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Analysis of Cotton Fiber Maturity. I. X-Ray Study of Phase Transformation in Various Cottons*

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Synopsis

An x-ray diffraction technique is described for the determination of the extent of conversion of cellulose I to cellulose II lattice in partly mercerized cottons. This technique has been applied to obtain the degree of phase transformation, after subjecting various cottons to swelling in 12% (w/w) NaOH at 65% R.H. and 27°C. For the various cottons studied, a direct relationship is found to exist between fiber maturity and the untransformed cellulose after swelling.

INTRODUCTION

The significance of fiber maturity in the context of cotton textile processing is widely known. Immature cotton fibers have physicochemical properties which are different from mature ones, and therefore their behavior during processing is different. An analysis of cotton, lapped on the top roller of a drawframe, indicated it to be immature.[1] Likewise, a study[2] of fibers broken in roving and yarn showed that these have maturity below the average maturity of the sample. It is also well known that the presence of immature fibers in a cotton sample during spinning gives rise to imperfections called "neps" in the spun yarn. These "neps" in a woven fabric create difficulties[3] in obtaining uniformity of dyeing.

The various definitions of cotton maturity, regardless of fiber fineness, employ a comparison of secondary wall thickness with the lumen dimensions. Various physical principles have been employed to assess the maturity of cotton fibers. Methods based on these principles are (a) examination of raw cotton fibers under a polarizing microscope, (b) microscopic examination of fibers swollen in 18% NaOH, and (c) use of instruments based on the principle of air flow through a plug of cotton, such as the Micronaire, Arealometer, etc. The relative advantages of these various approaches to measure cotton fiber maturity have been described earlier.[4]

With particular reference to the caustic soda swelling method, treatment with alkali brings about different changes in the physical appearance of

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mature and immature fibers. As a result of caustic treatment, the thick-walled, mature fibers are deconvoluted and assume a circular shape or cross section, whereas immature fibers are left practically unchanged in their original flattened, convoluted state. These changes in the "external structure" of fibers can be easily noticed under an optical microscope where mature and immature fibers are separately classified.

While reflecting upon this feature of the caustic swelling method, it occurred to the authors that it may be possible to classify various cottons according to their maturity by examining the differences in their "internal structure" employing x-ray diffraction techniques, after subjecting them to swelling in sodium hydroxide solution of optimum concentration.

The present paper deals with the analysis and assessment of the phase transformation from cellulose I to cellulose II of various cottons of different maturity after subjecting them to swelling in 12% (w/w) NaOH at 27°C. A refined experimental technique is described for the analysis of phase transformation in partly mercerized cottons. It is shown that the residual cellulose I, after treating cotton with 12% NaOH, can be related to its maturity.

EXPERIMENTAL

Material

Cottons selected for the present work included ten American cottons (mostly the Uplands), one fine Egyptian cotton, and two prematurely harvested Indian cottons, covering a wide range in maturity. All these cottons were Soxhlet extracted in order to remove waxy matter.

Determination of Maturity

Maturity determination for various cottons was done according to the standard ASTM procedure[5] for the randomly selected specimens, in which about 1000 fibers taken directly from a blended laboratory sample were microscopically examined after treatment with 18% (w/w) NaOH. Preconditioning of samples was done at 65% R.H. The parameter obtained from this classification is the per cent mature fibers (p_M).

Swelling of Cottons in Caustic Soda of Just Mercerizing Strength

Intracrystalline swelling of most cottons begins at 12% (w/w) concentration of NaOH and is complete at about 16% (w/w) NaOH concentration. For a study of proportions of cellulose I and cellulose II in various partly mercerized cottons, NaOH of 12% (w/w) concentration (having a specific gravity of 1.13 at 27°C) was found to be most convenient and suitable and has therefore been used throughout this work. This partial mercerization of various cottons at 12% (w/w) NaOH was done under standard conditions of temperature and humidity (27°C, 65% R.H.).

After swelling for 1 hr, the cotton samples were washed in water and dried in air. The analysis of the extent of phase transition in various cottons will be described later.

Apparatus for Obtaining Equatorial X-Ray Diffractograms

Transmission equatorial x-ray diffractograms from various treated and untreated cottons were taken using a vertical Philips X-Ray Diffractometer (PW 1050) equipped with a curved crystal focalizer (PW 1075) to minimize instrumental broadening effects. The source of x-radiation (CuK_α) was a Philips x-ray generator (PW 1009), and the monitoring of the x-ray beam diffracted by a specimen was done using a scintillation-type detector (PW 1964), a pulse-height discriminator (PW 1365) being used in the circuit for effective monochromatization of the diffracted x-rays.

