Swelling of Cotton in Ethylene Diamine: Variation of the Spiral Angle and the Angle of Crystallite Dispersion with Stress

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Synopsis

The swelling of cotton in ethylene diamine is well known. This paper analyzes the variation of the spiral angle and the angle of crystallite dispersion with variation in applied stress to a bundle of EDA-treated fibers. EDA treatment causes regular variation in the spirality of cotton. The variation in the angle of crystallite dispersion is irregular signifying the onset of decrystallization. Mechanical deformation of cotton fibers involves extension and compression of crystallite helices. The present analysis seems to point out that EDA treatment of cotton fibers cause a kind of order in the mechanical deformation of the fibers by aligning the helices and disordering the crystallites.

INTRODUCTION

Most fibers may be described as composed of linear polymers arranged in a partially oriented and partially crystalline structure. Attempts by Jackson et al.,[1] Krigbaum et al.,[2] Nielson and Stockton,[3] Takayanagi,[4] and Hearle[5-7] have been made to describe the mechanical properties of fibers in terms of crystallite regions and amorphous, disordered or noncrystalline regions. Peterlin and Ingram[8] indicate that the elementary fibrils are the basic element of the structure.

It is known that the main bulk of the cotton fiber made of the secondary wall consists of cellulose crystallites aligned as left- and right-handed helices with reversals occuring along the length of the fiber. The internal structure of the crystallites occur in such a way that the chains are partly stabilized by hydrogen bonds and partly by van der Waals forces. In certain regions, the minimization of energy is achieved by crystallization, and, in other regions, the polymer remains in a random configuration. When swelled in water, this minimum energy configuration competes with the energy minimization achieved by hydrogen bond formation. Thus, any type of swelling agent creates a change of configuration in the major arrangement of the polymer structure inside the fiber.

As outlined earlier, there are crystalline and amorphous areas inside the fiber, and, in the presence of swelling agents, decrystallization is known to occur. Thus, after swelling, due to minimum configuration of energy caused by hydrogen bonding, an appreciable change of order might be introduced in the internal structure and swelling would ultimately leave a disordered modification of the original arrangement.

Journal of Applied Polymer Science, Vol. 31, 2443–2455 (1986)

CCC 0021-8995/84/082443-13$04.00

Peterlin and Ingram[8] have concluded that the elementary fibril contains slightly extended cellulose molecules aligned in the cellulose I crystal lattice parallel to the fiber axis. The lattice coherence along the elementary fibrils is interrupted at irregularly spaced intervals so that the fibril contains a sequence of slightly mismatched crystal blocks (crystallites) with the same axial orientation of the cellulose chain but differing from each other in the orientation of the *a* and *c* axes. Thus, the geometry of the fiber warrants two kinds of arrangements, namely, one among the crystallites themselves stacked one over the other in a particular manner inside the fibril and, the other, the stacking of the fibrils forming two kinds of helices—the right-handed one and the left-handed one. This internal geometry would result as two overlapping intensities in the diatropic X-ray diffraction occuring in the reciprocal space when subjected to X-rays. If the spiral angle of the helical arrangement is small, these peaks due to the two helices would overlap one over the other and would appear as a single diffraction in the powder diffraction pattern. Thus, the diffracted intensity, though appearing as a single reflection, is due to two overlapping Gaussian distributions, and Deluca and Orr[9,10] have suggested an experimental procedure to separate these two overlapping distributions to obtain the spiral angle and the angle of crystallite dispersion along the helices.

Using the above procedure, Kalyanaraman[11,12] has calculated the spiral angle and the angle of crystallite dispersion for a number of cottons. This paper reports the variation of the spiral angle and the angle of crystallite dispersion of ethylene biamine (EDA)-treated cottons and its relation to the internal structural order of the natural cottons.

