Layer Morphology and Its Relation to Swelling and Structure: I. Cotton Fibers Treated in Alkali Metal Hydroxides

INTRODUCTION

In previous communications we noted that bilateral structure of cotton influences the conversion of cellulose I(CI) to cellulose II(CII)[1] and that in the same layered section both CI and CII type morphology could be obtained when fibers were swollen with 13% (3.7*N*) NaOH.[2] In the present investigation, the layer morphology of cotton fibers treated with a few selected concentrations of LiOH, NaOH, and KOH is examined and compared. The alkali-treated fibers were analyzed simultaneously by X-ray diffraction method (XRD) for CI and CII contents and other parameters related to structure. The results are summarized below, and the criterion for observing the bilateral structure in the layered cross section of the alkali treated fiber is brought out.

MATERIALS AND METHODS

Cotton fibers were swollen at room temperature (30 ± 1°C) in 3.4*N*, 3.7*N*, 4.0*N*, 4.7*N*, and 6.5*N* NaOH and 4.0*N*, 4.7*N*, 5.5*N*, and 6.9*N* KOH. In addition, fibers were swollen in 4.5*N* LiOH, NaOH, and KOH at 30°C and also in 4.5*N* LiOH at 0°C. After swelling the fibers in the given reagent for 15 min, they were washed free of alkali, soured in 2% acetic acid, washed further, and air-dried.

Layered cross sections of all the treated samples were obtained by the standard procedure.[3] Cross sections were coated with platinum and examined using a Hitachi HU 11E electron microscope at 75 kV.

All the treated fibers were cut in a Wiley mill to pass a 40-mesh screen, and their diffractograms were obtained by using a Philips stabilized X-ray generator employing CuK_a radiation. The X-ray diffractograms were analyzed to obtain the structural parameters by following the methods already reported.[4]

RESULTS AND DISCUSSION

The layered cross sections of the 4.5*N* LiOH and 4.0*N* KOH treated fibers are shown in Figures 1 and 2. Both clearly show the bilateral structure. It may be recalled[1] that 3.7*N* NaOH treated fibers also showed the bilateral structure. Further, Figures 1 and 2 reveal the fibrillar texture (characteristic of CI) at the terminal zone and the honey-comb structure (characteristic of CII) at the middle zone. This is in agreement with our earlier findings[1] where additional evidence was presented for the simultaneous existence of CI and CII in the same cross section.[2]

With higher concentrations of NaOH and KOH, the layers uniformly showed only honey-comb structure characteristic of CII. In the case of LiOH, as it was difficult to go for higher concentration, the temperature was lowered to 0°C to get increased swelling and higher conversion to CII. The layered cross sections revealed mostly a honey-comb structure as may be noted from Figure 3.

XRD data for the samples swollen in different concentrations of NaOH and KOH at room temperature and also that for samples treated with LiOH at room temperature and 0°C are given in Table I. It may be noted that, in the case of fibers swollen at room temperature with 4.5*N* LiOH, 3.7*N* NaOH, and 4.0*N* KOH, substantial amounts of CI are still present. This probably is a necessary condition to observe the bilateral structure after swelling. As we proceed to higher concentrations, the residual CI not only decreases, but the resolution parameter (RP) of the (110) and ($\bar{1}$10) of CI, indicative of perfection of crystallites of the residual lattice, also continues to reduce. Thus the perfection of the crystallites does influence the appearance of the layered section, in addition to the amount of cellulose I present. This is further substantiated by the observations given below.

XRD data of fibers treated with the same normality, viz., 4.5*N* of alkali metal hydroxides at room temperature, is given in Table II. The same normality implies the same number of cations in the solution. Hence, any difference observed either in the structural data or in the layered cross section should basically be due to the differential nature of swelling brought about essentially by the cationic size difference. Note that 4.5*N* NaOH gives maximum

