Orientation Behavior of Ethylene Diamine-Treated Cottons with Stress

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Synopsis

The decrystallization of natural cotton with Ethylene Diamine Treatment is well known. This paper analyzes the variation of X-ray orientation with stress on ethylene diamine-treated cotton fibers. For cotton fibers in the natural state, the elongation varies uniformly with the applied stress. It has also been pointed out by earlier work that the X-ray orientation does not vary uniformly with increase in applied stress. With ethylene diamine treatment on natural cottons, the above trends are reversed and this is reported in the present investigation. This paper also indicates a possible explanation to support the above observation.

INTRODUCTION

Ethylene diamine is known to swell cotton fibers and forms complexes with cellulose.[1,2] Recent investigations by Kalyanaraman[3] have shown that ethylene diamine (EDA) treatment improves the weak links in the cotton fiber and thereby gives a uniform tensile strength along the length of cotton fibers. Ethylene diamine treatment has no dependence on temperature and the reaction rate is fairly fast.[4,5] Although Segal and Creely[2] have reported that cotton treated for about 1 min in 98% EDA results in complete complex formation according to Hennige[4,5] 10 min are required for complete complex formation.

Although enough information is available regarding the decrystallization on EDA-treated cottons, information regarding the X-ray orientation measurement of EDA-treated cottons and the effects of stress on them are scanty. This paper reports the results of the investigation on the measurement of X-ray orientation on four different cotton fibers which are treated with EDA. This also reports the effect of the change in orientation with increase in stress.

In natural cotton fibers, the crystallites are arranged more or less parallel to the axis of the fiber. The degree of alignment along the axis of the fiber is generally known as orientation factor and Clark[6] was the first to measure it. Hermans et al.[7] have derived a mathematical expression to quantitatively estimate the orientation in cellulosic fibers. Using the Hermans' procedure, Kalyanaraman[8] has calculated the preferred orientation in a number of cotton fibers. Kalyanaraman and Ramakrishnan[9] have developed a microstress device to apply measured strain to a bundle of fibers and under the strained conditions to measure the orientation on the diffractometer. This microstress device is used for the present investigation.

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EXPERIMENTAL

Four cottons of American origin, namely Florence, S 2690, Acala, and T 4852 have been chosen. Their physical properties have been estimated using the regular lab techniques and they are reported elsewhere.[3]

EDA Treatment

A random sample of cotton belonging to each group has been taken and it is then dipped under slackened conditions in 100% ethylene diamine for 10 minutes[4,5] and then dried under ambient conditions.

Preparation of the Fiber Bundle

A random sample fo the representative treated cotton has been chosen and combed using fibrograph combs. One end of this parallel tuft is sandwiched between a pair of paper strips using quick-drying adhesives. After complete drying, the other end of the tuft was carefully recombed to remove the loose fibers and another pair of paper strips were pasted in the same configuration. The exposed middle region of the fiber bundle is adjusted to be about 10 mm in length. The thickness of the bundle is so chosen that it would be sufficient to produce enough X-ray diffraction and at the same time, be thin enough so as not to cause any absorption effects.

X-Ray Measurement

The method of measurement are discussed in detail by Kalyanaraman[8,10,11] in earlier papers. Ni filtered Cu Kα radiation is used and azimuthal scan of the diatropic reflection (040) is done utilizing the texture goniometer, a pulse height discriminator and a proportional counter. Point to point counting technique is used.

Scan of the Reflection

The bundle is mounted on to the texture goniometer. To start with, a radial scan is made and the 040 reflection is located. After locating the peak, the azimuthal scan is made from 0 to 90° on either side at equal intervals of 3° and the proportional counting is done for a fixed time of 32 s. The mean of the corresponding intensity values obtained on either side of the zero position is used for calculation. The background noise is assumed to be constant and equal to the count corresponding to the azimuth of 90°. For 040, the possible contamination at azimuth 90° from other reflections is not there at all and the noise level is about 2% of the peak intensity of the 040 reflection. The background noise is estimated on both sides of the peak and the average is taken and this average is substracted from all readings.

