Studies on Swelling of Cotton Fibers in Alkali Metal Hydroxides. IV. Influence of Initial Fiber Properties and Variations in Fine Structure on Tensile Behavior*

S. SREENIVASAN, P. BHAMA IYER, and G. S. PATEL

Central Institute for Research on Cotton Technology, ICAR, Adenwala Road, Matunga, Bombay-400 019, India

SYNOPSIS

Nineteen varieties of cotton, covering a wide range of fiber properties like maturity, fineness, and strength uniformity ratio were swollen in 5*N* KOH and NaOH at room temperature (30 ± 1°C). Tensile and fine structural properties of the resultant samples were measured and their relationship with initial fiber properties was examined. A comparative evaluation of fiber properties of KOH swollen fibers with those swollen in NaOH revealed that, irrespective of variety, fibers swollen in the former reagent retain higher tenacity. It was further noted that fine structural parameters like crystallite orientation and amorphous content which influence tensile properties become modified differently while swelling in the two reagents. While changes in crystallite orientation were found to be less drastic during KOH swelling, unlike in NaOH, the reverse was found to be true with crystalline content. These changes in fine structure could more or less explain the variation in tensile properties of fibers swollen in these two reagents. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Our earlier investigations[1-4] on the structure and properties of chemically treated cotton fibers revealed that KOH swollen fibers retain higher tenacities at all gauge lengths. This could be interpreted on the basis of fine structural variations such as higher accessibility, higher crystallite orientation, and more flexible and shorter crystallites. However, these studies were restricted to a few varieties having nearly the same maturity.

Swelling of cottons in NaOH has been known[5-7] to be influenced by their initial fiber properties like maturity, fineness, and strength uniformity. It was noted that, in general, the tenacity of fibers with low maturity and low strength uniformity increased substantially while fibers with high maturity showed drop in tenacity at 3.2 mm gauge length after slack swelling. Because of the varietal effect on swelling, the decrystallization brought about in *Gossypium hirsutum* cottons was found[8] to be more than in *Gossypium barbadesnse*. Further, it was shown[9] that both the decrystallization and the extent of conversion of Cellulose I to Cellulose II had profound influence on structure–property relations in swollen fibers.

A detailed investigation of the influence of fiber properties and the varietal effect on structure and properties of KOH swollen fibers is found to be lacking. Such a study would help in deciding the usability of this reagent for imparting desirable properties to cotton fibers irrespective of the variety. This knowledge is very essential for commercial exploitation of this reagent for finishing treatments. The present investigation was undertaken with this objective in view. This article summarizes the salient observations made during the study and discusses the results in comparison with those obtained after swelling these fibers in NaOH as well. The influence of structure, morphology, and initial fiber properties on structure–property relations of swollen fibers has been evaluated in detail.

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* Address correspondence to Dr. K. R. Krishna Iyer, Central Institute for Research on Cotton Technology, ICAR, Adenwala Road, Matunga, Bombay-400 019, Institute.

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Table I Physical and Structural Properties of the Selected Cottons

Cotton	Percent Mature Fibers ($Pm\%$)	Micronaire (μ)	Tensile Properties T_0 (g/tex)	$T_{3.2\text{mm}}$ (g/tex)	E (%)	Structural Properties f_x	Am
G. arboreum							
1. Abuharia	75.2	4.6	52.2	25.3	5.8	0.72	32
2. Kanwa	85.1	5.4	47.0	23.4	5.9	0.81	28
3. AK 235	75.0	5.8	43.1	17.7	5.0	0.73	29
4. AC-12	85.8	5.9	45.4	26.9	6.2	0.76	29
5. AC-10	89.6	6.1	47.2	26.6	6.9	0.73	30
6. AC-11	84.1	6.1	44.1	26.1	6.2	0.78	29
G. hirsutum							
7. B-61 18507	75.2	2.8	39.8	20.3	5.6	0.63	30
8. Auburnr-56	70.8	2.8	43.0	25.5	5.2	0.77	26
9. B-66-1803	50.1	3.0	41.7	23.2	5.1	0.78	26
10. Austhian	70.6	3.0	40.1	22.4	6.4	0.64	28
11. Aleppox-Empire-glander	55.7	3.2	47.5	23.3	5.1	0.69	28
12. Khandwa	75.0	4.6	46.6	18.7	4.9	0.65	30
G. barbadense							
13. GB-4	70.2	2.6	47.7	26.3	6.4	0.71	35
14. GB-2	66.6	2.8	50.4	26.4	6.0	0.71	31
15. Giza-45	77.3	3.0	47.2	22.2	5.8	0.68	33
16. SB-289E	56.5	3.0	47.2	30.4	6.7	0.70	28
17. Suvin	66.0	3.0	55.0	33.0	5.8	0.76	26
18. Ambrios	57.6	3.2	42.9	26.1	6.5	0.68	25
19. GB-0	56.8	3.5	50.0	29.0	6.1	0.70	31

EXPERIMENTAL

Materials

Nineteen varieties of cotton belonging to *G. arboreum* (6), *G. hirsutum* (6), and *G. barbadense* (7) were chosen for the study. Lint from each variety was purified by kier boiling using a standard procedure.

