

Properties of Cotton Fibers Containing the Cellulose IV Crystal Structure

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Synopsis

Complete conversion of the crystal form in cotton fibers to cellulose IV (cell IV cotton) was obtained by heat treatment of ethylamine-treated cotton cellulose in either saturated steam or formamide. Degradation of the fibers was not extensive during the conversion process; oxidative damage appeared to have been confined primarily to the accessible regions of the fibers. Examination by scanning electron microscopy indicated that the surface of the cell IV cotton was smoother than that of the same cotton with other crystal forms, namely, the starting cotton (cell I cotton), mercerized cotton (cell II cotton), and ethylamine-treated cotton (cell III cotton). Fiber accessibility increased in the order cell I cotton < cell III cotton \leq cell IV cotton < cell II cotton. Using leveling-off degree of polymerization as the measure, it appeared that the lengths of the crystallites in cell I cotton were much higher than those in cell II, III, and IV cotton. The strength of cell IV cotton was comparable to that of cell I cotton even though its degree of polymerization was significantly lower. It is suggested that heat treatments in formamide have an annealing effect on cotton that results in increases of strength.

INTRODUCTION

Five different crystal forms of cellulose have been characterized by x-ray diffraction methods, namely, cellulose I, II, III, IV, and x .^{1,2} Cellulose I normally is present in native celluloses. Cellulose II is prepared from native cellulose by either regeneration from solution or swelling with alkali metal hydroxides (mercerization). Cellulose III is obtained by treating products containing either cellulose I or cellulose II with liquid ammonia or selected anhydrous alkylamines and then decomposing the complex formed in the absence of water or other polar liquids. Heating samples containing cellulose II and/or III, under specified conditions, converts their crystal form to cellulose IV. Cellulose x is formed by treating cotton and wood pulp with concentrated phosphoric or hydrochloric acid.

The tensile properties and fine structure of fibers containing cellulose I, II, or III have been studied more than those containing cellulose IV. The probable reason is that most of the methods that have been described for complete conversion of the crystal form present in cellulose fibers to cellulose IV result in a badly degraded product. However, mercerized cotton and cotton treated with liquid ammonia have unique properties that make them attractive for textile use.³ It is possible therefore that a cellulose IV cotton,

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provided it could be prepared without degradation, would have potential value. Thus the objective of this research was to obtain a high efficiency of cellulose IV formation concomitant with minimal damage to the cotton fiber and then to characterize the tensile properties and fine structure of the treated fibers.

Methods for converting the crystal structure of a cellulose to cellulose IV have been reviewed.^{4,5} The extent of conversion is strongly dependent on the method used.⁶ In general, for any condition, the transformation to cellulose IV is easier and/or more complete for regenerated cellulose fibers than for mercerized native fibers because of the lower crystalline order of the former.⁷ The completeness of the transformation depends not only on the type of fiber but also on various other factors. Sueoka et al.⁸ reported that the ease of transformation can be related to crystal form and is in the order cellulose III_I, regenerated cellulose from cellulose III_I (cellulose I), cellulose III_{II}; and cellulose II. Hermans and Weidinger⁹ pointed out that a higher degree of swelling of the fibers by the heating medium is required to attain better penetration of the medium itself into the fibers. The medium acts as a protective plasticizer, allowing the chain molecules to retain sufficient mobility to arrange themselves into the stabler lattice form. Similar results have been observed by several workers.⁵

In this study, cellulose IV cotton was prepared from a cellulose III sample. To obtain a full appreciation of the changes caused by the treatment to convert the crystal structure of the cotton to cellulose IV, similar characterizations were made on the starting cellulose I fiber as well as the cellulose III and IV samples. Since mercerization is a common method of enhancing the properties of cotton, some data were obtained on mercerized fiber so that the differences between the cellulose IV sample and mercerized cotton could also be observed.

PROCEDURE

Materials

The Deltaphine-Smoothleaf variety of American Upland cotton was obtained from the Southern Regional Research Center, USDA, New Orleans, Louisiana. It had been scoured for 1 h in 2% aqueous sodium hydroxide. All chemicals were reagent grade. Cadoxen solution was prepared by the method of Segal and Timpa.¹⁰

Sample Preparation

Purification of Cotton

The cotton was further purified by refluxing for 8 h in 1% sodium hydroxide in a nitrogen atmosphere (40 g fiber per 2 L solution), washing with distilled water until free from alkali, and then drying.¹¹

Preparation of Cellulose II (Mercerization)

Cotton was mercerized using 5*M* sodium hydroxide (10 g cotton per 500 mL of solution) at 0°C for 1 h.¹² After filtering off the alkaline solution, the sample

was washed with distilled water at least 10 times over 60 min, steeped in 10% acetic acid for 30 min, and then washed again with distilled water until the water was free of acid. The cotton was dried by washing it three times with methanol and three times with ethyl ether before exposure to the ambient atmosphere. The product will be referred to as mercerized cotton or cell II cotton.

Preparation of Cellulose III (Ethylamine Treatment)

Cellulose III cotton was prepared by the method of Segal et al.¹³ Loose, air-dried cotton fibers were immersed in anhydrous ethylamine at an ice-bath temperature under an atmosphere of nitrogen for 4 h. The excess amine was displaced by nitrogen under pressure from the vessel, which was then connected to a condenser cooled by ice water and open to the atmosphere. A slow stream of nitrogen was passed through the system while a water bath was placed around the vessel and was kept boiling until ethylamine was not evolved. The cellulose sample was removed from the vessel, placed overnight under reduced pressure with a slow stream of dry air passing over it, and then kept in a desiccator.

Heat Treatments

Samples were subjected to one of two procedures. The first used a vessel in which the samples could be subjected to saturated water vapor in a nitrogen atmosphere under high pressure at temperatures up to 180°C for 4 h. In the other procedure, the samples were immersed in formamide and heated in a resin kettle at various temperatures for 4 h under a nitrogen atmosphere. The fibers were then washed with methanol three times and dried in a vacuum oven at 40°C. Samples in which the crystal structure was converted to cellulose IV by these treatments will be referred to as cell IV cotton.

Acid-Hydrolyzed Samples

Microcrystalline products were obtained by hydrolyzing the samples in 2.5 *M* hydrochloric acid (1 g sample per 150 mL solution) at the boil in the manner described previously.¹⁴ The products are also called leveling-off degree of polymerization (LODP) celluloses.

Product Characterization

Hygroscopicity

Adsorption moisture regains were determined at 59% RH and 21°C in duplicate, using 1-g samples in the manner described previously.¹⁴ The samples had been ground in a Wiley mill to pass through a 20-mesh screen.

