X-ray Diffractometric Study of Microcrystallite Size of Naturally Colored Cottons

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ABSTRACT: Cellulose crystallite sizes of naturally green and brown cottons as well as of white undyed and dyed cotton were studied by using X-ray diffractometry. Data were analyzed both by a peak stripping method using the program WinFit and by whole profile matching using the FullProf program. The fit obtained with WinFit agreed with the results from the FullProf except for a small difference centered on the 002 reflection. Crystallite sizes of white and colored cottons were estimated by the full-width-at-half-minimum (FWHM) method, and the results showed that compared to the white cotton, the crystallite sizes of green and brown cottons based on the 101 and 002 reflections were found to be comparable, whereas smaller $10\bar{1}$ crystallite sizes were observed. After dyeing, the crystallite size of dyed brown cotton displayed a slight increase in the 002 crystallite size compared to that of the undyed white cottons. The average crystallite size of 101, $10\bar{1}$, and 002 for each cotton determined by the WinFit program was comparable to that estimated by the FullProf program. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 76: 1466–1471, 2000

Key words: naturally colored cotton; cellulose crystallite size; X-ray diffraction; FWHM

INTRODUCTION

Naturally colored cottons, comprising fibers with natural pigments, have been cultivated for centuries,[1,2] but have received little attention until recent years, because of short fiber length and poor fiber strength.[3,4] With advanced genetic breeding technology, however, naturally colored cotton fibers in various shades of green and brown have been successfully processed on conventional textile machines.[5,6] Unlike traditional dyed cottons, the colors of which tend to fade, the natural color actually deepens after washing.[7] This character-

istic, plus other unique properties such as natural flame resistance,[8] have attracted much attention. In addition to these unique characteristics, naturally colored cottons are becoming increasingly important also because the presence of natural pigments eliminates the need for coloring textile products, thus saving not only a large amount of energy but also preventing dye chemicals from polluting the environment. These unique characteristics of naturally colored cottons, such as the deepening of color after laundering and the natural flame resistance, could be due to their special chemical characteristics (e.g., natural pigment composition and bonding between pigment and cellulose structures), physical characteristics (e.g., cellulose crystal size and percent crystallinity), or both. Characterization of the physical mi-

crostructure, which is the purpose of this research, will provide a partial understanding of the origins of the special properties of naturally colored cottons. For a more complete understanding, however, further research on the detailed chemistry of the fibers will also be needed. Although the crystallite size and other crystal parameter measurements of cotton and ramie have been extensively studied by X-ray diffraction based on the peak broadening,[9–11] the cellulose crystallites of naturally colored cottons have never been studied.

All fibers and polymers possess a certain amount of order–disorder in the structure, ranging from crystalline to amorphous molecular arrangement. In cotton cellulose, for example, the dominant crystalline regions form microfibrils that exhibit various shapes and sizes of crystallites.[12] The packing of long-chain molecules in the fiber crystalline regions does not result in a perfect crystal X-ray diffraction pattern; rather, the diffractograms usually contain broad peaks with large overlaps and background scatter.[13] Because the measurements of crystallite size from the Scherrer equation are based on peak broadening, valid measurements can be made only when peaks are resolved and separated from the background. To measure the cellulose crystallite size using the Scherrer equation, the full-width-at-half-maximum (FWHM) is commonly used as a measure of the true peak broadening due to the particle size effects.