Methods

Swelling was carried out in 5N KOH and NaOH at 30 ± 1°C for 10 min as described earlier.[1]

Measurements

Tensile and fine structural measurements on swollen fibers were carried out by using appropriate methods which have been described in detail in the earlier publications.[1-4,10] The results were expressed as ratios as shown below:

$$\text{(i) Tenacity ratio} = \frac{T_{3.2}(g/t)\text{ after swelling}}{T_{3.2}(g/t)\text{ before swelling}}$$

$$\text{(ii) Elongation ratio} = \frac{E(\%)\text{ after swelling}}{E(\%)\text{ before swelling}}$$

$$\text{(iii) Orientation ratio} = \frac{f_x\text{ after swelling}}{f_x\text{ before swelling}}$$

$$\text{(iv) Amorphous ratio} = \frac{\text{Am}(\%)\text{ after swelling}}{\text{Am}(\%)\text{ before swelling}}$$

RESULTS AND DISCUSSION

The physical and structural properties of the different varieties of cotton selected for the current study are summarized in Table I. Selection was made to bring in a maximum extent of variations in the physical properties. As may be noted from the table, the maturity has a range of 50–90%, while Micronaire varied from 2.5 to 6.1. The strength uniformity among cottons also had a range of 0.41–0.71. Such a wide choice would enable meaningful assessment of the influence of these physical properties on the swelling and consequent modification in the tensile properties of fibers.

Influence of Initial Fiber Properties on Tensile Behavior of Swollen Fibers

Maturity

The influence of fiber maturity on the tensile properties of swollen fibers is depicted in Figure 1. While Figure 1(a) and (d) contains the relationships between *Pm*(%) and the tenacity ratio (3.2 mm) for both KOH and NaOH swollen fibers, respectively, the corresponding relations with elongation ratio are shown in Figure 1(b) and (c), respectively. A significant correlation of $r = -.53$, relating maturity to tenacity ratio of KOH is noted. All other correlations relating maturity to fiber properties are nonsignificant.

It has been observed earlier[1-4] that the overall swelling in KOH is lower than in NaOH, although the swelling is more uniform in the former. Immature fibers have higher lumen and, hence, can swell more, leading to better uniformity along the length. As a result, increase in $T_{3.2}$ after swelling for these fibers is more for both KOH and NaOH. In the case of highly mature fibers which swell less, as the lumen space is very low, the effects produced by the reagents have some noticeable differences. Even this limited swelling in NaOH leads to a decrease in $T_{3.2}$ [Fig. 1(d)], while no such effect is shown after swelling in KOH. In short, irrespective of the maturity level, swelling in KOH is beneficial in improving the tenacity of cottons. The elongation ratio increases after swelling in both the reagents for fibers of all varieties irrespective of the maturity. However, the increase in *E*(%) is found to be more in favor of mature fibers.

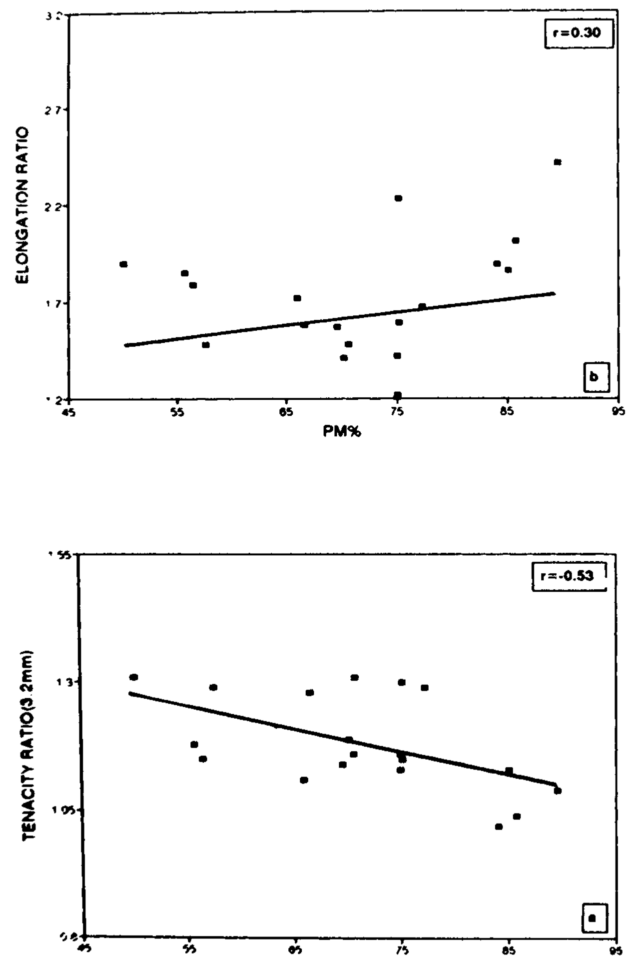

Figure 1 Dependence of (a, d) tenacity ratio and (b, c) elongation ratio of different varieties on percent mature (*Pm* %) fibers; (a, b) after swelling in KOH; (c, d) after swelling in NaOH.

