

Studies on Swelling of Cotton Fibers in Alkali Metal Hydroxides. I. Influence of Variations in Fine Structure on Tensile Behavior

S. SREENIVASAN, P. BHAMA IYER, G. S. PATEL, and
P. K. CHIDAMBARESWARAN, *Cotton Technological Research
Laboratory, Indian Council of Agricultural Research (ICAR),
Matunga, Bombay—400019, India.*

Synopsis

A study on cotton fibers swollen slack at ambient temperature in different concentrations of LiOH and KOH indicates that fibers swollen in KOH have higher disorder. Conversion to cellulose II results from swelling in both the reagents, although, with KOH swelling, it begins at a lower concentration. Further, retention of tenacity is higher at all gauge lengths after KOH swelling. Analysis of the influence of fine structure on tensile properties showed some specificity, mainly attributable to cationic size differences of the swelling agents.

INTRODUCTION

The technological importance of the mercerization process using caustic soda solutions has attracted the attention of many research workers and the excellent review by Warwicker and others¹ on the effect of this treatment on the fine structure of cotton bears testimony to the various research efforts in this field. It is generally accepted that swelling of cotton fibers in sodium hydroxide (NaOH) solutions of optimum concentration and temperature leads to an increased crystalline and molecular disorder, which results in an increase in chemical accessibility and a decrease in zero gauge tenacity. This process simultaneously releases internal strains existing in native fibers leading to an increase in the tenacity at higher gauge lengths.

In a series of communications, Vigo et al.,^{2,3} Zeronian and co-workers,⁴⁻⁶ and Pandey and Iyengar^{7,8} compared the performance of cotton treated with various alkali metal hydroxides. It was noted^{2-4,6} that the fine structure resulting from swelling is influenced by the size of the cations. It was also observed that fibers swollen in potassium hydroxide (KOH) had a higher breaking load at zero gauge length. However, Pandey and Iyengar⁷ did not find any appreciable difference in tensile behavior between the swelling agents. Studies conducted in this laboratory earlier,⁹ on the structure-property relations of fibers swollen in NaOH solutions of various concentrations, revealed that lattice type as well as decrystallization are important in deciding the tensile properties of the treated samples. However, such detailed investigations on fibers swollen with the other two alkali metal hydroxides, viz., lithium hydroxide (LiOH) and KOH, are not available. Hence the present investigation is undertaken with a view to study the concentration dependence of fine structural parameters and their influence on tensile properties of

fibers treated with LiOH and KOH and to evaluate the effect of cationic size if any on the structure-property relationship.

EXPERIMENTAL

Cotton fibers belonging to PSH variety were kier-boiled using 1% alkali solution prior to swelling treatments. The purified fibers were treated in various concentrations of LiOH and KOH at $30 \pm 1^\circ\text{C}$ for 10 min. At the end of the treatment, the fibers were washed in running tap water, scoured in 2% (v/v) acetic acid, and further washed and dried in air at room temperature. The normality of the alkali solutions before treatment was adjusted using standard procedure. The treated and dried fibers were conditioned at 65% RH at 27°C prior to measurements.

The tenacity at nominal zero gauge length (T_0) and 3.2 mm gauge length (T_3) was determined using Pressley fiber clamps on the Instron tensile tester. The extent of swelling was evaluated by measurement of increase in tex values of the fibers by a standard gravimetric method.¹⁰ Moisture regain (%) of both untreated and treated fibers was determined at 65% RH and 27°C using normal procedure.¹⁰

The radial X-ray diffractograms using powder samples and azimuthal intensity scans from fibers were obtained with a Philips stabilized X-ray generator, using CuK_α radiation, fitted with diffractometer and texture arrangements. The crystalline contents, viz., cellulose I (C I), cellulose II (C II), as well as amorphous values (Am) were evaluated from radial diffractograms using the method of Chidambareswaran et al.¹¹ The resolution of the cellulose I lattice was calculated by the method used earlier for cotton-jute fibers¹² based on the resolution of $(\bar{1}10)$ and (110) peaks of C I. The half maximum width of the (200) peak was measured essentially from the higher 2θ side of the peak as done earlier¹³ for C I lattice, the same way being carried out here even for the combined C I and C II lattices, by measuring the width of the combined (200) peak. [The notations for the designations of the peak have been done following the conventions for the first setting for monoclinic unit cell, setting *C*-axis unique, monoclinic angle $\gamma > 90^\circ$.] The crystallite orientation was quantitatively evaluated from the azimuthal intensity distribution of the (200) peak by the index $1/\phi_{1/2}$ of Warwicker,¹⁴ $\phi_{1/2}$ being the 50% X-ray angle.

