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WOODPULP CRYSTAL STRUCTURE AND ITS EFFECT ON NITROCELLULOSE PHYSICAL PROPERTIES

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The analysis of cellulose properties as determined by X-ray diffraction is described in this report. Results for several cellulose samples - both pulp and linter - are presented. A preliminary correlation between the measured properties of cellulose with properties of cellulose nitrate prepared therefrom is suggested.

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INTRODUCTION

The two major sources of cellulose for nitrocellulose (NC) production are cotton linters and woodpulp. Of these, cotton linters work well for both continuous or batch production of NC. However, availability and cost depend on weather fluctuations, so that in certain periods linters could be expensive and in short supply. In contrast, woodpulp offers a generally uniform, plentiful, less costly supply of cellulose. However, the physical and chemical characteristics of NC prepared from woodpulps have occasionally changed unexpectedly even though the pulps met the mil spec requirements for acceptance. These changes in properties resulted in a NC that was difficult to process into propellant. Stricter controls on the properties of NC are required with the development of the continuous nitration process and the new continuous propellant lines. At present, undesirable properties in a lot of NC are not detected until it is processed into propellant. With today's continuous nitration and propellant processing methods, the potential exists for the production of large quantities of NC that will be difficult to process. The cause of changes in NC properties is not known at present, but it is attributed to some uncontrolled variable in the woodpulp used to make the NC. This study was undertaken as part of a more comprehensive investigation of pulp variables in an attempt to identify causes of undesirable changes in NC characteristics.

Bracuti (ref 1) has reported on the initial phase of a study to determine the cause of button formation during nitration of sulfate pulp. Three possible causes were considered:

1. The presence of xylan and mannan.

2. The presence of phase II cellulose.

3. Variations in the degree of crystallinity of the cellulose.

In his report Bracuti described a computer program (refs 2 and 3) for the determination of percent crystallinity form X-ray diffraction measurements on cellulose. He demonstrated its utility by analyzing an X-ray diffraction measurement on filter paper as a test sample.

In the present work, we have extended and modified Bracuti's approach for the analysis of cellulose properties as determined by X-ray diffraction. In addition, we list results for selected samples of cellulose and correlate the physical properties of the cellulose with properties of NC prepared therefrom. Ultimately, this approach seeks to identify the causes of processing problems, and to assist in determination of corrective procedures.

RESULTS AND DISCUSSION

Cellulose Characterization

The determination of crystallinity in cellulose has been an active area of research for decades (reviewed in refs 4 and 5). Among the host of methods employed, X-ray diffraction, infrared, acid hydrolysis and water sorption have been described as most useful (ref 6). Results from these techniques indicate that the simple picture of cellulose as composed of two phases - highly ordered crystalline regions and completely disordered amorphous regions - is an oversimplification which has led to considerable controversy. That is, each technique has different sensitivity for each of the several degrees of order which occur in cellulose (ref 6). In the present work our concern is not with crystallinity per se but rather to develop a technique which allows a comparison of widely different types of cellulose for NC production. To achieve this, we follow Bracuti's X-ray diffraction approach (ref 1) with several important modifications.

The information obtainable by the X-ray diffraction technique in this application is considerable. Cellulose I, Cellulose II, amorphous cellulose and mannan and xylan differ crystallographically, so that each has a unique diffraction profile. Assuming that the interactions between different forms are negligible, the diffraction pattern for a composite sample can be treated as a superposition of the diffraction patterns of the individual components (ref 6). Furthermore, in a true "powder" sample, positions and relative intensities of peaks depend only on the structural type so that only the peak widths require determination (but see below).

In addition, X-ray diffraction has long been used as a probe of particle size ($\lesssim$ 1000 A) and elastic strains, both effects manifesting themselves through broadening of the diffraction lines. The separation of these two effects according to peak shape is an ongoing area of research (ref 9) in which several possibilities for peak profiles have been used. In our analysis we follow Hindelah and Johnson (ref 3) who assign the particle size effect broadening a Cauchy profile and the distortion broadening a Gaussian form.

The details of the X-ray diffraction measurements and the fitting procedure for three linter and four pulp samples are described in the next section and the Experimental Section. Important differences which contrast our approach from that of Bracuti (and Hindeleh and Johnson, refs 2 and 3) may be summarized as follows:

1. In the Bragg scattering angle range of interest $10° < 20_B < 30°$), four Cellulose I reflections are specifically included rather than three.

2. The amorphous fraction profile is described by a single analytical function obtained by fitting the X-ray pattern of a ball-milled sample (refs 6, 7, and 8) rather than by an arbitrary polynomial expansion, the coefficients of which are newly determined for each sample.

3. An approximate profile for Cellulose II content is explicitly included.

These modifications to Bracuti's method were made because in systems as complex as cellulose one wishes to minimize the number of adjustable parameters so that false minima are not obtained in the fitting procedure; also, the explicit inclusion of the appropriate profiles follows current trends in this field (ref 8).

