

Peak-Fitting Analysis of Cotton Fiber Powder X-ray Diffraction Spectra

Runying Chen,¹ Kathryn A. Jakes,² Dennis W. Foreman³

¹270A Rivers Building, East Carolina University, Greenville, North Carolina 27858

²1787 Neil Avenue, Ohio State University, Columbus, Ohio 43210

³305 W. 12th, Ohio State University, Columbus, Ohio 43210

Received 21 July 2003; accepted 3 March 2004

DOI 10.1002/app.20666

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The precision and accuracy of diffraction peak positions resolved from the powder X-ray diffraction spectra of cotton fibers by means of the residuals peak-fitting procedure of a commercial peak-fitting software package (PeakFit®) was investigated to explore the potential of such programs in providing reliable data that are not readily apparent in diffuse X-ray spectra. Each intensity spectrum was fitted by employing a Gaussian function as the peak profile. The precision of 15 pairs of the resolved diffraction peaks is 0.0017 mm; 9 of the 15 pairs fall into the 99% confidence interval. The precision in 2θ of four commonly identified peaks through four independent fittings is from

0.002 to 0.014°. The 2θ accuracy of the resolved peaks is good in comparison to data calculated for both the traditionally accepted and the more recently revised concepts of the cellulose I crystal structure. A peak resolved at about 15.3° may be attributed to the triclinic crystal structure component of cellulose I. Although distinct peaks are not readily apparent in the diffuse spectrum of cellulose, peak-fitting procedures may provide additional data for structure determination. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 2019–2024, 2004

Key words: X-ray; crystal structures; fibers

INTRODUCTION

Until relatively recently, a monoclinic unit cell structure (P2₁) was the commonly accepted model for the crystal structure of cellulose I, though some samples (e.g., algal cellulose, bacterial cellulose, and cotton) display contradictory evidence. Alternative crystal structure models were proposed to explain experimental data.^{1–3} One study, based on electron diffraction, proposed the existence of two polymorphs within cellulose I⁴; this concept has become the generally accepted model. Atalla and VanderHart⁵ report that cellulose I is composed of two crystal structures, I α triclinic (P1) and I β monoclinic (P2₁). The native celluloses vary in proportion of the two: the higher plants such as cotton are dominated by I β , whereas the lower forms of cellulose such as *Valonia* mainly consist of the metastable I α form. Questions regarding the details of the lattice structure of cellulose I still remain,^{6–8} as well as questions about the quantity of the two crystal forms in different native cellulose I materials.⁹

The results obtained in many X-ray diffraction studies of cotton fibers agree with the monoclinic unit cell structure, reflecting dominance of the I β crystal form

in cotton. Some structural variation exists between different higher plants (e.g., flax, ramie, and cotton).¹⁰ The X-ray diffraction spectrum of cotton is very broad and diffused with only a few sharp and identifiable diffraction peaks [i.e., the (1 $\bar{1}$ 0), (110), (200), and (004) peaks]. The diffraction lines from the single monoclinic crystal phase overlap with each other as well as with those of the triclinic crystal form. Further complication in discernment of crystalline structure is generated by the fiber's complex microfibrillar packing.¹¹

Being a well-studied subject, a very rich source of cellulose I structural data has been generated, especially that derived from diffraction studies. The objective of the research reported herein was to explore the precision and accuracy of the diffraction peak positions resolved from the diffraction spectra of cotton by means of a commercial peak-fitting software package to evaluate the suitability of such a method to disclose aspects of the fiber's crystalline structure not readily apparent in its diffraction spectrum. PeakFit® (Sea-Solve Software Inc., Richmond, CA), a commercial peak-fitting program based on a nonlinear curve fitting principle, was selected for this work because it has the reputation of not only being able to provide powerful data analysis but also being user friendly.¹² PeakFit® was used to analyze a variety of analytical spectra,^{13–17} including in fitting X-ray diffraction spectra.^{18–23} Rarely, however, do the studies that use commercial peak-fitting packages mention the particular