The effect of swelling in improving and retaining the tensile properties is substantially marked in varieties having low $Pm(\%)$. Hence, it is these varieties which stand to gain substantially by swelling in KOH. Using such varieties for preswelling treatments would be more beneficial and meaningful than for the highly mature cottons.

Micronaire

The relationships between Micronaire fineness and tensile properties of swollen fibers plotted in Figure 2 resemble those given in Figure 1. This is expected due to the interrelationship between Micronaire value (μ) and maturity ($Pm\%$) of cotton fibers. It can be noted that a highly significant r value of $-.71$ is obtained between the tenacity ratio and μ for KOH swollen fibers. The r value between μ and the $T_{3.2}$ ratio for NaOH ($r = -.46$) is higher than that obtained between $Pm(\%)$ and the $T_{3.2}$ ratio ($r = -.30$).

It is interesting to note that, even for varieties having $\mu > 5.5$, the tenacity does not decrease after swelling in KOH [Fig. 2(a)], although the increase is lower than that obtained for cottons having low μ values. On the other hand, in NaOH, the overall increase is less even in finer cottons, and in the case of coarser cottons, $T_{3.2}$ decreases, leading to a fall in the tenacity ratio [Fig. 2(d)] to below unity. The likely reason for this difference in behavior between coarse and fine varieties has been attributed to differences in cross-sectional shapes and fibrillar packing and has been amply dealt with in our earlier publications.[2,4] Decrease in tenacity could also occur due to fine structural changes like fibrillar disorientation. This is dealt with in detail in the section on orientation.

The breaking extension shows a tendency to increase with increase in μ as seen by the higher elongation ratios for coarser fibers after swelling. This is true for both KOH and NaOH.

