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Effect of Slack Mercerization and Tension Mercerization on the Breaking Load Distribution of Cotton Fibers

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Synopsis

It has been shown that the breaking load histograms of raw, slack-mercerized, and mercerized-stretched cottons can be represented by β-distributions. The breaking load distribution is positively skewed for raw cotton. The influence of slack mercerization is to make the distributions symmetric and to reduce the variability of the breaking load by the elimination of weak links. The mode of the distribution shifts toward higher breaking load upon mercerization, and this shift increases with the extent of applied stretch. For various raw and mercerized cottons, the effect of increasing the gauge length is to reduce the mean, mode, and variability of the breaking load and to make the distributions less and less asymmetric. The application of stretch to swollen fibers influences the load distribution on the side of higher load and renders the distribution asymmetric.

INTRODUCTION

Cotton fibers can be considerably modified in terms of crystallinity, orientation of crystallites, as well as tensile and mechanical properties by subjecting them to swelling and stretching treatments[1–4] with selected reagents. The swelling treatment causes a decrystallization[3] of cotton at certain optimal concentrations of the reagent. The orientation of crystallites in cotton is slightly improved upon slack swelling[4] (when the fibers are allowed to shrink freely in the swelling agent). When stretch is applied to cotton fibers after slack swelling and these swollen-stretched fibers are subsequently washed in water and air dried, substantial improvements occur[5] in the degree of crystallite orientation, static Young's modulus, and average single fiber tenacity. These improvements may be attributed to the removal of structural imperfections or weak links in cotton during the combined swelling and stretching process.

The methodology for obtaining and analyzing the breaking load distribution of single cotton fibers has been described in detail in an earlier investigation.[6] It has been found that the rupture load in various raw cottons studied follows a β-distribution,[6] and the shape of this distribution is influenced by factors such as fiber maturity and the presence of weak links in the fibers.

The present paper attempts to examine the influence of fiber mercerization on the distribution of the breaking load. For this purpose, cotton fibers have been modified by controlled swelling and stretching in a 24% (w/w) aqueous sodium hydroxide solution. The breaking load data for various modified fibers were obtained at several gauge lengths and were utilized to study the influence of mercerization on fiber weak links. The effect of applied stretch on the variability of breaking load in mercerized fibers was also studied.

EXPERIMENTAL

Materials

Karnak cotton belonging to *G. barbadense* species was selected for the present work because of its long staple length, which is desirable as there is considerable shrinkage in the length of fibers upon swelling. Waxes and pectinous materials were removed by 5 hr of Soxhlet extraction in chloroform, followed by 1 hr in 1% sodium carbonate at the boil.

Fiber Treatment

A parallelized bundle of fibers was subjected to 1 hr of swelling in 24% (w/w) aqueous sodium hydroxide solution at 65% R.H. and 27°C. Different degrees of stretch could be applied to fibers in the swollen state by making use of a stainless steel frame[4] provided with a vernier scale and a movable stud, which could receive one pair of jaws. The length of the fibers could be measured on this stretching device before and after swelling. The stretch applied to the fiber bundle during swelling is expressed in terms of the original length of the fiber bundle. Three levels of stretch were used:

(a) *Slack.* The bundle, which had contracted freely in the swelling agent, was stretched on the Instron tensile tester so that a very small tension was developed. The percent difference between this length and the original bundle length was expressed as the stretch for slack swelling (a negative value).

(b) *0% Stretch.* The jaws holding the slack-swollen fibers were transferred to the stretching device, and the bundle of swollen fibers was restored to original length (before swelling) prior to washing.

(c) *5% Stretch.* The swollen fiber bundle was stretched to 5% beyond the original length prior to washing.

Table I gives the designation of various swollen and stretched samples and also lists some of their useful properties.

