# *Birefringence of Native, Alkali-Swollen, and Crosslinked Cotton Fibers*

## INTRODUCTION

The refractive indices of cotton fibers are a measure of the overall polarizability with respect to the fiber axis and are influenced by orientation, crystallinity, and disposition of cellulosic chains. Chemical treatments, such as swelling in sodium hydroxide solution and crosslinking with formaldehyde, alter the refractive indices of the fibers. In this paper, the refractive indices of cotton fibers of different maturities before and after slack swelling in sodium hydroxide solutions of different concentrations, as well as after formaldehyde crosslinking, are considered.

## EXPERIMENTAL

### Materials

American Upland cottons, differing widely in maturity, were selected for this study. In addition, a number of cottons of about 70% maturity were also examined. All these cotton samples were Soxhlet extracted in a 1:2 mixture of ethyl alcohol and benzene at boil for 18 hr to remove the waxes present.

### Swelling

The six American cottons were slack-swollen in sodium hydroxide solutions of 10%, 16%, 24%, and 30% (w/w) concentration at 29°C for 30 min, washed in running water, and dried by exposure to the atmosphere.

### Crosslinking

The Soxhlet-extracted cottons were crosslinked with formaldehyde by the Form-D process for 1, 2.5, 5, and 10 min in a constant-temperature water bath maintained at 35°C. The crosslinked fibers were neutralized in sodium carbonate solution, washed, and air dried.

### Test Methods

The refractive indices of the extracted (control), swollen, and crosslinked cottons conditioned previously at 28°C and 65% R.H. for 24 hr were determined using the refractometric method developed by Neelakantan et al.[2] Samples in the form of a pad consisting of a few thousand highly parallelized fibers were immersed in a liquid of matching refractive index at 30°C and illuminated by highly collimated polarized white light. Measurements were made on duplicate bundles of fibers, and the average of these values is reported. The refractive indices of the extracted control cottons were also determined using the Becke line method. For each determination, about 30 fibers were immersed in paraffin oil–$\alpha$-bromonaphthalene mixtures of known refractive indices and the average refraction indices were determined. The birefringence was calculated in each case from the difference between the parallel and perpendicular refractive indices.

Two hundred fibers of each of the extracted control cottons were examined microscopically and the number of convolutions counted over a length of 1 cm in the central region of individual fibers. The average convolution angle was calculated for each cotton by the method described by Meredith.[3]

The crystallite orientation of the fibers is usually measured in terms of x-ray angle in degrees determined from the half-width of the azimuthal scan of the 002 arc at 50% of the maximum intensity by following the method of Creely et al.[4] However, in the present study, no x-ray measurement was made. The values reported in this paper are taken from the work of Orr and others,[5-7] and these values have been reported to be correct to ±1°.

TABLE I
Optical Properties of Untreated Cottons

| Cotton | Becke line method | | | Refractometric method | | |
|---|---|---|---|---|---|---|
| | $n_{\parallel}$ | $n_{\perp}$ | $\Delta n$ | $n_{\parallel}$ | $n_{\perp}$ | $\Delta n$ |
| Am. 947 | 1.584 | 1.536 | 0.048 | 1.585 | 1.537 | 0.048 |
| Am. 940 | 1.584 | 1.537 | 0.047 | 1.583 | 1.537 | 0.046 |
| Am. 193 | 1.585 | 1.537 | 0.048 | 1.588 | 1.536 | 0.052 |
| Am. 805 | 1.584 | 1.535 | 0.049 | 1.587 | 1.535 | 0.052 |
| Am. 888 | 1.586 | 1.534 | 0.052 | 1.596 | 1.534 | 0.062 |
| Am. 875 | 1.586 | 1.533 | 0.053 | 1.596 | 1.533 | 0.063 |