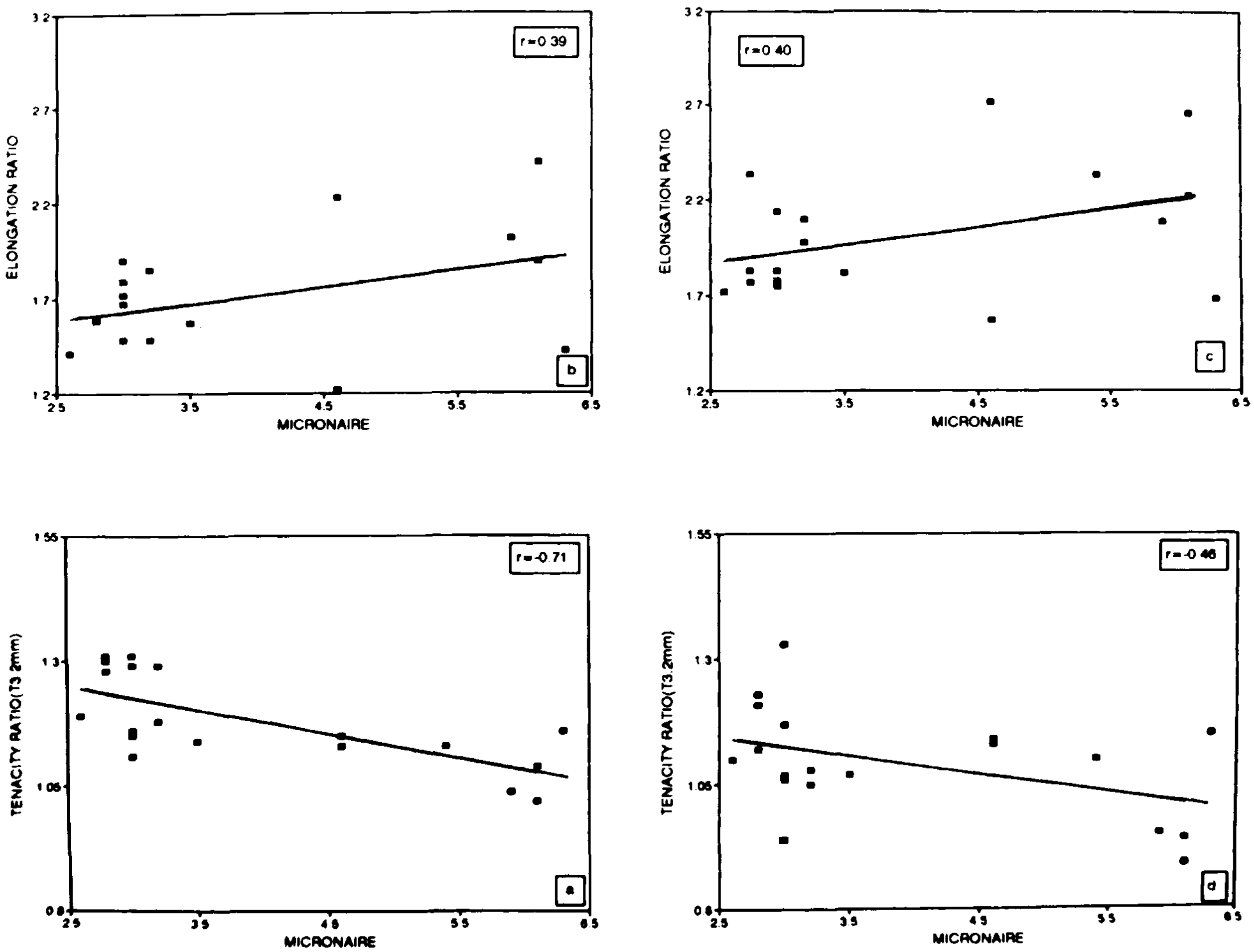

Figure 2 Plot of (a, d) tenacity ratio and (b, c) elongation ratio for different varieties against micronaire (μ); (a, b) after swelling in KOH; (c, d) after swelling in NaOH.

