Polymer Journal, Vol. 10, No. 3, pp 247—252 (1978)

Effect of Ethanol on Alkali and Acrylonitrile Treatments for Cotton

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(Received June 28, 1977)

ABSTRACT: Cotton fibers were pretreated with 5.4-*N* sodium hydroxide in an ethanol—water (volume ratio, 30 : 70) mixture and then cyanoethylated with acrylonitrile. The crystalline structure of the cyanoethylated cotton fibers was investigated by the X-ray method and compared with that of the cotton fibers, pretreated with 5.4-*N* aqueous sodium hydroxide and cyanoethylated under the same conditions. The presence of ethanol in the sodium hydroxide solution resulted in the increased accessibility of cellulose and a remarkable broadening of the X-ray profile. Cotton fabrics were also treated with alkali—acrylonitrile in the presence of ethanol; their physical properties are discussed.

KEY WORDS Cotton / Sodium Hydroxide / Ethanol / Acrylonitrile / Cyanoethylation / Crystalline Structure of Cellulose / X-Ray Spectra /

In the studies reported previously,[1-3] cotton was treated with aqueous alkali and then with acrylonitrile, and the crystalline structure and the properties of the resulting cyanoethylated cotton were investigated. Since the alkali-acrylonitrile treatment proceeds heterogeneously, the condition of alkali-pretreatment and hence the distribution of cyanoethyl residues affects the structural change of cotton.[3]

Jeffries[4] has recently investigated the swelling behavior and the structural change of cotton with sodium hydroxide in the presence of alcohol by X-ray and infrared deuteration techniques. When dissolved in water alone, aqueous sodium hydroxide at 2—3-*N* concentration level did not penetrate the fibrils nor cause any further lateral disorder in the original cotton. However, when the cotton was treated with 2-*N* sodium hydroxide in a mixture of ethanol and water (volume ratio 75 : 25), the X-ray study showed that a soda cellulose was produced. Washing with a mixture of ethanol and water (volume ratio 75 : 25) to remove the sodium hydroxide resulted in a recoversion of the soda cellulose to cellulose I. With 3-*N* sodium hydroxide in a mixture of ethanol and water (volume ratio 50 : 50), a similar result was obtained, but the conversion of the soda cellulose to cellulose II became predominant.

According to the observation by the infrared deuteration technique, the addition of alcohol to 6-*N* sodium hydroxide, that can give rise to the intrafibrillar swelling, had no marked effect on the degree of disorder of the hydrogen bonds in cellulose.

This paper is concerned with the treatment of cotton with 5.4-*N* sodium hydroxide in a mixture of ethanol and water (volume ratio 30 : 70), which leads to a high accessibility and remarkable broadening of the X-ray profile compared with the treatment with 5.4-*N* aqueous sodium hydroxide.

EXPERIMENTAL

Samples

Purified Egyptian cotton fibers and scoured and bleached 40's cotton fabrics (plain weave) were used.

Alkali—Acrylonitrile Treatment

Cotton samples were immersed in 5.4-*N* sodium hydroxide in a mixture of ethanol and water (volume ratio 30 : 70) for 1 hr at −5°C, squeezed to about 100% pickup, and then treated with acrylonitrile at 10°C for different periods of time with or without pre-immersion in acrylonitrile for 30 min at −5°C. The treated cotton samples were immersed in 1-% acetic acid in a mixture of ethanol and water (volume ratio 30 : 70) for 30 min below 10°C, washed with the mixture of ethanol and water (volume ratio 30 : 70) for 1 day below 10°C, and air-dried.

Treatment of the Alkali—Acrylonitrile-Treated Cotton in Boiling Water

Samples prepared by the alkali—acrylonitrile treatment were boiled in water for 3 hr and air-dried.

Moisture Regain

After being dried *in vacuo* for 3 hr at room temperature, samples were conditioned at 20°C and 65% R.H. until constant weight was reached, and then weighed. The samples were dried for 24 hr *in vacuo* at 40°C and then weighed again. The moisture regain was calculated by the following equation:

$$\text{Moisture regain } (\%) = \frac{W_b - W_a}{W_0} \times 100$$

Here W_b and W_a are the weight before and after drying. W_0 is the weight of residual cellulose estimated by considering an increase in weight due to the cyanoethyl residues from W_a, as follows:

$$W_0 = W_a \times \frac{5400}{5400 + 53 \times a}$$

where a is the degree of cyanoethylation in mol %.

