They were later dried at 110°C for 5 hr before determining their bone dry weights. The regain was obtained as the percentage of the dry weight of the fiber.

Crystallinity by Infrared Method

In the case of the control and the cyanoethylated samples, the crystallinity was estimated both from the 1372-cm^{-1} band (Index II) used by Nelson and O'Connor[7] and from the 342-cm^{-1} band (Index III) recently suggested by Iyer, Iyer, and Patil.[8] With the acetylated samples, the former could not be estimated because of interference of the 1372-cm^{-1} band with the absorption from the CH_3 group. Spectra of finely cut fibers in KBr matrix were recorded with a Perkin–Elmer model 457 spectrophotometer.

Crystallinity by X-ray Method

The x-ray crystallinity index was determined by following the method of Segal, et al.[9] Ni-filtered Cu radiation from Philips stabilized x-ray generator and diffractometer in the reflection mode were used to record the radial x-ray diffractograms of powdered specimens. The intensities were read out from the chart and used for calculating the crystallinity index.

Dye Uptake

Samples were dyed with a purified direct dye (Chlorazol Sky Blue FF) at 95°C using a dye liquor containing 0.3 g/liter dye and 5 g/liter sodium sulfate for 1 hr. The dye uptake was estimated from spectrophotometric analysis of the dye extract obtained by stripping the dye with 25% aqueous pyridine. A detailed study of the dyeing behavior of the decrystallized material is given elsewhere.[10]

RESULTS AND DISCUSSION

Preliminary Experiments

Figures 1 and 2 represent the results of preliminary experiments designed to identify substitution levels suitable for achieving high decrystallization combined with marginal strength loss. It is seen from these figures that tenacity decreased with increase in acetyl–nitrogen content, while the moisture regain (MR) increased, reached a maximum, and thereafter tended to fall. The deterioration in strength corresponding to the level of substitution giving maximum regain is, however, quite small in both cases. An acetyl content of about 6% and a nitrogen content of about 1.5% seem to combine a high degree of decrystallization with negligible strength loss.

Table I gives the various fiber properties for the two varieties of cotton decrystallized under identical conditions. It is observed that for a given preswelling treatment, PC samples show better decrystallization than PA samples as observed by the higher dye uptake and moisture regain values of the former as well as by their lower infrared and x-ray crystallinity indices. The difference between

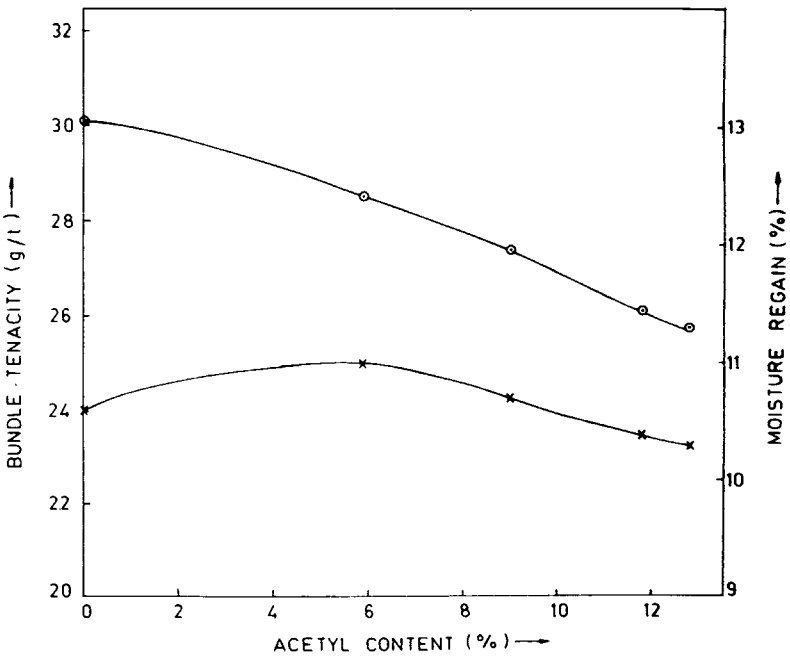

Fig. 1. Variation of bundle tenacity, ⊙, and moisture regain, with acetyl content (for 21% NaOH preswollen PA fibers).