RESULTS AND DISCUSSION

The mechanical, physical, and structural data obtained for the samples treated with LiOH and KOH are summarized in Table I. It may be observed from the table that fiber weight per unit length (expressed as mtex), which may be used as an index of swelling goes on increasing with increase in concentration. This confirms the swelling data obtained earlier⁴ by isopropanol technique. It is obvious from the table that moisture regain values very closely follow Am values and almost reach saturation beyond 4N for the KOH-treated samples. This is to be expected as the moisture is adsorbed by the amorphous regions in the fibers. However, with LiOH, swelling does not saturate at 4N, but continues to increase with increasing concentration, as is also the case with all the structural parameters including moisture regain.

TABLE I
Mechanical, Physical, and Structural Data of PSH Cotton Treated with LiOH and KOH Solutions at Ambient Temperature

Treatment	Tensile data				X-ray data			Fiber weight (mtex)	Moisture regain (%)
	T_0 (g/tex)	T_3 (g/tex)	SUR	E (%)	C II (%)	Am (%)	$1/\phi_{1/2}$ (deg ⁻¹)		
1. None	48.8	26.2	0.54	5.0	0	28	0.038	130	6.95
2. Treated slack (N LiOH)									
(a) 3.0	46.7	26.9	0.58	5.0	0	25	0.041	130	7.58
(b) 3.5	49.2	28.3	0.58	5.8	15	27	0.044	133	8.50
(c) 4.0	46.3	29.1	0.63	7.2	34	32	0.044	136	9.16
(d) 4.5	46.5	30.8	0.66	9.4	42	37	0.041	147	9.86
(e) 5.0	42.9	32.0	0.75	10.9	45	36	0.043	154	10.43
3. Treated slack (N KOH)									
(a) 2.0	49.3	26.3	0.53	5.0	0	29	0.038	130	7.22
(b) 3.0	46.5	29.2	0.63	6.1	26	32	0.042	133	8.33
(c) 4.0	48.4	32.1	0.66	7.8	39	40	0.042	138	9.62
(d) 4.5	50.7	31.6	0.62	8.4	38	41	0.042	143	9.95
(e) 5.0	48.2	30.5	0.63	9.4	38	38	—	148	10.05
(f) 6.5	46.9	31.7	0.68	10.5	43	40	0.043	157	10.52
(g) 8.0	47.1	31.2	0.66	11.1	45	40	0.042	—	10.57

Again, the strength uniformity ratio (SUR) for samples swollen beyond 4N in LiOH are higher than those corresponding samples produced from KOH swelling. An increase in SUR is normally associated with increase in T_3 and decrease in T_0 . Increase in T_3 , usually attributed to removal of weak zones, obtained in both LiOH and KOH was nearly equal beyond 4N. However, T_0 decreases only marginally after KOH swelling, leading to reduced SUR values. Hence, while comparing the performance of fibers swollen in different reagents, increased retention of tenacity at all gauge lengths will be a better index of performance than increased SUR, although, while comparing the response of cottons to the same reagent, higher SUR might be useful.^{15,16}

The variation in tensile properties, viz., T_0 , T_3 , and elongation at break E (%), as a function of concentration (normality) of the swelling agent is depicted in Figures 1(A) and (B). It is clear from the Figure 1(A) that T_0 decreases substantially by LiOH treatment, while the reduction is very marginal in KOH treated fibers [Fig. 1(B)]. A similar observation was made earlier by Zeronian et al.⁶ T_3 increases with increase in concentration, the maximum being almost the same for both swelling treatments. Note that T_3 reaches saturation at about 4N KOH, beyond which there is very little change. Elongation improves with increase in swelling concentration, but the relation seems to be nonlinear.