TABLE I
Properties of Swollen and Stretched Fibers

Series no.	Sample	Stretch,[a] %	Abbreviation used in the text	Density, g/cc	Tex
1	Karnak dewaxed	—	raw	1.564	0.14
2	Karnak swollen in NaOH (24%, 27°C, 1 hr	−15.0	NaOH (slack)	1.544	0.17
3	Same as 2.	0.0	NaOH (0)	1.536	0.16
4	Same as 2.	5.0	NaOH (5)	1.533	0.15

[a] Applied after swelling and maintained during washing and drying of fibers.

Measurement of Rupture Properties of Swollen Cottons

Three hundred single-fiber tests were carried out at 27°C and 65% R.H. on an Instron tensile tester, using a rate of extension of 50%/min and a full-scale sensitivity of 10 g. Various fiber samples were tested at five test lengths, namely, 0.2, 0.4, 0.6, 0.8, and 1.0 cm. The cross-head speed had to be changed accordingly so as to maintain the rate of extension at 50%/min. Vibroscopy of single fibers was not carried out. Instead, the average linear density was obtained by cutting, counting, and weighing 1-cm lengths of fibers.

Analysis of Breaking Load Distribution of Single Fibers

The breaking load data obtained from single-fiber tests were classified into frequency arrays. Using the detailed procedure published earlier,[6] the observed breaking load histograms of raw and swollen cottons were fitted by a *β-type* probability density function:

$$y = K.x^{m-1}(a - x)^{n-1}$$

where y is the frequency of any breaking load x, K is a constant, a is the range of distribution, and m and n are parameters determining the shape of the distribution.

The curve fitting of β-functions to the observed breaking load histograms was carried out on an IBM-360 computer. The program output consisted of observed and calculated frequencies of breaking load, chi-square, m, n, and a values. The mean and mode of the breaking load could be determined in terms of m, n, and a:

TABLE II
Criterion for Determining the Type of the Frequency Curve

Cotton sample[a]	Test gauge length, mm	*k* Factor	Type of breaking-load frequency curve
Raw	2	−0.3905	β
	4	−0.0051	β
	6	−0.0167	β
	8	−0.1438	β
	10	−0.0290	β
NaOH (slack)	2	−0.0066	β
	4	−0.0107	β
	6	−0.0023	β
	8	−0.0004	β
	10	−0.0188	β
NaOH (0)	2	+0.1016	Pearson type IV
	4	−0.0843	β
	6	−0.0641	β
	8	−0.0121	β
	10	−0.0196	β
NaOH (5)	2	−0.0341	β
	4	−0.6657	Pearson type IV
	6	+0.5438	Pearson type IV
	8	−0.2326	β
	10	+0.0002	Pearson type IV

[a] Egyptian Karnak.