Water Retention Value (WRV)

Samples, cut 0.65–1.3 cm in length, were immersed in distilled water for 24 h at 21°C. The amount of water retained by the samples was determined after centrifugation at 900 *g* for 30 min in an International clinical centrifuge

model CL. The procedure has been described previously.¹⁵ Results are the average of four determinations.

Tensile Properties

Bundle fiber testing was done on a Stelometer model 154, using procedures described in ASTM D 1445-75.¹⁶ Tenacities (gf/tex) were measured at zero and 0.3175 cm gauge lengths. Results are the average of six determinations.

X-ray Analysis

Diffraction patterns were obtained with a wide-angle precision x-ray diffractometer (Siemens Kristalloflex 4 Generator, Siemens Type F diffractometer), using nickel-filtered CuK_α radiation and a focusing technique essentially similar to that described by Segal et al.¹⁷ Instrumental conditions were 35 kV and 20 mA. Fibers were ground in a Wiley mill to pass through a 20-mesh screen. Powdered sample (0.3 g) was pressed into pellets at 8000 psi for 1 min.

Infrared Analysis

Infrared (IR) spectra were obtained with a Perkin-Elmer IR-257 grating spectrophotometer using the potassium bromide pellet technique.¹⁸ Fiber samples were ground in a Wiley mill to pass through a 20-mesh screen before mixing with potassium bromide.

Degree of Polymerization

The intrinsic viscosity of the samples was determined in Cadoxen with a Cannon-Ubbelohde four-bulb shear dilution viscometer. Intrinsic viscosity $[\eta]$ was converted to weight-average degree of polymerization (DP) using the following equation¹⁰:

$$[\eta] = 0.0184 \times [\text{DP}]^{0.76}$$

RESULTS AND DISCUSSION

Cellulose IV Formation

Treatment of cotton with aqueous alkali and with ethylamine resulted in essentially complete lattice transformation from cellulose I to II and III, respectively, and conversion to cellulose IV was obtained when cell III cotton was heated in formamide at 170°C for 4 h (Fig. 1). Complete transformation of the crystal structure to cellulose IV was also obtained by heating cell III cotton in steam at 180°C. The crystal form of cell II cotton heated in steam at 180°C or in formamide at 170°C remained predominantly cellulose II. Thus conversion to cellulose IV is easier from cellulose III than from cellulose II.

In these experiments, water and formamide were selected as the heating medium for their plasticizing effect on cellulose, which would therefore increase the mobility of the chain molecules. Both liquids are strongly hydrogen bonded. The solubility parameter of cellulose is 15.7, and those of water and formamide are 23.4 and 19.2, respectively.¹⁹

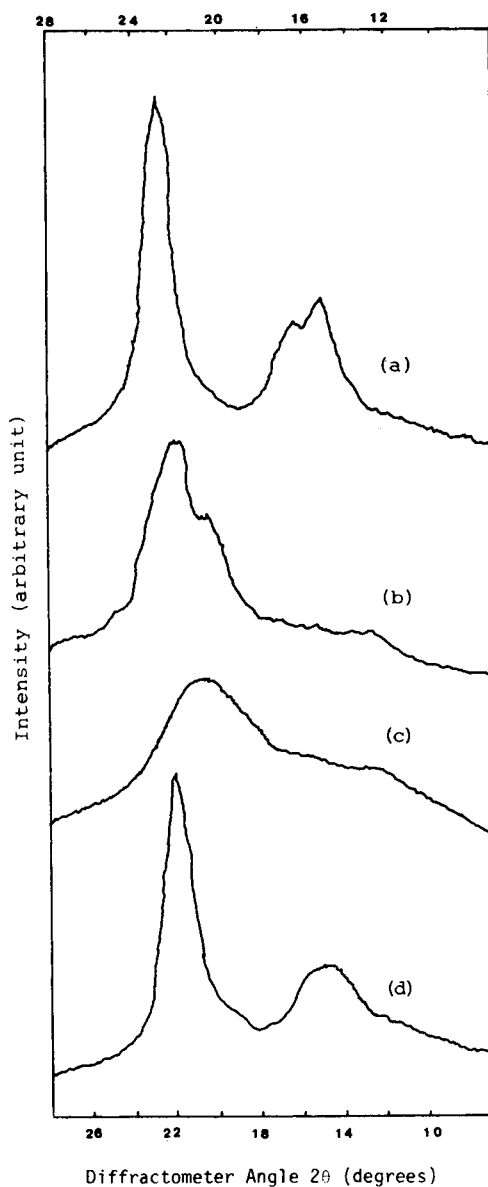


Fig. 1. X-ray diffractometer tracings of (a) cotton cellulose (cellulose I); (b) mercerized cotton (cellulose II); (c) ethylamine-treated cotton (cellulose III); (d) ethylamine-treated cotton heated at 170°C in formamide (cellulose IV).

In the next series of experiments, it was found that the treatment temperature of cell III cotton, in steam or formamide, could be lowered to 120°C without reducing the extent of the transformation to cellulose IV. Lowering the temperature reduced the amount of degradation suffered by the fiber (Table I). The DP of the sample fell as cell III cotton was being prepared. The further decrease in DP, which occurred when the cell III cotton was heated at 170°C in formamide, was small. However, when saturated steam at 180°C was

TABLE I
Degree of Polymerization (DP) of Ethylamine-Treated
Cotton Fiber After Heat Treatment for 4 h

Cotton pretreatment	Heating conditions		DP	Cellulose crystal type
	Medium	Temperature (°C)		
None	—	—	3350	I
Ethylamine treatment	—	—	2300	III
	S ^a	180	1500	IV
	S	120	2200	IV
	F ^b	170	2150	IV
	F	120	2200	IV

^aS = saturated steam.

^bF = formamide.

used as the heating medium, a large reduction in DP occurred. The DP of the fiber was the same when the treatment temperature was lowered to 120°C, irrespective of the heating medium. Since it was easier to control damage to the fiber when it was being heated in formamide, all the work on cell IV cotton discussed in the next section was done on samples prepared in this medium.

Properties of Cell IV Cotton Fibers

Fiber Morphology

As expected, cotton exhibited convolutions along its length (Fig. 2a) and a corrugated surface (Fig 2b). Ridges or compression marks are also evident. These ridges are thought to be caused by folds in the secondary layers, which are covered over by the primary wall.²⁰

The corrugations on the cotton fibers appear to have deepened after mercerization (Fig. 3a and b) but not after ethylamine treatment (Fig. 4a and b). Both mercerization and ethylamine treatments were conducted with the fibers in the slack state. The difference in appearance may be due to the reagents swelling the fibers by different amounts. The mercerizing treatment may cause greater swelling and greater collapse of the structure after removal of the sodium hydroxide.