EXPERIMENTAL

Four cottons of American origin, namely, Florence, S 2680, Acala and T 4852, have been chosen. Their physical properties have been reported earlier by Kalyanaraman.[13] The ethylene diamine treatment to the above natural cottons have been discussed in detail in an earlier work by Kalyanaraman.[13,14] The fibers are treated under slack conditions. Fiber bundles of the above treated cottons have been prepared as described by Kalyanaraman.[11,12,15] The bundles are mounted onto Kalyanaraman and Ramakrishman[16] bundle holder. This attachment facilitates the bundle to undergo elongation freely when subjected to tension with the Instron and at the same time, the expanded bundle could be clamped and mounted onto the texture attachment of the powder diffractometer.

X-ray Measurement

The crystallites in cotton fibers are arranged as a spiral structure along the fiber axis, and the degree of alignment along this axis is known as the orientation of the fiber. Clark[17] was the first to measure this orientation. Hermans et al.[18] have developed a mathematical expression to quantify this preferred orientation, and Segal et al.[19] and Creely and Conrad[20] have developed a diffractometric technique for its evaluation. The X-ray set up outlined here adopts the same procedure used by the earlier workers.

Ni-filtered CuKα radiation is used, and the azimuthal scan of the diatropic reflection (040) is done utilizing the texture goniometer, a pulse height discriminator, and proportional counter. The point-to-point counting method is used.

To begin, a radial scan is made and the 040 reflection is located at a 2θ angle of 34.5° after observing all usual precautions. From the zero position, the azimuthal scan of the intensity is obtained by counting the intensity from 0 to 90° on either side of the zero azimuth at equal intervals of 3° and 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 calculations. The background is assumed to be linear and equal to the intensity at an azimuth of 90°. At an azimuth of 90°, the background noise is about 2%, and there is no contamination from any other diffraction. The background noise is estimated on both sides of the zero, and the average of the two readings is determined and substracted from the other readings. Also, for the calculation of the spiral angle, the intensities at azimuths $E_1 = 15°$ and $E_2 = 30°$ for each cotton are used. This is also measured on both sides of the zero and the average is taken.

The bundle of fibers is stretched by the Instron machine to five extensions corresponding to elongations of 2, 4, 6%, etc., as described by Kalyanaraman[11,12] earlier. The orientation measurement and azimuthal scans were determined for each extension by transferring the bundle to the X-ray arrangement. After stretching, the bundle movement is frozen by clamping the bundle after the appropriate extension, and the bundle holder is transferred to the X-ray setup. The intensity values at azimuths of 15 and 30° on each side of the zero are taken so as to calculate the spiral angle and the angle of crystallite dispersion. To avoid relaxation phenomena, two or more separate bundles are used for each extension. All experiments are done in the conditioned atmosphere of 27 $\pm$ 2° celsius and a relative humidity of 65 $\pm$ 2%.

Orientation Factors, Spiral Angle and Angle of Crystallite Dispersion

The X-ray orientation factor is calculated using the above observations by the procedure suggested by Hermans et al.[18] for diatropic reflections. The spiral angle and the angle of crystallite dispersion are evaluated by using the intensity values at azimuths 15 and 30° and by the Deluca–Orr[9,10] procedure. The details are outlined elsewhere by Kalyanaraman.[21] The calculations were done by a BASIC program written by the author for the Challenger I.P. Desk Computer.

DISCUSSION

Swelling of cotton in ethylene diamine is well known. Evans and Jeffries[22] have quantitatively shown that there is an increase in the width of the cotton fiber if swollen in 100% EDA. EDA penetrates the cellulose substrate and causes internal structural changes by making hydrogen bonds of the intracrystallite and intercrystallite type. Rowland and Pittman[23] have pointed out that EDA increases the reactivity of cotton by 78% in slack

treatment. Thus, there is evidence for internal changes inside the fiber. Kalyanaraman[14] has pointed out that in EDA-treated cottons the stress developed vs. elongation do not follow the Hookean trend whereas X-ray orientation (f_x) vs. stress developed seem to follow the same. Since this observation is quite contrary to what has been observed in natural cottons as pointed out by Kalyanaraman,[15] it was considered worthwhile to further analyze and study the properties of the spiral angle and the angle of crystallite dispersion with stress for EDA-treated cottons.

