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Crystalline Structure of Polynosic and Cuprammonium Rayon Treated with Alkali and Acrylonitrile in the Presence of Ethanol

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Regenerated celluloses such as polynosic and cuprammonium rayon fibers were cyanoethylated after pretreatment with 5.4N NaOH in a mixture of ethanol and water (volume ratio 30: 70), and the crystalline structure of the products was investigated by X-ray method. The influence of cyanoethyl residues at least on the crystalline structure of cellulose was indistinguishable between regenerated cellulose and cotton.

INTRODUCTION

In a previous paper,[1] the crystalline structure of cotton, pretreated with 5.4N sodium hydroxide in ethanol-water (volume ratio 30: 70) mixture and then cyanoethylated, was investigated by X-ray method and compared with that of cotton cyanoethylated under the same condition except the absence of ethanol. The presence of alcohol in aqueous sodium hydroxide solution increased the accessibility of cellulose and broadened X-ray profile remarkably. In this paper, regenerated celluloses such as polynosic and cuprammonium rayon fibers are cyanoethylated after pretreatment with 5.4N sodium hydroxide in ethanol-water (volume ratio 30:70) mixture, and crystalline structure of the products is investigated by X-ray method.

Regenerated cellulose is soluble in 5.4N aqueous sodium hydroxide solution, but the addition of alcohol to sodium hydroxide solution prevents the dissolution of cellulose and the treatment in fibrous form can be performed.

EXPERIMENTAL

Samples. Polynosic fibers (Toramomen Advanced 61) supplied by Tachikawa Institute were subjected to extraction in a Soxhlet extractor with a mixture of ethanol and benzene (volume ratio 1: 1) for 6 hr and then with ethanol for 6 hr, and washed with water and air dried. Cuprammonium rayon 120(90) supplied by Asahikasei Co. was sampled before oil treatment. It was washed with water, then with hot water, and air dried. Egyptian cotton fibers were purified as described elsewhere.[2] Degrees of polymerization estimated by viscosity method (trinitrated in acetone at

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20°C) were 588, 456, and 4020 for polynosic, cuprammonium rayon, and cotton fibers, respectively.

Treatment. Cellulose immersed in 5.4N NaOH in a mixture of ethanol and water (volume ratio 30: 70) for 60 min at −5°C was treated with acrylonitrile at 10°C after being immersed in acrylonitrile for 30 min at −5°C. Then the treated cellulose was immersed in 1% acetic acid in a mixture of ethanol and water (volume ratio 30: 70), washed with the ethanol-water mixture, and air dried.

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

Moisture Regain and X-Ray Analysis. The method described previously was used.[2)]

RESULTS AND DISCUSSION

Figure 1 shows the relation between the immersing time in acrylonitrile at 10°C and the degree of cyanoethylation. The rate of reaction of regenerated cellulose is nearly equal to that of cotton. It is because the rate of reaction primarily depends on the concentration of sodium hydroxide solution.[3)]

Figure 2 shows the relation between the moisture regain and the degree of cyanoethylation. The values of moisture regain of original cotton and regenerated cellulose

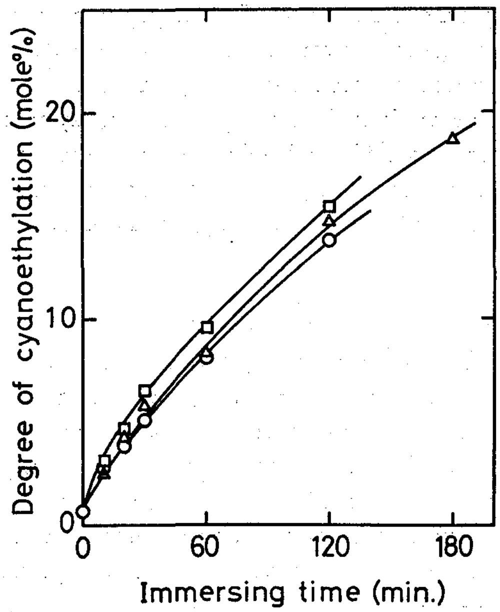

Fig. 1. Degree of cyanoethylation *vs.* immersing time in acrylonitrile at 10°C. The value at zero degree of cyanoethylation represents the value for cotton fiber immersed in acrylonitrile for 30 min at −5°C after immersing in alcoholic 5.4N NaOH. (□) polynosic fiber, (△) cuprammonium rayon fiber, (○) cotton fiber.