When untreated cotton was heated in formamide, the corrugations appeared to become smoother (compare Fig. 2a and b with Fig. 5a and b). However, longitudinal cracks were present in the fibers. Fibrils crossed over the cracks (Fig. 5b). These fibrillar separations were not observed on the surfaces of cell IV cotton (Fig. 6a and b) even when the sample had been heated to 170°C during preparation (Fig. 7a and b). Usually, wedge-shaped cracks are found on cotton fibers heated in air at high temperatures.²⁰ Such cracks were not observed on our samples, probably due to the plasticizing effect of the formamide. The surface of the cell IV cotton appeared to be smoother than that of the cell I, II, or III fibers.

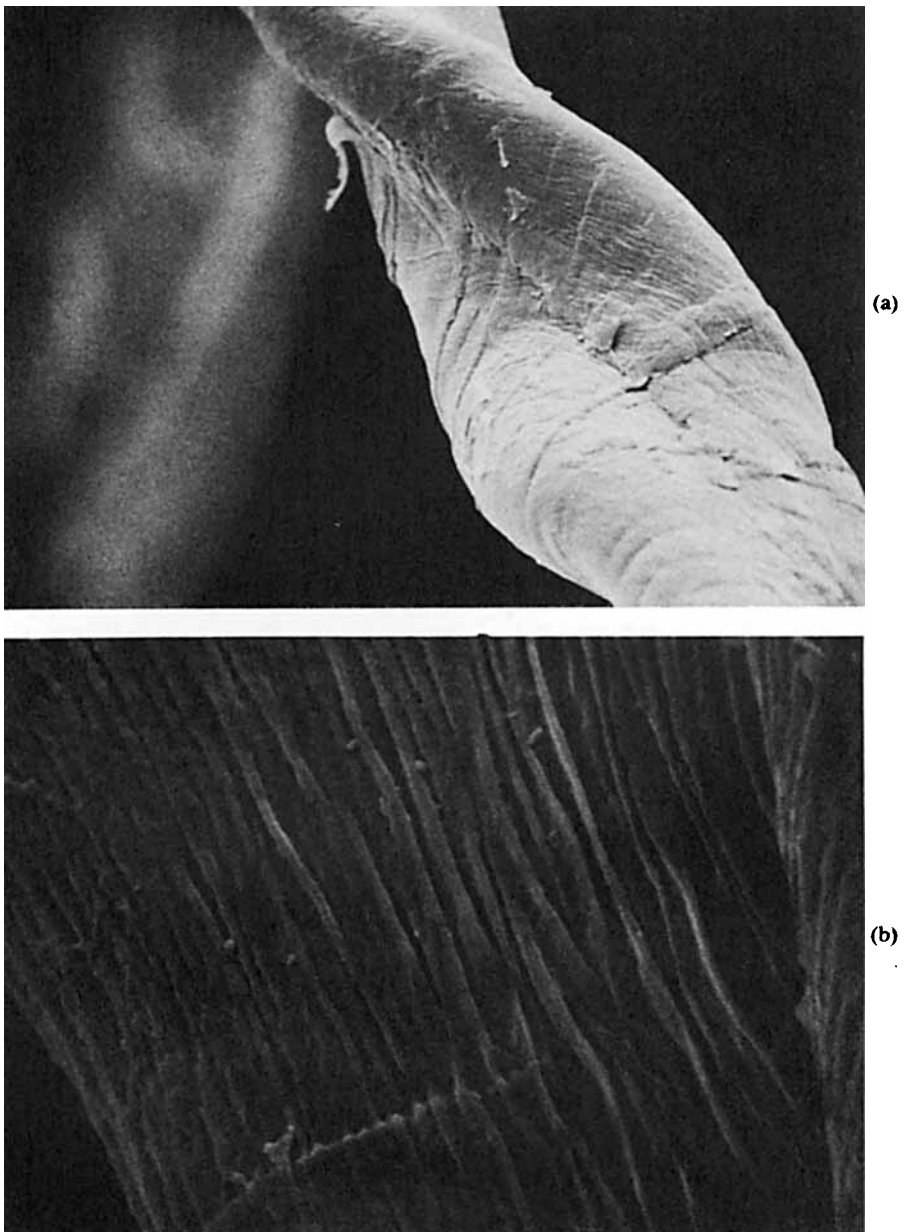


Fig. 2. Scoured cotton (a) ($\times 2550$); (b) ($\times 6560$).

Infrared Spectra

The IR spectra of heated cotton, cell III cotton, and cell IV cotton formed at both 120 and 170°C contained an absorption band at 1750 cm^{-1} that was not present on the spectra of either cell I or cell II cotton (Fig. 8). This band is due to carbonyl groups, and it indicates oxidation of the cellulose had