X-Ray Analysis

X-Ray analysis was made on the bundled fibers fixed with 1-% collodion. The equatorial scanning was made on a Rigaku Denki Geiger Flex wide-angle X-ray diffractometer with Cu-Kα beam at 40 kV and 15 mA. The X-ray profiles obtained were resolved into Gaussian curves with a *du* Pont 310 curve resolver.

RESULTS AND DISCUSSION

Figure 1 show the X-ray profiles of cotton fibers prepared by the alkali—acrylonitrile treatment in the presence or absence of ethanol. Perfectly mercerized cotton is obtained by the treatment in 5.4-*N* aqueous NaOH [see Figure 1(A)]. On the other hand, partially mercerized cotton is obtained by the treatment in 5.4-*N* NaOH is a mixture of ethanol and water (volume ratio 30 : 70), but its X-ray profile is much broader than that of the fibers treated with aqueous NaOH solution.

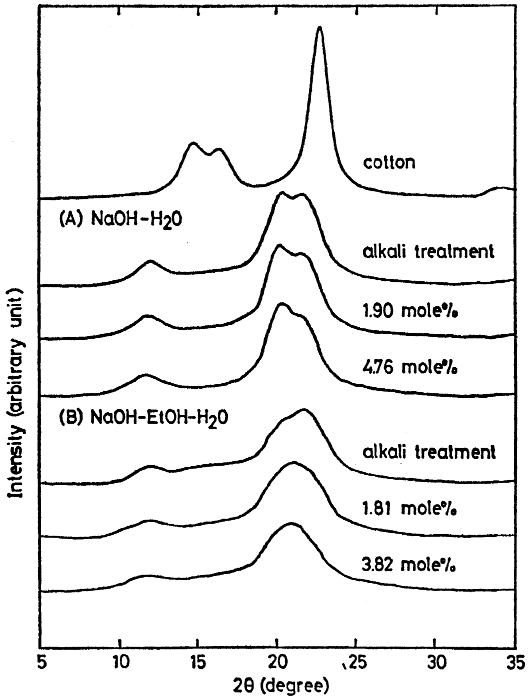

Figure 1. X-ray equatorial scannings of treated cotton fibers: (A), immersed in 5.4-*N* NaOH aqueous solution for 60 min at −5°C, and treated with acrylonitrile at 10°C; (B), immersed in 5.4-*N* NaOH in a mixture of ethanol and water (volume ratio 30 : 70) for 60 min at −5°C, and treated with acrylonitrile at 10°C. The degree of cyanoethylation of each sample is written in the figure.

Jeffries and Warwicker[4] reported that a soda cellulose was produced when the cotton was treated with 3-*N* NaOH in a mixture of ethanol and water (volume ratio 50 : 50), and the X-ray study showed that the conversion to cellulose II depended on the extent to which the cellulose sheets were pushed apart during the swelling and washing treatment. Hayashi, *et al.*,[5] showed that the transformation from cellulose I to II

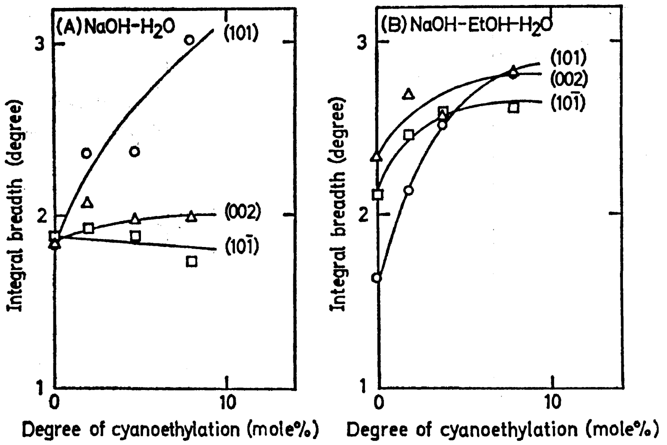

Figure 2. Integral breadth of X-ray diffractograms *vs*. degree of cyanoethylation for alkali—acrylonitrile treated cotton fibers: (A), immersed in 5.4-*N* NaOH aqueous solution for 60 min at −5°C, and treated with acrylonitrile at 10°C; (B), immersed in 5.4-*N* NaOH in a mixture of ethanol and water for 60 min at −5°C, and treated with acrylonitrile at 10°C. The values at zero degree of cyanoethylation represent the data for alkali-treated samples.

