A Comparison of the Dielectric Method with Density, Moisture Regain, and X-Ray Diffraction Methods of Determining Fine Structure in Cellulosic Materials

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Synopsis

A comparison between the dielectric method and density, moisture regain, and x-ray diffraction methods of estimating crystallinity in cellulosic materials is presented. The merits of the dielectric method compared to the other methods are discussed. Although the permittivities of completely crystalline and completely noncrystalline celluloses are not directly measureable, the use of extrapolated values for completely crystalline and completely noncrystalline celluloses make it possible to assign a percentage crystallinity to a given material from a single permittivity measurement. Capacitance measurements are very sensitive, accurate, and rapid. Therefore, the dielectric method is capable of following small and rapid changes in crystalline content arising from mechanical, chemical, or thermal treatments. In such a study, permittivities of completely crystalline and completely noncrystalline celluloses are not required. Since the relationship between permittivity and crystallinity is linear, it appears reasonable to continue to represent the fine structure of a cellulosic material by a simple model of a mixture or two hypothetical components: "crystalline" and "noncrystalline" cellulose and to retain the concept of "percentage crystallinity" in its present form.

INTRODUCTION

During the past several decades the fine structure of a wide variety of forms of cellulose has been studied. Any such study of a cellulosic material involves uncertainty because the material consists of a complex combination of long-chain molecules. It is now agreed that much of the evidence regarding fine structure is only qualitative.[1]

Many methods for the study of the fine structure of cellulosic materials have been reported in the literature. These include physical methods (x-ray diffraction, infrared absorption, isotopic exchange, dielectric properties, and density), physicochemical methods (adsorption of water vapor, heat of wetting, and iodine sorption), and chemical methods (hydrolysis, oxidation, esterification, and etherification). In this article we compare the dielectric method of measuring the crystalline content of a cellulosic material with density, moisture regain, and x-ray diffraction methods and then show how the dielectric method could be applied to estimate the crystalline content in a cellulosic material from a single permittivity mea-

surement. The application of the dielectric method to follow small changes in crystallinity also is discussed.

Permittivity and Loss Factor

When a voltage is applied across the plates of a condenser separated by a distance in vacuum, a certain electrical charge appears on the plates. If the condenser is now filled with a dielectric, the entire dielectric, as well as its individual molecules, will be polarized (the polarization may be induced or due to the alignment of permanent dipoles) thus increasing the charge on condenser. The ratio between the charge accumulated in the condenser with the dielectric and that accumulated without the dielectric is known as the permittivity or the dielectric constant of the material. The permittivity of the material depends upon the properties of the dielectric, on temperature, and on the frequency of the applied field.

The behavior of a cellulosic material in an alternating current field has been interpreted by three different models[2]: a capacitor and a resistor in parallel; a capacitor and a resistor in series; and a resistor in parallel with a series combination of capacitor and a resistor. A study with a capacitance bridge showed that the dissipation factor is independent of the model while the permittivity depends on the model.[2] In an ideal condenser in which polarization is instantaneous, the charging current is 90° out of phase with the alternating potential. When absorptive polarization occurs in addition to the charging current, there is also a loss current which is in phase with the applied voltage and which is associated with dissipation of part of the energy of the applied field. The total current is the vector sum of the charging current and the loss current. Because of the existence of the loss current, it is customary to introduce a complex permittivity

$$\epsilon^* = \epsilon' - i\epsilon'' \tag{1}$$

where the real part ϵ' is the measured value of permittivity and the imaginary part ϵ'' is the loss factor.

The term dielectric constant is commonly applied to sheet materials on an as-is basis. For example, a piece of paper of density 0.5 g/ml placed between the electrodes of a capacitor will produce an increase in capacitance from which the permittivity of paper can be calculated. However, this is not the permittivity of the cellulose from which the paper is made. The space between the electrodes is actually filled with a mixture of air and cellulose and is not well defined as to its geometry.[3,4] To obtain the needed information about the fine structure of the cellulose, it is necessary to postulate a property of the cellulose itself, "specific permittivity." This has also been called "intrinsic dielectric constant."[3]

The measurement of specific permittivity is not entirely straightforward. There are two approaches to this measurement. One is that of filling the void spaces in the fibers to be tested with a liquid mixture having the same permittivity as the fibers being measured.[5,6] This technique yields a direct value for the specific permittivity of the fibers. The

second approach is to employ a mathematical representation involving permittivity and density and then to calculate the permittivity at any common sheet density for purposes of comparison with other fibrous materials.[4,7]

Crystalline and Noncrystalline Regions in Cellulose

The terms "crystalline" and "amorphous," applied to regions in cellulosic materials, originated from x-ray investigations. Generally a crystalline region is defined as that part of the cellulosic material which gives rise to selective diffraction of x-rays, although minute regions of perfect order escape this definition.