X-Ray Orientation Factor

The orientation factor is estimated by using these readings and adopting Hermans' procedure[7] for diatropic reflections. The details are discussed in earlier papers.[8,10,11]

Bundle Tensioning

The specimen is now transferred to the instron machine and the locking device preventing the bundle to take a load is relaxed and the fiber is subjected to tension. The initial cross-head position is noted and the cross head is moved at a constant rate of 0.05 cm/min which is the smallest speed available in the machine used. Thirty seconds of loading at this rate corresponds to about 2% extension for the fiber bundle which is originally kept at about a length of 1 cm. After the desired extension, the cross head is stopped and the bundle is carefully transferred to X-ray apparatus for orientation measurements.

Thus, five extensions are planned for each cotton. However, further stages of elongation are stopped if the fibers start breaking even before the onset of the higher state of elongation.

For each extension, namely 2%, 4%, and 6%, the same bundle is not used since there is a time delay between extensions and orientation measurements. During this period, there is a possibility that the bundle might undergo relaxation phenomena and perhaps this could lead to change in parameters. For each extension, two individual bundles are taken and their original orientations are also measured before starting the investigation. The methods are discussed in detail by Kalyanaraman.[10,11]

All the experiments have been done in a conditioned atmosphere at 27 $\pm$ 2° celsius and a relative humidity of 65 $\pm$ 2%.

DISCUSSION

Table I gives the orientation factor, the percentage increase in elongation, the percentage increase in X-ray orientation, and the stress developed during the process for each cotton and for each state of extension. Since in each case, a new bundle is taken, the percentage increases are fairly accurate and do not involve any time relaxation phenomena. Table II gives the same parameters for the same cottons after EDA treatment. In all the cases, the orientation is estimated by monitoring the azimuthal intensity of the diatropic 040 reflection. Unlike the 002 diffraction, 040 does not change its structure with swelling or with the change of lattice. Therefore, any change in X-ray orientation, $f(x)$, as measured by this reflection directly indicates the change in the internal parameters discussed. Table III gives the average X-ray orientation under the slackened conditions for the natural cottons as well as for the same cottons treated with 100% EDA solution under identical conditions. Visibly, it appears that the X-ray orientation $f(x)$ of EDA-treated cottons seem to be smaller than the corresponding values for natural cottons. There appears to be an evidence of internal change inside the fibers. Evans and Jeffries[12] have quantitatively shown that there is an improvement in the width of the cotton fiber if swollen in 100% EDA. The EDA penetrates the microfibrils and forms interfibril and intrafibril cross linking by forming complexes with the cellulose substrate. Also, the cross linking of cellulose chain by diamine molecules has been pointed out by Howsman and Sisson.[13] Thus, this cross linking by diamine molecules results in the overall disorder in the interior of the microfibrils.

The amine complexing of cotton cellulose opens up the intermolecular

TABLE I[a]
Crystallite Orientation Before and After Stretching for Natural Cottons

