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An X-Ray Study of Crystalline Orientation and Mechanical Properties of Swollen Cotton Fibers Using Cadoxen Solution as Swelling Agent

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Synopsis

Bundles of cotton fibers were given swelling and stretching treatment using Cadoxen solution containing 3.58% cadmium. The fibers were stretched from −2% to +8% in steps of 2%. The crystallite orientation and mechanical properties of treated fibers are markedly improved. Results clearly indicate that the swelling of cotton in Cadoxen solution is intercrystalline and the swollen fiber has retained the cellulose I structure.

INTRODUCTION

It is well recognized that the swelling of cotton fibers in a reagent considerably modifies the molecular and crystallite orientation, and investigations[1-3] have been made to relate fibrillar and crystallite orientation to the various mechanical properties of swollen cotton fibers. Most of the work reported regarding the swelling of cotton and the resulting variation in orientation has been using caustic soda because it is commonly used as a mercerizing agent. The other swelling agents, namely aqueous solutions of ethylenediamine, zinc chloride, Cadoxen solution, etc., were investigated comparatively to a lesser extent.

In the previous work,[4] the optimum conditions for using Cadoxen as a swelling agent were reported. The present paper gives information about the improved crystallite orientation due to swelling of cotton fibers in Cadoxen solution. The preferred orientation is further improved by the combined action of swelling and stretching of the fibers. The effect of these stretching and swelling treatments on cotton fibers in relation to the mechanical properties, namely, static Young's modulus, tensile strength, and extensibility, of the swollen fibers are given. The x-ray studies also indicate the nature of the swelling.

EXPERIMENTAL

Preparation of Sample

Supima and Giza cottons were selected for the present study mainly because both have high degrees of polymerization and were readily avail-

TABLE I

X-Ray Orientation Factors and Mechanical Properties of Swollen and Stretched Cotton Fibers[a]

	Supima cotton[b]				Giza cotton[b]			
Stretch, %	X-ray orientation factor f_x	Breaking strength, g/d	Breaking extension, %	Static Young's modulus, g/d/unit strain	X-ray orientation factor f_x	Breaking strength, g/d	Breaking extension, %	Static Young's modulus, g/d/unit strain
Raw cotton	0.71	4.2 (36)	5.5 (37)	105.9 (42)	0.72	4.0 (35)	5.2 (34)	93.2 (41)
−2	0.74	3.9 (32)	7.9 (27)	81.2 (43)	0.79	4.1 (28)	8.1 (33)	94.5 (34)
0	0.78	4.0 (30)	7.6 (32)	87.2 (35)	0.82	4.2 (31)	7.6 (33)	101.8 (35)
+2	0.80	4.1 (26)	7.7 (32)	95.1 (46)	0.80	4.2 (31)	7.4 (42)	105.6 (32)
+4	0.82	4.1 (34)	7.2 (29)	95.0 (40)	0.83	4.2 (29)	7.2 (31)	106.6 (27)
+6	0.87	4.5 (35)	7.0 (33)	102.8 (36)	0.84	4.4 (31)	6.6 (35)	111.3 (35)
+8	0.87	4.4 (27)	6.9 (24)	106.1 (27)	0.86	4.5 (32)	6.4 (39)	121.2 (36)

[a] Swollen in Cadoxen containing 3.58% Cd for 1 hr.

[b] Figures in parentheses are c.v. %.

able. The cotton fibers were extracted using methanol in a Soxhlet apparatus to remove the particulate impurities.

The stretched cotton fibers were swollen in Cadoxen containing 3.58% Cd content. The details of the preparation of Cadoxen were given in a previous paper.[4] The stretching of the fibers has been done by a special fiber-stretching device similar to the one used by Radhakrishnan and co-workers. The fibers were stretched from −2% to +8% in steps of 2%. The details of the swelling conditions and stretching are given in Table I.