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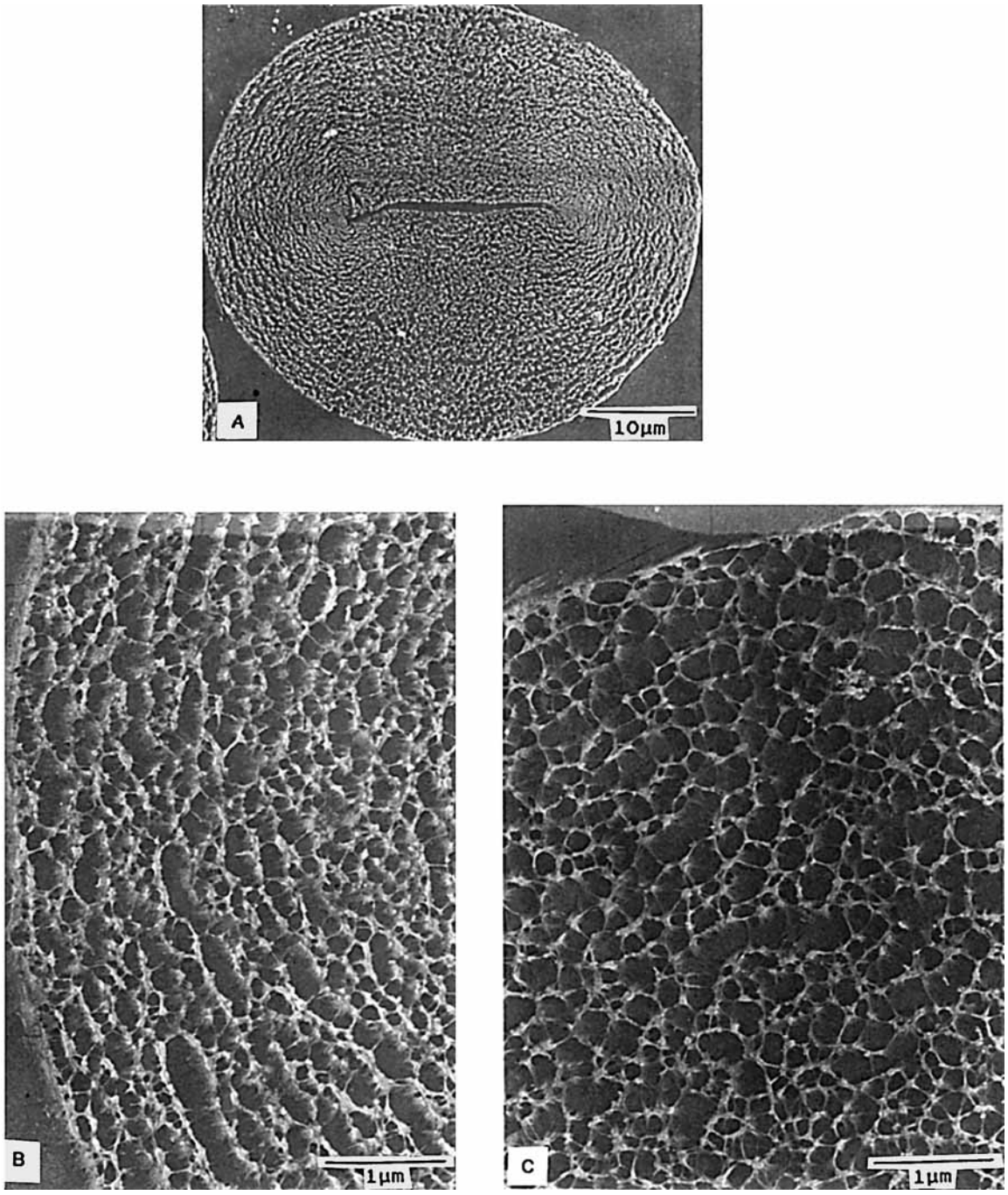

Figure 1 Layered cross section of fibers swollen in 4.5*N* LiOH at room temperature; (a) low magnification, (b) fibrillar texture of terminal zone at high magnification, and (c) honey-comb structure of middle zone at high magnification.

conversion to CII while 4.5*N* LiOH and KOH treated fibers show slightly lower conversion. The layered cross sections of these fibers also show some differences. 4.5*N* NaOH treated fibers show fully honey-combed layers [Fig. 4(a)] with no bilateral structure. Though 4.5*N* KOH treated fibers do not show any bilateral structure, the peripheral layers showed some fibrillar texture characteristic of CI [Fig. 4(b)]. On the other hand the layered section of 4.5*N* LiOH treated fibers shows a bilateral structure with the layers in the terminal zone revealing fibrillar tex-