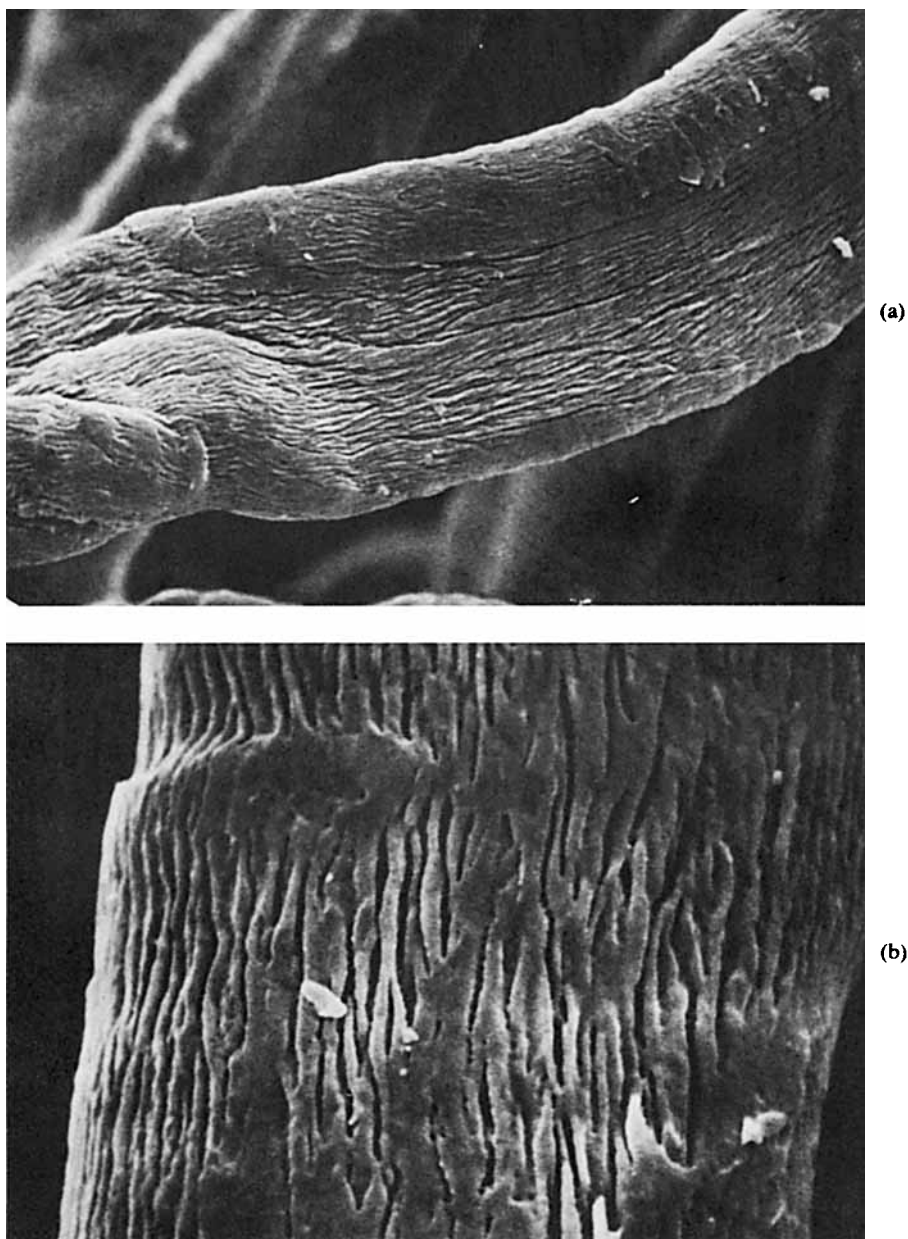


Fig. 3. Mercerized cotton (a) ($\times 2630$); (b) ($\times 6560$).

occurred during ethylamine treatment as well as during the heat treatments. It is interesting to note that the 1750 cm^{-1} absorption band was almost nonexistent on the counterpart microcrystalline products (Fig. 9). The non-crystalline parts of the cellulose would be removed by the acid hydrolysis. Thus it appears that the oxidative damage had occurred primarily in the accessible regions of the samples.

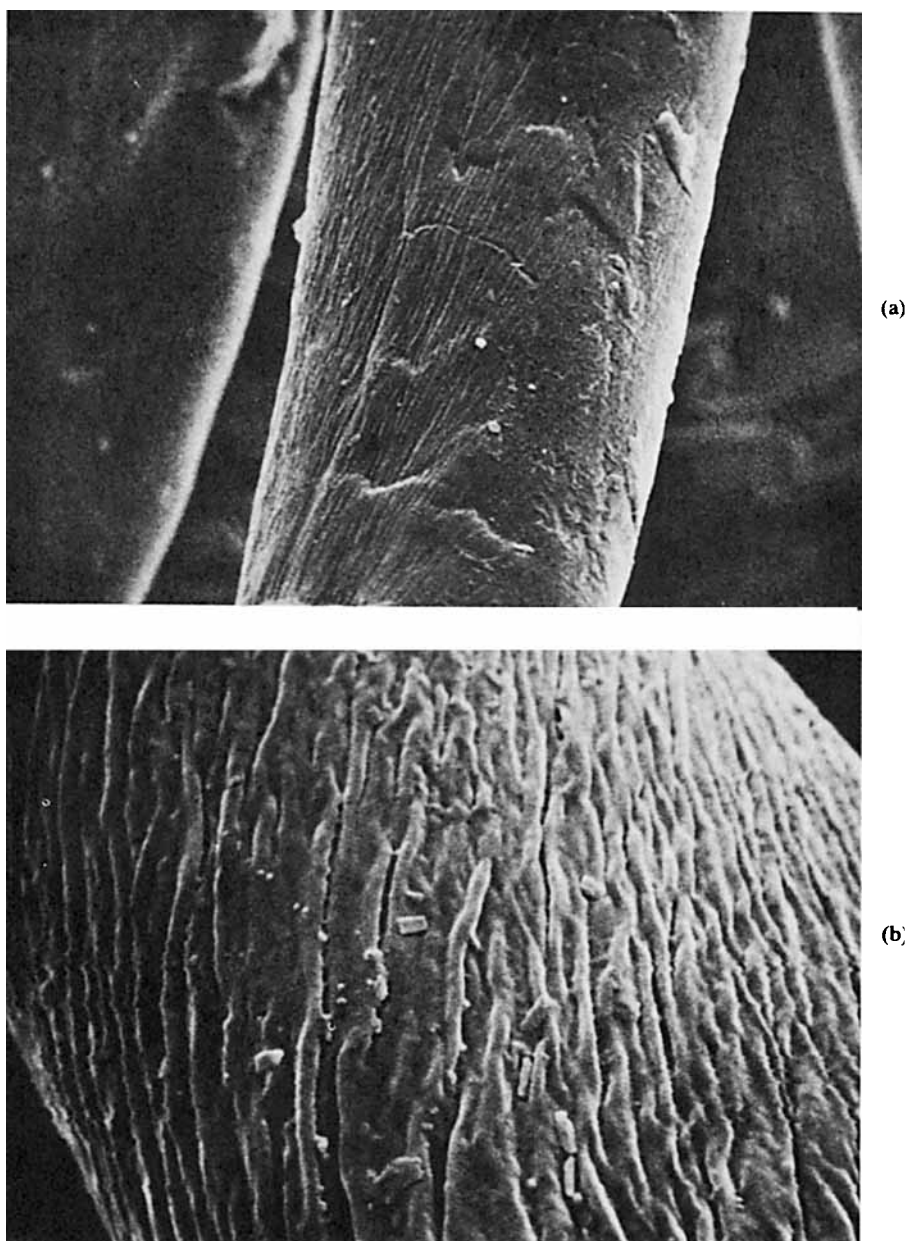


Fig. 4. Ethylamine-treated cotton (a) ($\times 2580$); (b) ($\times 6560$).