X-RAY DIFFRACTION ANALYSIS OF CELLULOSE SAMPLES

Experimental

Cellulose I is monoclinic in structure with lattice parameters a = 8.17A, b = 10.34A, c = 7.85A and β = 83.6°; Cellulose II is also monoclinic with a = 7.92A, b = 10.34A, c = 9.08A and β = 62.7° (ref 15). There is some controversy concerning the exact space groups (ref 10); however, this is not pertinent to the present study. In both forms I and II, the cellulose fibers are parallel to the b-axis. Within each fiber, the plane of each anhydroglucose ring is parallel to the (002) planes (Cellulose I) or parallel to the $(10\bar{1})$ planes (Cellulose II). Within the context of NC production, the structure of Cellulose II is less open than that of Cellulose I so that solvent penetration is more restricted (ref 1). The X-ray diffraction profiles of forms I and II cellulose have been measured separately and reported in the literature (refs 3 and 7, and citations therein). Profiles for these forms in our region of interest are shown in figure 1A and B.

Amorphous cellulose was obtained by vibratory ball-milling a sample of cotton-linter cellulose (following refs 6 and 7). The X-ray diffraction profile for our sample is shown in figure 1C. It is important to note that the contour exhibits some structure and could not be reproduced by a polynomial form of the type proposed in reference 3.

Mannan and xylan have been extensively studied because of their relationship to cellulose. However, powder diffraction profiles for both of these materials were not readily available. Consequently, they were not explicitly included in our analysis. A schematic representation of the mannan and xylan X-ray patterns, as obtained from tables in the literature (refs 11 and 12), is shown in figure 1D.

The X-ray diffraction measurements were made with a Norelco diffractometer equipped with a scintillation counter with 1/2° slits for incident and diffracted beams. CuK_α radiation filtered with nickel-foil was used. For the present work, we have not made corrections for air scatter, etc., since our principal emphasis here is to show the feasibility of cellulose characterization as it relates to NC production.

Least-Squares Fits

The principal peaks in the X-ray diffraction pattern of Cellulose I occur in the $10^0 \leqslant 2\theta_B \leqslant 30^0$ for $\lambda_{X\text{-ray}} = 1.542$ A. For partially ordered fibers, four peaks should be observable as listed in table 1. Three peaks corresponding to Cellulose II occur in the region of interest, the peak positions of which are also listed in table 1.

In the most general case, (neglecting the possible presence of mannan and xylan) the diffraction pattern for a composite Cellulose I/Cellulose II/amorphorous cellulose sample can be represented as

$$I(\theta) = B(\theta) + C(\theta) + \Sigma\, Q_i(\theta) \qquad (1)$$

where θ is the scattering angle, $C(\theta)$ is the profile for amorphous cellulose, $B(\theta)$ is the profile for the background, and the $Q_i(\theta)$ are the profiles for each of the distinct Bragg peaks arising from Cellulose I and II. The $Q_i(\theta)$ are given analytically by

$$Q_i(\theta) = fA_i \exp\left\{-\ell n2\left[\frac{2(\theta-\theta_i)}{W_i}\right]^2\right\} + \frac{(1-f)A_i}{1+[2(\theta-\theta_i)/W_i]^2} \qquad (2)$$

where A_i is the peak height, θ_i is the peak position, W_i is the full width at half maximum (FWHM) of the composite Gaussian/Cauchy peak profile and f is the fraction of Gaussian component of the total profile.

In principle, the background could be represented by a polynomial of arbitrary degree and each of the 21 parameters (7 peaks x 3 parameters) of the Cellulose I and II peaks, plus the Gaussian fraction and the amorphous profile amplitude could all be extracted from a fit to a given sample profile. In practice, this approach is very risky because of the high probability of multiple, essentially equivalent minima in the least-squares refinement.

We have reduced the number of adjustable parameters in the following way. First, since the structures of crystalline Cellulose I and II are well known, within an instrumental zero correction the positions of peaks are determined. Therefore, we fit only a single peak position, i.e., the P_i of the prominent (002) reflection of Cellulose I, and assign fixed angular differences between the (002-I) reflection and the other six that are included in the refinement. In addition, because in no sample studied were Cellulose II peaks prominent, relative intensities for the three relevant peaks were assigned from data presented in reference 7. For the same reason, the FWHM's of the Cellulose II peaks were fixed at a single value consistent with Cellulose I parameters.

The θ-dependence of the amorphous cellulose profile was obtained independently from a vibratory ball-milled sample of cotton linter. The profile was fit very well analytically with a function which included two broadened Cauchy/Gaussian contributions, the parameters of which are given in table 2. From inspection of the diffraction patterns from 5° to 35°, we chose the background to be of the form $B_1 + B_2\theta$ where B_1 and B_2 were determined from the data independent of the computer fitting.