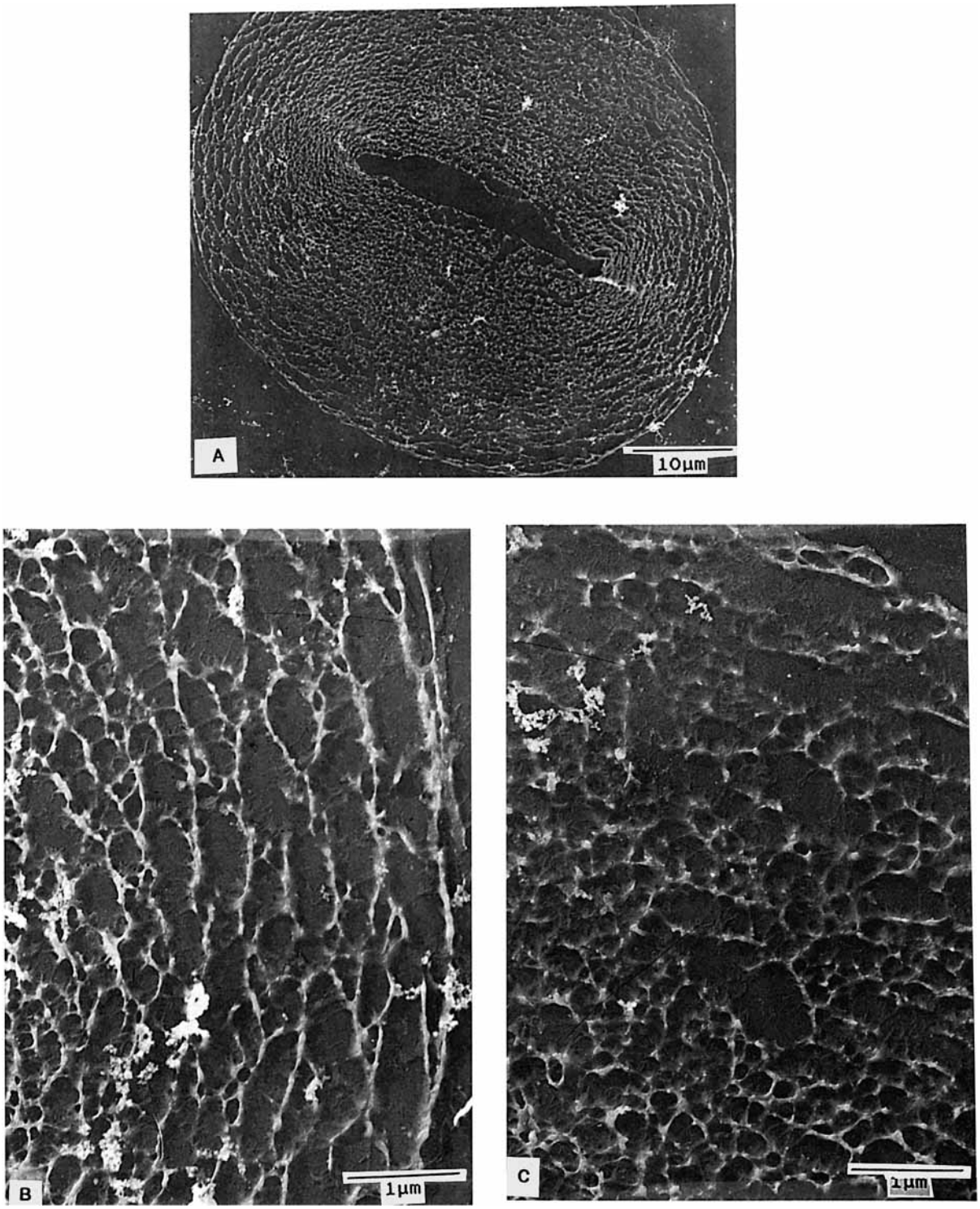

Figure 2 Layered cross section of cotton fibers treated with 4.0*N* KOH at room temperature: (a) low magnification, (b) fibrillar texture of terminal zone at high magnification, and (c) honey-comb structure of middle zone at high magnification.