Accessibility

Moisture regains can be taken as a measure of cellulose accessibility.²¹ Conversion of the crystal form in cotton from cellulose I to II, III, or IV results in each case in an increase in fiber accessibility (Table II). It will be noted that the accessibility of the cell IV cotton is decreased by raising the temperature during its preparation from 120 to 170°C; possibly due to an

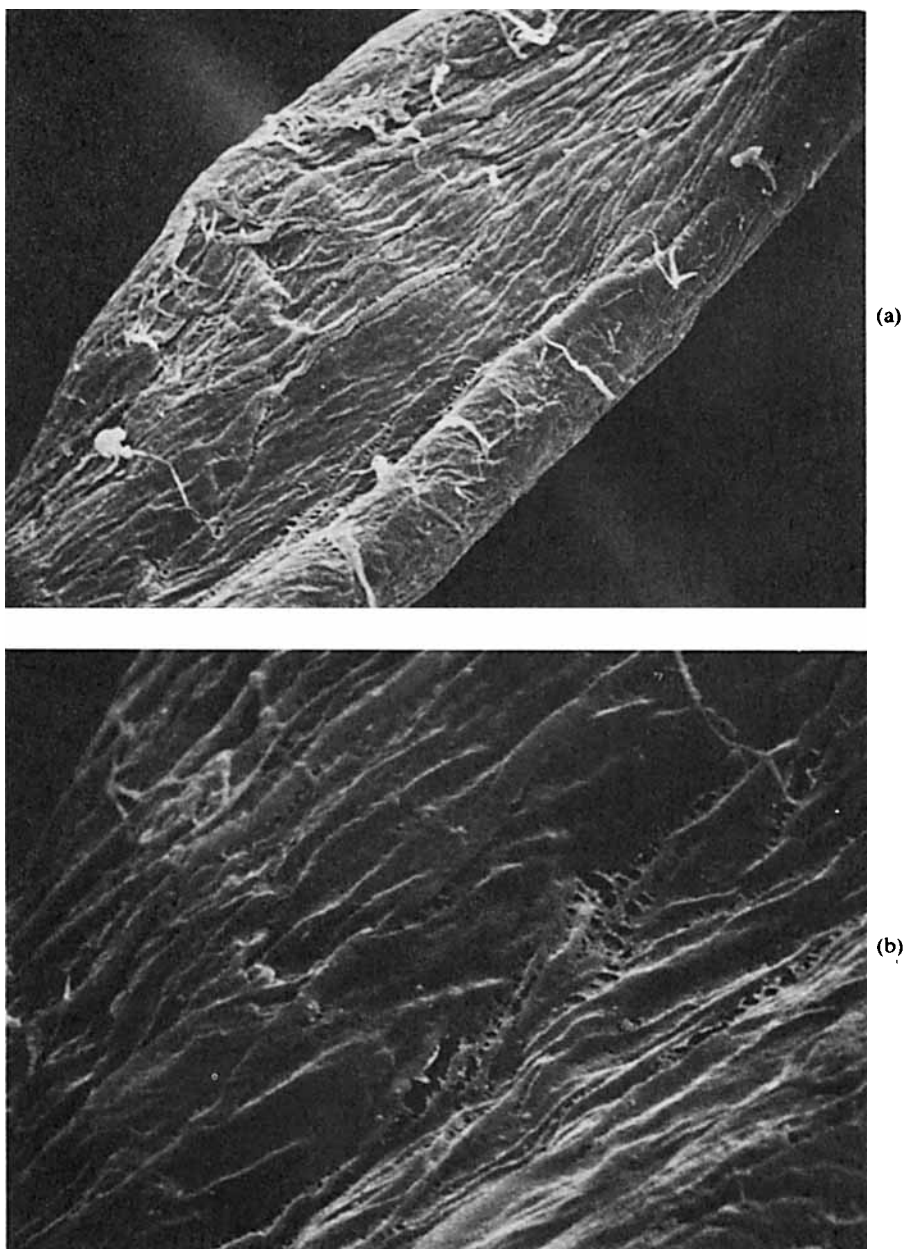


Fig. 5. Scoured cotton heated in formamide at 120°C for 4 h: (a) ($\times 2560$); (b) ($\times 6410$).

increased collapse of the structure as the temperature is raised. Crystallization does not appear to be the cause of the decreased accessibility since the weight loss after acid hydrolysis was greater for the sample heated at 170°C (see below). It can be observed also that heating cotton at 120°C for 4 h did not have a significant effect on its accessibility. However, the accessibility of the ethylamine-treated sample increased when it was heated under the same conditions to convert its crystal form to cellulose IV.