In order to obtain an equatorial x-ray scan, the cotton sample was mounted in the form of a well-parallelized bundle in a specially designed sample holder which could be positioned at the center of the diffractometer. The axis of the fiber bundle coincided with the diffractometer axis. In the transmission set up employed, both the incident and the diffracted beams make angles of $(90° - \theta)$ with the plane of the fiber bundle. Divergence and receiving slits of 4° and 0.3 mm, respectively, were used for these studies. The diffractograms were recorded on a chart, employing a scanning speed of 1 deg/min and a chart speed of 400 mm/hr.

ANALYSIS OF EQUATORIAL X-RAY DIFFRACTOGRAMS OF PARTLY MERCERIZED COTTONS FOR ESTIMATION OF PHASE TRANSFORMATION TO CELLULOSE II

In order to be able to analyze the equatorial diffractogram of a partly mercerized cotton sample, a series of equatorial diffractograms, with different proportions of cellulose I and cellulose II, were synthesized from the known equatorial x-ray diffractograms of pure cellulose I (raw cotton) and pure cellulose II (cotton twice slack-mercerized in 24% NaOH). Using this approach, one can compare the diffractogram of any partly mercerized cotton with the series of synthesized diffractograms (for which the cellulose I/cellulose II proportion is known) and obtain an approximate estimate of phase transformation to cellulose II in that sample. This approach can be made quantitative, as will be explained later.

Figure 1 illustrates the equatorial x-ray diffractograms of Egyptian Karnak and Karnak twice swollen in 24% (w/w) NaOH, normalized to equal areas. These represent the diffractograms of pure celluloses I and II, respectively. It must be noted that the 021 peak, which is present in transmission x-ray powder diffractograms of cellulose at 20.5° (2θ), is missing in these scans due to molecular orientation in these parallelized samples. Let us designate these diffractograms as C-I and C-II, respectively. The two-phase numerical synthesis of the equatorial diffractogram S_f of any

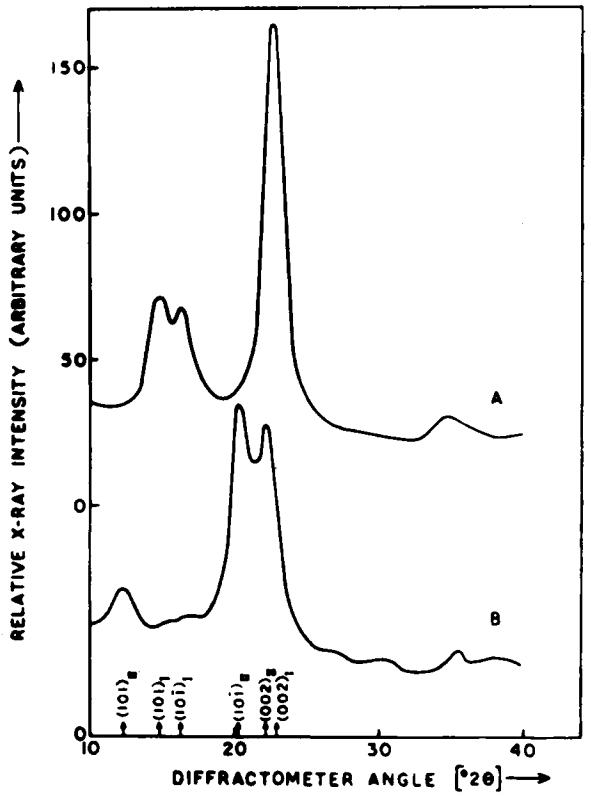

Fig. 1. Normalized equatorial x-ray diffractograms of (A) raw Egyptian Karnak and (B) twice-mercerized Egyptian Karnak, used as standards for synthesis of mixed patterns.

sample, having a degree of phase transformation f (to cellulose II), can be done every 0.25° in 2θ using the equation

$$S_f = fC_{II} + (1 - f)C_I$$

where $(1 - f)$ represents the fraction of residual cellulose I.