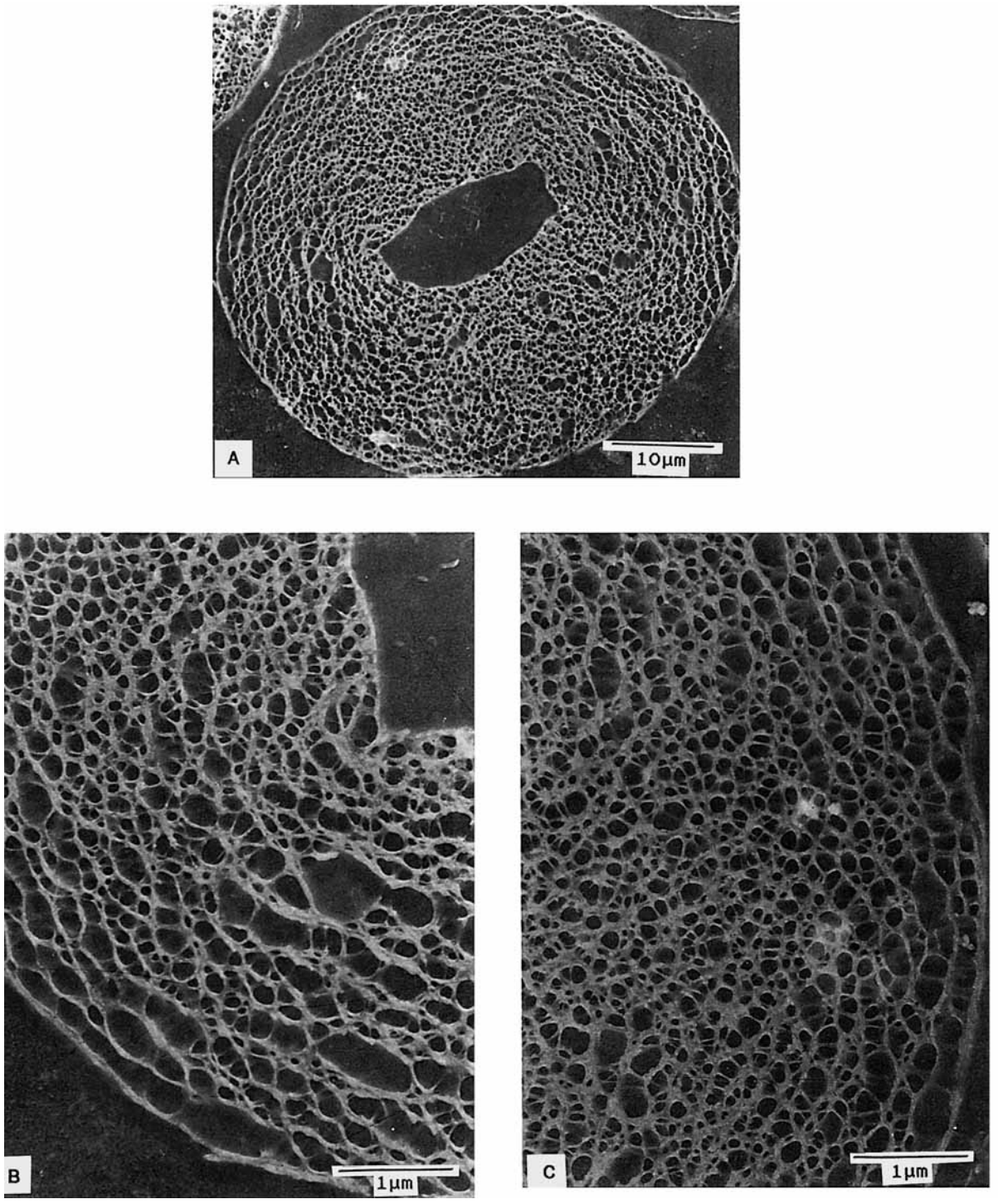

Figure 3 Layered cross section of cotton fibers swollen in 4.5*N* LiOH at 0°C: (a) low magnification, (b) texture of terminal zone at high magnification, and (c) honey-comb structure of the middle zone at high magnification.

ture characteristic of CI [Fig. 4(c)]. Table II indicates that residual CI though is nearly the same in both these reagents (i.e., LiOH and KOH); RP values for these residual celluloses are widely different. The RP is about 6.7 after LiOH swelling, while the same is only 2.9 after KOH treatment. This shows that LiOH is not able to penetrate the highly ordered regions of CI in the native cellulose and that the persistence of bilateral structure can be as-