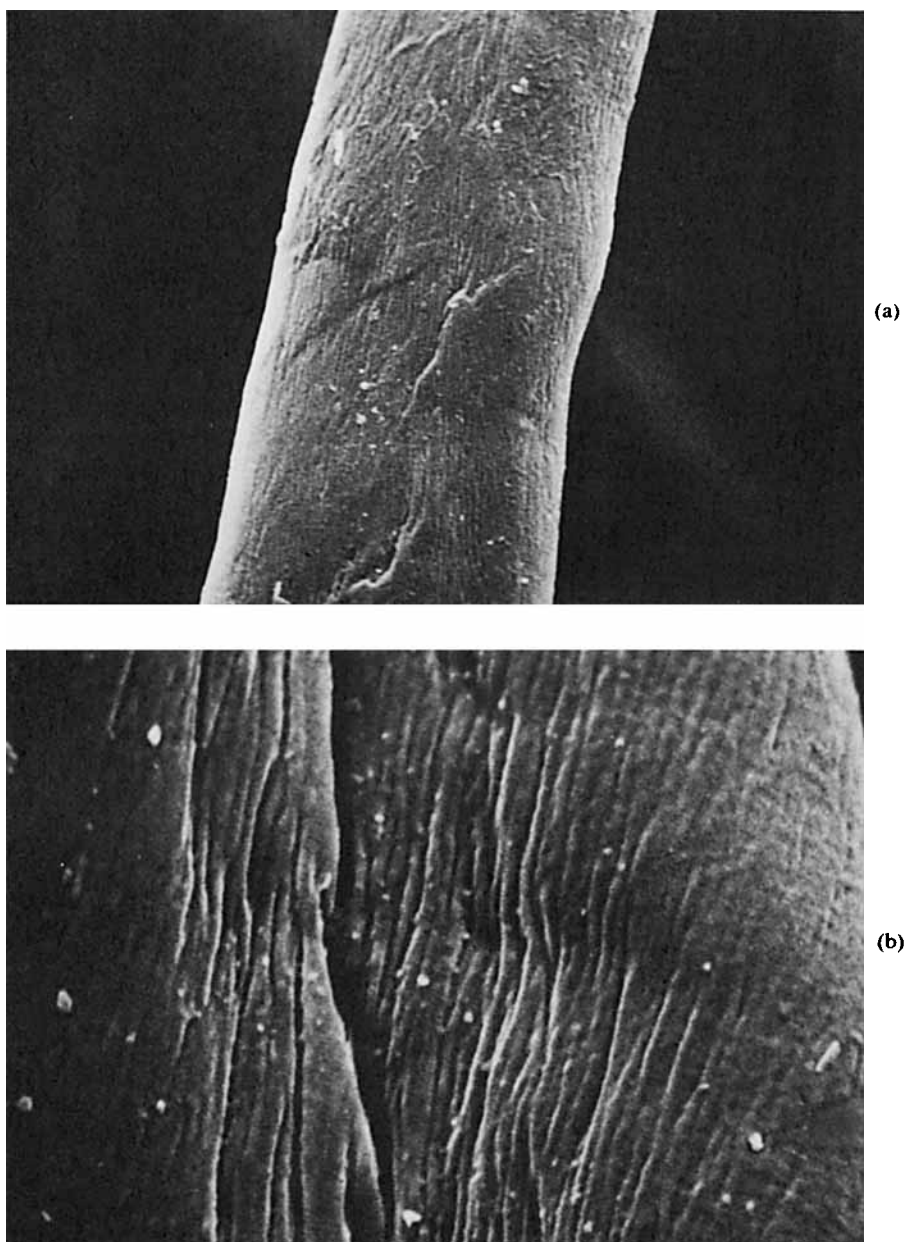


Fig. 6. Cotton, ethylamine treated and then heated in formamide at 120°C for 4 h: (a) ($\times 2650$); (b) ($\times 6560$).

Crystallite length in angstroms can be calculated by multiplying LODP by 5.15.²²⁻²⁴ It appears that the crystallite lengths of cell II, III, and IV are roughly equal and are all much less than that of cell I (Table III). Thus it is conceivable that, with shorter crystallites, the modified celluloses are easier to swell and thus more accessible to water.

It has been demonstrated that the water retention value of a cellulosic sample when determined after centrifugation at 900 g for 30 min is equivalent

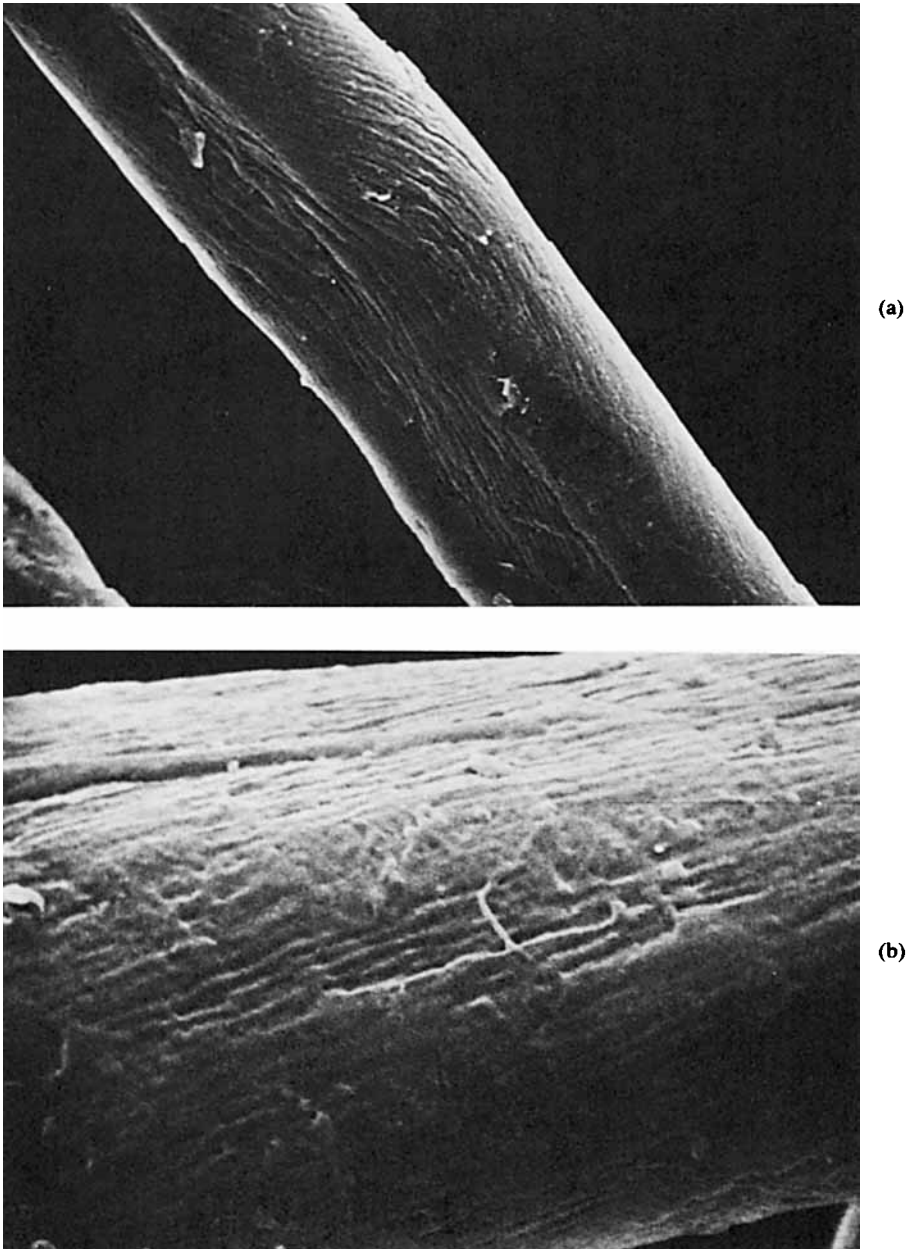


Fig. 7. Cotton, ethylamine treated and then heated in formamide at 170°C for 4 h: (a) ($\times 2630$); (b) ($\times 6560$).

to its fiber saturation point.²⁵ Thus WRV is a measure of the voids accessible to liquid water in the fibers. Heating cell I cotton or cell III cotton at 120°C for 4 h did not affect their WRV (Table II). The accessibility of the celluloses to liquid water increased in the order cell I cotton < cell III or cell IV cotton < cell II cotton. Thus the only apparent difference between accessibilities measured at 65% RH and 21°C and those measured with liquid water was