Hearle[1] gives a detailed description of different theories proposed for the fine structure of cellulose. All these theories agree that there are crystalline and noncrystalline regions in cellulose. Different terminologies for these two states, having approximately the same meaning, are also used. These include, for crystalline regions, the terms crystallinity index,[9,10,11] lateral order index (infrared),[12] index of order,[13] molecular order index,[14] and crystallinity ratio.[15] For noncrystalline regions, the terms amorphous or accessible portion of cellulose are used. This article considers cellulose to be a two-phase material, and these two phases are termed "crystalline" and "noncrystalline."

Permittivity of cellulose is largely determined by the freedom of movement of the various molecular components of the structure. At low frequencies, electronic, atomic, and dipole polarizations occur, while at high frequencies only electronic and atomic polarizations take place. In cellulose, polarization results partly from the rotation of free hydroxyl groups and partly from the rotational vibration of the chain segments. Since greater freedom of such movement exists in the noncrystalline regions of cellulose, the amount of crystalline material has a definite bearing upon the polarization. Consequently, the permittivity should be a direct function of the amount of noncrystalline material present in cellulose.

According to the dielectric method of estimating crystallinity in cellulosic materials, crystalline regions are those molecular chain segments that are well aligned and bound, including any regions so small as to be undetectable by x-ray diffraction. The noncrystalline regions include all those regions not bound in a crystalline structure and where freedom of oscillation of molecular segments is possible.

Relationship Between Permittivity and Density

The macroscopic density of a substance in its crystalline state is greater than that of the same substance in its noncrystalline state. Since cellulose fibers consist of a mixture of crystalline and noncrystalline states, their density is a function of the distribution between these two components.[16] The density of the fiber substance also depends on intrafiber voids[17] which, in turn, depend upon the physical history of the fiber.
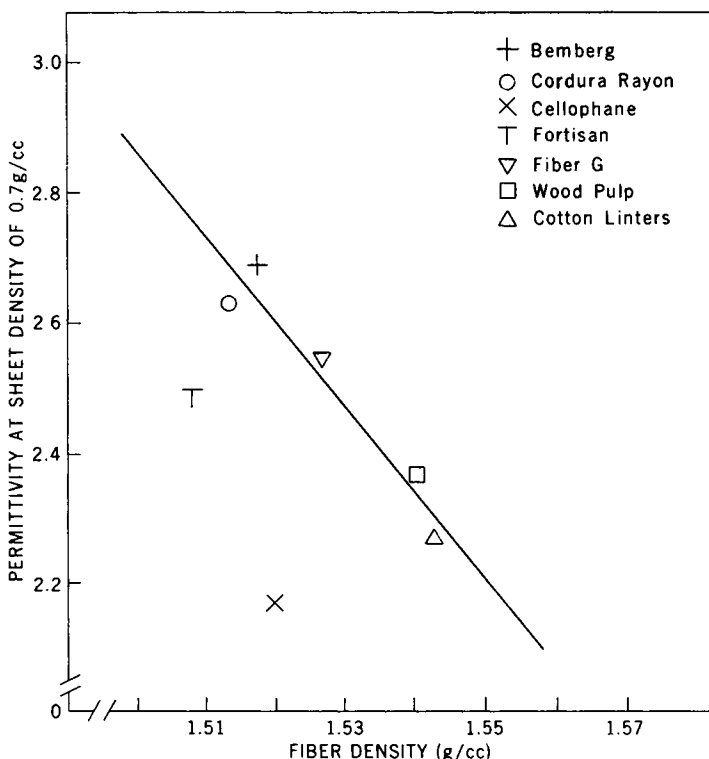
Fig. 1. Permittivity for several cellulosic materials (at sheet density 0.7 at 30°C and at 1000 Hz) versus fiber density. (From Verseput.[19])

Delevanti and Hansen[18] studied the dielectric properties of unbleached kraft pulp sheets of various densities. The permittivities of these sheets followed the Clausius-Mossotti relationship which postulates

$$\frac{\epsilon - 1}{(\epsilon + 2)d} = \text{constant} \qquad (2)$$

where ϵ is the permittivity, and d is the density (*sheet density*). They also found that the loss factor was directly proportional to the sheet density.

Later, Verseput[19] measured the permittivity and fiber density of many cellulosic materials by the carbon tetrachloride flotation method of Hermans[20] and found a correlation (Fig. 1) between permittivity calculated at a "standard" sheet density and the density of fiber substance. Neither Fortisan nor cellophane fit the correlation between fiber density and permittivity at 0.7 sheet density. The lack of agreement of fortisan was found to be due to microscopic gas occlusions within the fibers. According to Verseput, the low value of permittivity of cellophane was due to the possible "relatively rigid structure, with correspondingly lower polarization than is observed in regenerated fibers." The lack of exact agreement between permittivity and fiber density or between permittivity and accessi-

bility for cellophane is not surprising since the Clausius-Mossotti relation was used for correcting the permittivity measurements.[14]

Studies on dielectric properties and crystalline content of polymers other than cellulosic materials have also been reported. For oxidized polyethylene, it is well known that there are three absorption maxima in the loss factor–frequency curve, viz., at low, medium, and high frequencies, called α, β, and γ peaks, respectively. Booij[21] found that the magnitude of the α-maximum at low frequencies was proportional to the weight of crystalline material per cm^3 estimated by an infrared technique. He also concluded from his work that the density of the crystalline part of polyethylene (estimated by flotation method and infrared analysis) is determinative of the relaxation time of the low-frequency maximum.