With the several constraints described above, the diffraction profile for a given sample takes the analytical form:

$$
\begin{aligned}
I(\theta) = {} & BKG + P_A C(\theta) + P_{II} C_{II}(\theta_{002\text{-}I}, f) \\
& + \Sigma \left\{ fA_i \ \exp\left[-\ell n2 \ \frac{2(\theta-\Delta_i-\theta_{002\text{-}I})^2}{W_i} \right] \right. \\
& \left. + \frac{(1-f)A_i}{1 + [\ 2\ (\theta - \Delta_i - \theta_{002\text{-}I})/W_i\ ]^2} \right\} \qquad (3)
\end{aligned}
$$

In equation 3 the Δ_i are fixed differences between the adjusted parameter for the peak position of the Cellulose I (002) reflection and the three other Cellulose I reflections in the region of interest. P_A and P_{II} are adjusted amplitude parameters for the amorphous and Cellulose II profiles respectively. Values for the various fixed parameters are given in table 1.

The least-squares fitting program is one in which the nonlinear problem is linearized in the conventional way (ref 13).

X-Ray Results

Several observations can be made concerning the results summarized in tables 3 and 4. In general, it should be noted that each spectrum is arbitrarily normalized so that differences in the absolute values of the amplitudes, e.g., A(002-I), have no particular significance when comparing one sample to another. Similarly, differences in θ(002-I) from sample to sample are attributed to zero correction differences arising from sample geometry. It should also be mentioned that the conventional χ^2 goodness of fit (ref 14) is typically ~3 for the linter samples and ~1.7 for the pulp samples. This systematic difference probably occurs because the linter samples exhibit relatively sharp features while the pulp samples exhibit broader, easier-to-fit features.

The reliability of the obtained parameters can, to some degree, be inferred from the figure of merit values introduced in the previous section. It should be noted that the weighted-mean standard deviations listed in tables 3 and 4 are in themselves a measure of reliability. For example, the standard deviation of the amorphous amplitude of sample 4 (table 4) is 130% of the parameter itself. One cannot place very much confidence in this parameter even though the figure of merit is 0.2. Conversely, the obtained FWHMs of the (002-I) reflections for all samples have standard deviations of ~1% of the parameter value and figures-of-merit no greater than 1.5. This indicates that a high degree of confidence can be placed in the FWHM values. The only parameter that consistently shows a wide variation with region of spectrum fitted (i.e., 11°-25° vs 11°-29° for the same sample) is the fraction of Gaussian in the Gaussian/Cauchy/Bragg peak profile. Although this parameter is interpreted to be a measure of the ratio of internal strain to particle size effects, this point is somewhat open to question (ref 9), and this aspect will not be considered here.

Qualitatively, the following distinctions can be made among the various samples:

1. The linter samples show no evidence of the presence of Cellulose II whereas two of the pulp samples (Nos. 6 and 7) show clear evidence of substantial Cellulose II content.

2. Linter samples Nos. 1 and 2 appear to be virtually identical in all respects, whereas No. 3 exhibits a much higher relative amorphous content and much broader FWHMs for all peaks consistent with the notion of smaller regions of crystallinity.

3. The present results for the linter samples and those in the literature (ref 3 and citations therein) suggest that the FWHMs of the (101-I) and (10$\bar{1}$-I) reflections are comparable. The values for W(10$\bar{1}$-I) of samples Nos. 4 and 7 are much larger than the W(101-I) values for the same samples. This could be the result of the presence of mannan and/or xylan, reflections from which could result in apparent broadening of the (10$\bar{1}$-I) reflection (see schematic diffraction patterns in the Experimental Section.)

Quantitatively, one can define an index of crystallinity for these measurements as the total intensity contained in the amorphous portion of the spectra to the integrated intensity of the cellulose I (or II) reflections. However, because of preferred orientation effects in the sheet samples examined, reliable integrated intensities cannot be extracted. On the other hand, peak widths as extracted from the two fits for a given sample show excellent consistency so that some measure of particle size can be inferred.

Following reference 3, crystallite size values in a particular direction [hkl] can be determined from the Scherrer equation:

$$L(hkl) = K\lambda/\cos\theta \; d(2\theta)$$

where L is the dimension in the [hkl] direction, K=1, λ is the wavelength, θ is the Bragg angle and $d(2\theta)$ is the FWHM of the peak in radians. Crystallite dimensions for the samples studied are summarized in table 5. The three reflections considered all correspond to directions perpendicular to the fiber axis (i.e., *b* direction), so that one cannot infer the three-dimensional crystallite size. Nevertheless, it is clear that linter sample No. 3 is qualitatively different from Nos. 1 and 2. The somewhat low values for L(10$\bar{1}$) of pulp samples Nos. 4 and 7 may arise from a true particle size difference, but more probably are due to the presence of mannan and/or xylan, as mentioned previously.

NC Properties

All the pulps were nitrated in the laboratory with a mixture of nitric and sulfuric acids using a small scale batch nitration procedure. The nitrations and subsequent stabilizations were carried out to approximate plant processing conditions as closely as possible. The conditions of nitration and stabilization are given in table 6.

The pulps were nitrated to yield Grade B nitrocellulose, which has a minimum of 13.35% nitrogen and Grade A, Type II, nitrocellulose, which has 12.6% ± 0.15% nitrogen as required in MIL-N-244A. The NC molecular weight distributions (MWD) and molecular weight values were determined using a Waters Model 200 gel permeation chromatograph. Operating conditions are given in table 7.