Measurement of Crystallite Orientation

The crystallite orientation was determined according to the well-known Hermans orientation factor:[5]

$$f_x = 1\text{–}3\ \overline{\sin^2\alpha} \tag{1}$$

Equation (1) applies to native cotton and swollen fibers in which there is no lattice conversion.

The experimental setup for taking x-ray diffraction photographs of the fibers is similar to that of Gupta.[6] The fibers taken in the bundle form were combed to ensure parallelism, then gripped in jaws and held with nominal tension for x-ray exposure. A specimen-to-film distance of 4.5

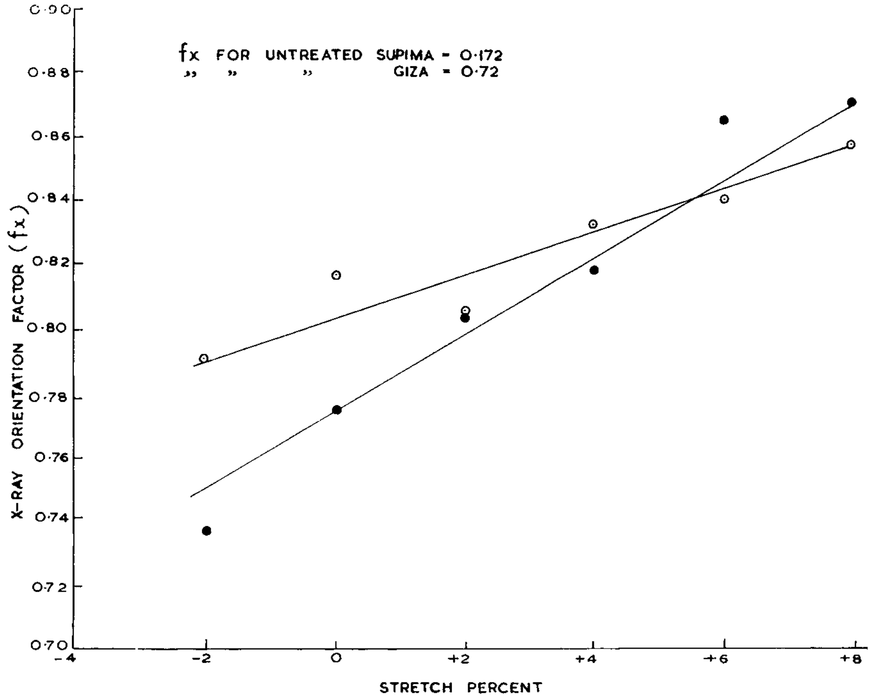
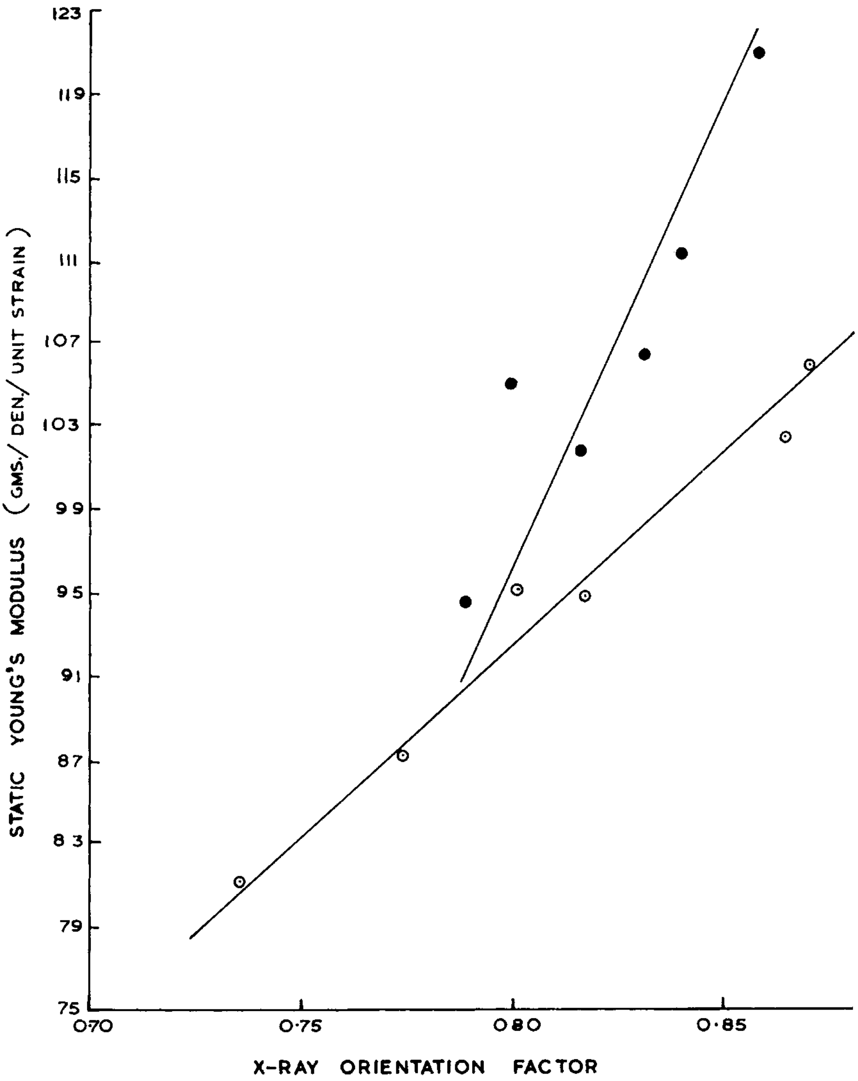