was caused by a change of the chain conformation from Cellulose I type to Cellulose II type. The change took place either through hydration of the chain or dehydration of the hydrated chain. When mercerization was carried out under the conditions where the cellulose crystallites were relaxed to a smaller extent (reaction at high temperature, at fixed length, and with a NaOH solution of a lower concentration), the crystallites of soda cellulose I were formed without passing the stage of fully hydrated cellulose. In this case, the chain conformation of cellulose I was retained in the cellulose I type and resulted in soda cellulose I_I.

Therefore, when cotton is treated with 5.4-*N* NaOH in a mixture of ethanol and water, the presence of the crystalline form of cellulose I may be due to reconversion of soda cellulose to cellulose I during the washing treatment, presumably because of a decrease in the degree of swelling due to the added ethanol.

The intensity of the (002) plane of the cotton treated in the NaOH—ethanol—water system was stronger than that of the (10$\bar{1}$) plane in the region of the lower degree of cyanoethylation. But, the intensity of the (002) plane of the cotton treated in the NaOH—water system was weaker than that of (10$\bar{1}$) plane.

Figures 2(A) and 2(B) show the relation between the integral breadth of the X-ray diffractograms and the degree of cyanoethylation for the NaOH—water system and the NaOH—ethanol—water system, respectively. Integral breadths of the (10$\bar{1}$) and (002) planes of cotton treated with NaOH in a mixture of ethanol and water are greater than those of cotton treated with aqueous NaOH. In the NaOH—water system, the integral breadth of the (101) plane of cellulose II increases with increasing cyanoethyl content, while those of the (10$\bar{1}$) and (002) planes stay nearly unchanged [see Figure 2(A)]. On the other hand, in the NaOH—ethanol—water system, the integral breadths of the (10$\bar{1}$) and (002) planes as well as that of the (101) plane increase as the cyanoethylation proceeds. When an aqueous sodium hydroxide solution containing alcohol is used, the disorder of the crystal lattice may be enhanced.

Lattice spacings are plotted against the degree of cyanoethylation in Figure 3. The lattice spacing of the (101) plane increases as the cyanoethylation proceeds, while those of the (10$\bar{1}$) and (002) planes stay nearly unchanged for the fibers prepared by alkali—acrylonitrile treatment either in the presence or absence of ethanol. In an attempt to enhance the penetration of

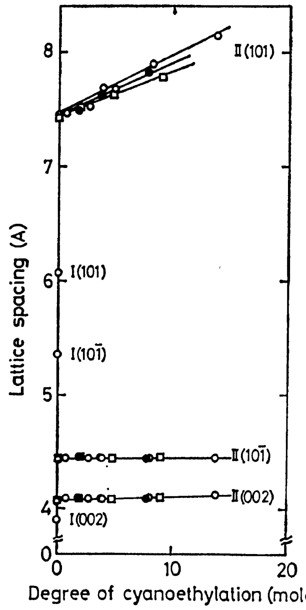

Figure 3. Lattice spacing *vs.* degree of cyanoethylation for treated cotton fibers: □, immersed in 5.4-*N* NaOH aqueous solution for 60 min at −5°C, and treated with acrylonitrile at 10°C; ●, immersed in 5.4-*N* NaOH in a mixture of ethanol and water (volume ratio 30 : 70) for 60 min at −5°C, and treated with acrylonitrile at 10°C; ○, immersed in 5.4-*N* NaOH in mixture of ethanol and water, and treated with acrylonitrile at 10°C after immersion in acrylonitrile for 30 min at −5°C. The values at zero degree of cyanothylation represent the data for alkali-treated samples.