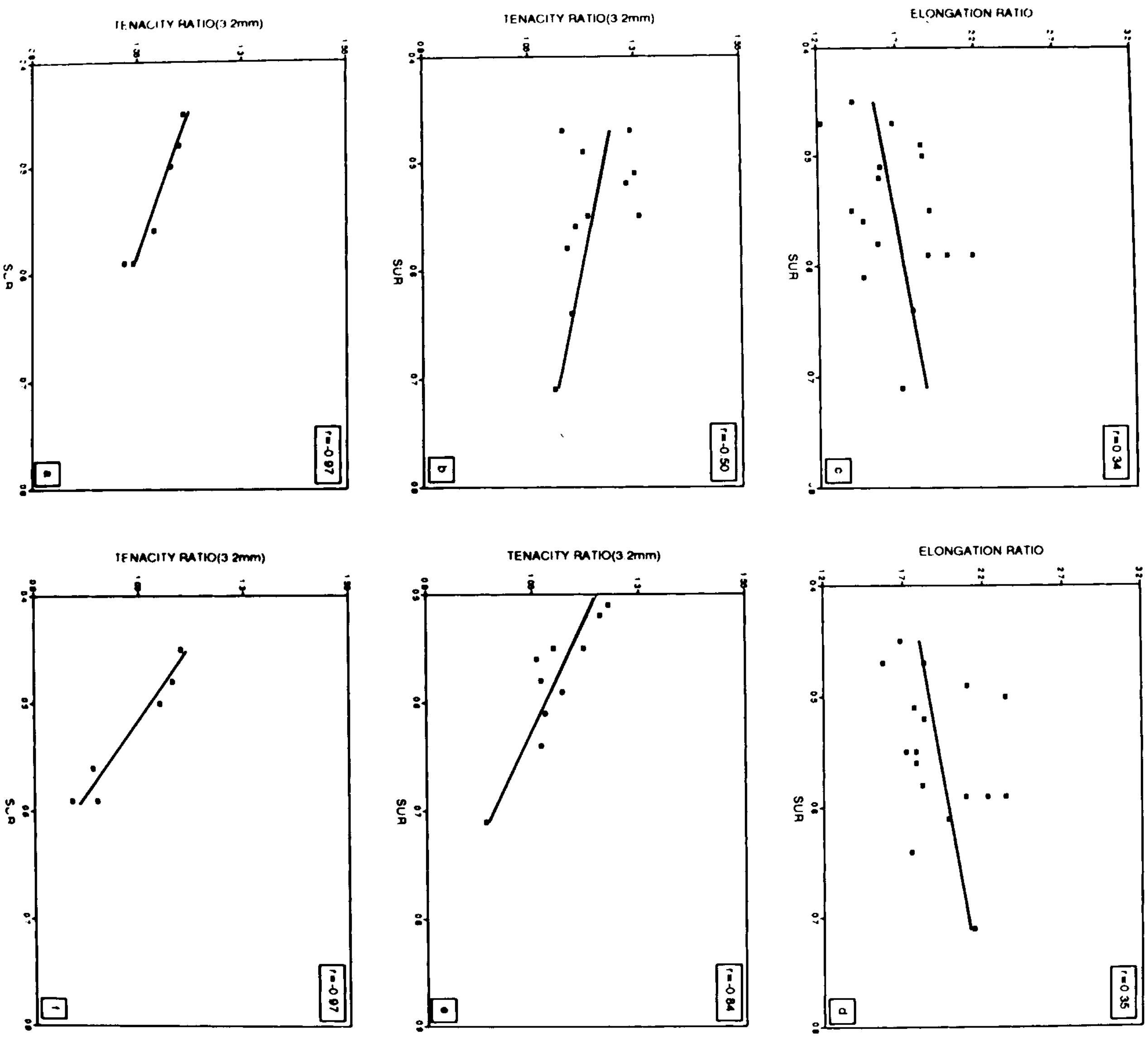

Figure 3 Dependence of (a, b, e, f) tenacity ratio and (c, d) elongation ratio on the initial strength uniformity ratio; after KOH swelling: (a) *G. arboreum* cottom; (b) *G. hirsutum* and *G. barbadense* cottons; after NaOH swelling: (f) *G. arboreum* cottons, (e) *G. hirsutum* and *G. barbadense* cottons.

Strength Uniformity Ratio (SUR)

SUR is a parameter that can indicate the extent of weak links and non-uniformity present in cotton fibers. In general, it can be expected that swelling should remove weak links and thereby increase the tenacity at higher gauge lengths. However, there appears to be a clear dependence of this increase on the initial uniformity of the cottons [see Fig. 3(a), (b), (e), (f)]. Further, a specieswise dependence of SUR on $T_{3.2}$ also becomes evident, and this effect is noted after swelling in both KOH and NaOH. From Figure 3(a) and (b), it is clear that with increase in uniformity the tenacity ratios decrease for all varieties irrespective of the species after KOH swelling. However, the improvement in $T_{3.2}$ on swelling is much higher for *G. hirsutum* and *G. barbadense* than for *G. arboreum*. In the case of *G. arboreum* cottons, it is rather difficult to find cottons of SUR of 0.6 or more. A variety having a SUR of 0.6 itself appears quite uniform, as swelling of these fibers did not produce any substantial increase in $T_{3.2}$ and the ratio remains close to unity. On the contrary, cottons of SUR of around 0.6 improve in strength substantially