In order to limit as much as possible the effects of other pulp variables, such as wood species, pulping process conditions, and the type of pulp, this study was made on pulps that came from the same source, mill, and geographic location. The wood fed to the pulp mill is as uniform as possible. Each of the pulps studied was processed under different conditions to achieve specific chemical and physical properties. The effect of these processing conditions on the variability of the amount and type of crystal structure present in the pulps was determined using X-ray diffraction techniques described in this report. The exact conditions used in processing each of the pulps is unknown. This is information that the supplier will not release. Therefore, the only definite knowledge concerning the pulps is their physical and chemical properties, method of pulping, and general process procedures.

The pulps used in this part of the study were from the Buckeye Cellulose Corporation. They are sulfate pulps made from 100% southern pine. Several are prehydrolyzed sulfate pulps and each received a bleach treatment. Each pulp was processed under different conditions as is evidenced by the differences in their physical and chemical properties given in table 8. The properties of NC derived from these pulps are also given in the table. A comparison of the properties of the NC samples and their MWD curves (fig. 2) shows that there is a significant difference in the MWD and related properties for the Grade B nitrocellulose. The pulp samples, E-1 and N-7, differ greatly in their alpha and pentosan content, but their Grade B nitrocellulose characteristics do not vary greatly and their MWD curves are similar. If the variations in the alpha and pentosan content were responsible for changes in NC molecular weight distribution, the MWD's for NC samples from N-7 (#5 of table 9) and N-5 (#7) would be expected to be fairly similar since they do not vary greatly in alpha and pentosan content. However, they are different and the cause is not attributable to the variation in alpha and pentosan content. The X-ray diffraction study of N-5 and N-7 has shown that these pulps vary in the type of cellulose structure present (sample E1 was not studied with X-rays). N-5 has a significant amount of the Cellulose II crystal structure. N-7 has none or such a small amount that it was not detected. The differences in the physical properties and MWD of Grade B nitrocellulose from N-7 and N-5 is attributed to the presence of Cellulose II crystal structure in the fibre. It does not appear to affect the properties of the Grade A nitrocellulose from these two pulps. From discussions with the supplier, the only basic difference in the production of these two pulps is in the use of a final strong caustic extraction on the N-5 pulp to increase purity and raise the alpha content. It, therefore, appears that this purification process is causing partial mercerization of the cellulose.

The source and designation of the three linter and four pulp samples examined are listed in table 9. The linter samples (excluding the filter paper) had the fibrous morphology of cotton; the pulp samples were in sheet form (~ 1.5 mm thick). Both types were examined in reflection geometry with no special effort made to minimize preferred orientation. This had the consequence that the ratios of integrated peak intensities could not be fixed and absolute crystallinity as such, could not be extracted. This is discussed further in the last section.

Representative X-ray diffraction patterns for one linter and two pulp samples are shown in figure 3. The various individual components which comprise the total spectra, as derived from the least-squares fits, are indicated in the figures. The detailed procedure for the least-squares fits was the following: For each sample, a linear (sloping) background was estimated from the data for the 5° to 35° angular range. This was then included but not adjusted in the actual spectral fits. As described in the Experimental Section, only the (002) reflection of Cellulose I was explicitly adjusted; all other peak positions were fixed relative to this peak. In addition, the width of the (021) reflection of Cellulose I was fixed at a value approximating the (002) Cellulose I width.

Two independent least-squares fits of each sample spectrum were performed: one for the region 11° to 25°; the other for the 11° to 29° range. The reason for this was the fact that some spectra showed an indication of very weak peaks in the 26° to 29° region. In the fitting procedure, this had the effect of artificially enhancing the Cauchy contribution to the peak profiles. As a consequence, parameters obtained from fits to the 11° to 25° region of certain spectra when used to reproduce the full 11° to 29° spectrum sometimes gave very poor agreement to the measurements for the 26° to 29° regions.

For completeness, and to illustrate the reliability of the least-squares fits parameters, the following procedure was decided on: The least-squares fits parameters for the linter and pulp samples are summarized in tables 3 and 4. The parameter values and indicated standard deviations are each the weighted mean (ref 14) of the values from the two independent fits to each sample spectrum. In addition, below each parameter values is shown a figure of merit (FM, defined as $FM = (PAR - \mu)/\sigma)$. Here, PAR is the parameter value from the 11° to 29° fit, μ is the weighted-mean parameter value, and σ is the weighted-mean standard deviation. The significance of the figure of merit is that it shows quantitatively, relative to the standard deviation, the difference in parameter values obtained from the two independent least-squares fits. Values of FM of ~ 1, or less, represent good consistency in a statistical sense; values of FM of ~ 2, or greater, indicate that the spectral region from 26° to 29° has an inordinate importance for the parameter in question.

Finally, it should be mentioned that in the fitting procedure, the best fit to a diffraction pattern might be obtained with a negative (unphysical) value for a parameter. When this occurred, that parameter was set to zero and held fixed.

