

## Structure of Decrystallized Cotton in Fabrics Prepared by Alkali and Acrylonitrile Treatments

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### Synopsis

The crystalline structure of decrystallized cotton, prepared by partial cyanoethylation with the use of sodium hydroxide aqueous solution and acrylonitrile, was examined by x-ray and IR data, in connection with such fabric properties as moisture regain. It was found that the moisture regain of the cotton fabric first increased, passed through a maximum at about 6 mole-% of cyanoethylation, and then slightly decreased with increasing degree of cyanoethylation. The increase of moisture regain in the region of the lower degree of cyanoethylation was well related to the decrease in the crystallinity of cotton. The x-ray diffraction studies revealed that the distension and disorder of the unit cell occurred primarily in the direction perpendicular to the (101) crystal plane as cyanoethylation proceeded.

### INTRODUCTION

We have previously found that cotton fibers could considerably increase their accessibility or decrease their crystallinity by treatment with acrylonitrile subsequent to sodium hydroxide treatment. A small quantity of cyanoethyl residues introduced onto cellulose molecules prevents the recrystallization of the decrystallized cotton during water washing and drying, whereby remarkably high accessibility and a low degree of crystallization are permanently attained.<sup>1</sup> We also pointed out<sup>2</sup> that the moisture regain of the cotton first increased, passed through a maximum at about 6 mole-% of cyanoethylation, and then slightly decreased with increasing degree of cyanoethylation.

Conrad et al.<sup>3</sup> examined the intensity of interferences (002) and (101) of cellulose cyanoethylated with a 6% NaOH and pointed out that the structure of cellulose I was retained because the concentration of sodium hydroxide used was not high enough to change cellulose into soda cellulose.

Also, Vasil'ev et al.<sup>4</sup> investigated by x-ray method the effect of mercerization on the distribution of the substituents in cellulose cyanoethylates. But, they only reported the profile  $2\theta$  versus x-ray intensity. In this report, we examine the structure of cellulose of various degrees of cyanoethylation (1.05–15.5 mole-%) prepared by using 18% sodium hydroxide solution and acrylonitrile, by means

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of x-ray and infrared studies together with the relationship between moisture regain and the amorphous fraction.

## EXPERIMENTAL

**Cotton Cellulose.** Scoured and bleached 40's cotton fabric (plain weave: Toyo Spinning Co.) was used. Various treatments were carried out with 10 cm × 10 cm sample fabrics in slack state.

**Treatment with Alkali.** Sample fabrics were immersed in an 18% (wt/wt) aqueous solution of sodium hydroxide for 30 min at 15°C, squeezed, water rinsed for 30 min, immersed in 0.2% acetic acid for 30 min, water rinsed again for 30 min, and air dried.

**Treatment with Alkali and Acrylonitrile.** Sample fabrics were immersed in an 18% (wt/wt) aqueous solution of sodium hydroxide for 30 min at 15°C, squeezed to about 100% pickup, immersed in acrylonitrile, squeezed, immersed in 0.2% acetic acid for 30 min, water rinsed for 30 min, and air dried.

**Nitrogen Analysis.** Nitrogen contents, N%, of samples treated with acrylonitrile were determined by the micro-Kjeldahl method. The degree of cyanoethylation was calculated from

$$\text{degree of cyanoethylation, mole-\%} = \frac{162 \times N}{42 - 1.59 \times N}$$

$$\text{degree of substitution (D.S.)} = \left( \frac{3}{100} \right) \times (\text{degree of cyanoethylation, mole-\%})$$

**Moisture Regain.** After being vacuum dried for 3 hr at room temperature, sample fabrics were conditioned at 20°C and 65% R.H. (over saturated aqueous solution of magnesium acetate) until constant weight was reached, and weighed. The samples were dried for 24 hr at 40°C in high vacuum and weighed. The moisture regain was calculated from the weights before and after drying. Dry weight was based on the residual cellulosic fraction.