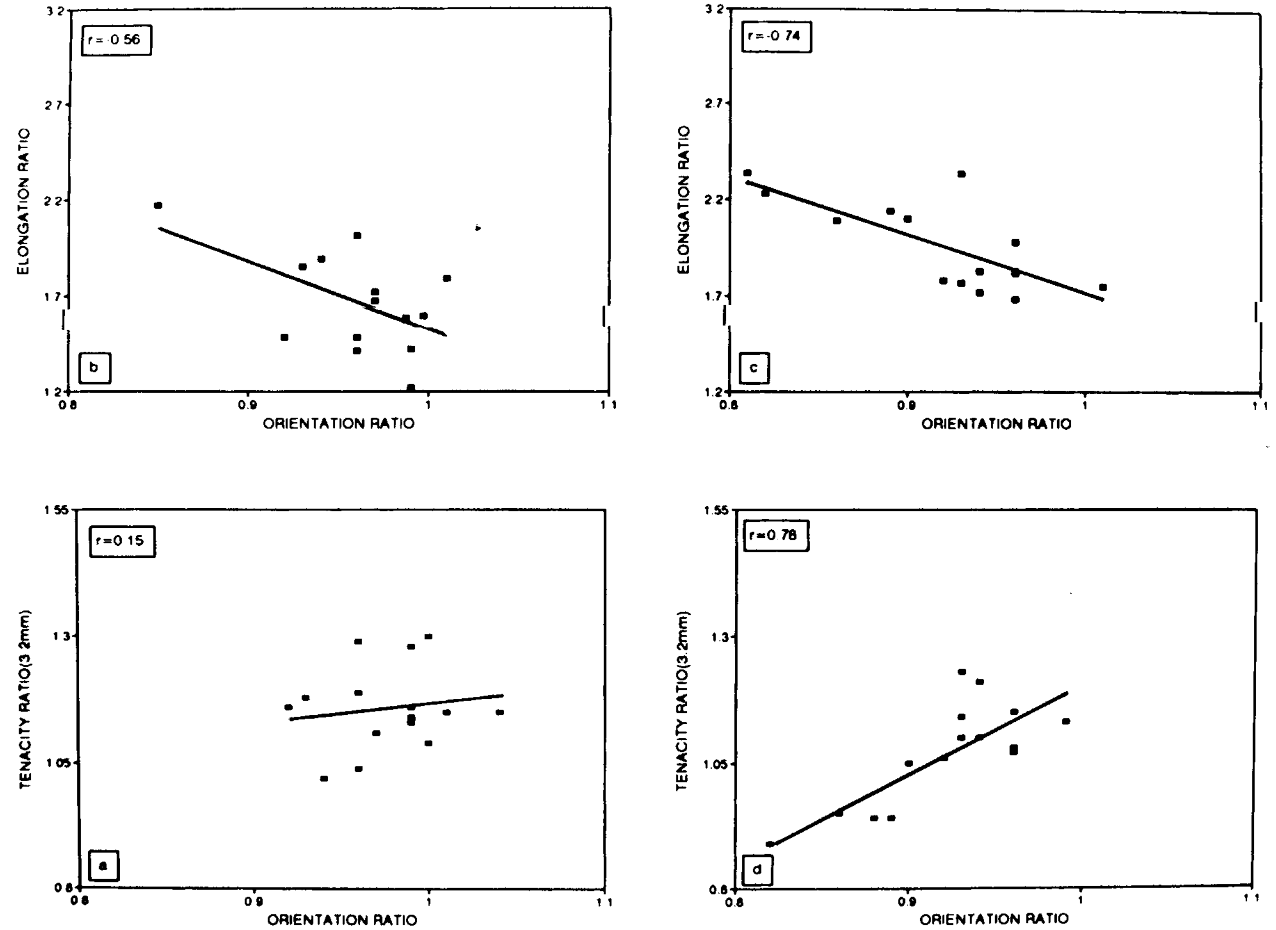

Figure 4 Dependence of (a, d) tenacity ratio and (b, c) elongation ratio on orientation ratio; (a, b) after KOH swelling; (c, d) after NaOH swelling.

in the case of *G. hirsutm* and *G. barbadense*. Even a variety having a SUR of about 0.7 showed an improvement of 10% in $T_{3.2}$ after swelling in KOH. However, after swelling in NaOH, $T_{3.2}$ decreased substantially in the case of *G. arboreum* cottons of a SUR 0.5 and above and the tenacity ratios fell much below unity [Fig. 3(f)]. The fall in $T_{3.2}$ is much faster in NaOH even for *G. hirsutum* and *G. barbadense* cottons [Fig. 3(e)], and for the variety having a SUR = 0.7, the tenacity ratio is less than unity (0.94). In other words, irrespective of the species, more uniform cottons show drop in $T_{3.2}$ after swelling in NaOH, while this does not happen during swelling in KOH. The change in fine structure brought about by excessive swelling is mainly responsible for this behavior, as will become evident from discussions on orientation in a later section. The elongation ratios after swelling improved substantially for both the reagents and the improvement is higher for more uniform cottons as seen from Figure 3(c) and (d).

Influence of Changes in Fine Structure on Tensile Behavior of Swollen Fibers

So far, we have discussed the change in tensile properties of swollen fibers based on the different initial fiber properties. All the fiber properties like maturity, fineness, and strength uniformity influenced the extent of swelling and thereby modified the tensile properties of the swollen fibers as evident from the relationships depicted in Figures 1–3. It is well known that swelling alters the fine structure considerably and it is important to ascertain how these fine structural changes influence the properties of the swollen fibers. The important fine structural parameters that become altered and which are known to influence the tensile properties of the swollen fibers are orientation and amorphous content. A brief discussion of the influence of these parameters on tensile properties are given below.

Orientation

Figure 4 contains the plots of tenacity ratios against orientation ratios for swollen fibers obtained by both the reagents. It is interesting to note that swelling in KOH produces minimal disorientation. As a result, a very poor correlation is noted between tenacity ratio and orientation ratio [Fig. 4(a)]. Low disorientation observed after swelling in KOH further substantiates the lower swelling produced by this reagent. On the other hand, swelling in NaOH produces substantial disorientation and thereby reduces $T_{3.2}$ values [Fig. 4(d)] as seen from the highly significant r value of +.78.

As already mentioned, in the present study, since all the fibers were kier-boiled prior to swelling, the restrictive influence of primary wall, if any, to swelling is absent. This leads to swelling of layers outward, particularly in mature cottons where inward swelling is highly restricted due to a lack of space. Although immature cottons could swell inward, the free secondary wall would enable these cottons also to swell outward to some extent. The substantial swelling in NaOH tends to produce misalignment in the fibrillar arrangement and creates nonuniformities in their original structure, especially for fibers having high initial orientation, maturity, and strength uniformity. On the other hand, optimal swelling in KOH even for these fibers enables them to retain higher orientation and thereby the tenacity.