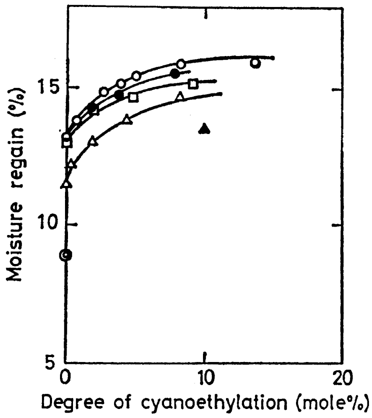

Figure 4. Moisture regain *vs.* degree of cyanoethylation. Cotton fibers: □, immersed in 5.4-*N* NaOH aqueous solution at −5°C and treated with acrylonitrile at 10°C; ●, immersed in alcoholic 5.4-*N* NaOH at −5°C and treated with acrylonitrile at 10°C; ○, immersed in alcoholic 5.4-*N* NaOH at −5°C and treated with acrylonitrile at 10°C after immersion in acrylonitrile for 30 min at −5°C. Cotton fabric: △, immersed in alcoholic 5.4-*N* NaOH at −5°C and treated with acrylonitrile at 10°C after immersion in acrylonitrile for 30 min at −5°C; ▲, immersed in 5.4-*N* NaOH aqueous solution at −5°C and treated with acrylonitrile at 10°C after immersion in acrylonitrile for 30 min at −5°C; ◎, original cotton.

acrylonitrile into the fibrils, the alkali-treated cotton was pretreated with acrylonitrile for 30 min at −5°C. But no difference in the lattice spacings was detected, compared with the results for the cotton treated without the pretreatment.

Figure 4 shows the relation between the moisture regain and the degree of cyanoethylation. The moisture regain of the cyanoethylated cotton fibers made after pretreatment with acrylonitrile for 30 min at −5°C is more than 16% at the degree of cyanoethylation of 10 mol %. The moisture regain of the cotton samples treated in the presence of alcohol is higher than that of the cotton samples obtained by the treatment in the absence of alcohol. Consequently, it is confirmed that highly accessible and highly disordered cotton is obtained by the treatment with the NaOH—ethanol—water system. The main factor causing such a result may be the structural change of soda cellulose by the addition of ethanol.

In order to determine whether recrystallization was induced, the alkali-treated and cyanoethylated cotton samples in the presence of ethanol were boiled in water for 3 hr. The degree of cyanoethylation ranged between 3.86 and 13.83 mol %. Figure 5 shows the X-ray diffractograms of the samples before and after the treatments. As shown in Figure 1, cotton treated with 5.4-*N* NaOH in a mixture of ethanol and water contains a very slight amount of cellulose I. Each diffraction peak of cellulose I and II increases on account of recrystallization after boiling in water, as shown in Figure 5. But no cellulose I diffraction is observed in the cyanoethylated samples even after boiling in water. Thus, these cyanoethylated samples remain highly disordered after boiling in water.

As shown in Figure 6, when the cyanoethylation with 5.4-N NaOH in a mixture of ethanol and water (volume ratio 30 : 70) was applied to cotton fabrics, the same tendency in the structural change as with the cyanoethylated cotton

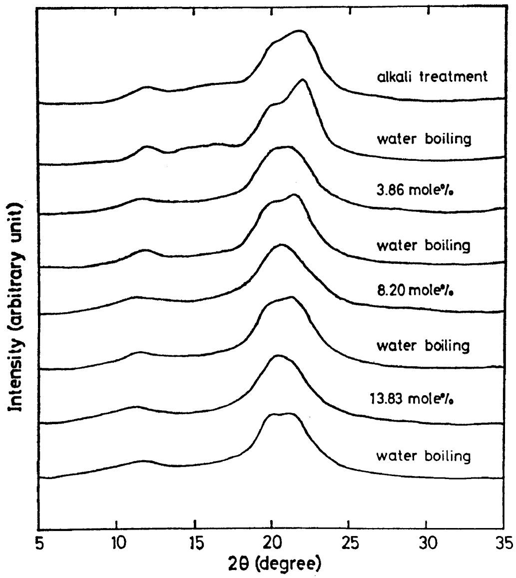

Figure 5. X-Ray diffractograms of treated cotton fibers before and after boiling in water for 3 hr. The cotton was immersed in alcoholic 5.4-N NaOH for 60 min at −5°C, and treated with acrylonitrile at 10°C after immersion in acrylonitrile for 30 min at −5°C. The degree of cyanoethylation of each sample is written in the figure.

