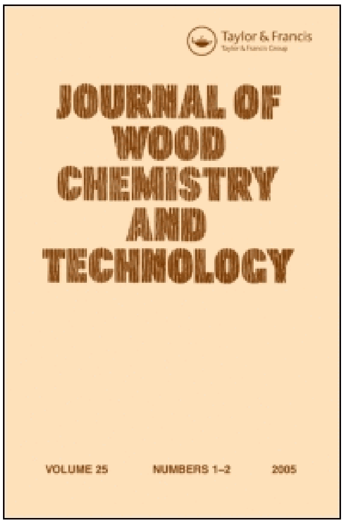

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Estimation of Cellulose Crystallinity Using Fourier Transform-Infrared Spectroscopy and Dynamic Thermogravimetry

T. P. Schultz[a]; G. D. McGinnis[a]; M. S. Bertran[b]
[a] Mississippi Forest Products Utilization Laboratory Mississippi State University, Mississippi, Mississippi State [b] Department of Agricultural and Chemical Engineering Colorado State University, Fort Collins, Colorado

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ESTIMATION OF CELLULOSE CRYSTALLINITY USING FOURIER TRANSFORM-INFRARED SPECTROSCOPY AND DYNAMIC THERMOGRAVIMETRY

T. P. Schultz and G. D. McGinnis
Mississippi Forest Products Utilization Laboratory
Mississippi State University
Mississippi State, Mississippi 39762

M. S. Bertran
Department of Agricultural and Chemical Engineering
Colorado State University
Fort Collins, Colorado 80523

ABSTRACT

Dynamic thermogravimetry (tga), differential thermogravimetry (dtg), and Fourier Transform-Infrared Spectroscopy (FT-IR) were performed on a variety of celluloses with different cyrstallinities. The data were compared to the crystallinity indices (C.I.) determined by X-ray diffraction. Highly significant correlations (99.9%) included: a positive linear correlation of the maximum dtg value; a logarithmic relation of the temperature at which the initial 10% weight loss occurred; and a linear relationship of three FT-IR absorbance ratios (1108/1091 cm^{-1}), (1430/1403 cm^{-1}), and (1459/1403 cm^{-1}). A significant logarithmic correlation was also found for the temperature at maximum dtg for cotton linter samples. These relationships are discussed.

INTRODUCTION

Researchers have used many different techniques to measure the crystallinity of cellulose, with the standard method being X-ray diffraction. A number of scientists have examined alternate methods to determine cellulose crystallinity. These alternate techniques often require a long analysis time, and/or give imprecise and nonreproducible results.

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Thermogravimetric Analysis

Thermogravimetric (tga) analysis has been extensively used by many carbohydrate chemists because it is a relatively simple, rapid, and straightforward analytical procedure. It should be remembered, however, that tga is affected by ash content and is also autocatalyzed by the formation of carbon dioxide and carboxylic acids. In addition, the rate of weight loss is not equal to the rate of the pyrolytic reactions.

Cabradilla and Zeronian[1] examined the dynamic tga results obtained when cellulose samples with different C.I. were pyrolyzed in nitrogen. They reported that as the crystallinity increased, the percent char formed decreased, the temperature at which the initial weight loss first occurred increased, the temperature at the maximum rate of weight loss increased, and the amount of levoglucosan produced increased. Lipska and McCasland[2] derivatized and decrystallized several cellulose samples. They also reported that the amount of residual char decreased as the cellulose crystallinity increased. In addition, they reported that the rate of weight loss was inversely correlated to crystallinity. Basch and Lewin[3] believed that only the amorphous regions are affected during the initial stage of weight loss. They reported that both cellulose crystallinity and orientation affected the rate of pyrolysis. Kato and Komorita[4] found that the pyrolysis of tobacco cellulose at 200° to 300°C resulted in a greater yield of furans from the amorphous than from the crystalline regions. They also noted a lower threshold temperature for less-crystalline cellulose, as did Cabradilla and Zeronian.[1]

In apparent disagreement with Cabradilla and Zeronian[1] and Lipska and McCasland[2], Weinstein and Broido[5] reported that char formation will occur preferentially in the ordered rather than the disordered regions of natural cellulose. Broido and co-workers[6] found that crystalline cellulose showed a large decrease in D.P. before any apparent weight loss occurred. Amorphous cellulose showed a more gradual D.P. change. X-ray analysis showed that amorphous cellulose became partially crystalline during pyrolysis.