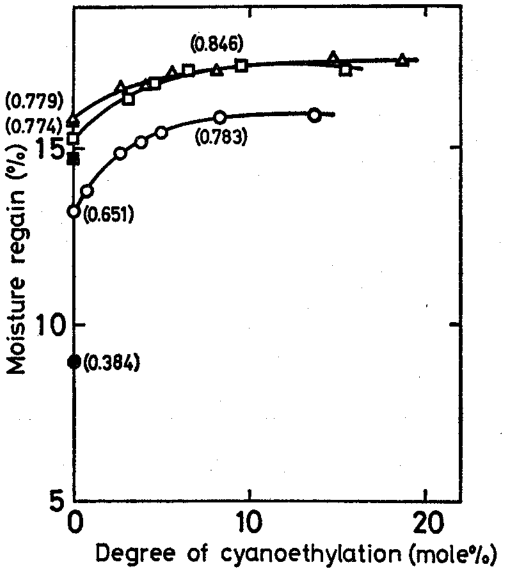

Fig. 2. Moisture regain *vs.* degree of cyanoethylation. The values at zero degree of cyanoethylation represent the values for samples immersed in alcoholic 5.4N NaOH. (■) original polynosic fiber, (▲) original cuprammonium rayon fiber, (●) original cotton, (□) treated polynosic fiber, (△) treated cuprammonium rayon fiber, (○) treated cotton fiber. Accessibility was designated in parentheses.

are about 8 and 15%, respectively. This high value of regenerated cellulose may be attributed to small crystal size and low degree of crystallinity. The moisture regain of cuprammonium rayon is 15.7% and that of alkali-treated rayon is 15.8%. The crystalline form of original regenerated cellulose is cellulose II, so the effect of alkali-treatment on accessibility is not observed. The moisture regain of each cellulose sample increases with increasing cyanoethyl content and levels off at about 10 mole%.

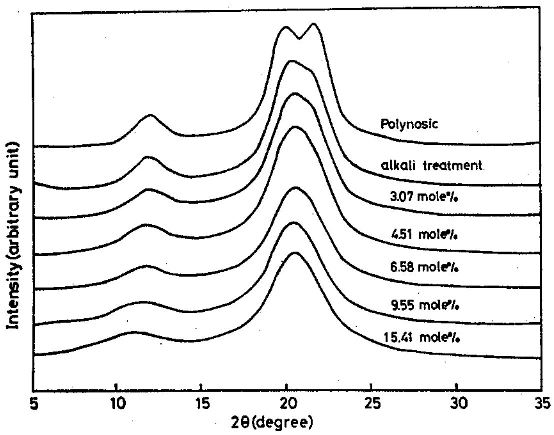

Fig. 3. X-Ray diffractograms for polynosic fibers treated with alkali-acrylonitrile in the presence of ethanol.

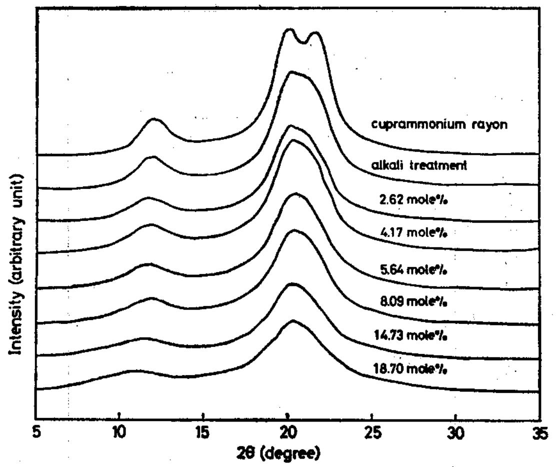

Fig. 4. X-Ray diffractograms for cuprammonium rayon fibers treated with alkali-acrylonitrile in the presence of ethanol.

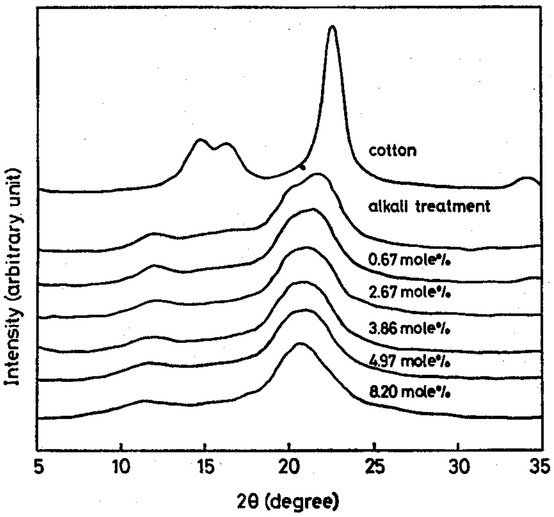

Fig. 5. X-Ray diffractograms for cotton fibers treated with alkali-acrylonitrile in the presence of ethanol.