## RESULTS AND DISCUSSION

### Optical Properties of Native Cottons

The optical properties of the American Upland cottons of different maturities are listed in Table I. It is seen from this table that the parallel refractive index and, hence, the birefringence increases with increasing cell wall thickness. It is also seen from this table that the parallel refractive indices and, hence, the birefringence values as determined by the refractometric method are higher than the corresponding values determined by the Becke line method. These results are in agreement with earlier observations.[8–10] The differences have been attributed to the fact that the spiral angle decreases in successive layers proceeding from the fiber surface toward the fiber axis[10–12] as well as to the fact that the Becke line method provides only an estimate of the refractive index near the fiber surface, while the refractometric method measures the average refractive index over the entire cross section consisting of several fibrillar layers parallel to the fiber axis.[8–12]

Hebert et al.[6] who studied the relationship between the birefringence as determined by the Becke line method and the convolution angle obtained a value of 0.057 for the birefringence of an unconvoluted cotton fiber with normal orientation. On the other hand, the relationship between

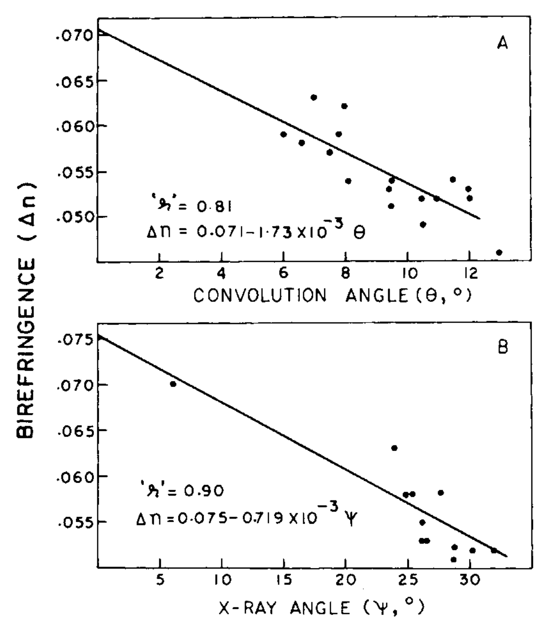


Fig. 1. Relationship between birefringence (refractometric method) and (a) convolution angle, (b) x-ray angle.

TABLE II
Optical Properties of Alkali-Swollen Fibers

| NaOH concentration, % | $n_{\parallel}$ | $n_{\perp}$ | $\Delta n$ |
|---|---|---|---|
| 0 | 1.596 | 1.534 | 0.062 |
| 10 | 1.584 | 1.529 | 0.055 |
| 16 | 1.576 | 1.528 | 0.047 |
| 24 | 1.572 | 1.527 | 0.045 |
| 30 | 1.572 | 1.527 | 0.045 |

the average birefringence (refractometric method) and the convolution angle is shown in Figure 1a. A statistical analysis of the data leads to a value of 0.071 for the birefringence of an unconvoluted fiber. This value is close to the birefringence of ramie with an orientation factor of 0.95% and having no convolutions.[13]

The relationship between the average birefringence of different cottons, as well as ramie, and the crystallite orientation (x-ray angles taken from the literature[5–7]) is shown in Figure 1b. A least-squares regression analysis of the data represented in the figure led to a birefringence value of 0.075 for an ideally oriented cellulosic fiber, which is close to the value of 0.076 derived by Iyer et al.[10] by the method described by Hermans.[13] On the other hand, Hebert et al.[6] have obtained from a graph of x-ray angle versus birefringence (Becke line method) a value of 0.071 for the birefringence of an ideally oriented cellulosic fiber. This value is significantly lower than the value obtained from the present study. An examination of their data[6] shows that the birefringence of ramie used by them was 0.066, while the widely accepted value is 0.070.[10,13] Insertion of this value in their graph leads to a birefringence of 0.075 for ideally oriented cellulosic fibers, which is close to the value derived by Iyer et al.[10] as well as that obtained by extrapolation in this study. In the present study, the coefficient of variation varied from 0.4% to 0.7% for different cottons.

### Birefringence of Swollen Fibers

The optical properties of slack-swollen cotton samples are given in Table II. It is seen that the perpendicular refractive index registers only a marginal decrease, while the parallel component decreases significantly with increasing concentration of sodium hydroxide solution. The birefringence is lowered even on swelling in 10% alkali, inspite of the decrease in the convolution angle. The tenacity as well as birefringence values level off on swelling in 24% alkali.