CONCLUSIONS

Because of preferred orientation effects in the cellulose samples and approximate profiles used for component phases, the present work has not exhausted the potential of X-ray diffraction for characterization of cellulose samples for NC production. Nevertheless, based upon the data presented, it can be concluded that the diffraction technique reveals significant differences in the physical properties of various woodpulps. More importantly, the relation of these properties to those of nitrocellulose in the context of propellant processing and mechanical properties should be investigated further.

In a broader scientific sense, the literature reviewed in the course of this study indicates that some fundamental difficulties exist in relating crystallinity as inferred, for example, from X-ray diffraction with that from infrared, deuteration measurements. In future work in this area, neutron diffraction, which is analogous to X-ray diffraction but is sensitive to deuteration, offers a possibility for resolving and understanding apparent differences.

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Table 1. Parameters for Cellulose I and II for equation 3.

Reflection	$2\theta_B$[a]	Δ_i	A_i	θ_i	W_i
(101-I)	14.845°	7.953°	--[b]	F1[c]	--
$(10\bar{1}$-I)	16.614°	6.184°	--[b]	F1	--
(021-I)	20.609°	2.189°	--[b]	F1	F2[d]
(002-I)	22.798°	0°	--[b]	--	--
(101-II)	12.327°	10.471°	80[e]	F1	2.0°[f]
$(10\bar{1}$-II)	20.191°	2.607°	260	F1	2.0°
(002-II)	22.032°	0.766°	300	F1	2.0°

---

[a] From ref 15 for $\lambda = 1.5418$A.

[b] Adjusted freely in least-squares fit.

[c] Fixed by Δ_i relative to θ(002-I)

[d] Fixed after initial fit to ~W(002-I).

[e] Relative intensities from ref 7.

[f] Arbitrarily fixed.

Table 2. Parameters for amorphous cellulose.

	f	A_l	θ_i	W_i
$Q_i(\theta)$[a]	0.348[b]	75.3	16.16°	3.316°
$Q_2(\theta)$	0.348	263.5	21.076°	6.357°

---

[a] $C(\theta)$ of eq. 3 = $Q_i(\theta) + Q_2(\theta)$ of eq. 2.

[b] Parameters obtained from least-squares fit to $C(\theta)$ to ball-milled sample data.

Table 3. Least-squares parameters for linter samples.

Parameter	Sample 1	Sample 2	Sample 3
Amorphous amplitude, P_A[a]	1.34±0.10 [0.8][b]	1.23±0.13 [1.5]	2.01±0.17 [1.5]
Cellulose II amplitude, P_{II}	0[c]	0	0
Gaussian fraction, f	0.20±0.026 [1.1]	0.30±0.03 [3.8]	0.59±0.04 [2.0]
A(002-I)	8325±70 [0.4]	8564±70 [1.0]	5588±57 [0.4]
θ(002-I)	23.55±0.004° [0]	23.70±0.004° [0]	23.49±0.007° [0.7]
W(002-I)	1.29±0.013° [0.3]	1.40±0.013° [1.5]	1.88±0.02° [0.5]

---

[a] Parameter notation of eq. 3.
[b] Figure of Merit as described in text.
[c] Parameter values without standard deviation were fixed in the least-squares refinement.

Table 3 (Contd)

Parameter	Sample 1	 2	 3
A(101-I)	3238±41 [0.2]	2545±38 [0.7]	1587±30 [0.6]
W(101-I)	1.62±0.03° [0.2]	1.56±0.03° [0]	2.15±0.05° [0.7]
A(10$\bar{1}$)-I)	2012±40 [0.02]	1843±36 [0.02]	1000±36 [0.7]
W(10$\bar{1}$)	1.44±0.05° [0.01]	1.57±0.05° [0.08]	1.81±0.09° [0.2]
A(021-I)	0	175±37 [1.1]	302±43 [0.3]
W(021-I)	1.5°	1.5°	1.8°

Table 4. Least-squares parameters for pulp samples.

	Sample			
Parameter	4	5	6	7
Amorphous amplitude, P_A[a]	0.16±0.21 [0.2][b]	0.44±0.15 [0.9]	0.75±0.14 [1.7]	0.06±0.1 [0.8]
Cellulose II amplitude, P_{II}	0.15±0.16 [0.2]	0[c]	0.87±0.13 [0.5]	2.21±0.1 [1.1]
Gaussian fraction, f	0.17±0.03 [4.2]	0.20±0.03 [3.5]	0.28±0.04 [5.7]	0.22±0.03 [1.8]
A(002-I)	5100±57 [1.0]	5069±49 [1.4]	4562±48 [1.5]	3597±34 [0.5]
θ(002-I)	23.45±0.01° [0]	23.44±0.01° [0.9]	23.64±0.007° [0]	23.60±0.007° [0.7]
W(002-I)	1.94±0.02° [0.2]	1.82±0.02° [0.26]	1.74±0.02° [1.4]	1.73±0.02° [0.5]

---

[a] Parameter notation of eq. 3.
[b] Figure of Merit as described in text.
[c] Parameter values without standard deviations were fixed in the least-squares refinement.