In Figures 2 and 3 are shown the normalized X-ray diffraction patterns (XRD) from fibers swollen in various concentrations of LiOH and KOH respectively, while Figures 4(A) and (B) depict the variation in fine structural parameters as a function of concentration of the swelling agent. From the above figures it is evident that, in LiOH, conversion to C II begins even at a lower concentration of about 3.5N at room temperature. However, Vigo

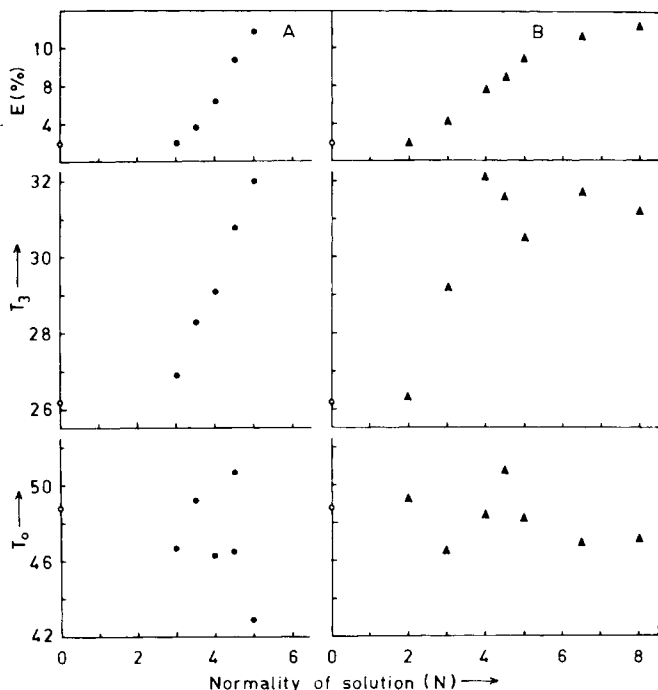


Fig. 1. Variation in tensile properties, viz., tenacity at nominal zero gauge (T_0), tenacity at 3.2 mm gauge (T_3), and breaking elongation ($E\%$) with concentration of the swelling agent: (A) LiOH; (B) KOH.

et al.,³ from lattice conversion measurements, pointed out that no conversion to C II occurred when kier-boiled yarns were swollen in 9.5% w/w ($\approx 4.4N$) LiOH. Studies by Zeronian and co-workers⁴ covering a wider range of concentration revealed that reflections corresponding to C II could be identified only from hydrolysates of 5.05N LiOH-treated fibers. It appears that techniques of recording and measurement adopted by these workers might have caused hindrance in identifying lesser amounts of C II, produced by swelling at room temperature at lower concentrations (of $\approx 3.5N$ and above but $< 5.0N$). However, conversion to C II has been observed at 3.5N LiOH at 0°C by earlier workers.⁵ Our XRD diagrams (Figs. 2 and 3) clearly show that, although C II starts appearing at an earlier concentration in KOH swelling, beyond 4N, the conversion to C II is not appreciably different in fibers treated in both reagents. Another interesting point that may be noted is that Am values are always higher after KOH swelling, even though the extent of swelling as measured by tex (Table I) is only marginally different, at any given normality. Thus we find that swelling and decrystallization always do not go hand in hand. Such an observation has been made by earlier workers^{5,17} as well. The above observations suggest some basic differences in the nature of swelling produced by both the reagents in creating disorder and conversion to C II. The extent of penetration of the swelling agent into crystalline regions, subsequent decrystallization and conversion to C II on washing out the alkali seem to be decided by the cationic size and degree of hydration of the swelling agent.