The above analysis has been done by the procedure of Deluca and Orr,[9,10] and whatever conclusion that is drawn is based on the basic assumption that the (040) X-ray diffraction is the result of two overlapping diffractions caused by the left-handed and the right-handed spiral stacking of the crystallites. Such an assumption appears to be valid, since, in certain species of cotton, it has been observed that the two peaks are resolved and the (040) intensity appears to have a distinctly visible bimodel distribution.

Table I gives the changes in X-ray orientation, stress developed, and elongation along with the ϕ and α values and their percentage changes with stress for the natural cotton. Table II gives the same parameters for the EDA-treated fibers. Since several bundles were used during the course of the investigation for each observation, it was thought to be more appropriate to study the percentage change in the parameters than the absolute changes in them. This method might partly remove the irregularities that might arise due to the use of different bundles. Figure 1(a) represents the change in stress and the percentage change in the spiral angle for natural cottons, and Figure 1(b) represents the same parameters after EDA treatment. It is seen from the plot that the scatter of the points for these parameters in natural cotton is slightly more than for EDA treatment. This is also evident from the correlation coefficient, as seen in Table III. The correlation coefficient is 0.8046 for the natural cottons, and it is 0.8421 for the EDA-treated cottons. The regression equation has also been given for the data and is available in Table III. The constants −2.147 and 0.79 as represented in the regression equations do not have any meaning, since the line must pass through the origin. These values perhaps may be due to the experimental errors or due to the use of bundles for this type of investigation. The increase in the correlation suggests that the stacking of helices have better contribution to orientation. This means that internal alignment of the crystallites have been brought about by making the spirals regular. This may explain the increase in tensile strength with gauge length, since an internal order has been brought about.[13] Also, if the stacking is made regular and better, it should show in the change in the yield point for the EDA-treated cottons. This has been reported by Kalyanaraman[13] in an earlier investigation.

The variation of the angle of crystallite dispersion correlates better with the applied stress for the normal cotton than after EDA treatment. This means that some kind of interaction has taken place between crystallites which suggests intercrystallite bonding and an increase in the mismatch of the crystallites. This fall in order shows as a slight decrease in orientation.[14] Thus, decrystallization is suggested, and the crystallite alignment has changed. From the measurement of crystallite size, Patil et al.[24] have

TABLE I
Stress Developed, Increase in X-Ray Orientation, Increase in Elongation, Increase in Spiral Angle, and Increase in Angle of Crystallite Dispersion for Natural Cottons

Cotton		Stress developed (g/tex)	% Increase in f_x	% Increase elongation	Before stretch		After stretch		% Change in spiral angle ϕ	% Change in α
					ϕ (°)	α (°)	ϕ (°)	α (°)		
2.	I	18.38	4.78	5.60	12.68	17.2	8.64	14.58	31.86	15.23
	II	16.29	4.92	7.00	13.81	18.44	9.42	14.52	31.79	21.26
	IIA	16.83	3.78	7.07	14.47	17.80	10.56	14.43	27.02	18.93
3.	I	8.77	3.54	1.45	13.55	16.41	12.90	14.14	4.8	13.83
	II	16.39	3.56	3.00	12.63	17.87	11.69	14.02	7.44	21.54
	IIA	11.93	1.62	2.90	13.61	14.13	12.25	13.54	9.99	4.18
	III	14.86	5.55	3.80	13.00	16.54	—	—	—	—
	IIIA	17.11	7.59	3.90	14.32	14.62	11.86	12.72	17.18	13.00
	IV	10.33	4.18	5.41	13.95	15.60	12.34	12.87	11.54	17.50
	IVA	12.84	7.50	4.31	13.84	16.30	11.95	14.10	13.66	13.50
	V	10.81	7.35	7.00	13.37	17.22	11.62	13.03	13.09	24.33
4.	I	—	—	—	17.6	16.58	16.95	15.80	3.69	4.70
	IA	4.39	5.93	1.70	17.18	16.64	16.83	16.39	2.04	1.50
	II	6.50	1.60	3.00	17.49	16.50	17.46	16.34	0.17	1.00
	IIA	7.85	3.49	3.50	17.32	18.51	15.85	15.02	8.49	18.85
	III	9.36	5.90	5.38	17.37	16.10	15.38	14.04	11.46	12.80
	IIIA	10.66	9.59	5.18	17.86	17.26	14.35	13.99	19.65	18.95
	IIIB	13.88	7.84	5.66	18.32	16.21	15.10	14.01	17.58	13.57
	IV	12.83	9.10	7.78	17.99	17.54	13.14	14.28	26.96	18.59
5.	I	2.24	2.71	1.54	15.38	16.04	14.36	14.67	6.63	8.54
	IA	4.88	1.03	1.74	14.82	16.16	14.29	14.72	3.58	8.91
	II	6.22	5.62	3.17	14.79	15.16	14.37	13.72	2.84	9.50
	IIA	5.92	1.68	2.91	15.08	15.74	14.38	13.98	4.64	11.18
	III	10.64	1.12	4.68	14.79	14.87	12.27	12.83	17.04	13.45
	IIIA	11.90	1.51	3.59	14.05	15.40	1.74	12.70	16.44	17.53
	IV	14.19	6.16	5.75	15.17	15.89	13.01	12.84	14.24	19.19
	IVA	12.67	2.64	5.93	13.72	15.76	11.43	12.35	16.69	21.64