Correspondence to: R. Chen (chenr@mail.ecu.edu).

fitting procedures chosen nor do they discuss the precision of the fitting results. In this study, the precision and accuracy of PeakFit®'s residuals peak-fitting procedure was investigated in resolving the peak positions of cotton powder X-ray diffraction spectra. This residual peak-fitting process falls into the third category of pattern-fitting programs summarized by Clark²⁴ (i.e., one in which no structural parameters or unit cell parameters are applied to the fitting). This type of fitting process has the advantages of flexibility, simplicity, and efficiency, but it may not be suitable for complex diffraction patterns with highly overlapped peaks.¹³ In view of the fact that the complex polymorphic crystalline structure of native cellulose I is still under investigation, as well as that the characteristic pattern of the powder X-ray diffraction patterns of cotton fibers are very diffuse, profile fitting using predetermined crystal structural parameters is inappropriate. Rather, employing the residuals peak-fitting process without supplying structural data was tested for its potential to show information in the powder diffraction pattern of cotton beyond that which is readily apparent in the diffuse spectrum. The fitting results of cotton powder X-ray diffraction spectra obtained in this study were compared with both the theoretical structure models of cellulose I and with experimental data reported in the literature. The results of this investigation provide reliability data of a residual peak-fitting analysis by using a commercial package and also by offering a possible means for the study of fiber polymer crystalline structure through peak-fitting analysis of their powder X-ray diffraction patterns.

EXPERIMENTAL

Samples

X-ray diffraction spectra were obtained from four different cotton fiber samples: an undyed, unfinished reference cotton (TestFabrics, No. 8588; Pittston, PA), the same reference cotton immersed at a deep-ocean site for 3 months, and two historic cottons recovered from a deep-ocean archaeological site (one dyed and one undyed) after 133 years of immersion. Further discussion of these materials and the implications of the results obtained are provided elsewhere.²⁵ The cotton fibers were cut into a fine powder and packed into a 0.5-mm glass capillary. All of the powder samples were packed in a consistent manner to achieve similar packing density. The capillary was then cut to about 1.5 cm with the sample located in the middle and then mounted onto the stage of the camera with wax. The capillary was carefully centered through an eyepiece while rotating the stage. For comparison, a sample of the same reference cotton was also prepared by packing a sample holder ($0.15 \times 1 \times 1.5 \text{ cm}^3$) and

examined by using the same diffractometer without the camera attachment.

Instrument

The powder X-ray diffraction spectra of the four cotton samples were obtained via a Debye–Scherrer powder camera (114.5-mm-diameter) mounted on a Philips Electronics PW 1316/90 model, which has a XRG 3100 X-ray generator, graphite monochromator, and copper target. The film was positioned by asymmetric (Straumanis) configuration in the camera. The advantage of this position is that the 2θ values can be determined directly from the distance between the symmetric pair of diffraction lines.

The X-ray operating parameters were 35 KeV and 20 mA. The camera was modified with the addition of an inlet through which helium was purged to reduce background air scattering. After experimentation with 6-, 4-, and 2-h exposures, a 2-h period was determined to be optimum, producing less diffused diffraction lines and lower background. A Mikrodensitometer Model II was employed to transform the blackening intensities on the X-ray diffraction film to diffraction intensity data. The accuracy of film translation by the upper sledge of the instrument is 0.02 mm. The step of film translation is 0.1 mm.

An X-ray spectrum of the reference cotton powder was obtained by using the same diffractometer without the camera attachment and directly measuring the intensity of the diffracted beam. The transformed diffraction intensity spectra obtained of the four powder cotton samples and the X-ray diffraction spectrum of the reference powder were then analyzed by using PeakFit®.