**X-Ray Analysis.** Fibers from warp yarns were fixed by using 1% collodion. The sample cake or pattern was 3 mm wide, 0.5 mm thick, and 35 mm long. X-Ray diffractions were recorded with a Rigaku Denki Geiger Flex wide-angle x-ray diffractometer, by using an x-ray beam generated with a copper target at 40 kV and 15 mA. X-Ray radial tracings were scanned between the angular

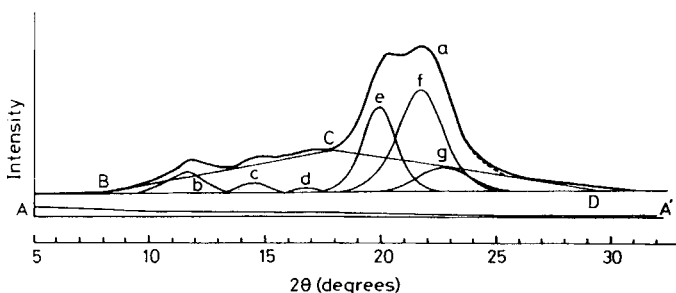


Fig. 1. Wide-angle x-ray scattering pattern for NaOH-acrylonitrile-treated cotton sample CN-4.04. Curve a: experimental curve; curves b, c, d, e, f, and g: resolved components; dotted line: curve calculated by summation of component curves.

limits of  $2\theta = 5^\circ$  and  $2\theta = 40^\circ$ . Figure 1 is an illustration of the resolution of a wide-angle x-ray scattering profile. Curve a is the experimental profile. Curve AA' is air scatter background. The region of amorphous scattering is assumed to be the area below BCD. The amorphous fraction is the ratio of the area of amorphous region to that below the experimental curve. The profile was resolved into six Gaussian curves, (101), (10 $\bar{1}$ ), and (002) of cellulose I, and (101), (10 $\bar{1}$ ), and (002) of cellulose II, by means of a du Pont 310 curve resolver. The dotted line is obtained by summing the component curves. This dotted curve falls exactly on the experimental curve in the range of  $2\theta = 5-24^\circ$ .

**Infrared Spectra.** Infrared spectra were obtained with a Perkin-Elmer Model 521 spectrophotometer by the use of the KBr pellet technique. Fibrous samples were cut with scissors into small pieces before mixing with KBr.

## RESULTS AND DISCUSSION

### Relationship Between Moisture Regain and Amorphous Fraction

Figure 2 is the relation between the moisture regain and the degree of cyanoethylation. As is obvious in Figure 2, the moisture regain of the treated samples first increases, passes through a maximum at about 6 mole-% of cyanoethylation, and then slightly decreases, with increasing degree of cyanoethylation. The increase in moisture regain at lower degrees of cyanoethylation may be attributed to the fact that the recrystallization during water washing and drying is prevented on account of the introduction of cyanoethyl residues and that, as a result, accessibility to water increases. The occurrence of the maximum moisture regain may result from a balance between the increase in accessibility and the decrease in the number of OH residues with increasing degree of cyanoethylation. The moisture regain, though being calculated based on the residual cellulosic fraction, shows a slight decrease at higher degrees of cyanoethylation. Such a behavior may be understandable if we assume an increase in the number of nonaccessible sites accompanied by the introduction of cyanoethyl residues.

The amorphous fraction from x-ray data was plotted against the degree of substitution in Figure 3. It is shown that the amorphous fraction increases gradually and levels off as the cyanoethylation proceeds. The increase of

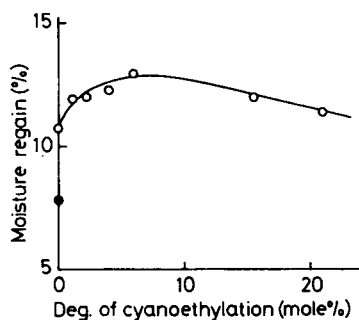


Fig. 2. Moisture regain vs. degree of cyanoethylation. Filled and open circles at zero degree of cyanoethylation express data for original and mercerized cotton fabrics, respectively.