Infrared Spectroscopy

Tsuboi[7] used polarized radiation to examine the IR spectra of cellulose. Using the polarizing technique along with deuteration, he was able to assign a number of bands. Liang and Marchessault[8-10] did an in-depth study on the IR analysis of cellulose. They used polarized light, as did Tsuboi[7], and also examined the differences between celluloses I and II. They assigned a number of bands using the polarization technique and reported differences in the spectra between cellulose I and II.

O'Connor and co-workers[11-13] also did a comprehensive study on the IR analysis of cellulose. They examined how crystallinity, cross-linkages, pyrolysis, and oxidation affected IR spectra. They suggested using an IR absorbance ratio (1372/2900 cm^{-1}) to estimate the crystallinity of celluloses I and II. Using this ratio, Nelson and O'Connor[13] reported a correlation coefficient

(R) of 0.860 between the IR ratio and X-ray analysis. Basch and Lewin[3] also correlated the crystallinity of cellulose using this IR ratio and X-ray diffraction and reported a R value of 0.882.

Solid polymeric samples have often been analyzed using KBr pellets. A major problem of using pellets to study polymers is that the IR light is scattered by the polymeric material. Since all the IR light is continuously passing through the sample with FT-IR, the light is partially scattered and this results in a spectrum with a sloping baseline.

This disadvantage can be avoided in Diffuse Reflectance Infrared Fourier Transform (DRIFT) Spectroscopy.[14-15] In DRIFT, a small amount of sample is mixed with a relatively large amount of a material of high reflectance but low interference, such as KCl or KBr. The matrix mixture is then placed into a sample cup. IR light is directed into the sample cup, where it is reflected and takes multiple paths. During some of the paths the IR light encounters some sample, where it either passes through (transmission) or is reflected by the sample. The IR light eventually exits from the matrix, and is refocused. By refocusing the IR light, a sloping baseline is avoided. Another advantage is that DRIFT samples are easier to prepare than KBr pellets. The DRIFT spectra is a combination of both transmission and reflection spectra, while spectra from KBr pellets are essentially transmission spectra.

Samples in which no KCl matrix is used can be run by DRIFT. However, poor spectra are obtained, especially when strongly absorbing samples such as wood are examined.

MATERIALS AND METHODS

Cellulose samples from four sources were used:

1) Cotton linter pulp (SR-210, Buckeye Cellulose Corp.), 99% α cellulose content and a D.P. of 2400;[16]
2) Foley Fluffs wood pulp (SR WP-2894, Buckeye Cellulose Corp.), from southern pine Kraft pulp, 97.7% α cellulose content and a D.P. of 1500;[16]
3) Whatman CF-11;
4) Avicel.

The cotton linter and Foley Fluffs samples were ground in a Wiley mill to pass a 0.5 mm screen, then ground in a ball mill for various lengths of time. Duplicate X-ray diffractograms of all samples were taken using a General Electric Model XRD-6 diffractometer. The X-ray diffractograms were analyzed for crystallinity by the empirical procedure of Segal et al.[17], and were used by Bertran and Dale[16] to determine enzymatic hydrolysis rates.

A Perkin-Elmer TGS-2 thermobalance controlled by a System 4 microprocessor was used for the tga and dtg analyses. The microprocessor was equipped with a first derivative computer. The nitrogen flow rate was 40 cm/min., and the sample size was approximately 3.0 mgs. Samples were heated to 110°C and held for six minutes to determine the sample dry weight and zero the instrument. The sample was then heated to 600°C at a rate of 10°C/min. All samples were run in duplicate, with the average result reported. The ash content was estimated by pyrolyzing the sample at 600°C for 20 minutes in air using the TGS-2. This method was used since only a small amount of each cellulose was available.

FT-IR spectra were obtained using a Nicolet 20DX equipped with a liquid-nitrogen cooled MCT detector. The samples were mixed with KCl in a 1:40 ratio (sample:KCl), and then ground using a Wig-L-Bug. A Harrick 2D, center-focus diffuse reflection (DRIFT) cell was used, with 600 scans per sample collected. The sample scans were ratioed against the spectra of pure KCl. The resolution was 2 cm^{-1}, and a Happ-Granzel apoidization function was used. Peak heights were determined using the absorbance value at 2000 cm^{-1} as the baseline. The cellulose:KCl grinding process may have partially affected the cellulose. However, it was felt that the short grinding time of two minutes would have only a minimal effect on the crystallinity. In addition, since all samples were ground using the same short grinding time, all samples may have been identically affected. It is possible, however, that the highly crystalline samples were affected more than the less crystalline samples since the process of crystallinity reduction is nonlinear. As discussed earlier, the DRIFT cell will give a slightly different spectrum than would be obtained by the pellet method.