Data analysis

A Gaussian function was chosen as the X-ray diffraction peak profile in this study. The mathematical advantage of using a Gaussian line is the analysis of possible error based on propagation theory. In comparison with a Cauchy line profile, a Gaussian function is a better approximation to the instrumental profile when the Debye–Scherrer technique is used.²⁶ Background intensity was subtracted before peak fitting. The residuals peak-fitting procedure provided in the PeakFit® software is an interactive peak-fitting process. The fitting process proceeded until a maximum r^2 and a minimum residual of random distribution were reached. The position of each diffraction line was calculated by using the symmetric peak pair positions resolved and identified from the residuals peak-fitting method of PeakFit®. The symmetry position of each pair of diffraction lines was calculated first and assessed by using a 99% confidential interval. Then, the 2θ positions of the four most commonly

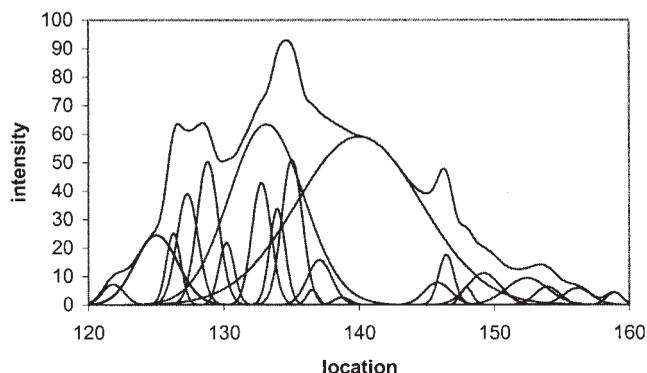


Figure 1 Diffraction peaks resolved from cotton fiber's camera X-ray spectrum.

identified diffraction lines resulting from four independent fittings of the reference cotton diffraction, (110), (110), (200), and (004), were analyzed by calculating the mean and standard deviation of each line. All the diffraction lines resolved from the four cotton samples in this study were compared with each other, and with those calculated line positions provided from both cellulose I α and I β structure models.

RESULTS AND DISCUSSION

At least 15 diffraction lines of cellulose I were resolved by PeakFit[®] from the translated X-ray spectrum of the reference cotton sample. Figure 1 provides an example of a typical cellulose I spectrum and of the peaks fitted

within that spectrum. Table I lists both the left and the right diffraction peak positions of each pair of diffraction lines, 2θ , calculated from each peak pair, and symmetry analysis results. The results indicate that each peak pair is symmetric about the center, with a standard deviation of 0.38 mm at an average of 224.31 mm. Of the 15 pairs of diffraction peaks, 9 pairs fall within the 99% confidence interval while 8 pairs lie within the 95% confidence interval. These results demonstrate that the residual peak-fitting procedure with PeakFit[®] produces good reliability in peak pair symmetry in resolving the overlapping diffraction peaks of cotton powder and that a larger number of diffraction lines of powder cellulose I can be identified in comparison to the four to six peaks observed without peak-fitting analysis.

An evaluation of the 2θ precision and accuracy with four commonly identified cellulose I X-ray diffraction lines, (110), (110), (200), and (004) of monoclinic crystal form, is listed in Table II. The resolved line at an average of 34.38° is closer to the (031) line than the (004) line based on the current cellulose monoclinic model suggested by Sugiyama et al.³⁰ The relative standard deviation of these lines resulting from the four independent fittings is from 0.002° for the (004) and (031) lines to 0.014° for the (110) line. The 2θ variation range between the four fittings is from 0.49° for the (200) diffraction line to 0.10° for the (004) or (031) lines. The average line positions of the selected four lines all fall within the data range reported in the literature. These results indicate that there is uncer-