The synthesized equatorial diffractograms for various values of degree of phase transformation f (as multiples of 0.1 to 0.9) are shown in Figure 2. From Figures 1 and 2 one can see a gradual transformation of the diffractogram from that of cellulose I to that of cellulose II, as f is varied from 0 to 1 in steps of 0.1. It can be seen from Figure 2 that, with increasing f, the height of the $10\bar{1}$ x-ray peak of the Cellulose II phase (at 20.4° 2θ) increases at the expense of the height of the 002 x-ray peak (at approx. 22.5°). The ratio of these two peak heights, R, can be related to the degree of phase transformation f according to Gjonnes et al.[6] In the present work, the peak heights are measured from the curves in Figure 2 after subtraction of a linear background obtained by joining the intensities at 10° and 32° (2θ), respectively. The ratio R of peak heights at 20.4° and 22.5° (2θ),

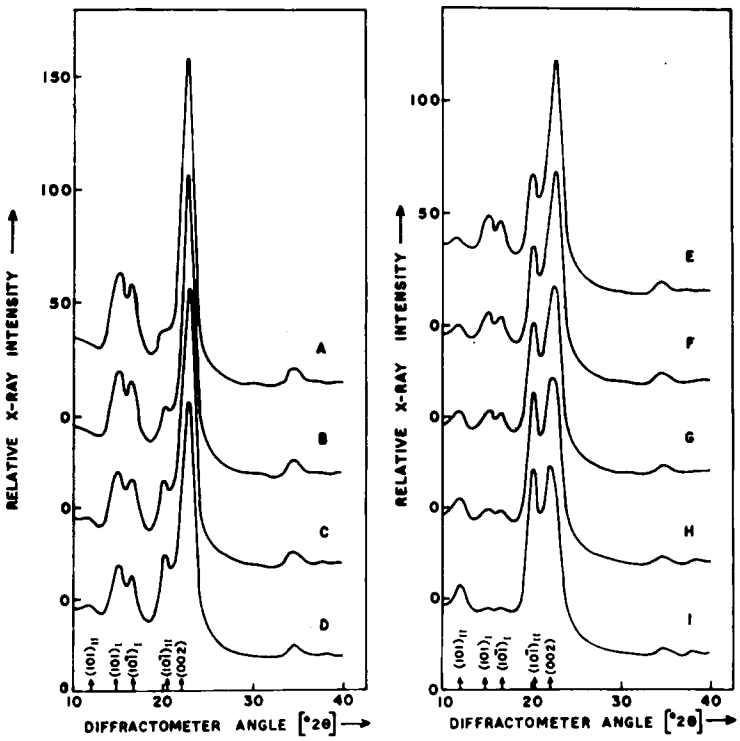

Fig. 2. Synthesized equatorial x-ray diffractograms of various mixtures of cellulose I and cellulose II: (A) 10:90 mixture, $f = 0.1$; (B) 20:80 mixture, $f = 0.2$; (C) 30:70 mixture, $f = 0.3$; (D) 40:60 mixture, $f = 0.4$; (E) 50:50 mixture, $f = 0.5$; (F) 60:40 mixture, $f = 0.6$; (G) 70:30 mixture, $f = 0.7$; (H) 80:20 mixture, $f = 0.8$; (I) 90:10 mixture, $f = 0.9$.

thus calculated from diffractograms of Figure 2, is plotted against the known values of degree of phase transformation f (Fig. 3).

This plot of Figure 3 can now be used as a calibration curve for obtaining the degree of phase transformation f from the ratio R observed from the diffractogram of a partly mercerized sample. It should be mentioned here that for obtaining this ratio R, normalization of the observed diffractogram is not necessary.

RESULTS OF THE PHASE TRANSFORMATION ANALYSIS OF PARTLY MERCERIZED COTTONS

Figure 4 illustrates the observed equatorial diffractograms of cottons of various maturities swollen in 12% (w/w) NaOH. One can appreciate the differences in the extent of phase transformation of various cottons on account of the differences in internal structure, which appear to be related to maturity. The peak height ratio R and the degree of phase transformation f deduced therefrom (using Fig. 3) are listed in Table I for various

cottons treated with 12% (w/w) NaOH. Table I also lists the experimentally observed values of mature fiber percentage p_M for these cottons. The values of residual cellulose I fraction are obtained by subtracting f from unity.

TABLE I
Relationship Between Maturity and Phase Transformation Upon Swelling for Various Cottons

Sample	Per cent mature fibers p_M	Ratio of peak heights R	Degree of phase transformation to cellulose II f, %	Residual cellulose I content $(1-f)$, %
1. Prematurely harvested Shanker-4 (30 days of growth)	0	0.975	89.5	10.5
2. American immature cotton	29	0.951	86.0	14.0
3. American upland cotton 947	45	0.883	79.8	20.2
4. American upland cotton 486	60	0.815	75.0	25.0
5. American upland cotton 940	69	0.789	73.5	26.5
6. American upland cotton 193	73	0.749	71.0	29.0
7. American upland cotton 934	77	0.714	69.0	31.0
8. American upland cotton 805	83	0.715	69.0	31.0
9. American upland cotton 922	94	0.563	59.0	41.0
10. American upland cotton 875	98	0.500	54.5	45.5
11. American Iquitos cotton 888	96	0.477	53.0	47.0
12. Egyptian Karnak	90	0.561	59.0	41.0
13. Prematurely harvested Kalyan (50 days of growth)	60	0.850	77.0	23.0