RESULTS AND DISCUSSION

Fourier Transform-Infrared Spectroscopy

A number of peak absorbances, peak areas, ratios of peak absorbances and areas, and ratios of peak absorbance to a nearby

TABLE 1

IR Absorbance Ratios Used to Estimate Crystallinity. The Bands Are All Measured Using the Absorbance Value at 2000 cm^{-1} as the Baseline.

Material	Crystallinity index, %	Absorbance ratio 1108/1091 cm^{-1}	 1430/1403 cm^{-1}	 1459/1403 cm^{-1}
Cotton linter	10	0.9435	1.0304	0.8756
Cotton linter	41	0.9586	1.0869	0.8881
Cotton linter	63	0.9813	1.1296	0.8962
Cotton linter	67	0.9830	1.1316	0.9159
Cotton linter	74	0.9956	1.1882	0.9592
Foley Fluffs	10	0.9183	0.9921	0.8207
Foley Fluffs	29	0.9410	1.0444	0.8580
Foley Fluffs	49	0.9577	1.0983	0.9211
Avicel	69	1.0219	1.1951	0.9399
Whatman	88	1.0499	1.2433	0.9819
R		0.915	0.966	0.906

valley were compared to cellulose crystallinity. The best correlations were found using the absorbance peak/valley ratio method, with the 2000 cm^{-1} absorptivity used as the baseline. The three ratios with the best correlation coefficient (R) values were: 1108/1091 cm^{-1} (X1); 1430/1403 cm^{-1} (X2); and 1459/1403 cm^{-1} (X3) (Table 1). All absorptivity values were corrected using the value at 2000 cm^{-1} as the baseline. The three R values (0.915, 0.965, and 0.906) are all significant at the 99.9% level. Previously, researchers using IR to estimate cellulose crystallinity had obtained R values of 0.860[13] and 0.880.[3]

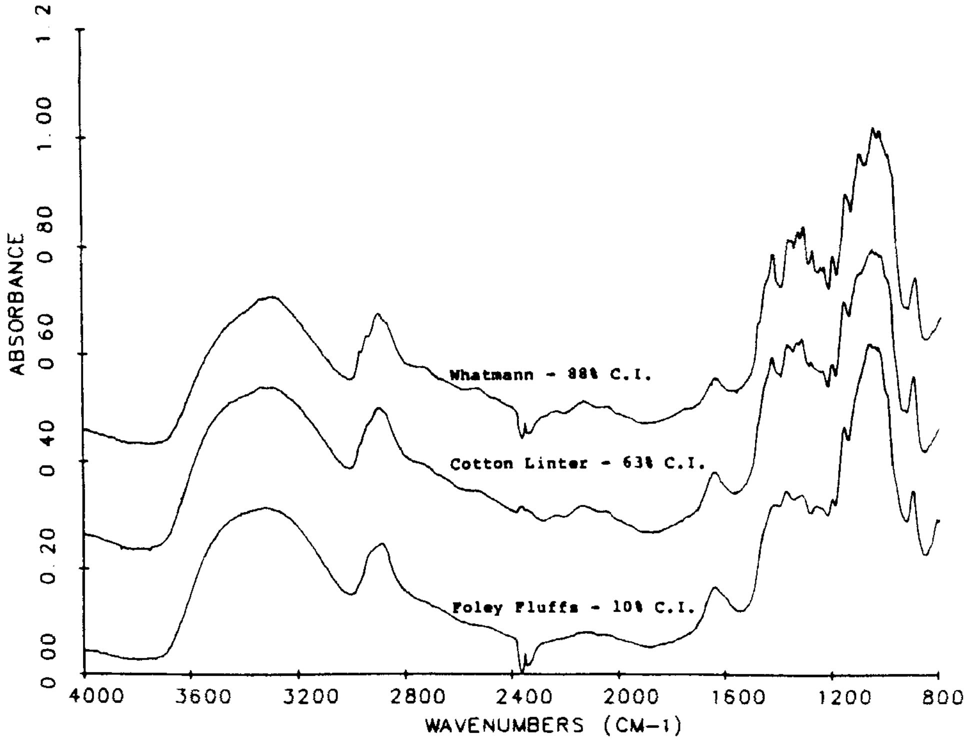

FIGURE 1. DRIFT FT-IR spectra of three cellulose samples.

Figure 1 shows the IR spectra of three samples. A graph of the 1430/1403 cm^{-1} absorbance ratio versus crystallinity is given in Figure 2.