TABLE I
Diffraction Lines Resolved by PeakFit[®] and Their Symmetry

Peak no.	Right arc position	Left arc position	$^\circ 4\theta$	$^\circ 2\theta$	symmetry (Right arc + Left arc)
1	121.83	101.97	19.98	9.93	223.80
2	125.02	99.70	25.32	12.66	224.72
3	126.28	97.87	28.41	14.21	224.15 ^{a,b}
4	127.31	97.03	30.28	15.14	224.34 ^{a,b}
5	128.81	95.45	33.36	16.68	224.26 ^{a,b}
6	131.36	92.83	38.53	19.27	224.19 ^{a,b}
7	132.78	91.52	41.26	20.63	224.30 ^{a,b}
8	133.94	90.45	43.49	21.75	224.39 ^{a,b}
9	135.03	89.24	45.79	22.90	224.27 ^{a,b}
10	137.06	87.20	49.86	24.93	224.26 ^{a,b}
11	146.44	78.11	68.33	34.17	224.55 ^b
12	149.22	75.49	73.73	36.87	224.71
13	152.43	72.70	79.73	39.87	225.13
14	153.93	70.09	83.84	41.92	224.02
15	156.16	67.38	88.78	44.39	223.54
				Average	224.31
				Standard deviation	0.38
				a. 95% confidence interval	(224.11, 224.50)
				b. 99% confidence interval	(224.05, 224.56)

TABLE II
Precision and Accuracy of 2θ from Repeated Fittings

Sample = reference cotton fiber				
Diffraction lines	(110)	(110)	(200)	(004)/(031) ^a
Diffractometer	14.67	16.39	22.50	34.30
Camera				
Fitting 1 $r^2 = 0.9992$	14.68	16.51	22.77	34.41
Fitting 2 $r^2 = 0.9993$	14.43	16.59	22.41	34.41
fitting 3 $r^2 = 0.9997$	14.59	16.42	22.57	34.31
fitting 4 $r^2 = 0.99998$	—	16.68	22.90	—
Average	14.57	16.55	22.66	34.38
SD (camera)	0.21	0.11	0.21	0.06
Literature (ref.)				
27	14.70	16.80	22.70	34.50
28 ^b	14.69–15.18	16.53–16.98	22.92–23.29	36.70
29	14.55	16.30	22.50	34.40
9	14.95	16.81	23.25	
30	14.59	16.57	22.40	34.64/34.36 ^a
31	14.83	16.63	22.85	34.80

^a This resolved diffraction line is more close to the (031) assignment than that of (004).

^b Calculated from the d-spacing range provided in the study.

tainty when identifying diffraction line positions through residuals peak-fitting using PeakFit®.

According to Toraya,³² the statistical uncertainty of a diffraction peak position depends on both the intensity and width of the peak and the counting statistics (i.e., low- or high-angle region), when individual profile fitting is used to determine the peak position of powder diffraction line. Another curve-fitting study reported that there are variations with replicating fitting analyses when a genetic algorithm is used and that the average value from the repeated fittings is more reliable.³³ When the average value of the four repeated fittings is calculated, the four diffraction line positions identified in this study (Table II) are closer to the cellulose monoclinic model proposed by Mark.²⁹ The peak position variation between the repeated fittings with the same spectrum at about the same r^2 level demonstrates the limitation of the residuals fitting procedure with diffuse X-ray diffraction spectra.

The results in Tables I and II indicate that the residual peak-fitting procedure offered by PeakFit® could be useful in resolving overlapping peaks in the powder diffraction pattern of cotton fiber or other diffraction patterns of a similar nature. However, some degree of uncertainty remains. Some researchers caution that good fitting results or high r^2 values do not necessarily lead to a valid physical structure determination and that the reliability of the fitting results is affected by the degree of peak overlapping, by the number of overlapping peaks in the fitting pattern, and by the determination of baseline position.³³ In response to these cautions, each of the diffraction peaks resolved by PeakFit® from the four cotton samples were compared with those reported in the literature to test the validity of the resolved diffraction lines

derived from a peak-fitting process in discerning physical structure.