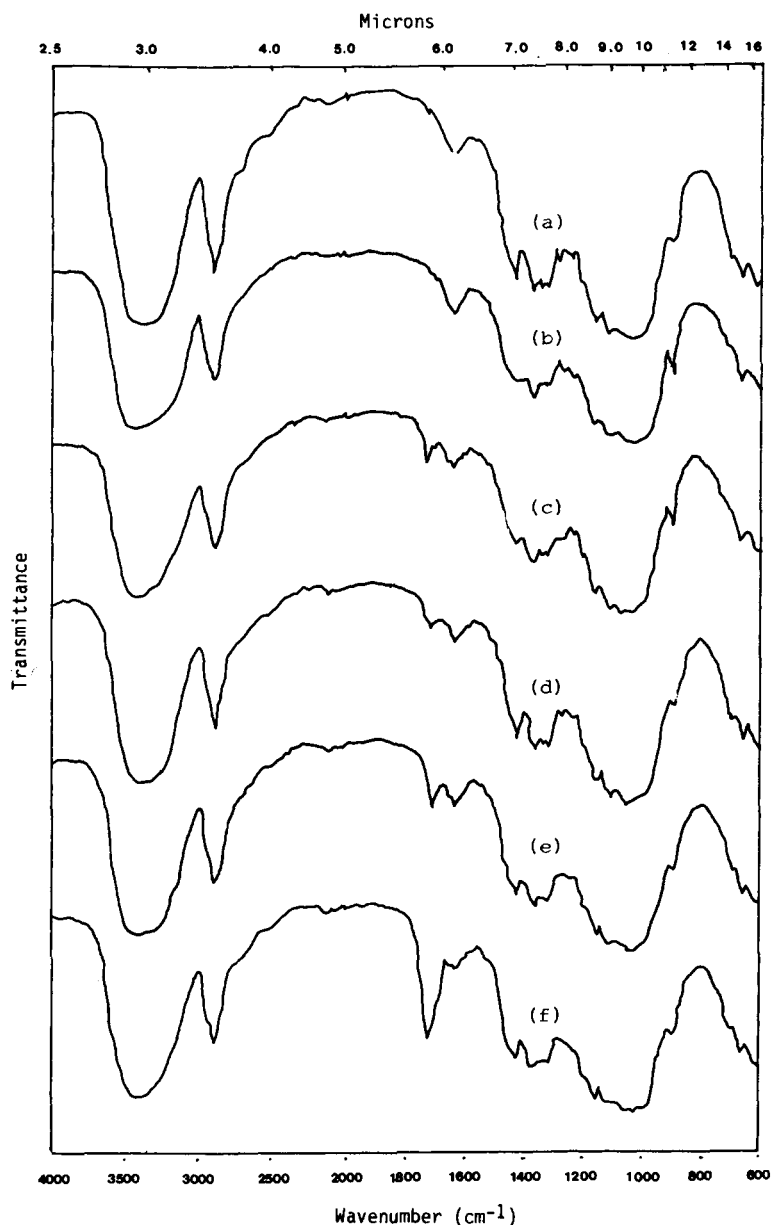


Fig. 8. Infrared spectra of cotton cellulose: (a) untreated control; (b) mercerized; (c) ethylamine treated; (d) heated at 120°C for 4 h in formamide; (e) ethylamine treated and heated in formamide at 120°C for 4 h; (f) ethylamine treated and heated in formamide at 170°C for 4 h.

for cell III and IV cotton. At 65% RH and 21°C, the latter appeared to have the higher accessibility. A possible explanation for the cell III and IV cotton having similar accessibilities by the WRV technique is that additional crystallization occurred while the cell IV cotton was immersed in water as it was being prepared for the test. It is known that water can have an effect on cell III cotton,¹³ and this may also contribute to the difference.

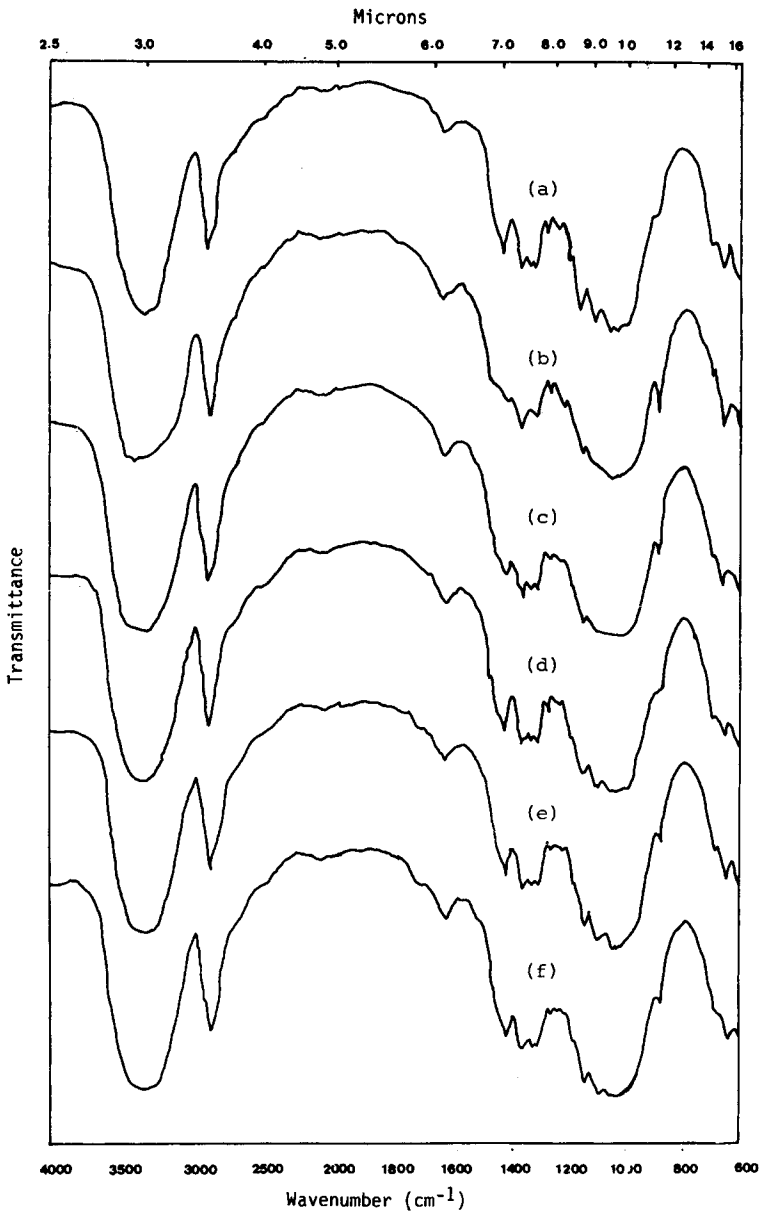


Fig. 9. Infrared spectra of microcrystalline cotton cellulose with following pretreatments: (a) untreated control; (b) mercerized; (c) ethylamine treated; (d) heated at 120°C for 4 h in formamide; (e) ethylamine treated and heated in formamide at 120°C for 4 h; (f) ethylamine treated and heated in formamide at 170°C for 4 h.