Table 4 (Contd)

Parameter	Sample 4	 5	 6	 7
A(101-I)	1190±26 [0.7]	1383±24 [0.3]	1204±24 [1.0]	1026±20 [0.24]
W(101-I)	2.22±0.06° [0.9]	1.92±0.05° [1.1]	1.84±0.05° [0.6]	1.96±0.05° [0.7]
A(10$\bar{1}$-I)	1429±35 [0.6]	1399±28 [0.9]	1173±25 [1.1]	1079±21 [0.3]
W(10$\bar{1}$-I)	2.68±0.10° [0.5]	2.11±0.07° [0.1]	2.10±0.08° [0]	2.33±0.08° [0.7]
A(021-I)	196±56 [0.7]	101±39 [0.4]	59±43 [0.8]	0
W(021-I)	2.0	1.9	1.8	1.8

Table 5. Crystallite dimensions from peak widths.

Sample	L(101)[a,b]	$L(10\bar{1})$	L(002)
1	55±0.6A	62±1.1	70±2.4
2	57±0.5	57±1.1	64±2.0
3	41±0.4	49±1.1	48±2.4
4	40±0.4	33±0.9	46±1.7
5	46±0.5	42±1.1	50±1.7
6	48±0.6	42±1.1	52±2.0
7	45±0.5	38±1.0	52±1.8

---

[a] From $L(hkl) = \lambda/\cos\theta d(2\theta)$, where θ is from table 2.
[b] Instrumental resolution neglected.

Table ~~6~~. Nitration conditions.

Temperature: 34°C

Time: 24 min

Mixed acid: 640 g

Pulp: 16 g (dried under vacuum @ 70°C)

	NC-13.4%N	NC-12.6%N
H_2SO_4	63.01	62.04
HNO_3	28.46	21.96
H_2O	8.53	16.00
Stabilization		
Acid boil	60 hr	24 hr
Acidity as H_2SO_4	0.3%	0.3%
Neutral boil (2)	5 hr	8 hr
Soda boil (0.025% Na_2CO_3)	4 hr	4 hr
Neutral boil (2)	2 hr	2 hr

All pulps were fluffed in a blender to eliminate effect of pulp sheet characteristics on nitration.

Table 7. GEL permeation chromatography.

Conditions used for the gel permeation studies are as follows:

Waters GPC Model 200
Solvent: Reagent grade acetone
Columns: Porasil

Type	MW exclusion limit
1500X	$1.5x10^6$
1000X	$1.0x10^6$
400X	$4.0x10^5$
250X	$2.5x10^5$
60X	$6.0x10^4$

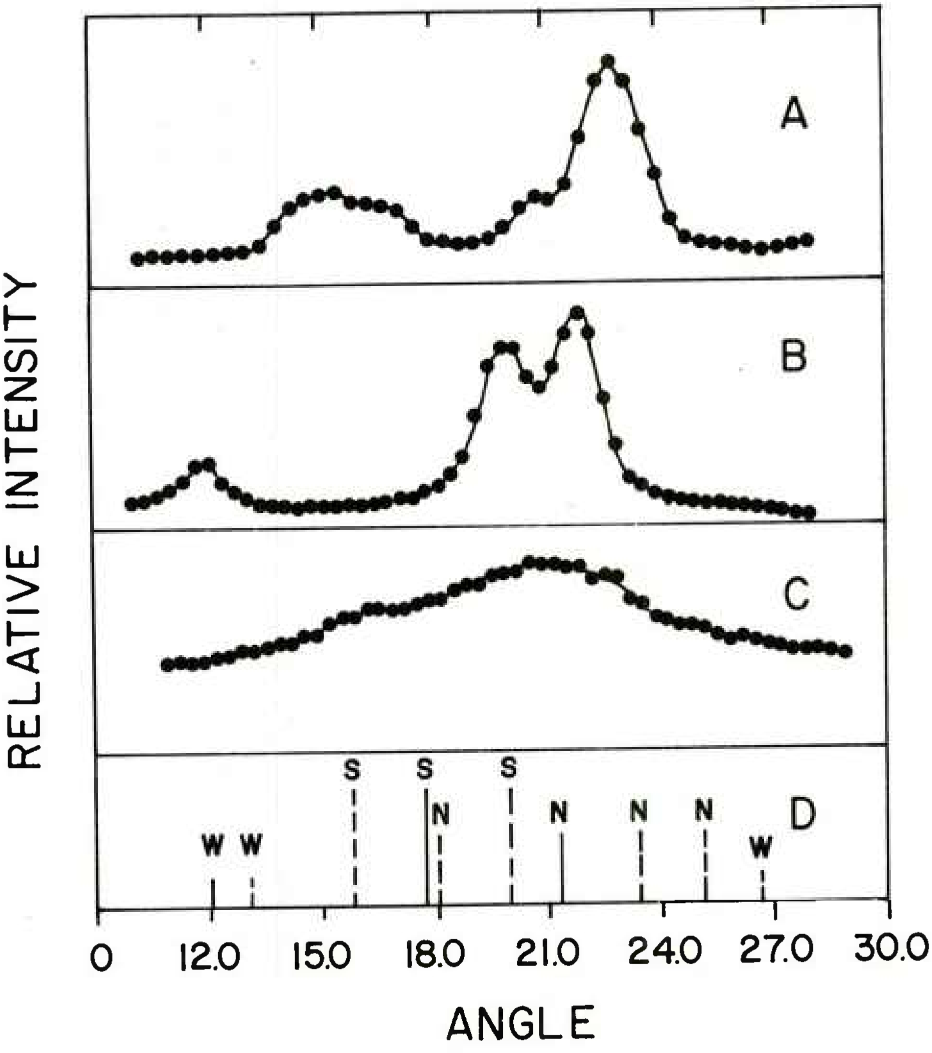
Flow rate:	1 mL/minute
Reference:	Static
Temperature:	Room temperature
Injection:	2 mL