Fig. 1. Effect of stretch on x-ray orientation factor: (O) Giza cotton; (●) Supima cotton.



(a)

Fig. 2 (*continued*)

cm was maintained for the entire study. Filtered Cu Kα radiation from a Philips sealed tube working at 35 kV and 25 mA was used. The exposure time was 2½ hr and the photograph was recorded on a flat film. The specimen size, exposure time, and the film-processing technique were standardized as far as possible. The microphotometer used for scanning the film was a Hilger and Watts nonrecording type. The film was mounted on a rotatable disc. The disc was rotated inside a stationary mount which was graduated in degrees and with its center coinciding with the center of the film. The whole body was fixed to the stage of the microphotometer.

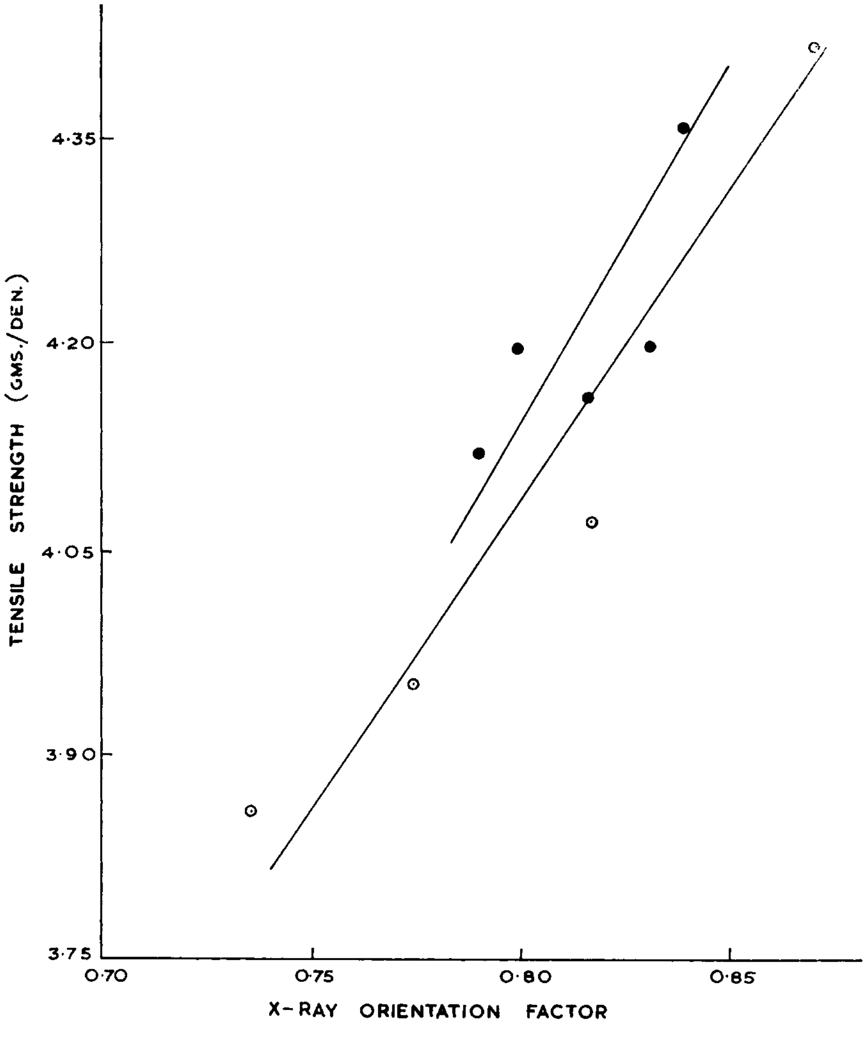


Fig. 2 (*continued*)

The rotation of the film was done in steps of 4° of arc about the center of the photograph, and at each setting the sickle was scanned radially by traversing the holder. Since the 101 and $10\bar{1}$ reflections overlapped, the outer reflection was scanned as representing the two along the length of the fiber.