Weight Loss

A negligible weight change occurred when cell I cotton was heated at 120°C (Table II). However, an 8% weight loss occurred when ethylamine-treated cotton was heated at this temperature to form cell IV cotton. The loss was slightly higher when the treatment temperature was raised to 170°C. Ethyl-

TABLE II
Properties of Cotton Cellulose After Various Treatments

Treatment ^a	DP ^b	Weight loss after heat treatment (%)	Moisture regain (%)	Water reten- tion value (%)
None (I)	3350	—	6.60	46.3
Mercerization (II)	2800	—	10.65	79.1
Ethylamine (III)	2400	—	8.23	57.7
Heated at 120°C, 4 h (I)	2700	0.02	6.74	46.2
Ethylamine treated and then heated at 120°C, 4 h (IV)	2250	7.89	9.46	56.8
Ethylamine treated and then heated at 170°C, 4 h (IV)	2100	8.95	7.34	60.5

^aCrystal form of product in parentheses.

^bDP = degree of polymerization.

TABLE III
Properties of Acid-Hydrolyzed Cotton Celluloses (Microcrystalline Samples)
After Various Treatments

Cellulose treatment before hydrolysis	LODP ^a	Weight loss after acid hydrolysis (%)
None	165	4.87
Mercerized	56	8.37
Ethylamine treated	59	23.47
Heated at 120°C, 4 h	160	3.51
Ethylamine treated and then heated at 120°C, 4 h	59	9.02
Ethylamine treated and then heated at 170°C, 4 h	61	11.08

^aLODP = leveling-off degree of polymerization.

amine treatment increases the accessibility of cotton, its moisture regain being 25% higher than that of the untreated sample (Table II). The higher accessibility appears to have increased the ease of degradation of the sample on heat treatment. The weight loss could be due to the extraction of low-molecular-weight oligosaccharides during washing treatments.

The weight loss after acid hydrolysis is roughly twice as high for cell IV cotton as for cell I cotton (Table III). It is even higher if the comparison is made with heated cell I cotton. The acid hydrolysis resulted in the elimination of the accessible cellulose in the samples. Accessibility, however, as indicated by the moisture regains of the nonhydrolyzed samples, does not appear to correlate well with acid hydrolysis weight loss. For example, the moisture regains of the untreated cotton and the cotton heated at 120°C for 4 h are similar, yet the latter sample loses less weight on acid hydrolysis. It appears other factors are involved, such as the DP of the sample. The DP of these two samples was 3350 and 2700, respectively. It has been suggested that crystallization occurs in the accessible regions of cotton as acid hydrolysis causes cellulose chain cleavage. It is feasible that if the starting sample has a

lower DP, the crystallization process can start sooner during the hydrolysis reaction than in the case of a cellulose with a higher DP. Thus more crystallization may occur in the former case, resulting in the smaller weight loss.

The loss in weight of the ethylamine-treated sample on acid hydrolysis is higher than might be expected when compared with the losses found with the other samples and is difficult to explain. Ethylamine treatment results in cotton decrystallization.³ However, as we have pointed out previously,³ the degree of crystallinity of ethylamine-treatment cotton determined by the acid hydrolysis technique is far lower than that measured by other methods, indicating the need for further work to explain the phenomenon.

The discrepancy between the moisture regain determination of accessibility and weight loss after acid hydrolysis can also be observed with the effect of temperature on the properties of cell IV cotton. The moisture regain data indicate that accessibility decreases with increased temperature, whereas the acid hydrolysis data indicate the reverse.

Tensile Properties

The heat treatment in formamide appeared to increase the strength of the cotton fiber irrespective of its crystal structure (Table IV), even though the DP of the products was decreased by the various treatments (Table II). Normally, a reduction in DP leads to a decrease in the tensile strength of cotton.^{26,27} Ethylamine treatment reduced the strength of the cotton. However, the heat treatment required to transform its crystal structure to cell IV induced an increase in strength. Consequently, the cell IV cotton had a

TABLE IV
Tensile Properties (Mean and Standard Deviation) of Cotton Cellulose
After Various Treatments

Treatment ^a	Breaking tenacity (gf/tex) at		Breaking elongation (%) at 0.3175 cm gauge	Strength retained (%) ^b at	
	0 gauge	0.3175 cm gauge		0 gauge	0.3175 cm gauge
None (I)	34.09 ± 1.52	16.11 ± 0.60 (47.3) ^c	8.20 ± 0.34	100	100
Ethylamine (III)	30.25 ± 0.82	13.45 ± 0.35 (44.5) ^c	9.05 ± 0.33	88.7	83.5
Heated at 120°C, 4 h (I)	36.55 ± 1.40	18.10 ± 1.01 (49.5) ^c	7.42 ± 0.46	107.2	112.3
Ethylamine then heated at 120°C, 4 h (IV)	33.38 ± 1.38	16.89 ± 0.92 (50.6) ^c	9.21 ± 0.53	97.9 (110.3) ^d	104.8 (125.6) ^d
Ethylamine then heated at 170°C, 4 h (IV)	33.69 ± 2.13	16.90 ± 1.10 (50.2) ^c	8.59 ± 0.29	98.8 (111.4) ^d	104.9 (125.7) ^d

^aCrystal form of product in parentheses.

^bStrength retained = $\frac{\text{breaking tenacity of sample}}{\text{breaking tenacity of control sample}} \times 100$.

^cPercentage decrease in tenacity between zero and 0.3175 cm gauge lengths.

^dStrength retained (%) = $\frac{\text{breaking tenacity of sample}}{\text{breaking tenacity of ethylamine-treated sample}} \times 100$.

strength comparable to that of the cell I cotton even though the DP had fallen from 3350 to less than 2300 during its preparation. Another indication of improved strength properties is that the ratio of the strength of the fiber at 0.3125 cm and zero gauge lengths was higher after heat treatments (Table IV). It is well known that the tenacity of cotton decreases as the test length is increased and that the decrease is more rapid the more irregular the fiber.²⁸ Thus it appears that the heat treatments have had an annealing effect on the fine structure of the cotton fiber, which results in an alleviation of the strains that had been set up in its structure during the drying and crystallization of the cellulose when the fibers were grown.³

CONCLUSIONS

Cell IV cotton can be formed with strength comparable to that of the starting cell I fiber but with higher accessibility. The surface of the cell IV cotton also appears to be smoother than that of the starting fiber, which may result in different fabric properties. Further work is recommended on cell IV cotton.

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