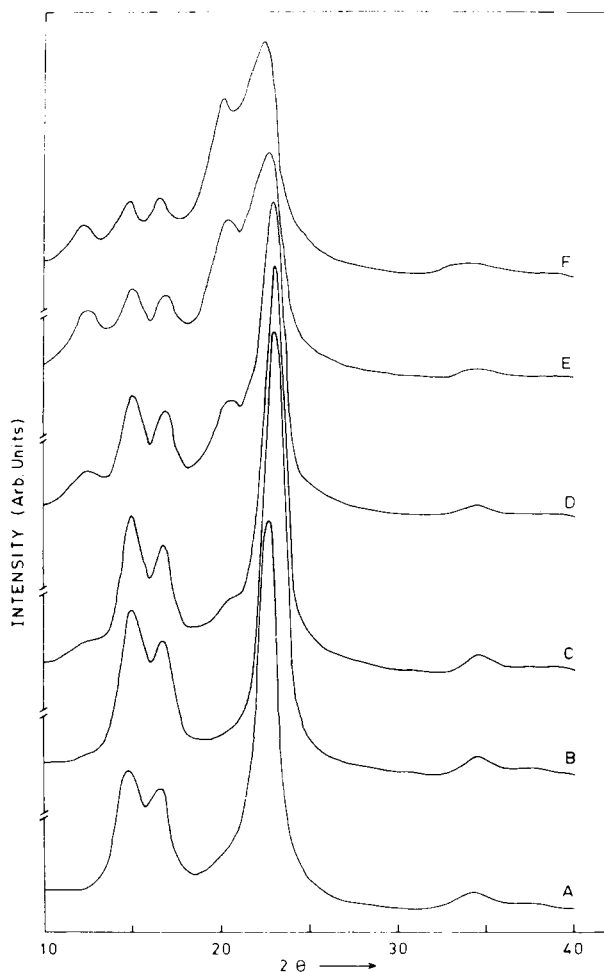


Fig. 2. Normalized X-ray diffraction (XRD) patterns of fibers swollen in LiOH solutions of various concentrations: (A) control; (B) 3.0*N*; (C) 3.5*N*; (D) 4.0*N*; (E) 4.5*N*; (F) 5.0*N*.

Warwicker and Wright proposed¹⁸ the occurrence of sheets of cellulosic chains to explain the various alkali and water celluloses obtained during swelling of cotton in NaOH and after subsequent washing in water of the soda celluloses. LiOH and KOH being alkali metal hydroxides similar to NaOH, the same swelling mechanisms should be valid in these cases as well. In cotton fibers, there exists a distribution of structural order, and this could be broadly classified into regions of high disorder (low order), intermediate order, and high order.¹⁹

At any concentration lithium ion (Li^+) will have the maximum degree of hydration. This ion with its surrounding hydration sphere can break some of the intersheet bonds and can penetrate only the very low-ordered-regions under concentrations below 4*N*. However, even at these concentrations, sufficient recrystallization into C II has been observed, as seen from Figure 2 and Table I. The formation of C II at this stage, mainly arising from swelling and recrystallization of amorphous and small- and less-ordered crystalline regions,