TABLE II

Stress Developed Increase in X-Ray Orientation, Increase in Elongation, Increase in Spiral Angle (ϕ) and Increase in Angle of Crystallite Dispersion (α) for the EDA-Treated Cottons

Cotton		Stress developed (g/tex)	% Increase in f_x	% Increase in elongation	Before stress		After stretch		% Change in spiral angle ϕ	% Change in α
					ϕ (°)	α (°)	ϕ (°)	α (°)		
2.	I	—	—	—	12.26	17.30	11.15	17.60	9.05	1.73
	IA	6.89	1.74	2.68	13.84	16.76	12.62	16.13	8.82	3.76
	II	8.88	4.26	5.60	14.01	17.90	11.60	14.52	17.20	18.88
	IIA	7.48	1.58	3.91	13.31	18.10	9.83	16.87	26.15	6.80
	III	17.70	6.30	5.88	13.65	15.80	10.15	14.40	25.64	8.86
	IIIA	16.38	6.36	6.06	14.16	16.66	9.73	15.44	31.29	7.32
	IIIB	24.20	5.98	3.59	13.89	16.36	9.62	14.72	30.74	10.00
	IV	21.23	6.98	5.31	13.88	17.25	8.62	15.95	37.90	6.96
	IVA	22.01	8.80	8.91	15.09	15.81	9.29	14.13	38.44	10.63
3.	I	8.03	2.04	0.92	14.25	15.32	12.79	13.44	10.25	12.27
	IA	6.17	2.16	4.79	13.33	14.38	12.74	13.92	4.43	3.20
	II	13.75	4.28	8.80	13.36	13.18	12.26	13.78	8.23	—
	IIA	14.12	4.04	2.52	13.66	14.00	11.74	13.01	14.06	7.07
	III	19.60	6.54	3.58	13.47	14.97	9.55	12.73	29.10	14.96
	IIIA	18.97	6.40	2.03	13.98	14.04	9.98	12.94	30.73	14.96
	IV	16.36	6.62	7.42	14.15	14.38	9.68	13.08	31.59	9.05
	IVA	15.20	6.54	9.23	15.00	15.60	9.99	12.61	33.66	19.17
4.	I	5.84	2.15	6.80	17.61	16.51	16.36	15.64	7.10	5.27
	II	11.75	4.20	4.24	19.96	18.86	15.36	14.04	23.05	25.56
	IIA	11.70	4.28	6.11	17.83	15.24	14.66	13.52	17.78	11.29
	III	12.83	6.82	9.11	16.99	16.46	12.51	13.35	26.37	18.89
	IIIA	13.23	5.16	5.16	16.37	16.76	12.94	13.71	20.95	18.20
5.	I	6.77	1.96	3.01	15.79	15.40	14.32	13.74	9.31	10.78
	IA	5.58	2.06	6.31	15.24	15.56	14.34	14.25	5.91	8.42
	II	14.28	4.08	3.95	14.73	14.13	11.83	12.69	19.69	10.19
	IIA	14.66	4.10	4.68	15.02	13.98	12.48	12.24	16.91	12.45
	III	15.16	6.62	8.66	15.94	17.25	10.04	13.13	37.01	12.29
	IIIA	11.39	6.77	7.46	15.08	15.20	11.34	12.79	24.80	22.43