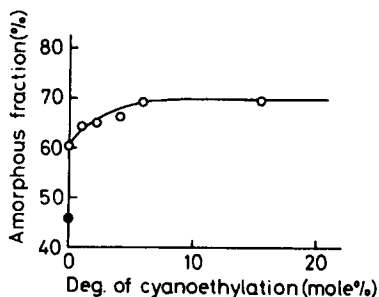


Fig. 3. Amorphous fraction vs. degree of cyanoethylation.

moisture regain in the region of the lower degree of cyanoethylation is well in accord with the lowering of the crystallinity of the samples.

Valentine<sup>5</sup> reported that the moisture sorption of completely accessible (amorphous) cellulose is 19.3% at 65% R.H. He obtained this value from the relation between the sorption ratio and the fraction of hydroxyl groups which were exchanged with D<sub>2</sub>O for various celluloses. Accessibility  $F_{am}$  was calculated from the moisture regain by using Valentine's relation,<sup>5</sup>  $F_{am} = SR/2.60$ . The results are shown in Table I.

Figure 4 shows the relation between the amorphous fraction obtained from x-ray data and the sorption ratio, where the sorption ratio is the ratio of the moisture regain of the cyanoethylated cotton to that of a standard cotton at the same relative humidity. The sorption ratio, obtained by extrapolating the straight line to an amorphous fraction value of 1, is 2.47; this corresponds to a moisture regain of about 19.3% at 65% R.H., in perfect agreement with Valentine's value.

#### Crystallinity of NaOH-Acrylonitrile-Treated Cotton by Infrared Spectra

Infrared spectra of the treated samples are shown in Figure 5. The evidence for the cyanoethyl residues introduced into cellulose molecules by NaOH-ac-

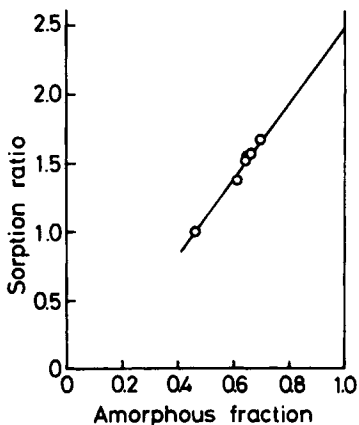


Fig. 4. Sorption ratio vs. amorphous fraction.

TABLE I  
 Accessibility, Amorphous Fraction, Infrared Absorption Ratio, and Dimension and Cross-sectional Area of Unit Cell of NaOH-AN-Treated Cottons

Sample	CN Deg., mole-%	Accessi- bility <sup>a</sup>	Amorphous fraction, %	Crystal- linity, %	Infrared ratio <sup>c</sup>	Unit cell dimensions			Cross-sectional area of unit cell, Å <sup>2</sup>	
						a	b	c		
Cellulose Id	—	—	—	—	—	8.35	10.3	7.9	84.0	65.6
Original cotton	—	0.38	45.7	54.3	0.535	8.20	10.34	7.91	83.5	64.4
Cellulose IIe	—	—	—	—	—	8.14	10.3	9.14	62.0	65.7
Mercerized cotton	—	0.53	60.3	39.7	0.400	8.15	10.34	9.17	61.8	65.9
C101	1.05	0.59	64.3	35.7	0.381	8.17	10.34	9.18	62.2	66.3
C102	2.25	0.59	64.9	35.1	0.368	8.28	10.34	9.34	60.9	67.6
C103	4.04	0.61	66.3	33.7	0.364	8.32	10.34	9.37	60.9	68.1
CE5-1	5.93	0.64	69.3	30.7	0.343	8.41	10.34	9.40	60.5	68.8
C104	15.5	0.59	69.6	30.4	0.368	8.71	10.34	9.68	58.4	71.8

<sup>a</sup> Definition of accessibility is given in the text.

<sup>b</sup> Crystallinity = 100 - amorphous fraction.

<sup>c</sup> Infrared absorption ratio  $a_{1372} \text{ cm}^{-1} / a_{2900} \text{ cm}^{-1}$ .