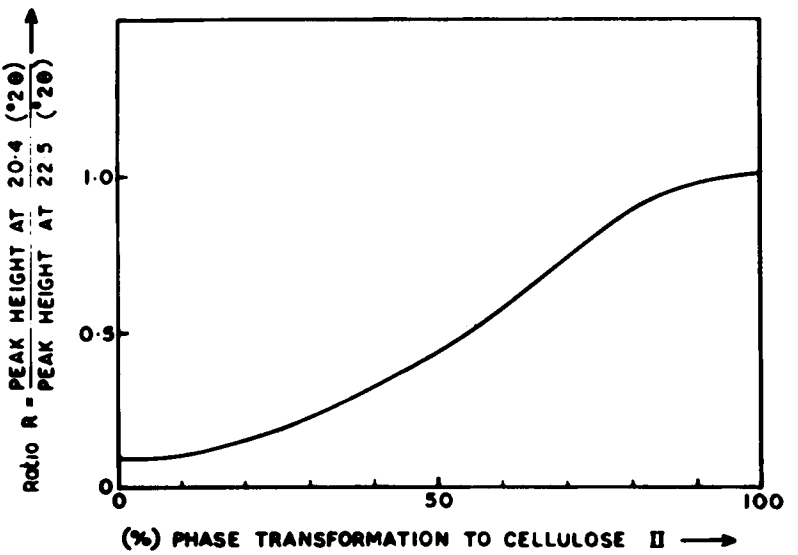

Fig. 3. Calibration curve depicting plot of $10\bar{1}/002$ peak ratio R against degree of phase transformation f for various synthesized curves of Fig. 2.

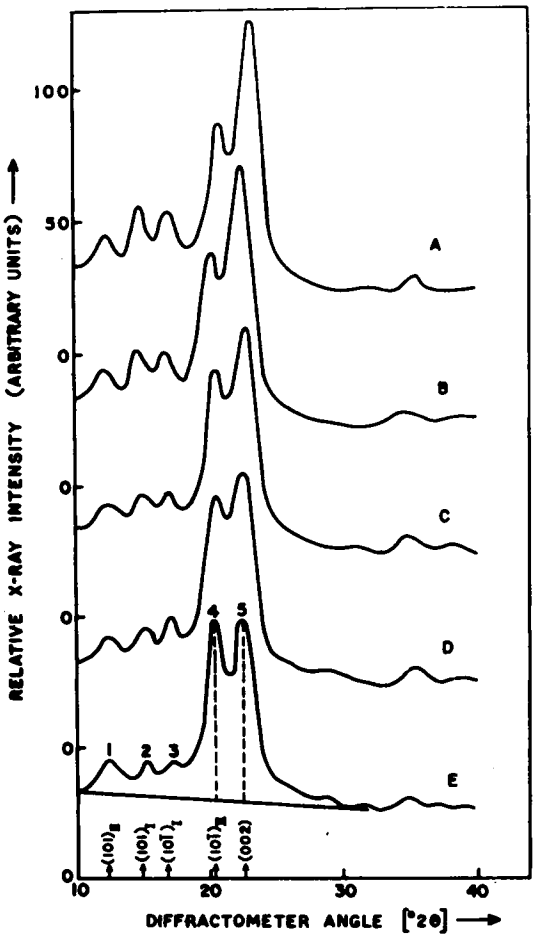

Fig. 4. Observed equatorial x-ray diffractograms of cottons of different maturity swollen in 12% (w/w) NaOH: (A) 875, p_M = 98; (B) 934, p_M = 77; (C) 486, p_M = 60; (D) 947, p_M = 45; (E) Shanker-4 harvested at 30 days after flowering, p_M = 0.

Finally, Figure 5 shows the relationship between the residual cellulose I content $(1 - f)$ of various cottons (after treatment with 12% NaOH) and their mature fiber percentage p_M. A curvilinear relationship exists between the residual cellulose I fraction $(1 - f)$ and the mature fiber percentage p_M for various cottons. However, when log $(1 - f)$ is plotted as a function of p_M, a linear plot is obtained (Fig. 6).