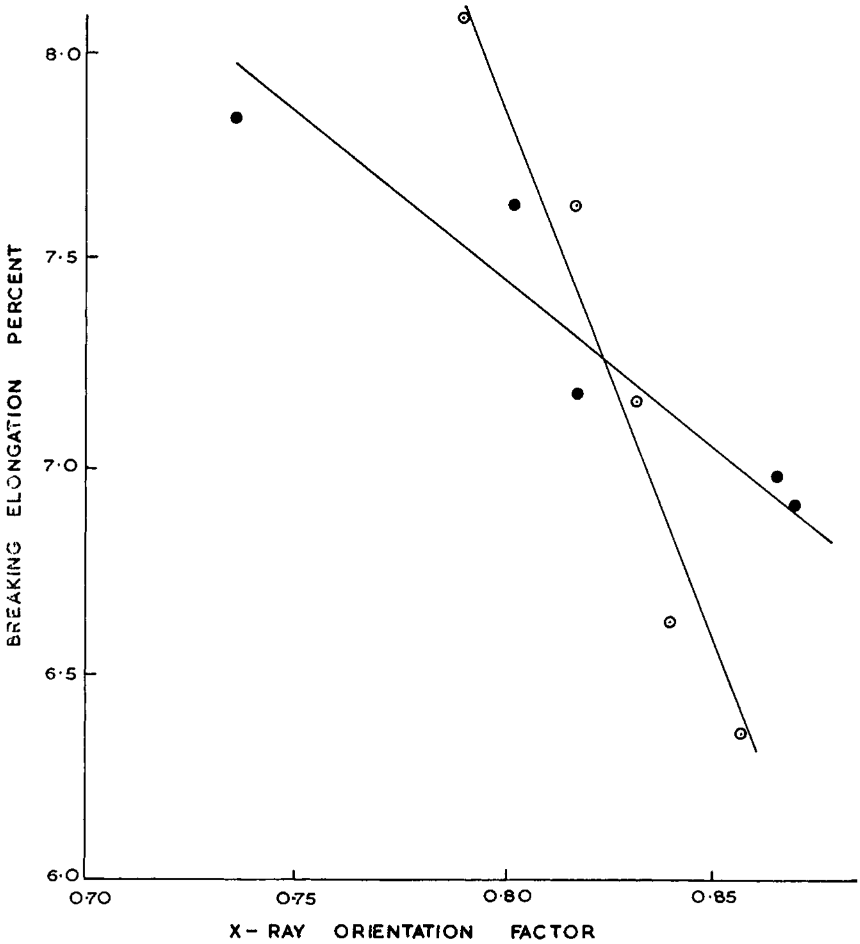
Measurement of Mechanical Properties

The tensile properties of native cotton fibers and swollen cotton fibers in Cadoxen were determined using Instron according to standard procedure. A gauge length of 0.5 cm was taken in order to obtain greater accuracy in tensile properties measurement as suggested by a number of workers.[1,7,10] The cross-head and chart speeds were kept 0.5 cm/min and 30 cm/min, respectively. Load Cell A (0–50 g range) with a 10-g full scale load calibration was used. Fifty fibers