To overcome the problem introduced by the overlap of broad peaks, computational methods have been developed for peak profile resolution.[14,15] Recently, a computer program created by Dr. S. Krumm at the University of Erlangen, Germany called "WinFit"[16] became available for
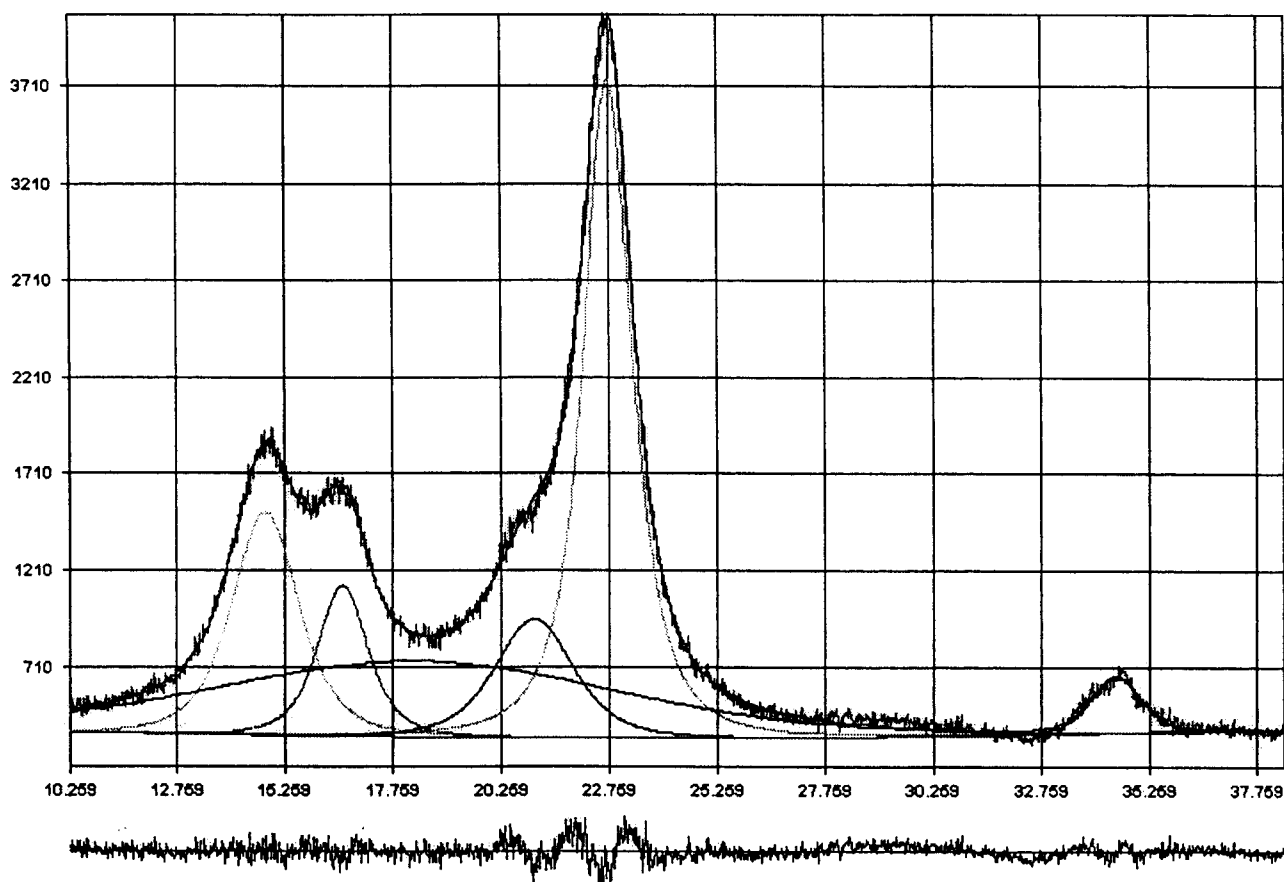

Figure 1 Experimental X-ray diffraction pattern of green cotton, its approximate decomposition into six peaks (including the very broad one which was treated as background) obtained using the program WinFit, and the difference plot (between the experimental curve and the six peaks).

line profile analysis. The program has been used for line profile analysis of materials that yield broad and heavily overlapping peaks for crystallite size in the range of 2–100 nm (20–1000 Å). Although the WinFit program has been employed to measure the crystallite sizes of cotton,[17] it was not designed originally for the study of cellulose crystallites. Therefore, for comparative purposes, we also employed a second program called Full-Prof[18] for the X-ray diffraction data fitting. Unlike the WinFit program, which decomposes the diffractogram into a sum of Pearson VII functions[19] without taking into consideration any structural parameters, the FullProf program fits the data by placing peaks with pseudo-Voigt shape[19] in positions calculated from the known lattice dimensions and space group. After the data fitting, the FWHM for each reflection was used to assess the crystallite size.