A close look at the azimuthal distribution curve of (200) peak for swollen fibers given in Figure 5 (for a highly mature and oriented variety) reveals certain interesting information. The azimuthal distribution curve for fibers swollen NaOH has intensity changes at all azimuths which are substantial particularly at higher angles as compared to untreated and KOH swollen fibers. The intensity corresponding to higher azimuth has contributions from scattering by crystallites which are more inclined to the fiber axis. As the outer layers have fibrils having a higher inclination to the fiber axis, and since the intensity corresponding to higher azimuths shows an increase, the distribution curve can be taken to be suggestive of the outward swelling in NaOH, particularly for highly mature cottons. As a result, the Hermans' orientation factor computed for NaOH swollen fibers considerably decreases. As noted in an earlier publication,[3] f_x is a more realistic measure of orientation in swollen fibers as compared to $1/\phi_{1/2}$ ($\phi_{1/2}$ being 50% X-ray angle) which generally gives a good account of orientation in normal fibers.

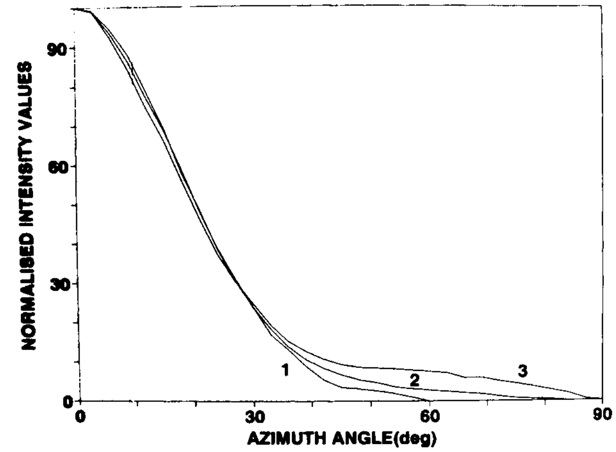

Figure 5 Azimuthal intensity distribution curves of (200) arc for (1) control, (2) KOH, and (3) NaOH swollen fibers.

The disorientation brought about by swelling in NaOH results in considerable improvement in elongation as seen from Figure 4(c). The breaking elongation of the swollen fibers bears a highly significant inverse relationship with the orientation as seen from the r values of −.74 and −.56 for NaOH and KOH, respectively. Preservation of higher orientation after swelling in KOH is reflected in the marginally reduced elongation ratios for these fibers [Fig. 4(b)].

Amorphous Content

Swelling produces a substantial increase in the amorphous fraction in cotton fibers. The increased amorphous fraction results due to combination of factors such as conversion of crystalline to noncrystalline cellulose as well as reduction in the crystallite dimensions. The latter phenomenon leads to an increase in amorphous content due to an increased surface area of the crystallites, as surface of crystallites are also viewed as amorphous by X-rays. The effect of this overall increased amorphous content on fiber properties is depicted in Figure 6. It is seen that, irrespective of the species, cottons which had a lower amorphous fraction showed less change in the amorphous fraction upon swelling. The increase in amorphous content, after swelling in KOH, is substantially higher and values of the amorphous ratio vary from 1.3 to 1.9. It has already been noted[1] that, due to its higher cationic size, KOH produces more uniform swelling, resulting in a substantial in-