were tested from each specimen. All experiments were performed at 65% R.H. and 20°C.

RESULTS AND DISCUSSION

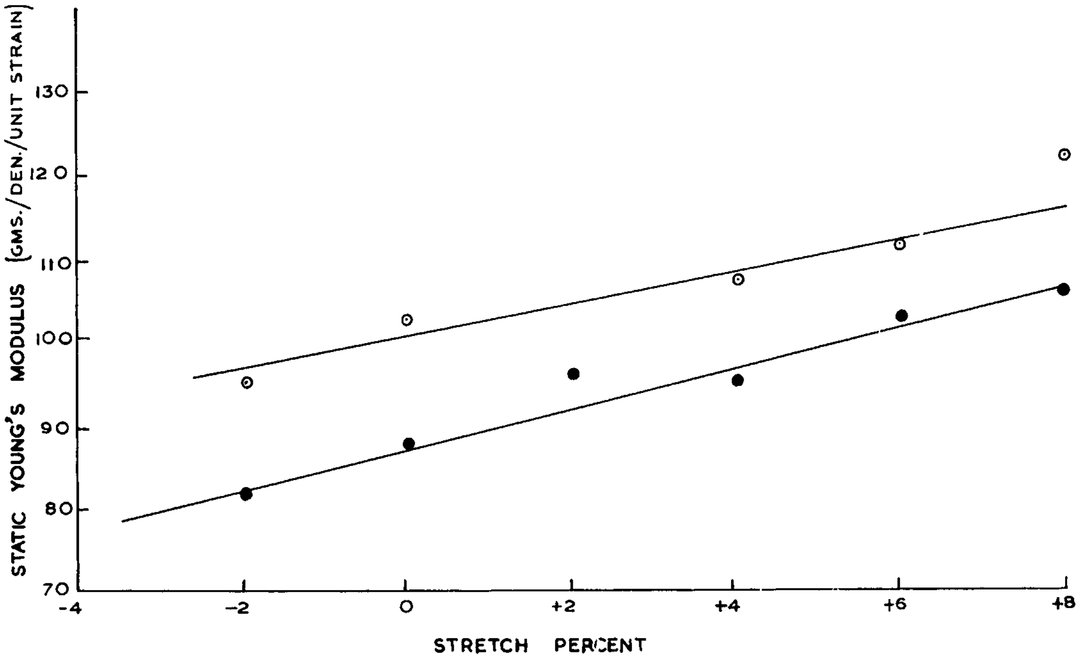
Crystal Structure and Intensity Profiles

A comparison of x-ray diffraction photographs indicates that the swelling treatment has not brought about any shift in the position of the 101, 10$\bar{1}$,



(c)

Fig. 2. Relation between x-ray orientation factor and: (a) static Young's modulus; (b) single fiber tensile strength; (c) single fiber breaking elongation; (●) Giza cotton; (O) Supima cotton.