There are few studies available with data comparable to this study's peak-fitting results in the range of diffraction lines of cellulose I at both lower and higher 2θ . Therefore, the calculated diffraction lines, provided by both the more recently proposed allomorph composite cellulose I structure model³⁰ and the traditionally accepted cellulose I monoclinic crystal structure model,³¹ were used for comparison.

All the fitting results from the four cotton samples are listed in Table III, along with the calculated 2θ data and their indices from cellulose I crystal structure models. The diffraction line indices of the cellulose monoclinic model from Mann et al.³¹ are converted to those based on the current cellulose crystal structure coordination convention illustrated by Sugiyama et al.³⁰ Only the portion of the calculated 2θ data and their indices that match the data range resulting from the peak-fitting performed in this research with PeakFit® are listed.

Table III demonstrates that, with the four camera diffraction cotton powder samples, many more cellulose I diffraction lines can be resolved than those derived from the diffractometer alone. The advantage of the camera diffraction method lies in the data provided in both the lower and the higher 2θ range. In contrast, no diffraction lines below the (110) line and above the (004) line are resolved from the cotton powder diffraction spectrum obtained from the diffractometer. Similar to the repeated fittings demonstrated in Table II, variations exist with fitting results of the four different cotton samples' camera diffraction spectra. There are 14 diffraction lines consistently resolved from at least three cotton samples, while another 13

TABLE III.
2 θ Position of Cotton Diffraction Lines Resolved through PeakFit®

Resolved diffraction line 2 θ positions from spectra by camera and diffractometer					Calculated 2 θ positions from cellulose I crystal structure models (monoclinic and triclinic) and their indices								
Camera method				Diff.									
SD	M3	MD	MU	SD	Indices			Indices					
$R^2 = 0.99998$	$R^2 = 0.99991$	$R^2 = 0.99994$	$R^2 = 0.99992$	$R^2 = 0.99985$	Monoclinic ^a	Monoclinic ^b	h	k	l	Triclinic ^a	h	k	l
9.93		9.37											
	10.67	10.92	10.92			10.91	1	0	0				
12.66		12.45											
		13.63			13.88	13.83	0	1	1				
14.21			14.15			14.28	1	0	1	14.26	1	0	0
	14.73	14.78	14.81	14.67	14.59	14.83	1	-1	0				
15.14	15.38	15.20								15.41	0	-1	1
16.68	16.47	16.70	16.51	16.39	16.57	16.63	1	1	0	16.79	0	1	0
				17.25	17.12	17.20	0	0	2				
	18.14	18.57	18.27		18.68	18.70	1	1	1				
19.27				20.08	20.37	20.40	0	1	2	20.28	-1	-1	2
20.63	20.51	20.46	20.51		20.47	20.64	1	0	2	20.67	0	0	2
21.75		21.61		22.13		21.92	0	2	0				
22.90	22.75	22.64	22.41	22.50	22.40	22.85	2	0	0	22.39	1	1	0
				23.46	23.60	23.54	0	2	1	23.29	0	1	1
						24.01	1	1	2				
24.93	24.70		24.86			24.41	2	0	1				
		25.70				25.70	2	-1	1				
	30.86	30.17			30.83	30.93	1	1	3	31.16	0	-2	2
					31.28	31.25	1	2	2	31.73	-1	1	2
	32.60	32.87	32.68										
34.17					34.09	34.17	0	2	3				
	34.35	34.34	34.55	34.55	34.36	34.27	0	3	1	34.63	-1	-1	4
					34.64	34.80	0	0	4				
	35.97	35.45				35.73	2	-1	3				
36.87			36.92		36.84	36.94	1	2	3				
	37.72	37.90	38.13		37.48	37.52	0	3	2	37.80	-2	-2	2
	38.40	38.51			38.64	38.80	1	1	4	38.30	-1	-2	4
					38.82		-2	3	1	38.48	1	1	2
39.87						39.32	2	-3	1	39.17	-1	0	4
	41.69	41.34			41.42	41.46	0	2	4	41.22	-2	-2	4
41.92			41.82		41.82		-2	3	2				
44.39	44.95	44.81	44.11		44.64	44.66	0	4	0				
					47.09		1	1	5				
	47.95	47.90	47.57			47.57	1	4	0	47.61	0	-3	3

SD, reference cotton; M3, 3-month immersed cotton; MD, historic dyed cotton; MU, historic undyed cotton.