The crystallinity of native cottons and ramie has been found to be substantially constant and equal to 74%.[14] The wide variation in birefringence ($\Delta n$ = 0.04 to 0.07) of different cellulosic fibers with cellulose I structure is mainly due to the differences in the orientation of the fibrils.[10,14] On slack mercerization, the crystallinity of all cottons and ramie is reduced to about 54%.[14] However, all varieties of cotton and ramie show substantially unchanged or slightly improved crystallite orientation. On the other hand, the amorphous orientation has been found to decrease significantly on slack mercerization with sodium hydroxide because of shrinkage. However, the decrystallization and consequent increase in the amorphous portion alone cannot account for the large reduction in birefringence. It is seen from Table III (data taken from ref. 14) that the process of decrystallization and disorientation without lattice change (i.e., EDA slack swelling which reduces the crystallinity of native cottons to 44%) does not produce very large reductions in birefringence. The process of reorientation by stretching the EDA slack-swollen fibers back to original length leads to birefringence values comparable to those obtained for the native fibers. On the other hand, stretching the fibers slack swollen in sodium hydroxide does not improve their birefringence significantly. This, therefore, suggests that the significant reduction in the range of birefringence values (0.038–0.047) of the slack-mercerized cottons and ramie should, therefore, be attributed mainly to the change in the disposition of the molecular cellulosic chains on mercerization. In this configuration (cellulose II lattice), it appears that the orientation differences cannot result in significantly different birefringence values for different cottons and ramie.

TABLE III
Optical Properties of Swollen Fibers[a]

| Cotton | $n_{\parallel}$ | $n_{\perp}$ | $\Delta n$ | X-Ray orientation factor |
|---|---|---|---|---|
| Giza-45 | | | | |
| Raw | 1.586 | 1.532 | 0.054 | 0.70 |
| NaOH Slack | 1.570 | 1.529 | 0.041 | 0.75 |
| NaOH 0% Stretch | 1.577 | 1.529 | 0.048 | 0.92 |
| EDA Slack | 1.582 | 1.531 | 0.051 | 0.73 |
| EDA 0% Stretch | 1.584 | 1.531 | 0.053 | 0.77 |
| Ramie | | | | |
| Raw | 1.599 | 1.529 | 0.070 | 0.95 |
| NaOH Slack | 1.573 | 1.526 | 0.047 | 0.84 |
| NaOH 0% Stretch | 1.576 | 1.526 | 0.050 | 0.95 |
| EDA Slack | 1.587 | 1.527 | 0.060 | 0.91 |
| EDA 0% Slack | 1.589 | 1.527 | 0.062 | 0.94 |

[a] Data of Iyer et al.[14]

### Changes in Optical Properties with Crosslinking

To study the changes in birefringence, the refractive indices of crosslinked fibers were determined by the refractometric method, and the data are given in Table IV. It is seen that there is no perceptible change in the perpendicular refractive index with increasing bound formaldehyde, while the parallel refractive index progressively decreases. As a result of the significant decrease in the parallel index, the birefringence values are lowered.

## CONCLUSIONS

From the graphs of birefringence determined by the refractometer method as a function of convolution angle as well as x-ray angle, the value of the birefringence of the unconvoluted as well as the perfectly oriented cellulose fibers have been obtained.

The parallel refractive index, and consequently the birefringence, progressively decrease in the case of fibers swollen in sodium hydroxide solution of increasing concentration.

Formaldehyde crosslinking has been found to lower the refractive indices of cotton fibers parallel to the fiber axes, and, hence, the birefringence values are progressively lowered.

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TABLE IV
Optical Properties of Crosslinked Fibers

| % Bound formaldehyde content | $n_{\parallel}$ | $n_{\perp}$ | $\Delta n$ |
|---|---|---|---|
| 0.0 | 1.588 | 1.536 | 0.052 |
| 0.14 | 1.585 | 1.535 | 0.050 |
| 0.24 | 1.583 | 1.534 | 0.049 |
| 0.54 | 1.582 | 1.534 | 0.048 |
| 0.79 | 1.580 | 1.534 | 0.046 |

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