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, as already reported.[4] Much difference in the effect of cyanoethyl residues on the increase of accessibility to water between cotton and regenerated cellulose is not observed. Accessibility calculated by Valentine's relation[5] is designated in parentheses in Fig. 2. High value can be obtained by alkali-acrylonitrile treatment in the presence of ethanol.

To clarify the crystalline structure of alkali-acrylonitrile treated cellulose in the presence of ethanol, X-ray profiles were analyzed by a curve resolver as described in the previous papers.[2,4] Figures 3, 4, and 5 show X-ray diffractograms for polynosic fiber, cuprammonium rayon fiber and cotton fiber, respectively. Lattice spacings of samples determined from the peaks of the resolved curves, were plotted against the degree of cyanoethylation in Fig. 6. For each cellulose sample, the lattice spacing of (101) plane increases as the cyanoethylation proceeds, while those of (10$\bar{1}$) and (002) planes stay nearly unchanged. Consequently with increasing cyanoethyl content, *a* and c of the unit cell increase, while *b* remains constant and β decreases.

Figures 7, 8, and 9 show the relation between the integral breadth and the degree of cyanoethylation for treated polynosic fiber, cuprammonium rayon fiber and cotton fiber samples, respectively. All figures show that integral breadth of each crystalline plane increases as the cyanoethylation proceeds. It is suggested that highly disordered structure of celluloses can be obtained by alkali-acrylonitrile treatment in the presence of alcohol.

Effect of boiling in water for 3 hr, on the X-ray diffractograms of alkali-acrylonitrile treated cellulose in the presence of alcohol, is shown in Figs. 10 and 11 for polynosic and cuprammonium rayon fibers, respectively. Regenerated cellulose treated with

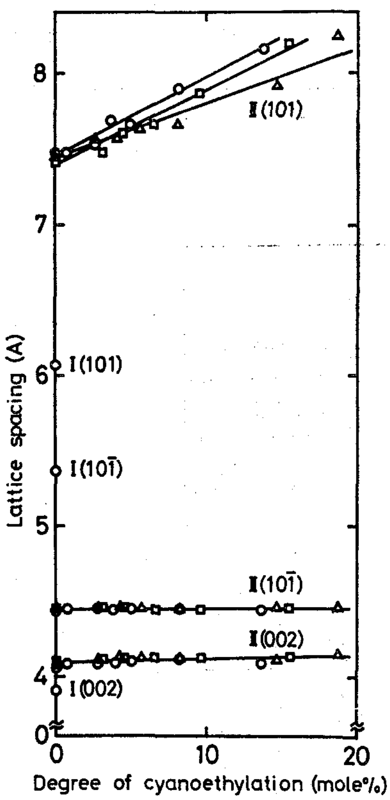

Fig. 6. Lattice spacing *vs.* degree of cyanoethylation. The values at zero degree of cyanoethylation represent the values for samples immersed in alcoholic 5.4N NaOH. (□) polynosic fiber, (△) cuprammonium rayon fiber, (○) cotton fiber.

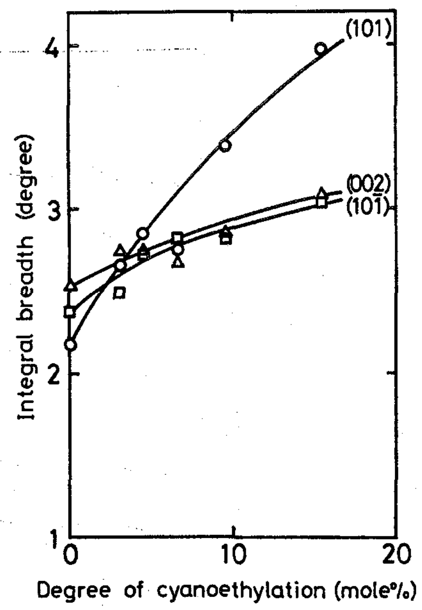

Fig. 7. Integral breadth *vs.* degree of cyanoethylation for polynosic fibers.

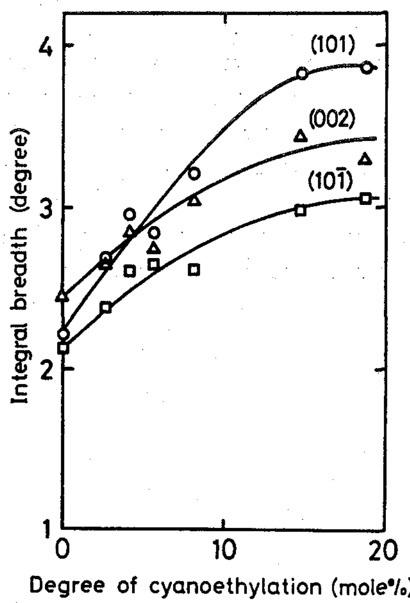

Fig. 8. Integral breadth *vs.* degree of cyanoethylation for cuprammonium rayon fibers.