Species		Crystallite orientation Initial	After stretch	Elongation %	Increase in $f(x)$	Stress developed g/tex
Florence	I	0.750	0.790	1.45	5.33	4.95
	II	0.770	0.782	3.16	1.56	8.48
	III	0.772	0.802	4.34	3.88	12.58
	IV	0.794	0.832	5.60	4.78	18.38
	V	0.772	0.810	7.00	4.92	16.29
	Va	0.768	0.797	7.07	3.78	16.83
S 2690	I	0.790	0.818	1.45	3.54	8.77
	Ia	0.755	0.800	1.80	3.24	7.48
	II	0.787	0.815	3.00	3.56	16.39
	IIa	0.802	0.815	2.90	1.62	11.93
	III	0.775	0.818	3.80	5.55	14.86
	IIIa	0.764	0.822	3.95	7.59	17.11
	IV	0.790	0.823	5.44	4.18	10.33
	IVa	0.760	0.817	4.31	7.50	12.84
	V	0.748	0.803	7.00	7.35	10.81
Acala	I	0.751	0.768	1.70	2.26	—
	Ia	0.725	0.768	1.70	5.93	4.39
	II	0.751	0.763	3.00	1.60	6.50
	IIa	0.746	0.772	3.50	3.49	7.85
	III	0.746	0.790	5.38	5.90	9.36
	IIIa	0.740	0.811	5.18	9.59	10.66
	IIIb	0.739	0.797	5.66	7.84	13.88
	IV	0.736	0.803	7.78	9.10	12.83
	IVa	—	0.790	6.95	—	11.34
	V	0.733	0.811	8.40	10.64	13.13
T 4852	I	0.775	0.796	1.54	2.71	2.24
	Ia	0.776	0.784	1.74	1.03	4.88
	II	0.766	0.809	3.17	5.62	6.22
	IIa	0.775	0.788	2.91	1.68	5.92
	III	0.806	0.815	4.68	1.12	10.64
	IIIa	0.794	0.806	3.59	1.51	11.90
	IV	0.779	0.827	5.75	6.16	14.19
	IVa	0.794	0.815	5.93	2.64	12.67

[a] To convert g/tex into SI units (kNm/kg), multiply by 9.807.

regions and possibly the hydrogen-bonding order is changed because of the presence of the amine groups. Rowland and Pittman[14] have pointed out that EDA increases reactivity of cotton by 78% in slack treatment. Also, the degree of activation with EDA treatment and its response to restretching are remarkably similar to that generally realized in mercerization. All these indicate that there is a structural change in the internal architecture of the fiber which is seen as the change in value of the X-ray orientation factor.

Figures 1(a) and (b) and 2(a) and (b) represent the stress developed vs. elongation and stress developed vs. increase in $f(x)$, namely the X-ray orientation for two of the cottons. In both the cases, Figure 1(a) and Figure 2(a) elongation vs. stress developed follows a Hookean trend in the natural state. But EDA treatment in both cases seems to destroy the direct proportionality of the Hookean trend of the stress elongation relationship.

TABLE II[a]
Crystallite Orientation Before and After Stretching for Ethylene Diamine-Treated Cottons

Species		Crystallite Orientation Initial	Crystallite Orientation After stretch	Elongation %	% Increase in $f(x)$	Stress developed g/tex
Florence	I	0.764	0.767	0.39	—	—
	Ia	0.746	0.766	2.68	1.74	6.89
	II	0.745	0.787	5.60	4.26	8.88
	IIa	0.742	0.771	3.91	1.58	7.48
	III	0.765	0.810	5.88	6.30	17.70
	IIIa	0.759	0.805	6.06	6.36	16.38
	IIIb	0.781	0.809	3.59	5.98	24.20
	IV	0.753	0.793	5.31	6.98	21.23
	IVa	0.748	0.815	8.95	8.80	22.01
S 2690	I	0.762	0.779	0.92	2.04	8.03
	Ia	0.752	0.788	4.79	2.16	6.17
	II	0.750	0.816	8.80	4.28	13.75
	IIa	0.795	0.815	2.52	4.04	14.12
	III	0.781	0.809	3.58	6.54	19.60
	IIIa	0.788	0.804	2.03	6.40	18.97
	IV	0.768	0.825	7.42	6.62	16.36
	IVa	0.758	0.828	9.23	6.54	15.20
Acala	I	0.720	0.745	3.47	2.20	5.53
	Ia	0.735	0.749	6.80	2.15	5.84
	II	0.730	0.761	4.24	4.20	11.75
	IIa	0.736	0.781	6.11	4.28	11.70
	III	0.740	0.800	8.11	6.82	12.83
	IIIa	0.755	0.794	5.16	6.82	13.23
T 4852	I	0.765	0.788	3.01	1.96	6.77
	Ia	0.729	0.775	6.31	2.06	5.58
	II	0.785	0.816	3.95	4.08	14.28
	IIa	0.769	0.805	4.68	4.10	14.66
	III	0.751	0.816	8.66	6.62	15.16
	IIIa	0.750	0.806	7.46	6.77	11.39

[a] To convert g/tex into SI units (kNm/kg), multiply by 9.807.