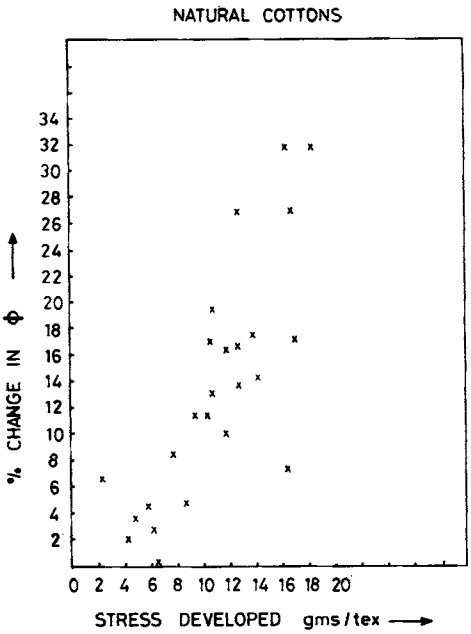

Fig. 1(a). Stress developed vs. percentage change in spiral angle for natural cottons. To convert g/tex to SI units (kNm/kg) multiply by 9.807.

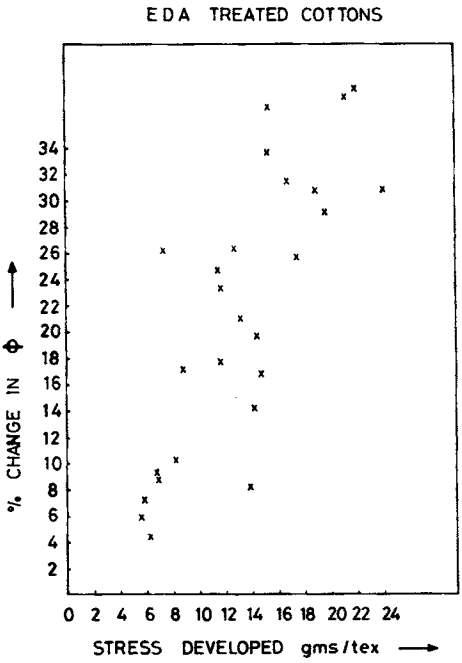

Fig. 1(b). Stress developed vs. percentage change for EDA-treated cottons. To convert g/tex to SI units (kNm/kg) multiply by 9.807.

TABLE III
Correlation Coefficients of Parameters and the Corresponding Regression Equations[a]

Parameters	Correlation coefficient	Regression equation
	Natural Cottons	
S vs. $\Delta\phi$	0.8046	$\Delta\Phi = -2.147 + 1.459S$
S vs. $\Delta\alpha$	0.7352	$\Delta\alpha = 2.96 + 0.976S$
ΔL vs. $\Delta\Phi$	0.8648	$\Delta\Phi = -2.39 + 3.84\Delta L$
ΔL vs. $\Delta\alpha$	0.7475	$\Delta\alpha = 3.35 + 2.43\Delta L$
Δf_x vs. $\Delta\Phi$	0.4489	
Δf_x vs. $\Delta\alpha$	0.5197	
	EDA-treated cottons	
S vs. $\Delta\Phi$	0.8421	$\Delta\Phi = 0.79 + 1.568S$
S vs. $\Delta\alpha$	0.322	
ΔL vs. $\Delta\Phi$	0.5047	
ΔL vs. $\Delta\alpha$	0.3094	
Δf_x vs. $\Delta\Phi$	0.8756	$\Delta\Phi = 1.34 + 4.28f_x$
Δf_x vs. $\Delta\alpha$	0.51	

[a] S = stress developed; Φ = spiral angle; α = angle of crystallite despersion; f_x = X-ray orientation; Δ represents percentage variation of the parameters from their original value.

pointed out that EDA treatment of cotton tends to reduce the size of the crystallite regions. However, the above observation only suggests a disorder in the stacking of the crystallites about the helix.