Table 8. Chemical properties.

Properties	Pulp description	Buckeye E-1 southern pine sulfate		Buckeye N-7 southern pine prehydrolyzed sulfate		Buckeye N-5 southern pine prehydrolyzed sulfate	
NC	Nitrogen (%)	13.42	12.71	13.44	12.57	13.48	12.70
	Viscosity (sec)	183.2	188.0	185.5	146.6	161.1	140.4
	Intrinsic vis	0.330	0.400	0.340	0.275	0.300	0.290
	DP	206	308	234	220	190	212
	Mw	263,030	285,777	205,616	219,745	192,768	199,457
	Mn	51,435	65,568	50,491	59,258	60,602	61,096
Pulp	Viscosity (cps)	14.00		11.00		10.5	
	Alpha (%)	89.0		95.7		97.7	
	Pentosan (%)	7.4		1.8		0.6	
	Density (g/cm^3)	0.57		0.65		0.75	

Table 9. Samples.

Sample No	Type	Source/description
1	Cotton linter	Whatman #42 ashless filter paper
2	Cotton linter	NS-70 sheet
3	Cotton linter	Hercules lot No. 5718
4	Wood pulp	Alaska lumber bleached sulfite
5	Wood pulp	Buckeye S.R.WP-2803 (N-7)
6	Wood pulp	International paper (BH-S)
7	Wood pulp	Buckeye S.R. WP-2803 (N-5)



In 1D, the dashed lines represent mannan, the solid lines xylan; W=weak, N=normal, S=strong.

Figure 1. X-ray diffraction patterns for cellulose I (A, ref 16), cellulose II (B, ref 7), amorphous cellulose (C, this work) and mannan and xylan (D, refs 11 and 12).