Elongation results from the restructuring of the stacking of the crystallites and the stacking seems to be thrown out of order with EDA treatment. Thus, it supports the phenomenon of decrystallization caused by EDA treatment as claimed by earlier workers by the measurement of several other physical parameters.

TABLE III
Comparisons of X-Ray Orientations of Natural and EDA-Treated Cottons

Cotton	X-ray orientation: Natural cotton	X-ray orientation: EDA-treated cotton
Florence	0.771	0.756
S2690	0.774	0.769
Acala	0.741	0.736
T4852	0.783	0.758

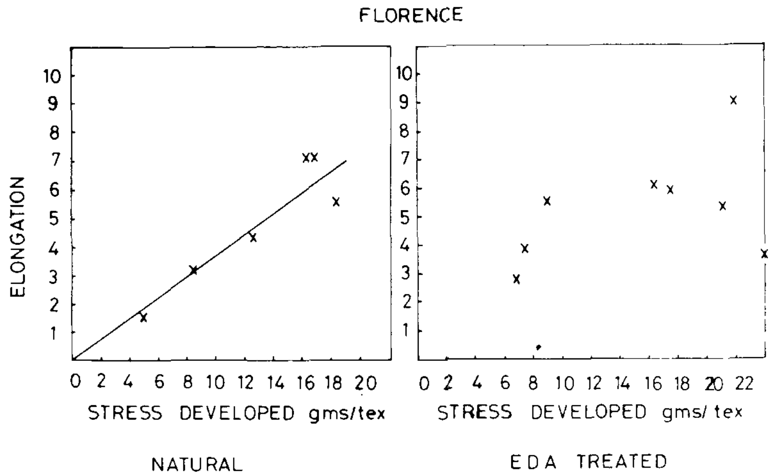

Fig. 1(a). Stress-developed vs. percentage increase in elongation for natural and EDA-treated Florence cottons.

However, it is very interesting to note that stress developed vs. % increase in $f(x)$ does not obey the proportionality relation namely Hooks law in the natural state, whereas after EDA treatment, the % in stress developed vs. % increase in $f(x)$ seems to conform to the Hook's law.

This is indicated in Figures 1(b) and 2(b) and the straightline trend is seen in the other cottons investigated as well (refer to Tables I and II). With stress, the percentage increase in $f(x)$ fails to obey the Hookean trend in natural cottons, this has been already pointed out by Kalyanaraman.[8] However, a possible explanation for reversing this trend by EDA treatment may as follows. The amine moiety by being inside the intermolecular space might perhaps result in a great deal of hydrogen bonding and thus may be responsible for the ordering of chromopheres in the intermolecular space. Since the X-ray brings out the time and space average of the diffracting

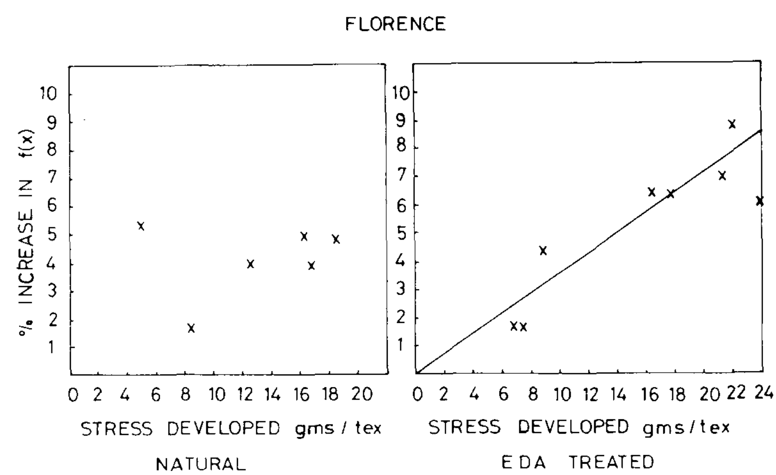

Fig. 1(b). Stress-developed vs. percentage increase in X-ray orientation for natural and EDA-treated Florence cottons.