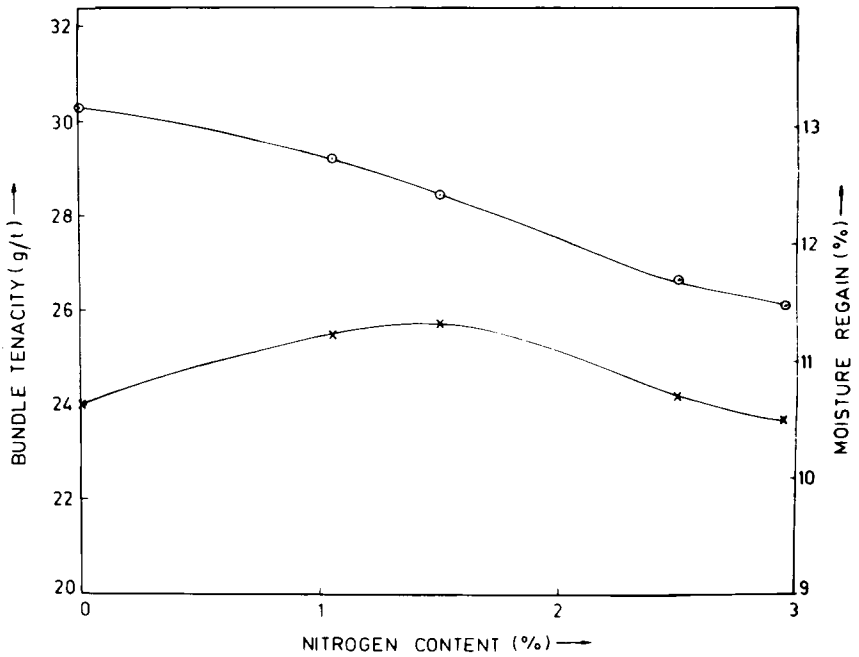

Fig. 2. Variation of bundle tenacity, ⊙, and moisture regain, with nitrogen content (for 21% NaOH preswollen PC fibers).

the PA and PC samples in respect of the extent of decrystallization is more marked for preswelling concentrations of 12 and 15%.

Table II shows the mechanical properties of the decrystallized fibers along with those of the controls. It may be seen that at the very low levels of substitution as is used here, the strength loss is very negligible after the preswelling treatments in 12 and 15% NaOH concentrations. On decrystallization, the strength uniformity ratio either improved slightly or remained nearly the same. While PC treatments gave a higher strength uniformity ratio for 12 and 15% NaOH swelling, PA produced a higher uniformity ratio for the 21% swollen fibers, especially for the coarse variety of cotton, Digvijay. Single fiber data did not convey much information except to indicate that PC samples had a slightly higher percentage of extension over the control and PA samples. This is a direct consequence of the higher decrystallization produced by partial cyanoethylation. While structural and physical properties did not show any marked difference between the varieties, the mechanical properties show the superiority of the finer variety, both before and after decrystallization treatments. For the finer variety of cotton, PSH, strength and strength uniformity ratio remained high throughout while % CV for single fiber strength and extension remained low. Table III summarizes data showing the effect of crosslinking on the bundle strength of the decrystallized fibers. It may be noted that decrease in % N due to crosslinking, as the preswelling NaOH concentration is reduced from 21 to 12%, results largely from the fewer accessible OH groups available for crosslinking when the preswelling concentration is decreased. For the same degree of crosslinking, the decrystallized fibers showed a higher strength and strength uniformity ratio than the controls. This indicates a better distribution of crosslinks in the

TABLE I
Physical and Structural Properties of Decrystallized Fibers for Two Varieties of Cotton

Sample	Variety of cotton: Digvijay						PSH					
	Nitrogen/ acetyl, %	MR, %	Dye uptake, g/kg	Crystallinity: IR index II	Crystallinity: IR index III	Crystallinity: X-ray index	Nitrogen/ acetyl, %	MR %	Dye uptake, g/kg	Crystallinity: IR index II	Crystallinity: IR index III	Crystallinity: X-ray index
Dewaxed and kiered	—	7.4	8.76	0.66	0.63	0.83	—	7.6	8.86	0.68	0.63	0.84
Control (12% NaOH swollen)	—	8.9	12.70	0.61	0.56	0.80	—	9.1	13.07	0.67	0.57	0.81
PA (12% NaOH preswollen)	6.2	9.1	29.74	—	0.50	0.74	6.6	9.5	29.06	—	0.51	0.74
PC (12% NaOH preswollen)	1.35	9.9	36.16	0.53	0.42	0.70	1.39	10.1	36.06	0.59	0.42	0.70
Control (15% NaOH swollen)	—	9.5	17.10	0.54	0.36	0.67	—	9.8	16.88	0.61	0.36	0.66
PA (15% NaOH preswollen)	6.97	10.1	38.00	—	0.27	0.59	6.53	10.4	35.75	—	0.29	0.56
PC (15% NaOH preswollen)	1.72	10.6	48.50	0.44	0.26	0.56	1.53	10.9	47.22	0.49	0.25	0.55
Control (21% NaOH swollen)	—	10.6	18.10	0.51	0.32	0.62	—	10.5	18.60	0.59	0.34	0.64
PA (21% NaOH preswollen)	8.18	10.8	38.50	—	0.24	0.52	8.05	10.8	37.39	—	0.27	0.48
PC (21% NaOH preswollen)	1.50	11.3	44.75	0.45	0.22	[a]	1.40	11.3	43.33	0.49	0.24	[a]

[a] The index could not be measured because of a shift in the (002) peak.