<sup>d</sup> K. H. Meyer and F. Misch, *Ber.*, **70(B)**, 266 (1937).

<sup>e</sup> I. Sakurada and K. Fuchino, *Scient. Pap. Inst. Phys. Chem. Res.*, **34**, 1164 (1938).

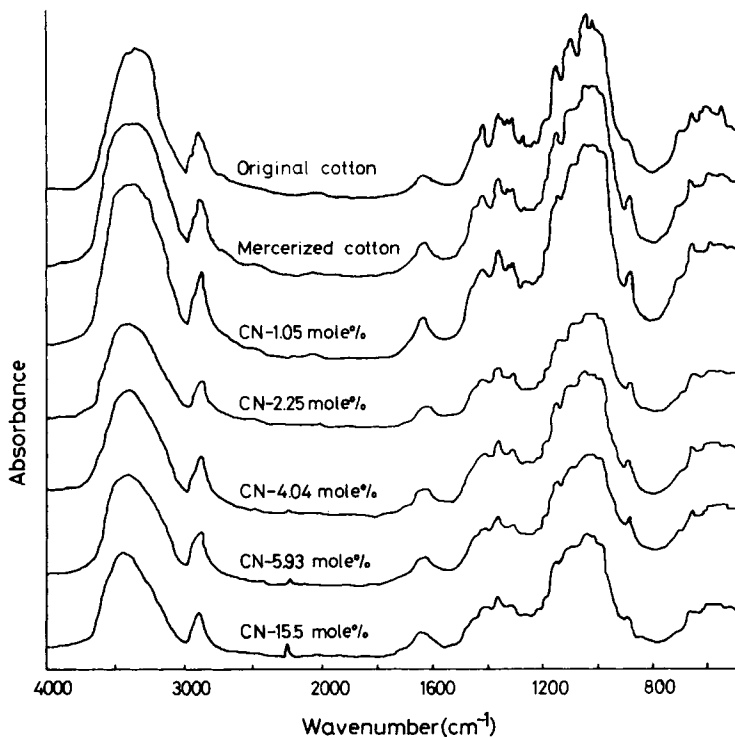


Fig. 5. Infrared spectra of cottons of different degrees of cyanoethylation prepared with NaOH and acrylonitrile.

rylonitrile treatment is shown by the  $\text{C}\equiv\text{N}$  stretching band at  $2240\text{ cm}^{-1}$ . At lower degrees of cyanoethylation, the  $2240\text{ cm}^{-1}$  absorption band did not appear. But when we increased the sample weight in the disk, the absorption band at  $2240\text{ cm}^{-1}$  did appear.

As a measure of the crystallinity, the infrared absorption ratio  $a_{1372\text{ cm}^{-1}}/a_{2900\text{ cm}^{-1}}$  was adopted according to Nelson and O'Connor,<sup>6</sup> with slight modification. Namely, for the band at  $2900\text{ cm}^{-1}$ , a baseline was drawn between  $3900\text{ cm}^{-1}$  and  $2400\text{ cm}^{-1}$ . Results obtained are shown in Table I. The infrared spectra of these modified cottons should be examined in more detail hereafter, but the correlation of the crystallinity obtained from infrared spectra with the amorphous fraction obtained by x-ray analysis has a linear relation as shown in Figure 6.

X-Ray and infrared data showed that the crystallinity of cotton could be decreased by these alkali and acrylonitrile treatments. The relative precision of these data is undoubtedly high, despite some uncertainty in absolute accuracy.

#### Crystalline Structure of Cotton Treated with NaOH and Acrylonitrile by X-Ray Analysis

To clarify the crystalline structure of decrystallized cotton by alkali and acrylonitrile treatments, we tried to analyze x-ray diffractograms of samples with various degrees of cyanoethylation.