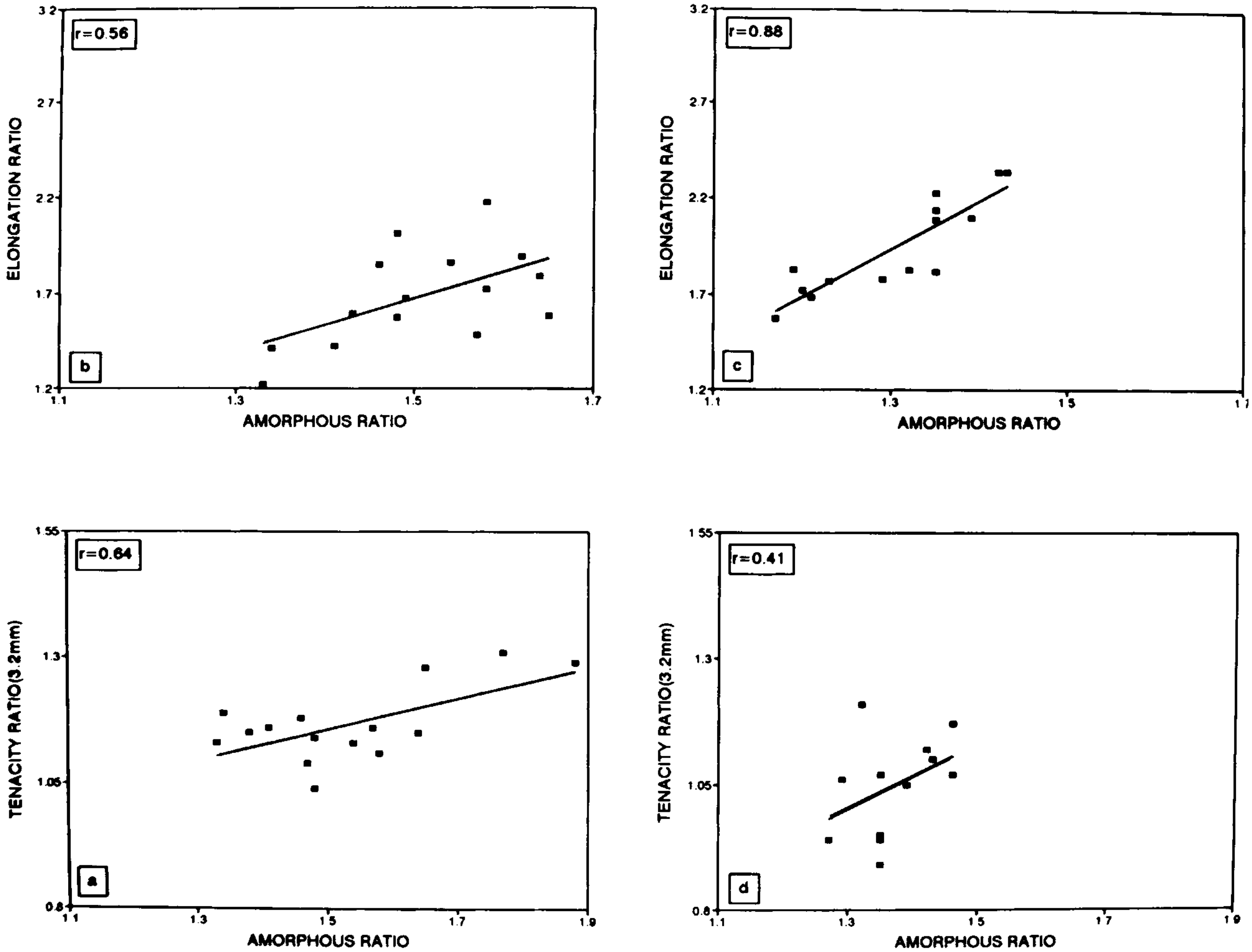

Figure 6 Plot of (a, d) tenacity ratio and (b, c) elongation ratio against amorphous ratio; (a, b) after KOH swelling; (c, d) after NaOH swelling.

crease in the amorphous fraction. Swelling in KOH also brings about a marked reduction in crystallite dimensions, particularly in crystallite length, as seen from the half-breadth at half-maximum of (004) presented in Table II. It is interesting to note from the table that, irrespective of the species, swelling in KOH produced a higher reduction in crystallite dimensions (indicated as increased half-breadths) for cottons with lower SUR values. These reduced crystallite dimensions offer better flexibility to the load-bearing elements, and, hence, at a given strain, higher load bearing is possible for fibers swollen in KOH than in NaOH. This is a key factor that helps in the retention and increase in tenacity after swelling in KOH even for fibers where some disorientation has occurred.

On the contrary, swelling in NaOH produces a much lower enhancement in amorphous content [Fig. 5(d)]. The crystallite size reduction is also not as pronounced as in KOH. Hence, it appears that orientation plays an upper hand in deciding the tenacity of NaOH swollen fibers unlike in fibers swollen in KOH where increased amorphous content and reduced crystallite dimensions are responsible for the superior tensile behavior. A clear dependence of the elongation ratio and amorphous ratio is noticeable for both KOH and NaOH swollen fibers as seen from the significant *r* values of .56 and .66, respectively.

CONCLUSIONS

(i) Irrespective of the species and initial fiber properties, all cottons retain higher tenacities and also reasonably high elongation after swelling in KOH, although swelling in NaOH

Table II Crystalline Dimensions After Swelling

		Half-maximum Breadths of Peaks in Degrees	
Cotton	Treatment	(200)	(004)
G. arboreum			
1. Abuharia	Nil	1.40	0.300
(SUR = 0.48)	NaOH	2.25	0.375
	KOH	2.40	0.375
2. AC-11	Nil	1.43	0.325
(SUR = 0.59)	NaOH	2.20	0.340
	KOH	2.20	0.360
G. barbadense			
1. GB-2	Nil	1.38	0.290
(SUR = 0.52)	NaOH	2.10	0.340
	KOH	2.40	0.400
2. GB-0	Nil	1.40	0.300
(SUR = 0.58)	NaOH	2.18	0.350
	KOH	2.20	0.390
3. Suvin	Nil	1.40	0.290
(SUR = 0.71)	NaOH	2.20	0.350
	KOH	2.30	0.380

increases the breaking elongation to a greater extent.

(ii) Highly mature and more uniform cottons deteriorate in tenacity after swelling in NaOH. This deterioration is a direct consequence of the higher disorientation.

(iii) Swelling in KOH enables even the highly mature and more uniform cottons to retain higher tenacities due to the formation of higher amorphous material and flexible smaller crystallites after swelling in this reagent.

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