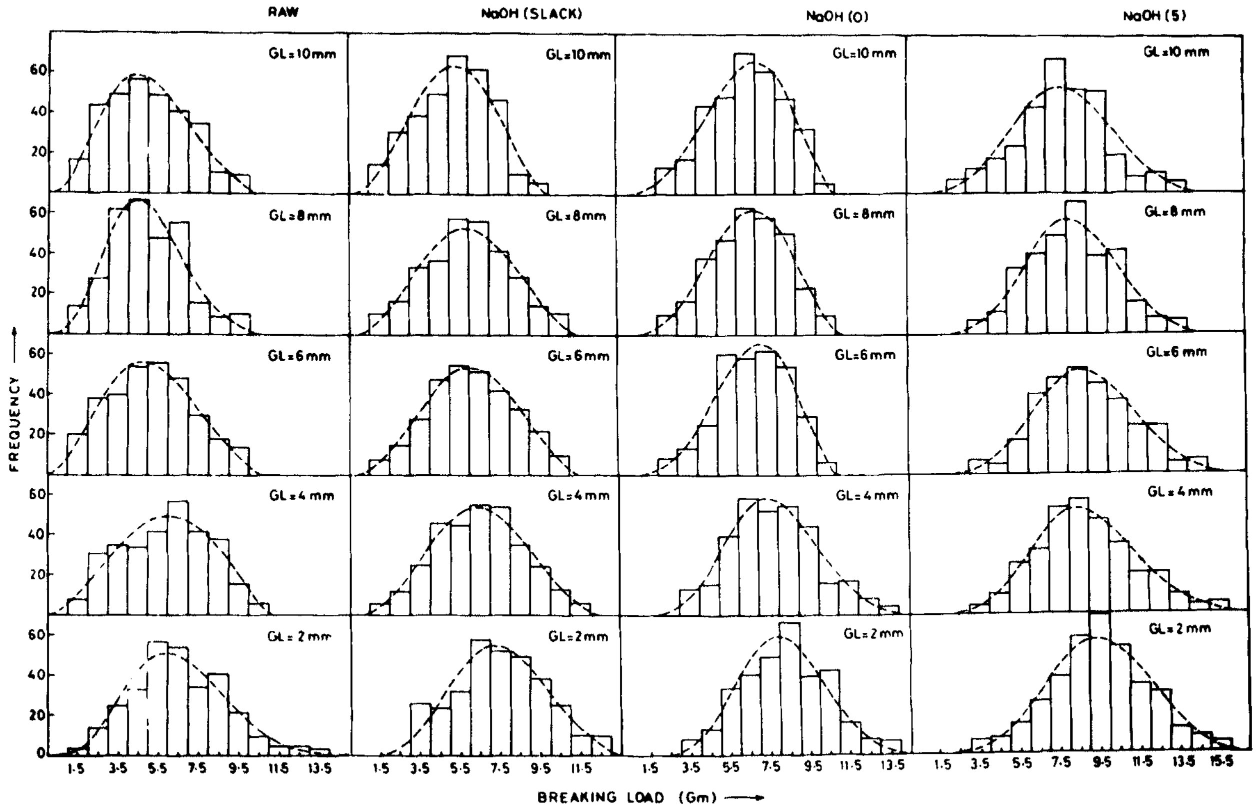

Fig. 1. Observed breaking load histograms (—) and Calculated β-distributions (- - -) for raw, swollen, and stretched cottons.

$$\text{mean} = \frac{m}{(m+n)} \cdot a$$

$$\text{mode} = \frac{(m-1)}{(m+n-2)} \cdot a$$

Prior to curve fitting, the information regarding the nature of the distribution was obtained using the k criterion of Pearson. The k factor was computed from the values of β_1 and β_2 determined[6] from the observed frequency data.

RESULTS

Table II lists the k criteria for raw, slack-swollen, and swollen-stretched samples at various test lengths. It turns out that 16 out of 20 breaking load histograms can be represented as β-distributions. In the remaining cases, all swollen-stretched samples NaOH (0) or NaOH (5), there is evidence regarding the existence of a Pearson type IV distribution. However, β-functions were fitted to all the histograms. The reasons for deviation of some of the histograms from a β-type frequency curve will be discussed later. The values of β_1 and β_2 listed in Table II also provide information regarding the asymmetry and breadth of the observed breaking load distributions. Since $\sqrt{\beta_1}$ is a measure of skewness, it would appear from the data presented in Table II that when the gauge length is increased, the distributions tend to become increasingly symmetric.

The observed breaking load histograms for raw, NaOH (slack), NaOH (0), and NaOH (5) cottons obtained at five different gauge lengths are shown in Figure 1. The fitted β-distributions are represented by the broken curves. It can be seen that the breaking load distribution becomes broader as the gauge length is decreased and also when the stretch applied subsequent to swelling is increased. Table III lists the values of the parameters m, n, a, χ^2, and the mean, mode, standard deviation, and coefficient of variation (*C. V.*) of the breaking load, obtained from the parameters of the fitted β-distributions. The chi-square values show that β-distributions give satisfactory fits to the observed histograms in most cases, with very few exceptions (marked "a" in Table III). The causes of unsatisfactory fits, particularly in the context of NaOH (5) cotton, will be discussed later.