EXPERIMENTAL

Cellulose samples used in this study were white pima and naturally green and brown cottons (*Gossypium hirsutum L*). For comparative purposes, some of the white pima cottons were dyed with a brown reactive dye to the same shade as that of the naturally brown cotton. In preparation for the X-ray goniometer, fiber samples were chopped with a scissors to about 0.5 mm. The samples were then reduced to a fine random powder by mechanical action prior to mounting on a plastic sample holder consisting of a cylindrical depression 10 mm in diameter and 1 mm in depth. To further diminish the possibility of preferred orientation effects, the sample holder was spun about its main axis during data collection.

The diffraction patterns of all samples were recorded using a Siemens D5000 diffractometer. The source was a Cu X-ray tube operating at 50 kV and 30 mA. Neither an incident beam nor a diffracted beam monochromator was used, but a pulse height discriminator was set so that only the Cu $K_{\alpha 1}/K_{\alpha 2}$ doublet would be recorded. Scans were performed over the 5–60° 2θ range using steps 0.02° in width; intensities were recorded for 10 s per step. The contribution of the sample holder to the background was measured using an empty sample holder under identical conditions. Because this background scan was devoid of features that could significantly affect the sample patterns, no attempt was made to subtract this background from the sample patterns recorded.

The data were first analyzed without smoothing by using the WinFit program.[20] This program fits the observed profile with a series of split Pearson VII functions and a polynomial background correction and yields individual peak positions and peak widths. The peak widths were then used to compute crystallite. The instrumental contribution to the peak width was corrected using sample of LaB_6 scanned under identical conditions. The cell dimensions were determined for

Table I   Experimental Data of Peak Parameters for the White, Green, and Brown Cottons

Sample	Reflection	Position (2θ)	Intensity Maximum[a]	Integrated Area[a]	FWHM	Exponent[b]
White	101	14.610	1052	2914	1.875	1.104
	10$\bar{1}$	16.457	684	1273	1.473	1.696
	002	22.586	2456	4137	1.312	1.589
Green	101	14.667	713	1932	1.750	1.021
	10$\bar{1}$	16.432	526	1424	1.760	1.032
	002	22.625	1243	1840	1.258	2.542
Brown	101	14.570	485	1273	1.906	1.286
	10$\bar{1}$	16.422	334	935	1.782	1.000
	002	22.553	1033	1624	1.273	1.880
Dyed brown	101	14.716	1229	3642	2.059	1.162
	10$\bar{1}$	16.507	724	1575	1.385	1.000
	002	22.592	2934	4554	1.190	1.503

[a] Relative values.
[b] Pearson VII exponent (m); $m = 1$ corresponds to a Lorenzian shape, $m \to \infty$ to a Gaussian shape, and $m \approx 1.4$ to a shape with approximately equal Lorenzian and Gaussian contributions.[19]
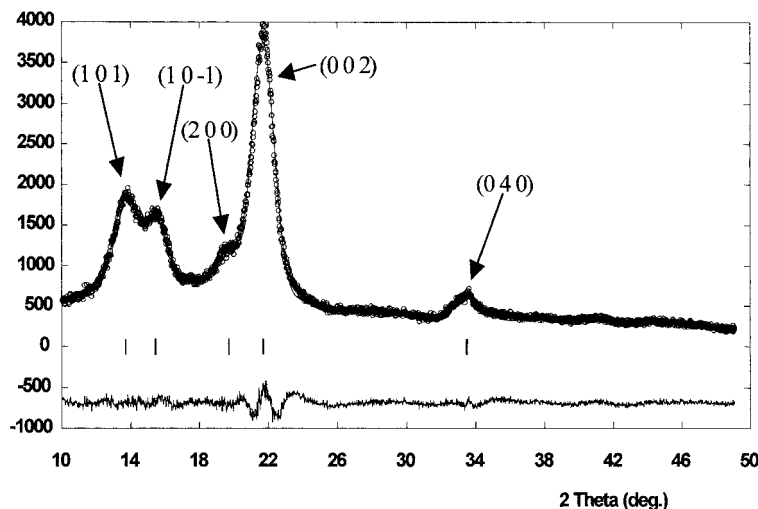
Figure 2 Experimental X-ray diffraction pattern of green cotton (small circles), the fit obtained using the program FullProf (thin solid line), and the difference plot (at the bottom of the figure).

each of the samples by a nonlinear least-squares refinement from the peak positions obtained from the profile fitting.