Figure 2 represents the percentage variation in the spiral angle with respect to the percentage variation in X-ray orientation factor. Here, the correlation is poor whereas with EDA treatment the correlation between

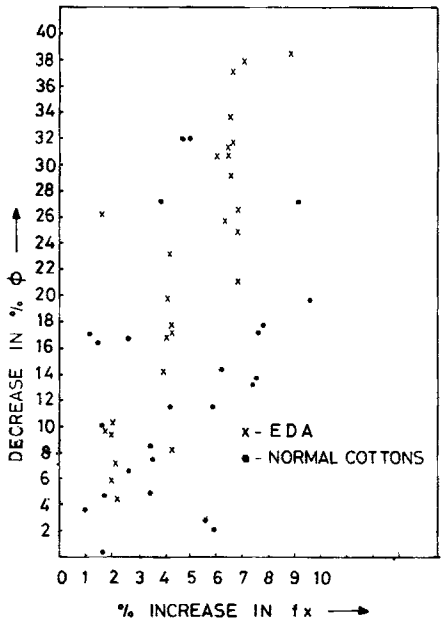

Fig. 2. Increase in fx vs. decrease in % spiral angle for normal (●) and EDA-treated (×) cottons.

the same parameters is fairly good. This means that, after EDA treatment, the improvement in orientation mainly depends upon the improvement in the alignment of the helices. This suggests a better yield stress and shift in yield point, and this has been observed to be true.[13]

Figure 3 gives the variation of elongation with percentage decrease in spiral angle ϕ. The correlation is equal to 0.8648 for natural cottons and is 0.5047 for the EDA-treated cottons. This again signifies the increase in disorder in the crystallites due to decrystallization after EDA treatment. This also means that the dependence of the alignment of the helices on elongation is disorderly. Figure 4 represents the variation of the percentage change in α with the percentage change in stress. The correlation coefficient is good in natural cottons and is equal to 0.7352. After EDA treatment, there is a large scatter of this relation and the correlation is very poor, namely, 0.322 (Table III). This also indicates the decrystallization that has taken place inside the fibre after EDA treatment. Figure 5 represents the variation of percentage increase in the X-ray orientation factor with percentage decrease in α. The scatter seems to be the same for both natural and EDA-treated cottons. Figure 6 gives the percentage variation of elongation with percentage change of α for both the cottons. The correlation is fairly good for natural cottons and the correlation coefficient is, respectively, equal to 0.7475 and 0.3094 for the natural and the EDA-treated cottons. α represents the angle of crystallite dispersion and its percentage variation correlates well with the percentage variation in elongation in natural cottons means that the applied stress causes a regular order in the crystallite stacking about the helix. The poor correlation of the same parameters in

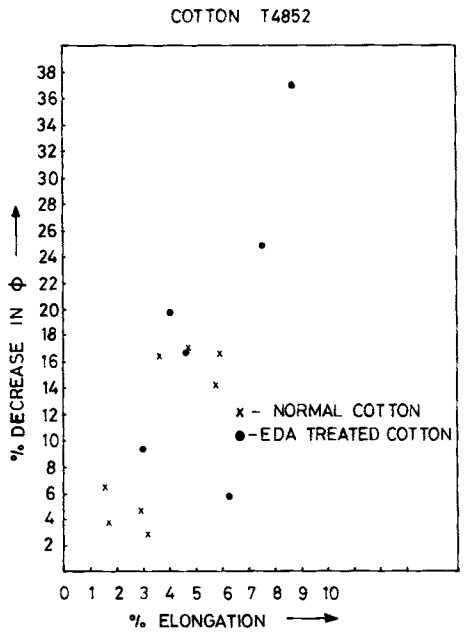

Fig. 3. Percentage elongation vs. percentage decrease in spiral angle for one of the cottons: (×) normal; (●) EDA-treated.