The effect of increasing the gauge length is to reduce the constants m, n, and a, and the mean, mode, and standard deviation and to increase the *C.V.* of the breaking load (Table III). The mode shifts to lower breaking loads as the gauge length is increased (Fig. 1). The decrease in breaking load with increase in gauge length is undoubtedly due to the "weak link effect." [7,8] Increase in *C.V.* is merely a consequence of decreasing the mean breaking load. The variability of the breaking load decreases with increasing gauge length, as demonstrated by a reduction in the range a and the standard deviation (Table III).

Figure 2 shows a plot of the frequency constants m and n as a function of (a) applied stretch and (b) gauge length. The parameter n is more variant than m when the gauge length is changed. For raw cotton, n values are higher than m values at different gauge lengths, thus indicating a positively skewed distribution of the breaking load. For the slack-mercerized cotton, NaOH (slack), n, and m become nearly equal at all gauge lengths except the lowest, reflecting that the breaking load distributions have become symmetric or very nearly so. For NaOH

TABLE III
Variability of Breaking-Load in Raw Cotton and Various Swollen and Stretched Cottons

Series no.	Cotton sample[b]	Gauge length, mm	Parameters of fitted frequency curve			Goodness of fit χ^2	Measures of the Variability of Single Fiber Breaking Load				Skewness
			m	n	a		Mean, g	Mode, g	Standard deviation, g	*C.V.*, %	
1	Raw	2	5.3	14.8	25.2	14	6.65	5.99	2.5	37.6	0.26
		4	2.8	2.6	11.2	11	5.81	5.93	2.4	41.3	−0.05
		6	2.9	3.5	11.5	8	5.21	4.97	2.1	40.3	0.11
		8	4.8	12.2	17.5	21[a]	4.94	4.43	2.0	40.5	0.26
		10	3.3	5.2	12.8	7	4.97	4.53	2.0	40.2	0.22
2	NaOH (slack)	2	6.4	12.1	21.5	18[a]	7.44	7.04	2.4	32.2	0.17
		4	4.1	4.5	13.7	4	6.53	6.43	2.3	35.2	0.04
		6	3.7	3.8	12.5	3	6.17	6.14	2.2	35.7	0.01
		8	3.6	4.0	12.6	9	5.97	5.85	2.3	38.5	0.05
		10	3.4	3.2	10.3	12	5.31	5.37	1.9	35.8	−0.03
3	NaOH (0)	2	8.7	13.8	21.0	11	8.12	8.29	2.3	28.3	−0.07
		4	8.1	16.0	23.1	14	7.76	7.42	2.2	28.4	0.15
		6	5.1	3.3	11.2	7	6.80	7.18	2.0	29.4	−0.19
		8	4.9	3.8	11.8	4	6.65	6.87	1.9	28.6	−0.12
		10	4.3	2.9	11.0	8	6.57	6.98	2.0	30.4	−0.20
4	NaOH (5)	2	8.6	18.8	30.3	26[a]	9.51	9.07	2.6	27.3	0.17
		4	8.9	21.9	30.5	10	8.81	8.37	2.6	29.5	0.17
		6	7.8	11.0	21.4	17	8.88	8.66	2.5	28.2	0.09
		8	8.3	12.2	20.5	14	8.30	8.09	2.5	30.1	0.08
		10	6.0	7.1	17.2	32[a]	7.88	7.75	2.5	31.7	0.05

[a] Empirical fits of β-distribution to the observed histograms are poor in these cases.
[b] Egyptian Karnak.