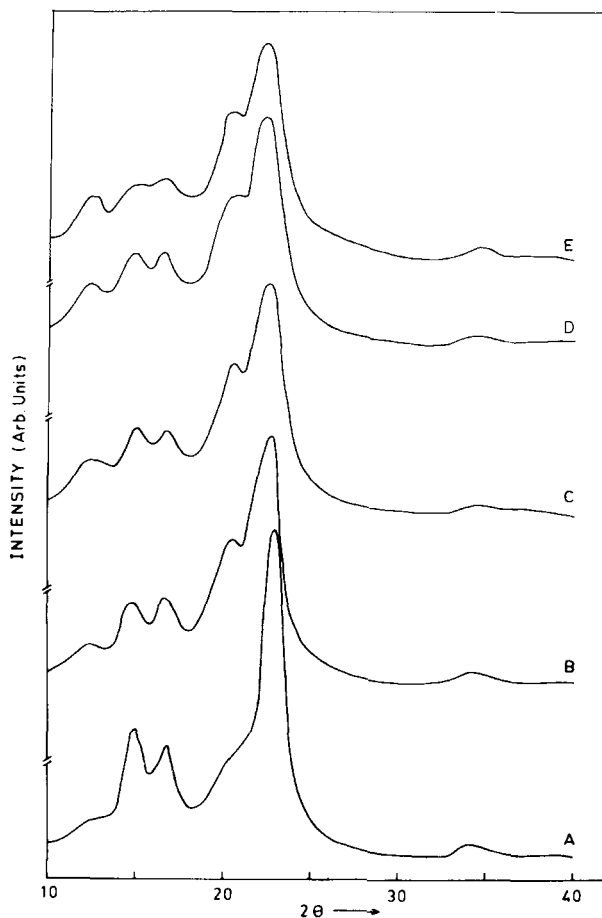


Fig. 3. Normalized XRD patterns of fibers swollen in KOH solutions of various concentrations: (A) 3.0*N*; (B) 3.5*N*; (C) 4.0*N*; (D) 4.5*N*; (E) 5.0*N*.

might have been facilitated by the existence of cellulosic chains with different polarity (parallel as well as antiparallel) in the original material as suggested by Nishimura and Sarko^{20,21} in their studies on NaOH swelling of ramie fibers. However, as the concentration is increased further and reaches near saturation ($\approx 5N$), the bulk of the hydration sphere decreases so that these ions can penetrate even the well-ordered regions and most of the interchain linkages could be broken and the Li^+ ions form complexes with glucosidic residues. Thus the amount of C II formed would be limited to the noncrystalline and lesser-ordered crystalline regions at concentrations below 4*N*, though this amount would increase with increasing concentration owing to penetration into the high-ordered regions. However, even after swelling in 5*N*, considerable C I remains, and it is interesting to note that the residual C I has a very high order. This is evident from Table II, where the resolution of the resulting C I lattice after swelling in various concentrations of both the reagents have been summarized.

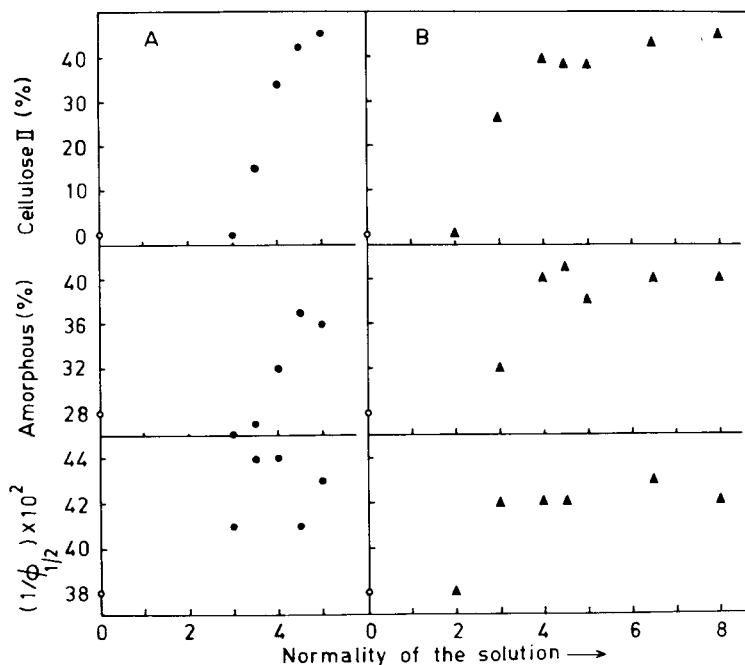


Fig. 4. Variation in fine structural parameters, viz., crystallite orientation ($1/\phi_{1/2}$), amorphous (%) and cellulose II (%) with normality of the solution: (A) LiOH; (B) KOH.

The very high values of resolution parameter (RP) (Table II) might suggest the possibility of LiOH unable to penetrate highly ordered regions. However, it appears more likely that the lithium cellulose formed does not have sufficient energy to overcome the barrier for rotation about the glucosidic linkage, and, since chains involved in this process may now become favorably aligned, on removal of alkali, they revert to C I, with better intermolecular hydrogen bonding, thus retaining higher order. In other words, interchain linkages broken during swelling in some regions (very-high-ordered regions) do not contribute to C II formation, but reform in a better way to result in a

TABLE II

Amount and Resolution of Residual Cellulose I Lattice and Half-Width of (200) after Swelling in Various Concentrations of LiOH and KOH at Ambient Temperature.