^a From Sugiyama et al.³⁰

^b From Mann et al.³¹

diffraction lines are resolved from either one or two cotton samples, resulting in a total of 27 diffraction lines of cellulose I. Most of the 27 diffraction lines obtained from the four cotton powder samples are comparable to those calculated from the traditionally accepted cellulose I monoclinic structure model (Table III). These resolved diffraction lines of cotton cellulose, then, are valid evidence of physical structure rather than being statistical artifacts of the fitting procedure. The differences noted in the diffraction lines between historic cotton fibers submerged for 133 years and the modern reference cotton may then be attributed to the structural alteration incurred due to the long-term storage context.²⁵

There are some differences between the diffraction line positions of the models of Sugiyama³⁰ and Mann³¹, ranging from 0.02° for the (111) and (040) lines to 0.45° for the (200) line. Sugiyama defines the parameters of the revised cellulose monoclinic model as $a = 0.801$ nm, $b = 0.817$ nm, c (chain axis) = 1.036 nm, and $\gamma = 97.3^\circ$. Mann's cellulose monoclinic model parameters are $a = 0.787$ nm, $b = 0.817$ nm, c (chain axis) = 1.034 nm, and $\gamma = 96.3^\circ$. It is also noticeable that most of the diffraction lines from the triclinic crystal structure are either overlapping with or close to those of the monoclinic structure.

In our work, a few diffraction lines resolved from residual peak fitting of the cotton powder diffraction

spectrum cannot be indexed on the basis of either of the two monoclinic structure models (e.g., lines at about 12.50, 15.30, and 32.70°). However, the diffraction line at 15.14–15.38° resolved from the three cotton samples is closer to the (011) line at 15.41° in the triclinic crystal structure model proposed by Sugiyama et al.³⁰ It would be interesting to compare the peak-fitting results with more diffraction lines obtained from the cellulose triclinic crystal structure model. The diffraction line at about 32.70° is also resolved consistently from three cotton samples, so it is hard to attribute this line as a statistical artifact. However, we could not index this line with the information currently available.

CONCLUSION

This study demonstrates that the residual peak-fitting procedure provided by a commercial software program (PeakFit®) can resolve a large number of overlapping diffraction peaks in the cellulose I powder diffraction spectra. The pairs of diffraction peaks identified by this peak-fitting process exhibit good reliability but with some degree of uncertainty, as do the 2θ positions obtained by repeated fittings from one sample as well as by fittings from multiple samples. In comparison with both the revised and the traditional cellulose I crystal structure models, most of the cotton cellulose I diffraction lines identified by the peak-fitting procedure can be related to valid physical structures, while only a few lines cannot be indexed. The peak resolved at about 15.3° from three different cotton samples may be attributed to a triclinic crystal structure component of cellulose I. Overall, the results of this study support the use of the residuals peak-fitting procedure to resolve overlapping peaks in powder camera diffraction spectra but some precautions are warranted as well. It would be beneficial to compare the results of this study with additional cellulose I structural information, and also with other peak-fitting analysis studies of natural cellulose fibers. The potential outcome of such research would be the determination of additional cellulose structural features that are not readily apparent in the X-ray spectra.

The authors thank Dr. John C. Mitchell for assisting with the X-ray diffraction experiment.