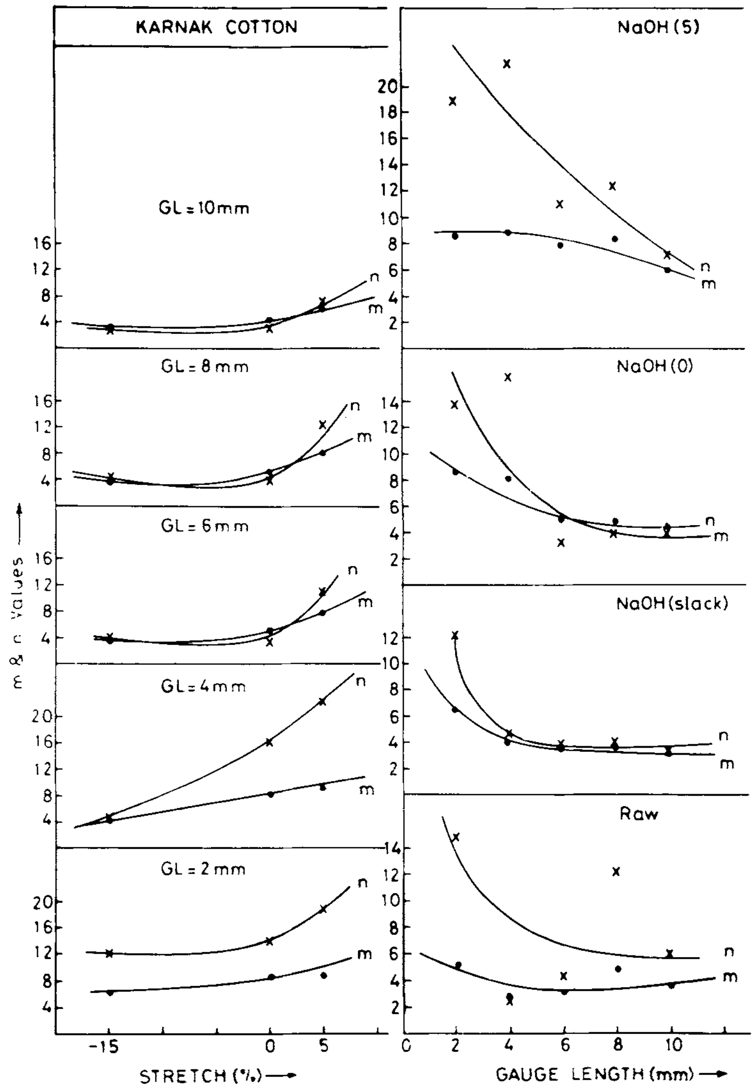

Fig. 2. Plot of *m* and *n* vs percent stretch and gauge length.

(0) and NaOH (5) cottons, *n* tends to be greater than *m*, particularly at lower gauge lengths. This difference between *n* and *m* is a function of applied stretch. The effect of increasing gauge length is to make the breaking load distributions less asymmetric. The increase in stretch makes the distributions more asymmetric, particularly at lower gauge lengths, where the difference between *n* and *m* is larger (Fig. 2).

On slack mercerization, the mode shifts to higher breaking loads at all gauge lengths (Fig. 1, Table III). The breaking load distributions become nearly symmetric. For NaOH (0) cotton, the mode shifts to still higher breaking load values, and, as a consequence, the breaking load distributions appear to be negatively skewed (Fig. 1, Table III). With further increase in applied stretch, i.e., for NaOH (5) cotton, the mode attains a maximum value. The breaking load distributions for NaOH (5) cotton become postively skewed again (Fig. 1) due to the strengthening of fibers on the higher load side of the distribution. The asymmetry, however, decreases with increasing gauge length.

The variability of breaking load, as inferred from standard deviation, is less for NaOH (slack) and NaOH (0) cottons than for raw cotton. NaOH (5), however, shows a greater variability of breaking load than raw cotton (Table III). This may also be inferred from values of the range a, which is not as reliable as standard deviation as a measure of variability. Mercerized cottons show a lower *C.V.* than raw cotton.

When the gauge length is increased from 2 mm to 10 mm, the drop in average breaking load is 25%, 29%, 19%, and 17% for raw, NaOH (slack), NaOH (0), and NaOH (5), respectively. Stretching the cotton fibers subsequent to slack mercerization thus reduces the effect of weak-links and improves the uniformity of strength along the length of the fiber.