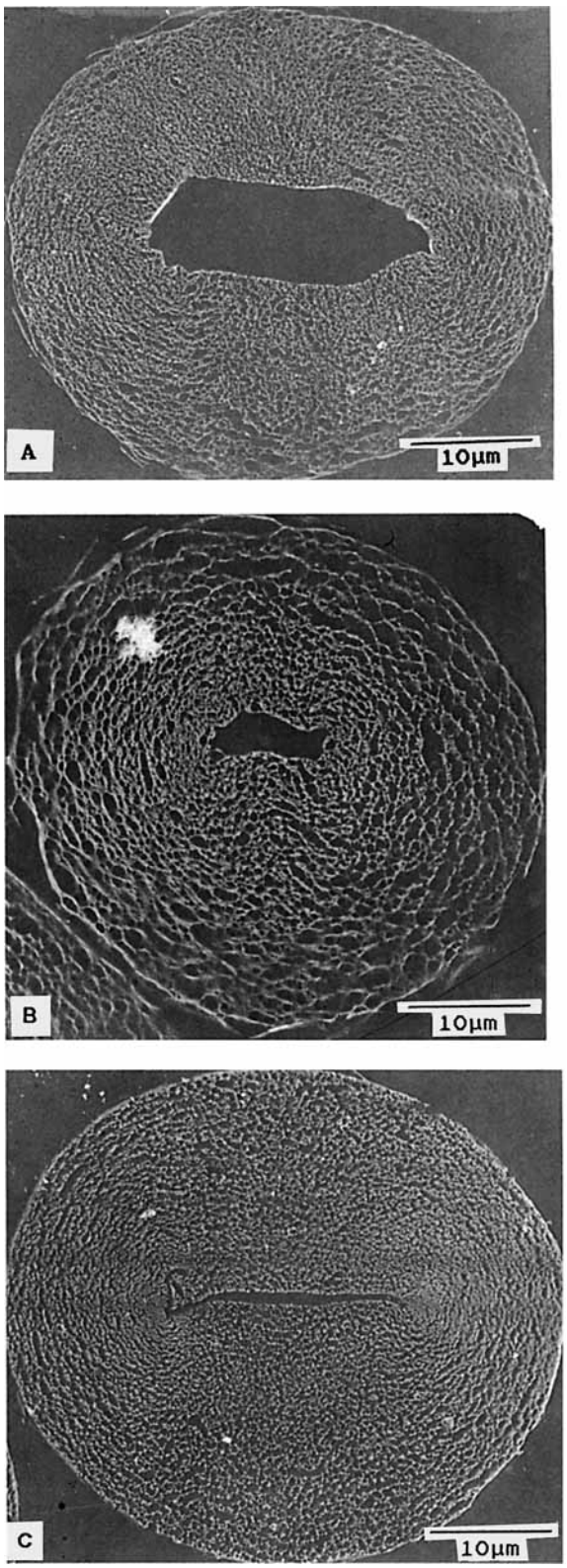

Figure 4 Layered cross section of cotton fibers treated at room temperature: (a) 4.5*N* NaOH, (b) 4.5*N* KOH, and (c) 4.5*N* LiOH.

Table I X-ray Data of Fibers Treated with Alkali Metal Hydroxides of Different Concentrations

	X-ray Data				
Treatment	CI	CII	Total	Am	RP of CI
1. None	70	0	70	30	2.6
2. LiOH					
(a) 4.5*N* RT	17	43	60	40	6.7
(b) 4.5*N* 0°C	10	47	57	43	3.5
3. NaOH					
(a) 3.4*N* RT	50	15	65	35	3.8
(b) 3.7*N* RT	33	34	67	33	5.0
(c) 4.7*N* RT	13	55	68	32	3.8
(d) 6.5*N* RT	14	49	63	37	3.1
4. KOH					
(a) 4.0*N* RT	22	38	60	40	3.6
(b) 4.7*N* RT	19	43	62	38	2.1
(c) 5.5*N* RT	14	41	55	45	3.0
(d) 6.9*N* RT	14	42	56	44	2.6

sociated with the above X-ray data. With the nearly same percentage of CI, KOH treatment did not show the bilateral structure, as the residual CI is of very poor order (lower RP). This observation also implies that KOH produces a more extensive and uniform swelling than LiOH and that it is able to disrupt the very highly ordered regions of CI. The residual CI, though poorly ordered, is responsible for the appearance of fibrillar texture at the outer layers.

CONCLUSIONS

The variations in the layered morphology of fibers treated identically with LiOH, NaOH, and KOH may be traced to differences produced by the swelling agents at the ultrastructural level. X-ray data also supports this presumption. The persistence of bilateral structure in the layered section of the alkali swollen fibers is decided not only by the

Table II X-ray Data of Fibers Treated in Alkali Metal Hydroxides of Same Concentration[a]

	X-ray Data				
Treatment	CI	CII	Total	Am	RP of CI
4.5*N* LiOH RT	17	43	60	40	6.7
4.5*N* NaOH RT	13	53	66	34	4.3
4.5*N* KOH RT	19	39	58	42	2.9

[a] RT (room temperature) = 30° ± 1°C.

quantity of residual lattice but also by the nature of crystalline order present in the residual lattice. Absence of bilateral structure after swelling is related to higher conversion to cellulose II in addition to higher amorphous content. Availability of higher amounts of amorphous material in fibers swollen in KOH should make them more reactive and hence more amenable for subsequent finishing treatments.

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S. ARAVINDANATH*
P. BHAMA IYER
S. SREENIVASAN

Central Institute for Research
on Cotton Technology,**
Matunga, Bombay 400019 India

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* Present address: Reliance Industries Limited, Patalganga, Raigad (Dist.), Maharashtra
** Formerly Cotton Technological Research Laboratory