(a)

Fig. 3 (*continued*)

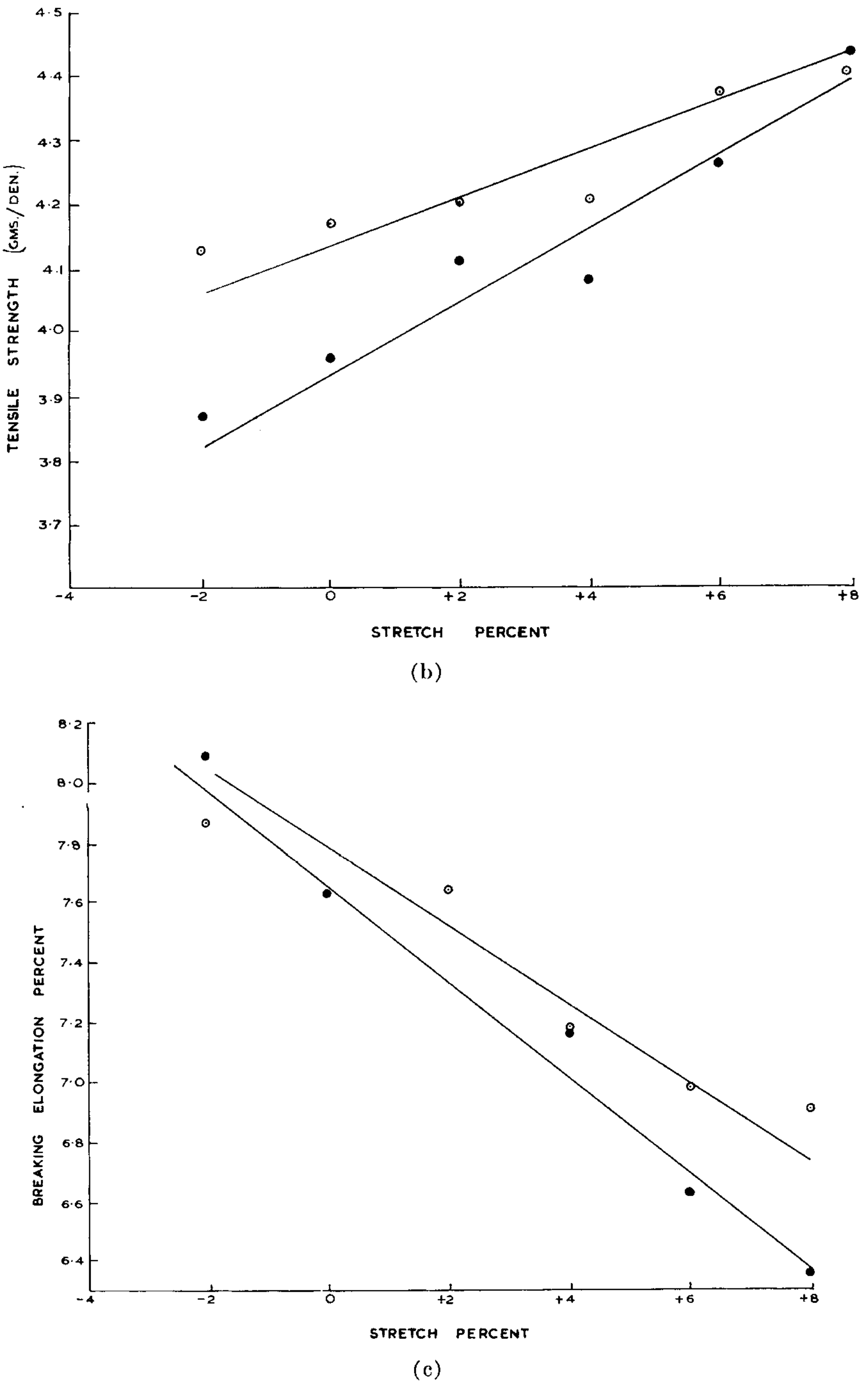


Fig. 3. Effect of stretch on: (a) static Young's modulus; (b) single fiber tensile strength; (c) single fiber breaking elongation; (O) Giza cotton; (●) Supima cotton.

and 002 planes. Therefore, it appears from the unchanged position of the crystallographic planes that the swollen fiber has retained the cellulose I structure. This clearly shows that the swelling of cotton in Cadoxen containing 3.58% cadmium is intercrystalline.