If the peak and valley at 1108/1091 cm^{-1} are closely examined, it appears that the 1108/1091 cm^{-1} ratio is affected by the absorbance at 1091 cm^{-1} decreasing as the crystallinity increases (Figure 1). Nelson and O'Conner[12] noted a strong, broad band near 1090 cm^{-1}, which reportedly occurred only in amorphous cellulose. Nelson and O'Conner did not propose an assignment for

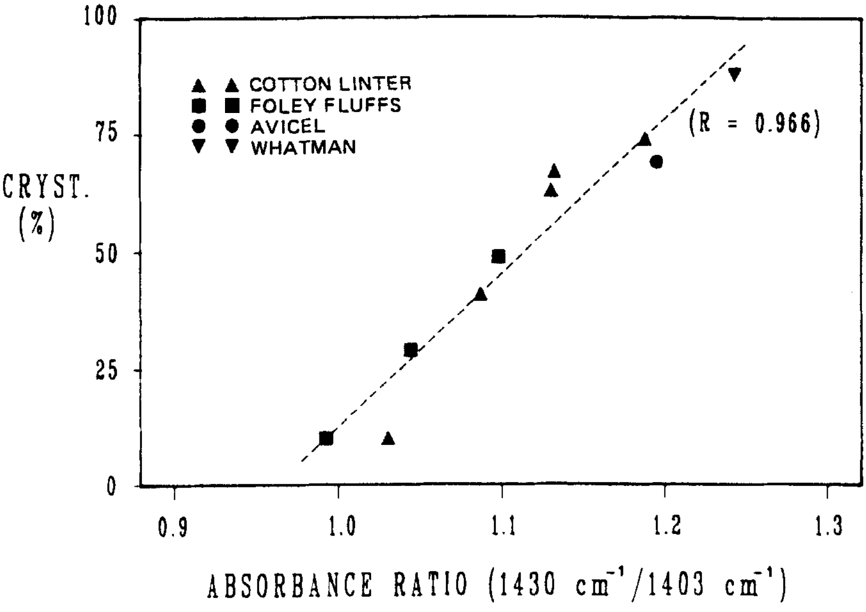

FIGURE 2. Correlation of the 1430/1403 cm^{-1} absorbance ratio to crystallinity.

the 1090 cm^{-1} band. They did call the 1111 cm^{-1} peak a hydroxy association band, using assignments given by Higgins et al.[18] The association bands in alcohols have been attributed to the effect of hydrogen bonding on the vibrations caused by stretching of the C–O bond. Liang and Marchessault[9], however, called the 1110 cm^{-1} peak the antisymmetrical, in-phase ring-stretching mode.

The 1430/1403 cm^{-1} ratio is believed to be affected by both the absorbance increasing at 1430 cm^{-1} and decreasing at 1403 cm^{-1} as the crystallinity increases. Tsuboi[7] and Liang and Marchessault[9] assigned the peak at 1426 cm^{-1} as CH_2 symmetrical bending vibrations. Nelson and O'Conner[12] assigned the CH_2

bending peak to 1429 cm^{-1}. They pointed out that the peak would be affected by the environment of the C-6 group, such as inter- and intramolecular hydrogen bonding at the O-6.

The 1459/1403 cm^{-1} ratio also appears to be dependent on both the shoulder at 1459 cm^{-1} and the valley at 1403 cm^{-1}. Tsuboi[7] assigned a peak at 1446 cm^{-1} as the OH in-plane bending mode, and noted that the 1446 cm^{-1} peak decreased upon deuteration. Liang and Marchessault[9] assigned a shoulder at 1455 cm^{-1} to the OH in-plane bending.

Since amorphous and crystalline cellulose have identical chemical bonds, the IR spectra of amorphous and crystalline samples should be essentially identical. However, the sharpness of certain IR peaks can be directly correlated to the cellulose crystallinity. This was expected since crystalline samples will have bonds of identical strengths and orientation. In an amorphous sample, however, a particular bond would have a wide range of strengths and orientation environments. Thus, an amorphous sample should give an IR spectra with broad peaks. In the same way that the sharpness of an X-ray diffraction peak is correlated to crystallinity, so should the sharpness of an IR peak be correlated to crystallinity. In short, while the chemical structure of amorphous and crystalline cellulose are identical, differences in the physical environment of the bonds will give IR spectra with slightly different characteristics.

TABLE 2

Tga and dtg Data For the Ten Cellulose Samples.