Concentration	LiOH			KOH		
	C I (%)	RP of C I	$\beta_{1/2}$ (deg) (200)	C I (%)	RP of C I	$\beta_{1/2}$ (deg) (200)
None	72	2.80	1.40	72	2.80	1.40
3.0N	75	2.94	1.25	42	3.80	1.40
3.5N	58	3.68	1.20	26	3.35	1.50
4.0N	34	4.63	1.30	21	3.34	2.00
4.5N	21	6.42	1.50	24	3.50	2.00
5.0N	19	6.08	1.70	24	2.40	2.10

highly ordered native cellulose fraction. In this connection, it may be recalled²² that even wetting and drying treatments can cause an increase in the perfection of H bonding in crystalline regions.

During swelling in KOH, the basic mechanism should be similar to what is described above. However, because of the larger cationic size and lower hydration sphere, potassium ion (K^+) can break not only the intersheet linkage but also intrasheet bondings in some of the highly ordered regions as well even at concentrations below 4*N*. When potassium cellulose is formed by interaction between K^+ and cellulose, the disruption within the structural elements would be higher than that due to lithium basically due to the larger cationic size of potassium. At regions where K-cellulose has sufficient energy to produce configurational changes favorable for C II formation, the new lattice results during alkali removal. However, at regions where rotation of alternate chains has not taken place, the chains would reform into C I or amorphous depending on the proximity and disposition of the adjacent chains to form interchain hydrogen bonds. In this approach, the higher Am values are a direct consequence of greater disturbance to the structural elements. This could also explain why the residual C I lattice formed after KOH swelling, although of nearly the same amount (Table II) as that after LiOH treatment, has a poor crystallite size, as indicated by the poorer resolution of

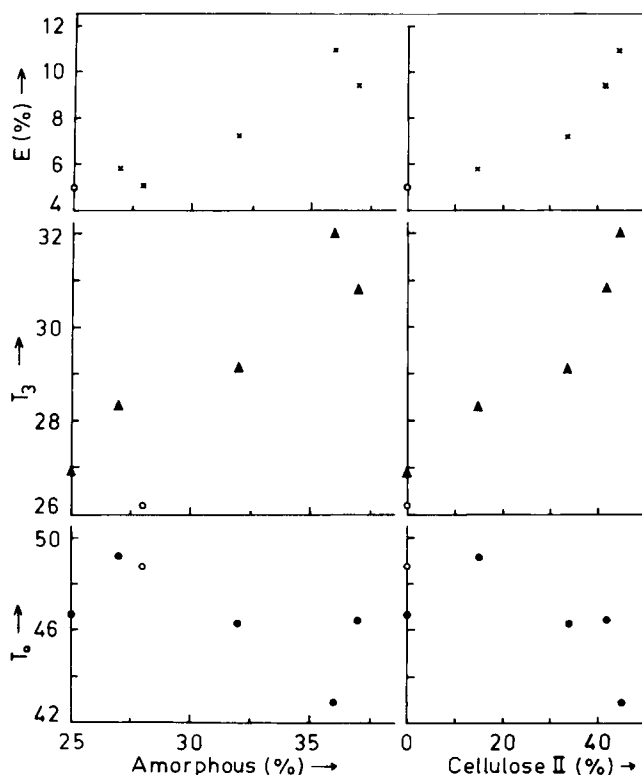


Fig. 5. Influence of amorphous (%) and cellulose II (%) on tensile properties, viz., tenacity at nominal zero gauge (T_0), tenacity at 3.2 mm gauge (T_3), and breaking elongation ($E\%$) for fibers swollen in LiOH.

the $(\bar{1}10)$ and (110) peaks of C I (Fig. 3). Another interesting consequence of KOH swelling is the poorer crystallite size even for the newly formed lattice as made evident from $\beta_{1/2}$ values of the combined (200) peak (Table II). A reduction in the crystallite dimensions which includes reduction in crystallite length as well⁶ can make the crystallites flexible enough to withstand higher loads, thus leading to increased retention of tenacity especially at zero gauge length, in spite of higher decrystallization with only marginal change in crystallite orientation $1/\phi_{1/2}$. The small improvement observed in $1/\phi_{1/2}$ after slack swelling in both the reagents could be attributed mainly to removal of convolutions.