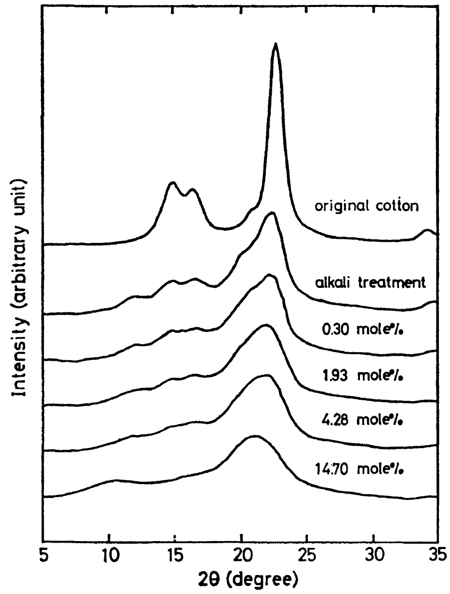

Figure 6. X-Ray diffractograms of treated cotton fabric. Cotton fabric was immersed in 5.4-N NaOH in a mixture of ethanol and water, and treated in acrylonitrile at 10°C after immersion in acrylonitrile for 30 min at −5°C. The degree of cyanoethylation of each sample is written in the figure.

Table I. Properties of NaOH—acrylonitrile-treated cotton fabric (effect of alcohol)

Treatment	Crease recovery, %		Strength,[a] g	Elongation,[a] %	Moisture regain, %
	Dry	Wet			
—	42	32	285	6.7	7.8
NaOH—EtOH—H_2O[b]	44	41	277	10.7	11.5
NaOH—EtOH—H_2O, AN (4.28 mol %)[c]	42	46	266	10.0	13.3
liq. NH_3[d]	48	42	254	7.4	9.5
NaOH—H_2O[e]	36	44	265	8.7	11.1
NaOH—H_2O, AN (3.90 mol %)[f]	18	38	260	9.3	12.1

[a] Values of warp yarns taken from fabric.
[b] Cotton was treated with alcoholic 5.4-N NaOH for 60 min at −5°C.
[c] Cotton was treated with alcoholic 5.4-N NaOH for 60 min at −5°C, and treated with acrylonitrile at 10°C after immersion in acrylonitrile for 30 min at −5°C.
[d] Cotton was immersed in liquid ammonia for 1 min and air dried.
[e] Cotton was immersed in 5.4-N NaOH aqueous solution for 30 min at 15°C.
[f] Cotton was immersed in 5.4-N NaOH aqueous solution for 30 min at 15°C and treated with acrylonitrile at 20°C.

fibers is observed, except that strong peaks of the (101) and (10$\bar{1}$) diffractions of cellulose I remained in the region of low degrees of cyanoethylation on account of the fabric construction.[3,4]

After cyanoethylation, when the never-dried cyanoethylated cotton samples were immersed in 1-% aqueous acetic acid, they swelled to a great extent and partially lost their fibrous form. Consequently, after the cyanoethylation with the NaOH—ethanol—water system, it was necessary to immerse the treated cotton in 1-% acetic acid in a mixture of ethanol and water and then to wash with a mixture of ethanol and water.

Table I shows the physical properties of NaOH—acrylonitrile treated cotton fabrics. Cotton fabrics treated with the alcohol system retain their softness together with the same degree of dry crease recovery as the original cotton fabric, while cotton fabrics treated with aqueous NaOH have high stiffness and low crease recovery. Once dried, the fabrics made with the alcohol system retain their softness even after boiling in water. Cyanoethylated cotton fabrics made in the NaOH—ethanol—water system show no change in tensile strength, but exhibit an increase in elongation and show a high moisture regain.

Acknowledgment. The authors wish to thank Dr. Masao Hosono for his useful discussions.

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