References

- Honjo, G.; Watanabe, M. *Nature* 1958, 181, 326.
- Ellis, K. C.; Warwicker, J. O. *J Polym Sci* 1962, 56, 339.
- Sarko, A.; Muggli, R. *Macromolecules* 1974, 7, 486.
- Hebert, J. J.; Muller, L. L. *J Appl Polym Sci* 1974, 18, 3373.
- Atalla, R. H.; VanderHart, D. L. *Science* 1984, 223, 283.
- Baker, A. A.; Helbert, W.; Sugiyama, J.; Miles, M. J. *J Struct Biol* 1997, 119, 129.
- Findenstadt, V. L.; Millane, R. P. *Macromolecules* 1998, 31, 7776.
- Kono, H.; Yunoki, S.; Shikano, T. *J. Am Chem Soc* 2002, 124, 7506.
- Wada, M.; Sugiyama, J.; Okano, T. *J Appl Polym Sci* 1993, 49, 149.
- Wellard, H. J. *J Polym Sci* 1954, 13, 471.
- Morton, W. E.; Hearle, J. W. S. *Physical Properties of Textile Fibers*; Textile Institute: Manchester, 1993.
- Bergbreiter, D. E.; Srinivas, B. J. *J. Am Chem Soc* 1992, 114, 7961.
- Grun, R. *Ancient TL* 1998, 16, 51.
- Franco, R.; Ma, J.-G.; Lu, Y.; Ferreira, G. C.; Shelnut, J. A. *Biochemistry* 2000, 39, 2517.
- Bhaskar, S.; Dobal, P. S.; Majumder, S. B.; Katiyar, R. S. *J Appl Phys* 2001, 89, 2987.
- Sokol, M. *Med Sci Monitor* 2001, 7 (3), 496.
- Vreeland, W. N.; Slater, G. W.; Barron, A. E. *Bioconjugate Chem* 2002, 13, 663.
- Clogston, J.; Rathman, J.; Tomasko, D.; Walker, H.; Caffrey, M. *Chem Phys Lipids* 2000, 107, 191.
- Kaszur, Z. J. *Appl Cryst* 2000, 33, 87.
- Manna, L.; Scher, E. C.; Alivisatos, A. P. *J Am Chem Soc* 2000, 122, 12700.
- Saxena, S. K.; Dubrovinsky, L. S. *Am Mineralogist* 2000, 85, 372.
- Breen, M. L.; Dinsmore, A. D.; Pink, R. H.; Qadri, S. B.; Ratna, B. R. *Langmuir* 2001, 17, 903.
- Tas, A. C. *Powder Diffr* 2001, 16, 102.
- Clark, S. M. *J Appl Cryst* 1995, 28, 646.
- Chen, R.; Jakes, K. A. in *Historic Textile and Paper and Polymers in Museums*; Cardamone, J.; Baker, M. T., Eds.; American Chemical Society: Washington, DC, 2000; pp. 38–54.
- Klug, H. P.; Alexander, L. E. *X-ray Diffraction Procedures*; John Wiley & Sons: New York, 1974.
- Krässig, H. A. *Cellulose: Structure, Accessibility and Reactivity*; Gordon and Beach Science Publishers: Philadelphia, 1993.
- Tripp, W. W.; Conrad, C. M. in *Instrumental Analysis of Cotton Cellulose and Modified Cotton Cellulose*; O'Connor, R. T., Ed.; Marcel Dekker, Inc.: New York, 1972; pp. 339–374.
- Mark, H. J. *Phys Chem* 1940, 44, 764.
- Sugiyama, J.; Vuong, R.; Chanzy, H. *Macromolecules* 1993, 24, 4168.
- Mann, J.; Roldan-Gonzalez, L.; Wellard, H. J. *J Polym Sci* 1960, 19, 165.
- Toraya, H. *J Appl Cryst* 2001, 34, 558.
- De Weijer, A. P.; Lucasium, C. B.; Buydens, L.; Kateman, G. *Anal Chem* 1994, 66, 23.