Material	Whatman	Avicel	Cotton linter	Cotton linter	Cotton linter	Cotton linter	Cotton linter	Foley Fluffs	Foley Fluffs	Foley Fluffs
Crystallinity index, %	88	69	74	67	63	41	10	49	29	10
Ash, %[a]	0	0	3	0	4	0	14	0	2	4
dtg maximum[b]	6.4	7.0	5.4	5.2	4.7	4.7	2.4	4.4	4.0	3.3
Temperature at dtg maximum, °C	390	372	405	402	399	387	353	401	387	372
Temperature at 10% weight loss, °C	364	348	365	362	354	344	285	345	331	302
Char at 600°C, %	6	3	7	9	9	12	28	11	10	14
% Char-Ash	6	3	4	9	5	12	14	11	8	10

[a] The percent ash was determined by pyrolyzing the sample in air at 600°C.
[b] The dtg maximum is the maximum rate of weight loss per mg of sample.

TGA/DTG

The dynamic tga and dtg data are summarized in Table 2. A review of the literature suggested that % char, temperature at start of weight loss, temperature at maximum dtg, and maximum dtg may be correlated to cellulose crystallinity.[1-6]

A positive linear correlation (R = 0.895) was found when crystallinity was correlated to the maximum dtg value. (The maximum rate of weight loss was determined by measuring the maximum height of the dtg curve above the baseline and dividing by the initial weight of sample.) A relationship (R = 0.976) was also observed for the correlation of the natural log of the crystallinity versus the temperature at which 10% weight loss occurred (Figure 3). The temperature at 10% weight loss was used rather than the temperature at which weight loss first occurs because the 10% value was less arbitrary. Both R values are significant at the 99.9% level. These findings generally agree with the results reported by other researchers—that as the cellulose crystallinity decreases the temperature at which weight loss first occurs and the rate of weight loss both decrease.

The % char, and % char corrected for ash content, was not highly correlated to cellulose crystallinity. However, it was noted that the residual char value increased as the cellulose crystallinity decreased. The increased char value, however, may have been caused by an increase in the ash content rather than a decrease in crystallinity.

An extremely significant correlation (R = 0.998) was found for the natural log of crystallinity versus the temperature at

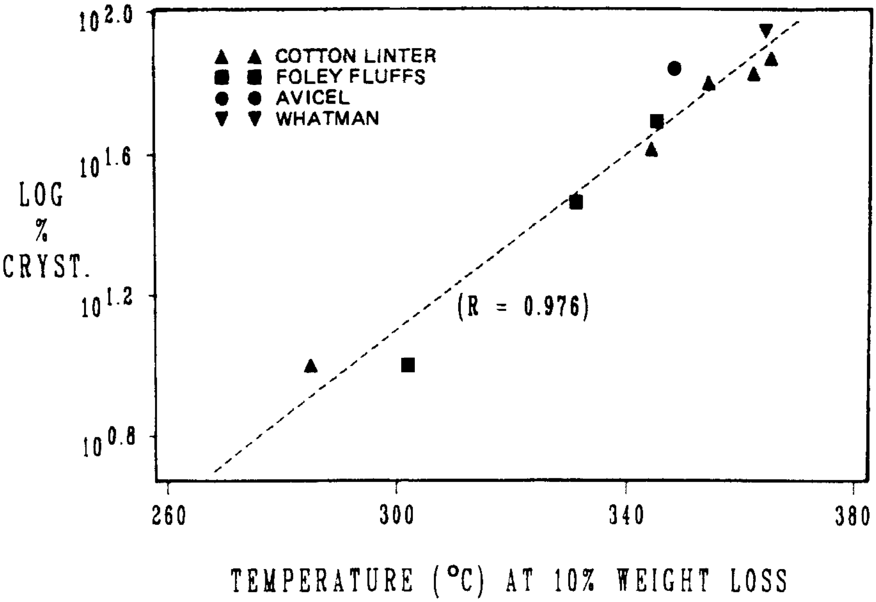

FIGURE 3. Temperature (°C) at 10% weight loss versus the log of % crystallinity.

maximum dtg for the cotton linter samples. However, this correlation was good for only the cotton linter samples, suggesting that other factor(s) besides crystallinity probably also have a significant effect. One possibility is that minor constituents of the cellulose may act as a catalyst, or that the degree of polymerization affects cellulose pyrolysis.

When examining these correlations, it should be remembered that most samples were ball-milled to decrease crystallinity, which may have caused an increased ash content due to contamination from the steel balls. Since ash can act as a catalyst, the effects which were observed may be due, in part or totally, to the ash present. In addition, the orientation and degree of polymerization of the cellulose may affect the tga and dtg curves.

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