From the foregoing discussion it is evident that as a result of swelling of native cellulose in aqueous alkali metal hydroxides of appropriate concentration, decrystallization of C I lattice takes place, leading to increased disorder and part of the disordered material recrystallizes into C II during subsequent washing and drying. We have already noted that C II and Am (%) change with concentration as also the tensile behavior of the swollen fibers. Hence it is reasonable to expect that the tensile properties of the treated fibers should be related to the extent of newly formed lattice as also to the disordered fraction. In Figures 5 and 6, an attempt is made to analyze graphically how

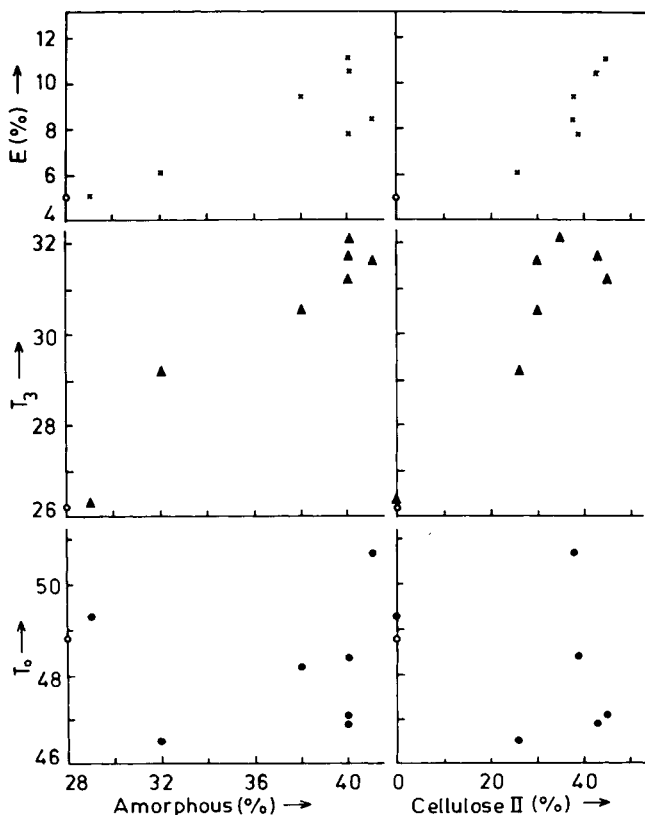


Fig. 6. Influence of amorphous (%) and cellulose II (%) on tensile properties viz.: tenacity at nominal zero gauge (T_0), tenacity at 3.2 mm gauge (T_3), and breaking elongation ($E\%$) for fibers swollen in KOH.

these structural parameters affect the tenacity. These figures, represent the changes in T_0 , T_3 , and E (%) as a function of Am (%) and C II for the LiOH- and KOH-treated fibers, respectively. Orientational changes are not included as only very little variation was shown for the differently treated fibers and, in the case of slack swelling, orientation influences the tensile properties least.⁹ T_0 seems to have less bearing on the structural variations as may be noted from the scatter of points connecting T_0 with Am or C II. This observation is almost equally true for fibers treated in both the reagents. Although there is less scatter between T_3 and Am, the relationship seems to improve further when T_3 is plotted against C II, especially for LiOH-treated fibers, and the relationship appears nonlinear, for this reagent. Between E (%) and Am and E (%) and C II, the scatter seems to be slightly higher for the former, especially after KOH treatment. However, the trend is the same for both the reagents and the points seem to lie on a curve rather than a straight line, probably due to the subtle influence of some other factors than those already considered here.