Figure 7 shows x-ray radial tracings of samples with various degrees of cy-

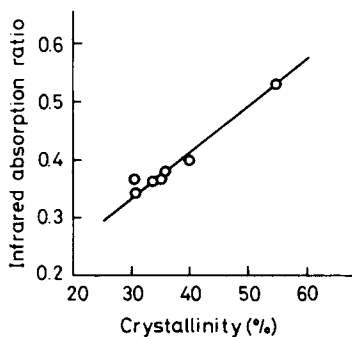


Fig. 6. Infrared absorption ratio  $a_{1372\text{ cm}^{-1}}/a_{2900\text{ cm}^{-1}}$  vs. crystallinity obtained from x-ray data.

anoethylation. For cotton fabrics treated with an 18% sodium hydroxide solution, the curve clearly shows an incomplete mercerization of the fabric, arising from a restraining influence of the fabric structure itself on the mercerizing process. The diffractometer tracing of sample CN-4.04 shows the (101) and (10 $\bar{1}$ ) interferences of cellulose I. But in the case of sample CN-5.93, only cellulose II interferences are observed. In other words, the intensities of cellulose I interferences decrease as the cyanoethylation proceeds. This shall be discussed later.

With respect to the cellulose II structure, the change of the x-ray diffraction can be more clearly seen by resolving the experimental profiles into six Gaussian

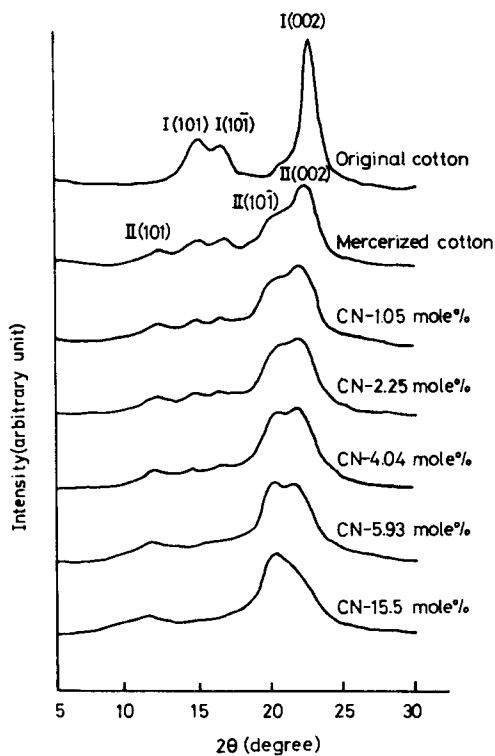


Fig. 7. X-Ray profiles for cyanoethylated cotton fabrics.

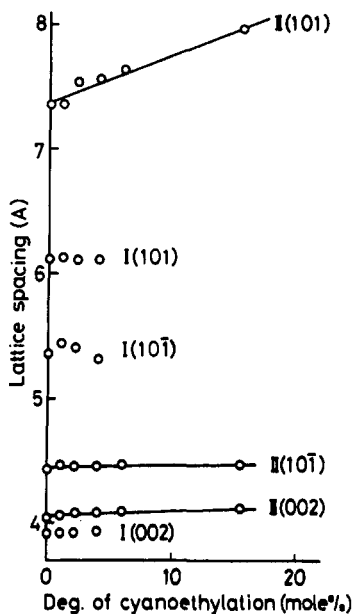


Fig. 8. Lattice spacing vs. degree of cyanoethylation.

curves as mentioned earlier. From the peaks of the resolved curves, we determined lattice spacings and unit cell dimensions, which are shown in Figure 8 and Table I, respectively. The lattice spacing of the (101) plane of treated samples increases with increasing cyanoethyl content, while those of the (101̄) and (002) planes are nearly constant. With increasing cyanoethyl content,  $a$  and  $c$  of the unit cell increase, while  $b$  remains constant and  $\beta$  decreases. The change in cross-sectional area of the unit cell is shown in Table I. As is obvious in Figure 9, the half-widths of the (101) and (002) reflections increase as the cyanoethylation proceeds, and that of the (101̄) reflection is nearly constant. As is well known, half-widths are associated with lattice perfection as well as crystallite dimensions. But, as shown in Figure 3, the amorphous fraction increases gradually and levels off as the cyanoethylation proceeds. It seems reasonable