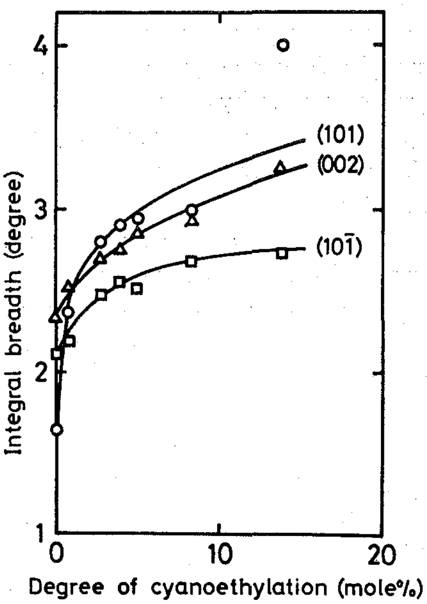

Fig. 9. Integral breadth *vs.* degree of cyanoethylation for cotton fibers.

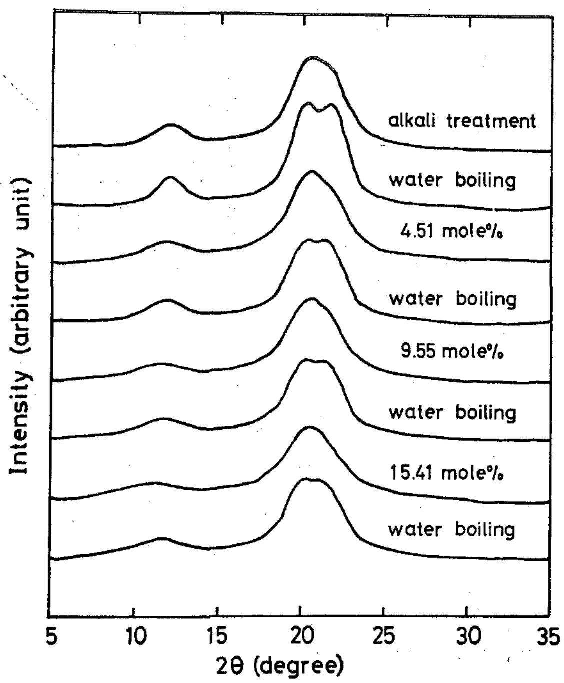

Fig. 10. Effect of boiling in water for 3 hr on the X-ray diffractograms of alkali–acrylonitrile treated polynosic fibers in the presence of alcohol.

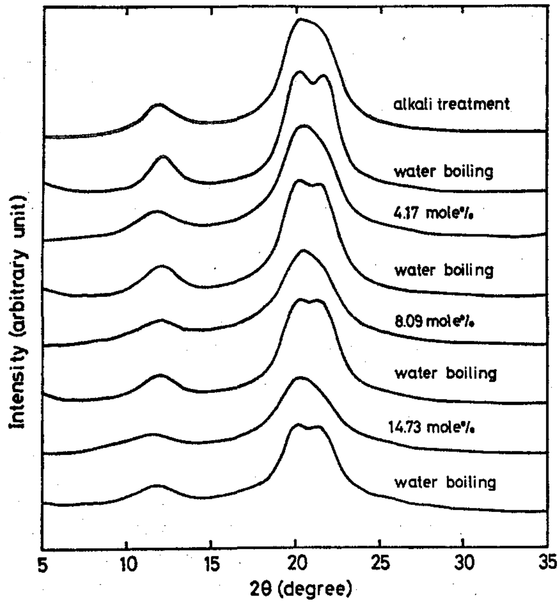

Fig. 11. Effect of boiling in water for 3 hr on the X-ray diffractograms of alkali-acrylonitrile treated cuprammonium rayon fibers in the presence of alcohol.

5.4N NaOH in a mixture of ethanol and water is recrystallized to the same order as original cellulose. Contrary, in the case of cotton, as described elsewhere, alkali-treated cotton is not so recrystallized as regenerated celluloses.[1] But as the cyanoethylation proceeds, intensity of each crystal plane decreases in both cases, and thus prevention of recrystallization by cyanoethyl residues is obvious. The influence of cyanoethyl residues at least on the crystalline structure of cellulose is indistinguishable between regenerated cellulose and cotton.

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