DISCUSSION

The x-ray orientation factors f_x for raw, NaOH (slack), NaOH (0), and NaOH (5) cottons are 0.70, 0.71, 0.84, and 0.88, respectively.[4] The improvement in breaking load in various slack and stretch-mercerized samples can largely be accounted for by an increase in the orientation of crystallites[9] in the fibers. The "weak links" in cotton fibers[10] can be places of low diameter, high internal strain (e.g., reversals), or nonglucosidic residues distributed randomly along the fiber length. Mercerization tends to strengthen each of these types of weak links. Wakeham and Spicer[11] showed that the tendency of cotton fibers to break preferentially at reversals is reduced by mercerization. Mercerization also improves the uniformity of the breaking load along the fiber length as is evident in the case of cottons NaOH (0) and NaOH (5) by the decreased effect of gauge length on the mean breaking load and also by the decreased *C.V.* at a particular gauge length. The swelling and stretching treatments thus have an "annealing" effect on the fibers.

The distribution of single-fiber breaking load in raw cotton is due to the following: distortion of fiber shape, variation in fineness and intrinsic strength between fibers, and a variation in the breaking load along the length of fibers (i.e., the influence of weak links). Mercerization, which improves breaking load and the uniformity of fiber diameter, and removes some of the weak links, should, therefore, profoundly influence the distribution of the breaking load. In practice, however, the variation in breaking load between different fibers persists even after slack mercerization, hence the distribution is not greatly affected.

The breaking load distribution in raw cotton[6] is positively skewed. Upon slack mercerization, the distribution becomes nearly symmetric and shifts to a higher mode. This may be attributed to a relaxation of internal stresses and strains within fibers and also to the improved uniformity of fibers. For fibers which have been swollen and stretched to their original length, NaOH (0), the breaking load distribution shifts still further toward higher load values but becomes negatively skewed. The effect of stretch is not only to increase the crystallite orientation, but also to induce a reversion to a cellulose I lattice,[3,4] which is a more strained molecular configuration than cellulose II. The skewness may be due to this induced strain or may be produced by a strengthening of fibers on the higher load side of the mode. The breaking load distribution becomes positively skewed again and shifts to a still higher mode when the maximum stretch is applied to fibers after swelling [NaOH (5)]. This cotton has[4] as much as 17% cellulose I and a very high orientation factor of 0.88. The increase in crystallite orientation thus accounts for the development of very strong fibers, which contribute to the side of higher load in the distribution. The range (i.e., variability) of the distribution increases for NaOH (5); this may be partly explained in terms of recrystallized cellulose I.

It appears from Tables II and III that the distributions may not be conforming to the β-type for NaOH (5) cotton. This could be an artifact produced as a result of experimental difficulties in imparting uniformly the maximum stretch to alkali-swollen fibers. When fibers, with their ends gripped between jaws and wet with NaOH, are stretched, there may be some slippage of the fibers relative to each other, particularly at high levels of stretch. As a consequence, all the fibers may not be stretched to the same extent. This possibility, coupled with a reversion to cellulose I lattice,[4] induces a variability in the breaking load of NaOH (5) cotton and the standard deviation is consequently increased (Table III).

CONCLUSIONS

Mercerization influences the initial portion of the breaking load frequency curve (i.e., the portion of low breaking loads) by strengthening the weak fibers. As a result, the frequency curve becomes symmetric, the mode shifts to higher load values, and a higher mean and a lower *C.V.* are obtained for breaking load. With increasing stretch applied after swelling, a progressive increase in the mean and a decrease in the *C.V.* of the breaking load are obtained. However, the frequency curves for swollen-stretched cotton become skewed, presumably due to the development of stronger fibers which affect the tail on the high load side. With a few exceptions, the breaking load histograms of mercerized cottons can be satisfactorily represented by a β-distribution. The breaking load variability in cotton is reduced by slack mercerization as well as by increasing the gauge length.

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