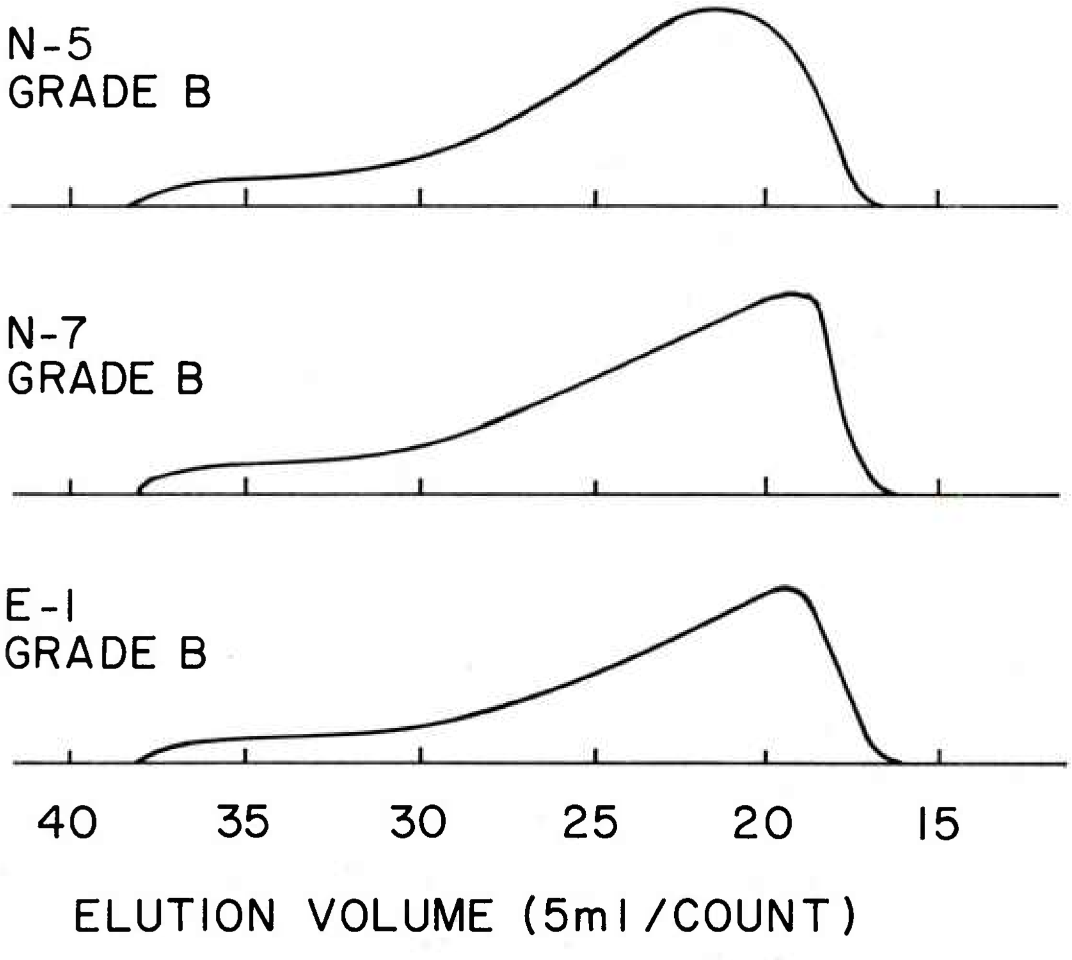
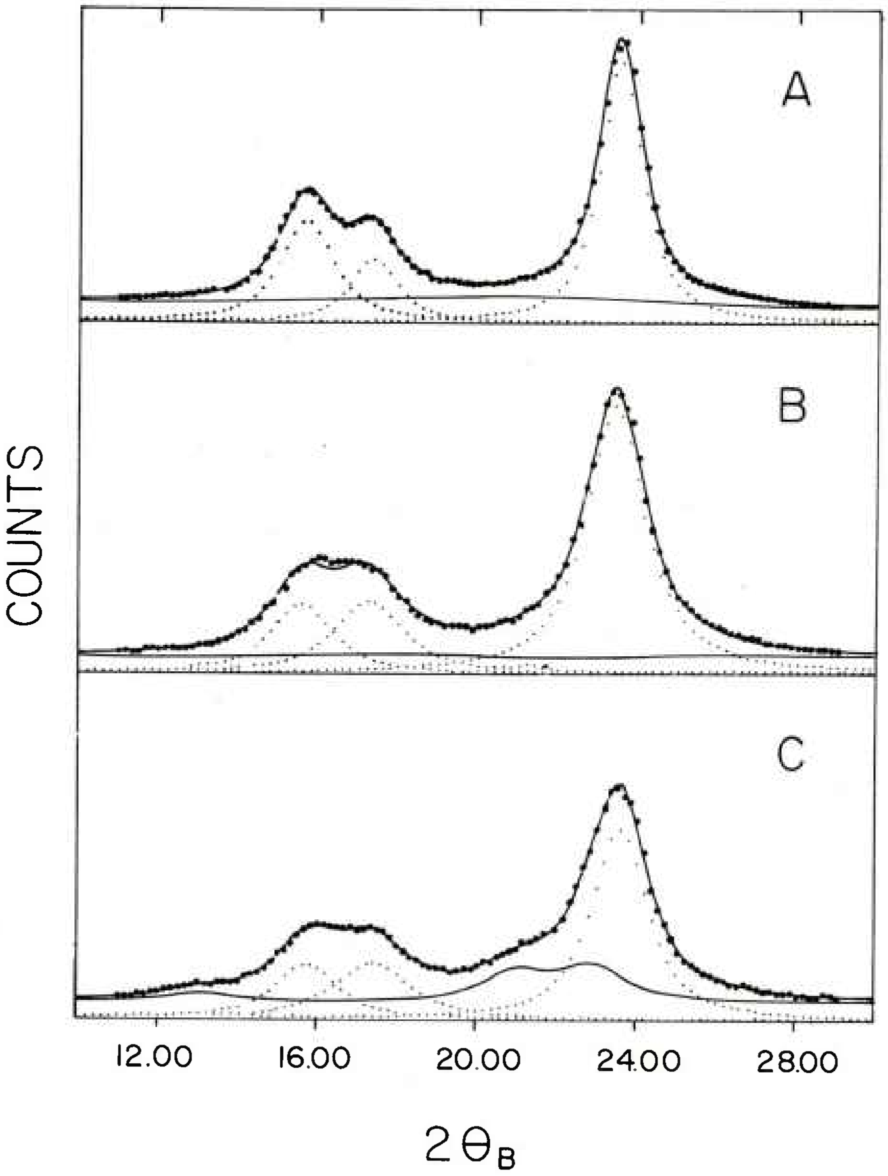


Figure 2. Nitrocellulose molecular weight distribution.



The solid line through the data points represents the least-squares fit value with all contributions. The symmetric dotted peaks correspond to the fitted cellulose I Bragg peak profiles. The slowly varying solid line going across the bottom of each figure is the composite profile of background, amorphous and cellulose II contributions.

Figure 3. X-ray diffraction data and least-squares fit results for cellulose samples 1(A), 5(B), and 7(C).

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