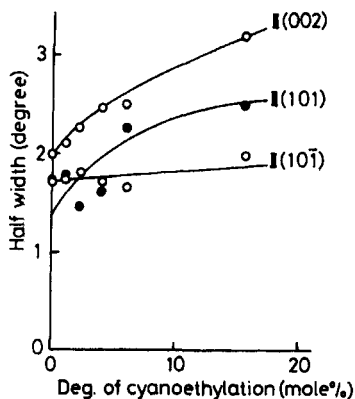


Fig. 9. Half-width of resolved curves vs. degree of cyanoethylation.



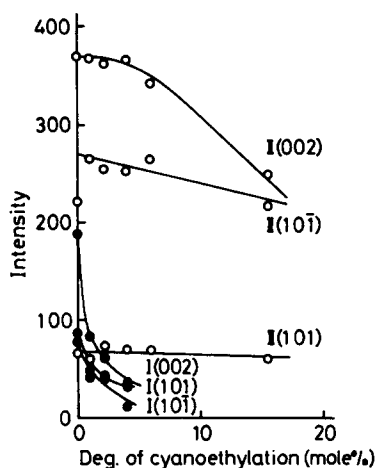


Fig. 10. Intensity at the peak of resolved curves vs. degree of cyanoethylation.

to assume that half-widths are mainly related to lattice perfection in this case. From these data, it is suggested that the distension and disorder of the unit cell arise primarily in the direction perpendicular to the (101) crystal plane with increasing cyanoethyl content.

The relationship between the degree of substitution and the intensity at the peak of the resolved curves is shown in Figure 10. The intensities of cellulose I peaks decrease rapidly; on the other hand, the intensities of cellulose II peaks decrease less rapidly as the substitution increases.

Jeffries et al.<sup>7</sup> have investigated the mechanism of the interfibrillar and intrafibrillar swelling of cotton by infrared and x-ray methods. The x-ray results showed that complete penetration of sodium hydroxide solution into cotton yarns took place in 5.0*N* sodium hydroxide under free swelling and also under tension. However, on washing out the sodium hydroxide, the cotton yarn held under tension showed some cellulose I content. Recently, Hayashi et al.<sup>8</sup> reported a similar effect on ramie fibers.

Taking into account these facts, the cellulose I structure found in the final products may be mainly due to a reversion of soda cellulose I to cellulose I during the washing treatments, because tension is present throughout the mercerization.

Warwicker et al.<sup>7,9</sup> pointed out the mechanism of swelling as follows. During intrafibrillar swelling, the hydrogen bonds between the sheets are broken and a complex is formed in which water molecules of the hydrated dipole of the swelling solution are replaced by the hydroxyl groups of cellulose. On washing out the swelling agent, the complex is replaced by water or by another solvent. On subsequent removal of this solvent, the choice whether the cellulose I or cellulose II type of sheet is reformed will, to some extent, depend on the disposition of the group (probably the primary alcohol group) that provided the internal hydrogen bonding of the cellulose I sheet. If this group is in an appropriate position, and the swelling is sufficient to allow the necessary movement, it will swing into a position required for the formation of a cellulose II type of sheet.

The swelling of the cotton fabric treated with NaOH aqueous solution may be insufficient to allow a full hydrogen bond rearrangement necessary for the

conversion to cellulose II. So, a reconversion of soda cellulose I to cellulose I may take place during the washing treatments. When cyanoethyl groups are introduced onto cellulose molecules swollen with NaOH solution, the distended cellulose structure is obtained and a hydrogen bond rearrangement necessary for the conversion to cellulose II will take place. So, by introducing the cyanoethyl group, the conversion to cellulose II from soda cellulose I may be promoted, and the decrystallization will then proceed.

The authors are grateful to Assistant Professor K. Nakamae, Faculty of Engineering, Kobe University, for valuable suggestions in this work.

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Received November 28, 1975

Revised January 20, 1976