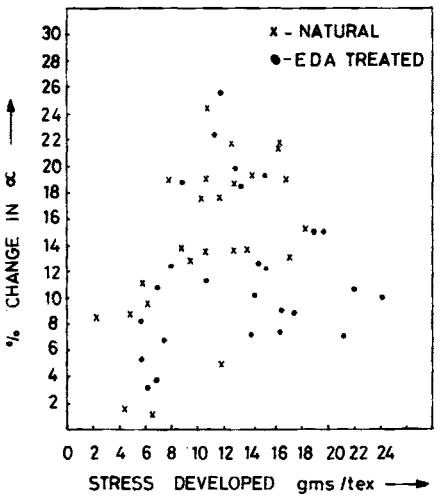

Fig. 4. Stress developed vs. percentage change in angle of crystallite dispersion to convert g/tex to SI units (kNm/K/g) multiply by 9.807: (×) natural; (●) EDA-treated.

EDA-treated cotton suggests a kind of disorder in the movement of crystallites on the application of stress implying the onset of decrystallization. Also this indicates that in natural cottons the observed elongation is contributed by the rearrangement of crystallite stacking about the helix and the straightening of the helix about its axis (suggested by fall in spiral angle ϕ).

Peterlin and Ingram[8] have concluded that mechanical deformation of cotton fiber involves extension or compression of microfibrils. Each deformation demands a sliding motion of the adjacent helices down to the smallest structural elements. Many hydrogen bonds that keep the elementary

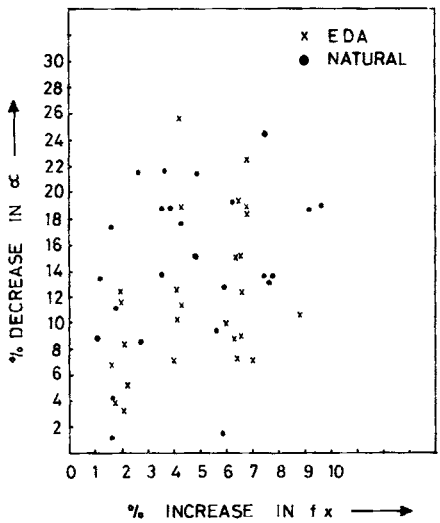

Fig. 5. Percentage increase in fx vs. Percentage decrease in α for normal (●) as well as EDA-treated (×) cottons.

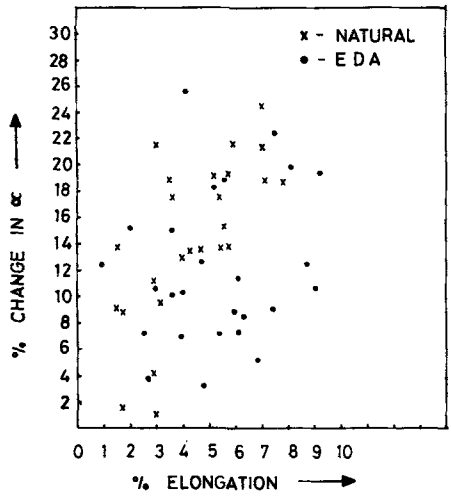

Fig. 6. Percentage elongation vs. percentage change in α for natural (×) and EDA-treated (●) cottons.

fibrils as tie bonds are very likely to block the sliding so that the block would perform as a single helix. The above observation suggesting the helical deformation with stress supports the conclusion of Peterlin and Ingram.[8]

Thus, the individual microfibrils bundled into macrofibrils by strong hydrogen bonds may perhaps provide the mechanical properties of the fiber. Between natural cottons and EDA-treated cottons, there could be a totally different arrangement of the hydrogen bonds or the tie bonds between polymer chains may be different. Thus, the spiralling fibrils in both cases may have individual extensibility with the helix angle. It is well known from the work on twisted yarns that increasing the helix angle reduces the resistance to extension. Hearle[6] suggested that this was due to the occurence of two modes of deformation: Either the fibrils may stretch as the fiber extends at constant volume or the fibrils may change their helical configuration like spiral springs without change in length but with a reduction in volume giving the resistance to the fiber extension. Since in EDA treatment the correlation between change in elongation and the spiral angle is poor, the second situation seems to prevail and the EDA-treated fiber behaves like a spiral spring.