The intensity profiles for both Supima and Giza cottons are long and even, which indicates that the spread of the fibrils is at proportionally longer angles to the fiber axis. The swelling treatment shortens the length of the arcs for both the 101, $10\bar{1}$, and 002 planes. In the case of the 002 plane, the arcs shorten further with stretch, but the 101, $10\bar{1}$ do not show any appreciable change. The shortening of the arcs indicates a shift in the mean statistical distribution of fibrils, showing that they lie more parallel to the fiber axis. It is also accounted by the crowding of the high-intensity values for short azimuth angles followed by a sharp decline.

Effect of Swelling Conditions on Crystallite Orientation

Figure 1 indicates the linear relationship between the stretch (%) and x-ray orientation factor for both the cottons. The swelling treatment has been found to increase the fiber orientation even when the cottons are negatively stretched (−2%). Here, the conditions are very close to slack swelling, and so this behavior may be attributed to the partial straightening of the convoluted fiber during swelling. Such a deconvolution would align the axes of the crystallites more nearly parallel to the fiber axis. Radhakrishnan and others[1] who worked on the swelling behavior of NaOH on various cottons obtained similar results.

Figures 2a and 2b show a linear variation of static Young's modulus and tensile strength with orientation factor. The breaking elongation decreases linearly with the increase in orientation factor, as shown in Figure 2c. The swelling treatment of cotton fibers under various conditions in Cadoxen solution improves orientation, which in turn accounts for the variation in mechanical properties of the fibers.

Effect of Swelling Conditions on Mechanical Properties

The effects of stretch on static Young's modulus, tensile strength, and breaking elongation are shown in Figures 3a, 3b, and 3c. Supima cotton exhibits a considerable decrease in modulus after slack swelling (106 g/d/unit strain for untreated cotton, but 81 g/d/unit stain). On the other hand, the modulus of Giza cotton fibers increases owing to slack swelling. The tensile strength behavior of both the varieties of cotton under different conditions of swelling is roughly similar. The stretch swelling improves the tensile strength for both the cottons. As expected, there is an overall increase in the breaking elongation of fibers due to slack swelling. But with the increasing stretch during swelling, a drop in elongation of swollen fibers is obtained (Fig. 3c).

Whether the negative stretching during swelling treatment of fibers should result in an increase of strength and modulus is not clear. The behavior seems to differ from cotton to cotton, as shown in Figures 3a and 3b. If we consider the -2% stretch swelling conditions analogous to that of slack swelling, then it is evident that the modulus and strength of the fibers are controlled by more than one factor. For example, the reactivity of Cadoxen may affect the chain length and chain length distribution, yet improvement in crystallite orientation due to accompanying swelling may give better and close packing. There are contradictory reports available. Pandey and Iyengar[7] and Segal and co-workers[8] reported decrease in tensile strength in the case of NaOH-treated cotton fibers. On the other hand, Grant[9] and Radhakrishnan and co-workers[1] observed an increase in tensile strength of slack swollen cotton fibers.

CONCLUSIONS

When cotton fibers are swollen in Cadoxen solution at optimum conditions for maximum swelling, the crystallite orientation and mechanical properties are markedly improved.

Results clearly indicate that the swelling of cotton in Cadoxen solution is intercrystalline and the swollen fiber has retained the cellulose I structure.

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