From the above results, it can be stated that fibers swollen in KOH have higher disorder and that the conversion to C II begins at a lower concentration. It is also observed that the retention of tenacity at all gauge lengths is better after swelling in KOH. In spite of these differences, the tensile behavior of fibers swollen in the two reagents, viz., LiOH and KOH, can be seen to be almost governed fully by the variations in the same fine structural parameters. However, notwithstanding the fact that the mechanism of swelling cotton fibers in aqueous solutions of alkali, viz. formation of alkali-cellulose and transformation of the same to C II during washing are similar, the present study shows that the structure-property relations are not all that identical and seems to have some specificity to the swelling agent, mainly attributable to their cationic size differences.

The authors express their gratitude to Dr. N. B. Patil, Head Physics Division, CTRL, for helpful discussions and suggestions. They are also thankful to Dr. V. Sundaram, Director, CTRL, for encouragement and permission to publish this paper.

References

1. J. O. Warwicker, in *A Review of the Literature on the Effect of Caustic Soda and Other Swelling Agents on the Fine Structure of Cotton*, Shirley Institute Pamphlet No. 93, Manchester, U.K., 1966.
2. R. H. Wade and T. L. Vigo, *Text. Res. J.*, **39**, 148 (1969).
3. T. L. Vigo, R. H. Wade, D. Mitcham, and C. M. Welch, *Text. Res. J.*, **39**, 305 (1969).
4. S. H. Zeronian and K. E. Cabradilla, *J. Appl. Polym. Sci.*, **16**, 113 (1972).
5. S. H. Zeronian and K. E. Cabradilla, *J. Appl. Polym. Sci.*, **17**, 539 (1973).
6. S. H. Zeronian, K. W. Alger, and K. E. Cabradilla, *J. Appl. Polym. Sci.*, **20**, 1689 (1976).
7. S. N. Pandey and R. L. N. Iyengar, *Text. Res. J.*, **39**, 24 (1969).
8. S. N. Pandey and R. L. N. Iyengar, *Text. Res. J.*, **39**, 993 (1969).
9. P. K. Chidambareswaran, S. Sreenivasan, N. B. Patil, and V. Sundaram, *Text. Res. J.*, **54**, 682 (1984).
10. V. Sundaram, K.R. Krishna Iyer, V. G. Munshi, M. S. Parthasarathy, and A. V. Ukidve in *Handbook of Methods of Tests for Cotton Fibers, Yarns and Fabrics*, Cotton Technological Research Laboratory, Bombay, India, 1979.
11. P. K. Chidambareswaran, S. Sreenivasan, and N. B. Patil, *Text. Res. J.*, **57**, 219 (1987).
12. P. K. Chidambareswaran, S. Sreenivasan, N. B. Patil, V. Sundaram, and B. Srinathan, *J. Appl. Polym. Sci.*, **20**, 3443 (1976).

13. P. K. Chidambareswaran, S. Sreenivasan, N. B. Patil, and V. Sundaram, *J. Appl. Polym. Sci.*, **25**, 1825 (1980).
14. J. O. Warwicker, *J. Polym. Sci., A-2*, **4**, 571 (1966).
15. R. Lawson and K. L. Hertel, *Text. Res. J.*, **44**, 975 (1974).
16. R. S. Orr, A. W. Burgis, J. Creely, and T. Mares, *Text. Res. J.*, **29**, 355 (1959).
17. B. E. Dimick and R. H. Atalla, in *Mercerization of Cellulose, a Re-examination of the Mechanism*, abstracts of papers, 169th National Meeting ACS, Philadelphia, 1975.
18. J. O. Warwicker and A. C. Wright, *J. Appl. Polym. Sci.*, **11**, 659 (1967).
19. S. P. Rowland and E. J. Roberts, *J. Polym. Sci., A-1*, **10**, 2447 (1972).
20. H. Nishimura and A. Sarko, *J. Appl. Polym. Sci.*, **33**, 855 (1987).
21. H. Nishimura and A. Sarko, *J. Appl. Polym. Sci.*, **33**, 867 (1987).
22. R. Jeffries, *Polymer*, **4**, 375 (1963).

Received January 28, 1988

Accepted 1988