DISCUSSION

The data presented in Table I and Figure 5 do not rule out the possibility of using a standard swelling treatment for various cottons followed by a phase transformation analysis for the determination of their maturity. However, the results presented here are only of a preliminary nature, and much more data are required on cottons of different species and origin to

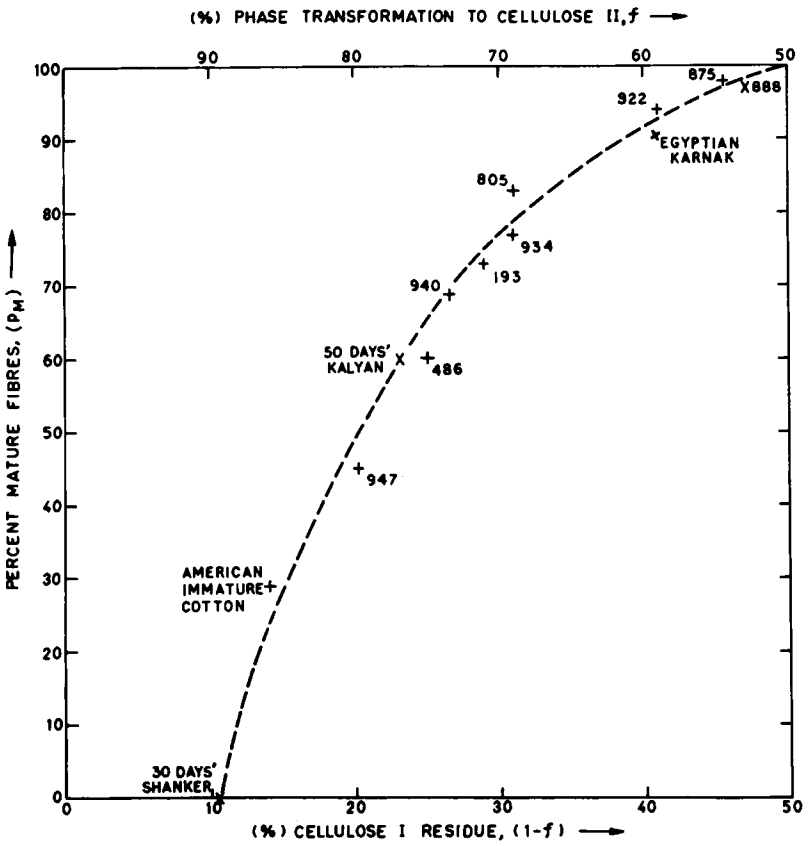

Fig. 5. Relationship between degree of phase transformation to cellulose II (f) and per cent mature fibers (p_M) for various cottons treated with 12% NaOH.

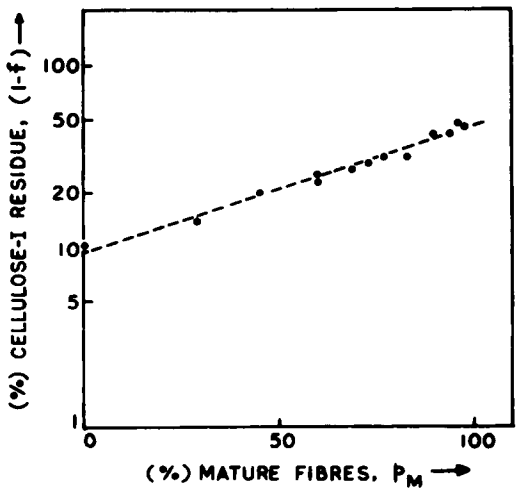

Fig. 6. Plot of log $(1 - f)$ vs p_M.

establish a relationship between maturity and the extent of phase transformation in 12% NaOH. It may be worthwhile to mention, in passing, that other estimates of maturity, such as those obtained using the Micronaire or Arealometer, may be better related to phase content. For cottons of interest in textile spinning, p_M should be greater than 60, otherwise excessive fiber damage may occur during processing, leading to an increase in card waste.

The greater extent of conversion to cellulose II in the case of more immature cottons after swelling in NaOH of concentration as low as 12% (w/w) is probably due to the following reasons: (i) immature cottons have a less perfect lattice structure than mature cottons, and (ii) immature cottons adsorb more alkali[7] than mature cottons because of the higher porosity of their structure.

These results have implications for the use of deconvolution count[8] as a measure of degree of mercerization. If the sample contains a large fraction of immature cotton fibers, deconvolution count obtained would be high, despite better phase transformation. This happens because immature fibers fail to deconvolute while they readily undergo phase transformation in alkali of mercerizing strength.

This x-ray technique of phase analysis, though applied here to study cotton maturity, can also be used to advantage in other applications, such as analysis of blends of cotton and viscose, measurement of degree of mercerization of cellulosic textiles, etc.

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