The data were also analyzed by a whole pattern fitting by using the FullProf program. Here the initial lattice dimensions used were those obtained from the previous refinements carried out with WinFit. The profile function used was TCH Pseudo Voigt function,[21] in which all the peak width parameters were obtained from the same sample of LaB_6 and not refined. Peak broadening due to size effects was included as an isotropic size parameter of Gaussian character. Domain size was calculated from this size parameter and a value of 0.9 for the Scherrer constant was assumed. The background was refined as a second-order polynomial centered on $2\theta = 20°$, given that the background generated by amorphous cellulose appears as a broad bump centered at this position.[22]

RESULTS AND DISCUSSION

Figure 1 shows the result of fitting naturally green cotton using WinFit. The major reflection peaks typical of cellulose I (101, 10$\bar{1}$, and 002) are immediately obvious. The figure includes raw data, the five separate peaks obtained, a trace of the calculated background, and the difference

plot. Peak parameters obtained from the four cotton samples are summarized in Table I.

Figure 2 summarizes the fitting by using Full-Prof. Again, the experimental pattern, calculated pattern, and difference plot are also shown. Comparing the difference plots at the bottom of Figures 1 and 2, one can see that the fits obtained from the two programs are in fair agreement with each other: they both fit the observed data well except for the slight difference centered on the 002 reflection. At this time the origin of this discrepancy is unclear. One possible explanation is that other reflections close to the 002 peak may exist and are not included in the analysis.

The monoclinic unit cell parameters of the cellulose crystallites of the white and naturally green and brown cottons obtained from WinFit are shown in Table II. They are found to be comparable to the lattice parameters that have

Table II   Lattice Parameters of Cotton Samples

Cotton Sample	a (Å)	b (Å)	c (Å)	β
Cellulose I[a]	8.35	10.30	7.90	84.0
White	8.34	10.40	7.89	83.2
Green	8.35	10.40	7.91	83.2
Brown	8.32	10.40	7.88	83.5
Brown (dyed)	8.22	10.39	7.91	83.5

[a] Unit cell parameters from Mauersberger.[19]

Table III Cotton Cellulose Crystallite Sizes (Å) Determined by WinFit and FullProf Programs Based on the FWHM and FullProf Methods

Cotton Sample	WinFit				FullProf
	101	10$\bar{1}$	002	Average	Average
White	42	54	61	52	51
Green	45	45	64	51	52
Brown	42	45	63	50	52
Dyed brown	39	57	67	54	53

urally green and brown cottons, estimated by the FWHM, may be considered insignificant. This finding indicates that the differences in properties between the white and naturally colored cottons, such as color darkening behavior and natural flame resistance, cannot be attributed to microcrystallite size differences. This suggests that these property differences may be chemical in nature and other avenues of pursuit must be sought to understand the special properties of naturally colored cottons.

been generally adopted for native cellulose I.[23] Crystallite sizes of white and naturally green and brown cottons determined from the peak parameters given by both the WinFit and Full-Prof programs are given in Table III. In comparison to white cotton, the crystallite sizes of both green and brown cottons showed comparable sizes in the 101 and 002 directions but slightly smaller sizes in the 10$\bar{1}$ direction. Because these calculations may have some uncertainties, these size differences may not be significant. In addition, the average crystallite sizes estimated by the FullProf program are comparable to the average of 101, 10$\bar{1}$, and 002 estimated by the WinFit program.

Table III also shows the crystallite sizes of brown dyed cotton. The results indicate that after dyeing with the reactive dyes, there was no significant change in the 101 and 10$\bar{1}$ crystallite sizes but a slight increase in the 002 crystallite size. Other research has indicated that increasing the fiber moisture content[24] or hydrolytically degrading the fibers[25] will cause an increase in the average crystallite size due to the rearrangement of associated chains in the amorphous areas. Hence, the slight increase of the 002 crystallite sizes from the undyed white cotton to the dyed brown cotton is likely due to the effect of moisture during the dyeing process.

In conclusion, this study found that the WinFit program has provided a convenient technique for cellulose peak analysis, and both the WinFit and FullProf programs showed a fair agreement in the peak profile fitting, although after data fitting by both programs, there exists an unexplainably small difference between the observed and calculated data. Therefore, the slight difference in the 10$\bar{1}$ crystallites between the white cotton and nat-

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