Figure 7 represents the variation of 50% X-ray angle with the spiral angle ϕ. For both normal and EDA-treated cottons, it is linear in the middle regions and the scatter increases for the EDA-treated cottons. The trend is the same as observed by Kalyanaraman.[11]

CONCLUSIONS

1. In EDA-treated cotton, the increase in stress causes variation in the spirality of the cotton fiber, and the variation is regular.

2. Increase in stress causes irregular dispersion of the crystallites, implying, thereby, the onset of decrystallization.

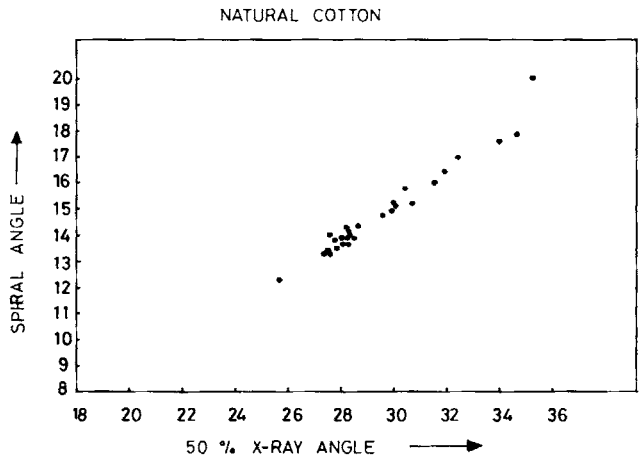

Fig. 7(a). 50% X-ray angle vs. spiral angle for natural cottons.

3. The orientation enhancement is directly proportional to the spiral angle decrement in EDA-treated cottons.

4. In normal cottons, the elongation causes the realignment of the helices as well as the crystallites, since both show a good correlation. EDA treatment reflects a modification of the above phenomenon because of the decrystallization.

5. Mechanical deformation of cotton fiber involves extension or compression of the helically arranged microfibrils. EDA treatment appears to increase the order in the hydrogen bonding of the microfibrils.

6. EDA-treated cottons enables the fibrils to change their helical configuration as in spiral springs without change in length.

The above conclusions are made on the assumption that the diffracting crystallites are arranged in the form of helices and the distribution of the crystallites are normal about the mean. Physical observation seems to agree with the above hypothesis, but it is also the limitation of the analysis. Also,

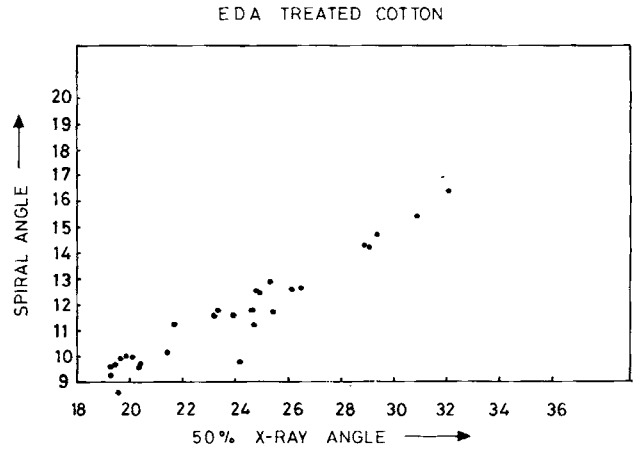

Fig. 7(b). 50% X-ray angle vs. spiral angle for EDA-treated cottons.

the results presented here pertain to a bundle of fibers and not to single fiber, and, consequently, this is also a limitation of the above study.

The author expresses his thanks to Mr. R. Ramakrishnan and Mr. A. Siveramakrishnan for the collection of the data and for part of the calculations. The author thank Mr. T. V. Ratnam, Director, SITRA, for his keen interest in the work and for the encouragement. The financial assistance from the Agricultural Research Service of the United States Department of Agriculture in a PL 480 grant is gratefully acknowledged.

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Received April 10, 1985
Accepted July 2, 1985