TABLE II
Mechanical Properties of Decrystallized Fibers for Two Varieties of Cotton

Sample	Variety of cotton: Digvijay					PSH				
	Bundle tenacity, g/tex at		Uniformity Ratio	Single fiber[a] Strength, g	Single fiber[a] Extension, %	Bundle tenacity, g/tex at		Uniformity Ratio	Single Fiber Strength, g	Single Fiber Extension, %
	0 in.	1/8 in.				0 in.	1/8 in.			
Dewaxed and kiered	47.30	28.56	0.60	6.18	6.9	49.60	37.94	0.76	5.44	7.5
12% NaOH swollen	40.50	32.80	0.81	7.24	10.4	47.80	40.33	0.84	6.13	12.4
				(36.9)	(30.9)				(27.1)	(24.7)
12% NaOH swollen and PA	37.60	31.50	0.84	7.04	10.9	45.20	38.55	0.85	6.80	12.5
				(41.8)	(28.9)				(23.5)	(26.5)
12% NaOH swollen and PC	35.90	32.26	0.90	7.78	11.3	42.60	37.47	0.88	6.88	12.5
				(40.4)	(32.6)				(26.2)	(26.6)
15% NaOH swollen	40.00	32.50	0.81	7.68	13.3	39.90	36.16	0.91	6.60	17.6
				(39.7)	(31.3)				(24.3)	(27.0)
15% NaOH swollen and PA	37.30	30.75	0.82	7.69	13.4	41.20	37.10	0.90	6.55	17.8
				(34.3)	(36.6)				(25.7)	(28.2)
15% NaOH swollen and PC	37.40	32.75	0.88	7.58	15.3	38.20	33.26	0.87	7.02	19.1
				(36.4)	(32.6)				(23.1)	(25.5)
21% NaOH swollen	36.00	30.13	0.84	7.34	14.8	40.50	37.93	0.94	6.15	17.2
				(37.4)	(27.5)				(27.3)	(23.1)
21% NaOH swollen and PA	32.50	28.24	0.87	7.04	15.0	37.10	34.41	0.93	6.24	18.9
				(37.2)	(29.1)				(33.0)	(26.4)
21% NaOH swollen and PC	32.80	28.17	0.86	7.16	15.2	35.80	33.49	0.94	5.80	19.9
				(35.3)	(30.2)				(27.4)	(28.5)

[a] Values in parenthesis give corresponding CV%.

TABLE III
Mechanical Properties of Decrystallized and Crosslinked Fibers of PSH Cotton

Sample	Nitrogen due to Crosslinking alone, %	Bundle Test Data: Tenacity, g/tex at gauge length 0 in.	Tenacity, g/tex at gauge length 1/8 in.	UR	Extension, %	Percent Retention of tenacity at gauge length 0 in.	Percent Retention of tenacity at gauge length 1/8 in.
12% NaOH swollen and crosslinked (control)	0.35	20.4	11.9	0.58	5.7	42.67	29.50
12% NaOH swollen, acetylated, and crosslinked	0.38	28.9	19.9	0.69	7.2	63.93	51.62
12% NaOH swollen, cyanoethylated, and crosslinked	0.40	28.2	20.8	0.74	7.3	66.19	55.51
15% NaOH swollen and crosslinked (control)	0.66	24.4	15.6	0.64	5.8	61.15	43.14
15% NaOH swollen, acetylated, and crosslinked	0.70	26.4	19.1	0.72	7.8	64.07	51.48
15% NaOH swollen, cyanoethylated, and crosslinked	0.72	25.0	16.5	0.66	5.7	65.44	49.60
21% NaOH swollen and crosslinked (control)	0.68	15.4	9.5	0.62	5.1	38.02	25.04
21% NaOH swollen, acetylated, and crosslinked	0.72	21.6	15.4	0.71	7.1	58.22	44.75
21% NaOH swollen, cyanoethylated, and crosslinked	0.75	20.5	13.5	0.66	6.2	57.26	40.31

decrystallized fibers. Decrystallization by partial cyanoethylation gave a higher uniformity ratio when preceded by 12% NaOH swelling while 15 and 21% NaOH swollen materials gave a higher uniformity ratio in the case of PA samples. The "percent tenacity retention," defined as (100 × tenacity of crosslinked sample)/(tenacity of corresponding uncrosslinked sample), shown in the last two columns clearly indicate the superiority of the decrystallized and crosslinked fibers over the crosslinked control.

The results indicate that partial cyanoethylation or acetylation treatment does not produce as bad a starting material, for subsequent crosslinking treatments, as observed by earlier workers, provided substitution is limited to very low levels and is preceded by proper swelling treatments.

CONCLUSIONS

Partial cyanoethylation and acetylation treatments, when carried out after suitable preswelling treatments, produce effective decrystallization which can be used to advantage in getting samples with better strength retention after crosslinking. Acetyl content of nearly 6% for the PA and nitrogen content of nearly 1.5% for the PC samples seem to be ideal for good decrystallization without any serious mechanical deterioration. While a low preswelling NaOH concentration of 12% appeared to be favorable for good strength uniformity in the case of PC samples, a concentration of 21% was found to be necessary to achieve the same degree of strength uniformity in PA fibers. For a given preswelling treatment, partial cyanoethylation produced better decrystallization than partial acetylation. On crosslinking with DMDHEU, decrystallized fibers showed a

higher strength and strength uniformity ratio than the controls for nearly the same degree of crosslinking.

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