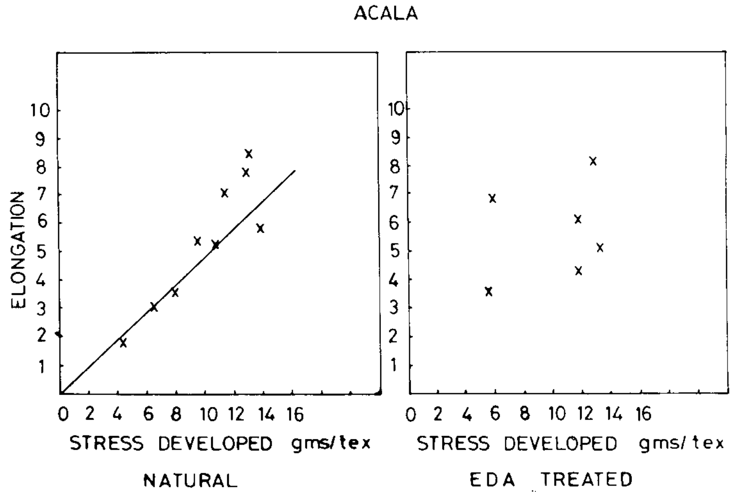

Fig. 2(a). Stress-developed vs. percentage increase in elongation for natural and EDA-treated Acala cotton.

matter, there may be a gradual and regular rearrangement of hydrogen bonds with stress, and this might reflect in the linear behavior of X-ray orientation with stress. However, whether the improvement is in space order or time order can be easily concluded by investigating the optical orientation which gives the time average of the interacting chromophore as pointed out by Kalyanaraman.[15] Work in this direction is in progress.

CONCLUSIONS

1. EDA treatment on natural cottons seems to bring a change in internal order, namely decrystallization. The X-ray method of investigation reported here for the first time agrees with the conclusions obtained by earlier workers using different techniques.

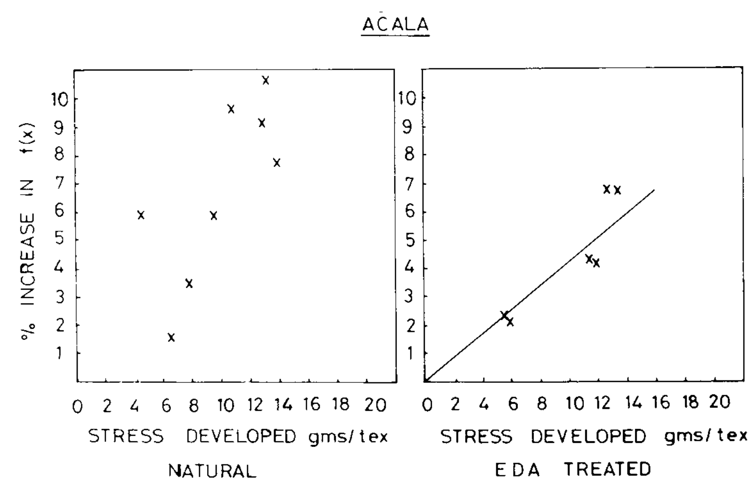

Fig. 2(b). Stress-developed vs. percentage increase in X-ray orientation for natural and EDA-treated Acala cotton.

2. Study of stress developed vs. elongation seems to reconfirm such an observation.

3. Stress developed vs. X-ray orientation in EDA-treated cottons seems to obey a regular relationship.

4. The above observation seems to indicate that in the decrystallization brought in by EDA, there seems to be an order brought into the diffracting matter which seems to behave regularly with stress.

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