Nakajima and Saito[22] studied the dielectric properties and densities of three samples of polymonochlorotrifluoroethylene. One sample was cooled slowly from the melting temperature. A second sample was quenched to room temperature and a third sample was quenched to $-30°C$. After the initial dielectric measurements, the third sample was annealed at $180°C$ for 4 hr to produce further crystallization. In all the cases they found that the area under the ϵ'' versus $\log f$ curve increased roughly in proportion to the extent of noncrystalline region in the material estimated from density measurements.

Relationship Between Permittivity and Noncrystalline Regions Estimated By Moisture Regain

Hermans[23] pointed out that there is a direct relationship between the capacity of a fiber for water absorption and the quantity of noncrystalline material in the fiber; and that sorptive capacity should be regarded as a function mainly of the noncrystalline regions and can confidently be expected to stand in close relation to the percentage of noncrystalline matter.

Several studies have been reported in the literature regarding the correlation between permittivity and the noncrystalline content of cellulosic materials determined by moisture regain. Calkins,[24] in an interesting study, found a linear relationship between permittivity (corrected to a standard density) and the moisture regain of various regenerated celluloses.

Ishida et al.[3] measured the dielectric properties of viscose rayon, Bemberg, and cotton sliver over a frequency range of 500 Hz to 3 MHz and over a temperature range of $-60°$ to $+20°C$. They found that the quantity $\epsilon_0 - \epsilon_\infty$ (where ϵ_0 and ϵ_∞ are the permittivities at static field and at infinite frequency, respectively), which is proportional to the concentration of the dipoles contributing to the orientation, gave the following ranking over the observed temperature range: viscose rayon $>$ bemberg $>$ cotton sliver. This ranking parallels that of the noncrystalline matter[6] in the three samples. This was explained on the basis that the dipoles in the noncrystalline region and on the surface of crystallites make a substan-
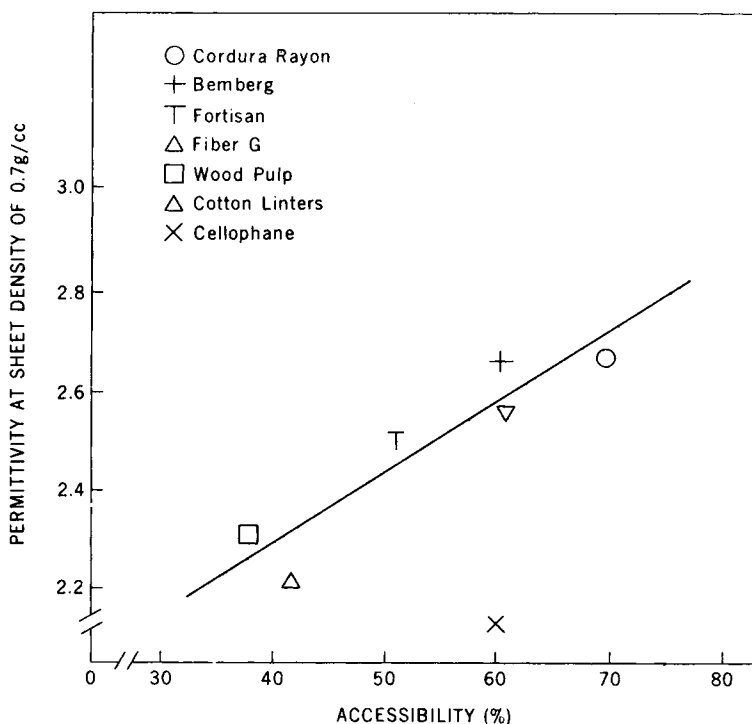
Fig. 2. Permittivity for several cellulosic materials (at sheet density 0.7 at 30°C and at 1000 Hz) versus accessibility. (From Verseput.[19])

tial contribution to dielectric dispersion. A similar hypothesis had earlier been advanced by Calkins,[24] Verseput,[19] and Kane.[6]

Verseput[19] confirmed Calkins' discovery for a number of native and regenerated fibers (Fig. 2).

Kane carried out a similar study using the liquid mixture technique,[6] which did not require the use of the Clausius-Mossotti relationship for density corrections. He found an excellent linear correlation (Fig. 3) between specific permittivity and noncrystalline content (accessibility) of various cellulosic materials.

Both Verseput and Kane determined water vapor adsorption isotherms on all samples by the method of Wink.[25] The moisture regain values were then interpreted by the Hailwood and Horrobin equation[26]

$$\frac{Mr}{1800} = \frac{\alpha h}{1 - \alpha h} + \frac{\alpha \beta h}{1 + \alpha \beta h} \tag{3}$$

where M is the molecular weight of the polymer unit, r is the moisture regain in g/100 g of dry sample, h is the per cent relative humidity, and α and β are constants. In deriving the above equation, Hailwood and Horrobin postulated that unhydrated cellulose, hydrated cellulose, and water molecules formed an ideal solid solution and consequently their
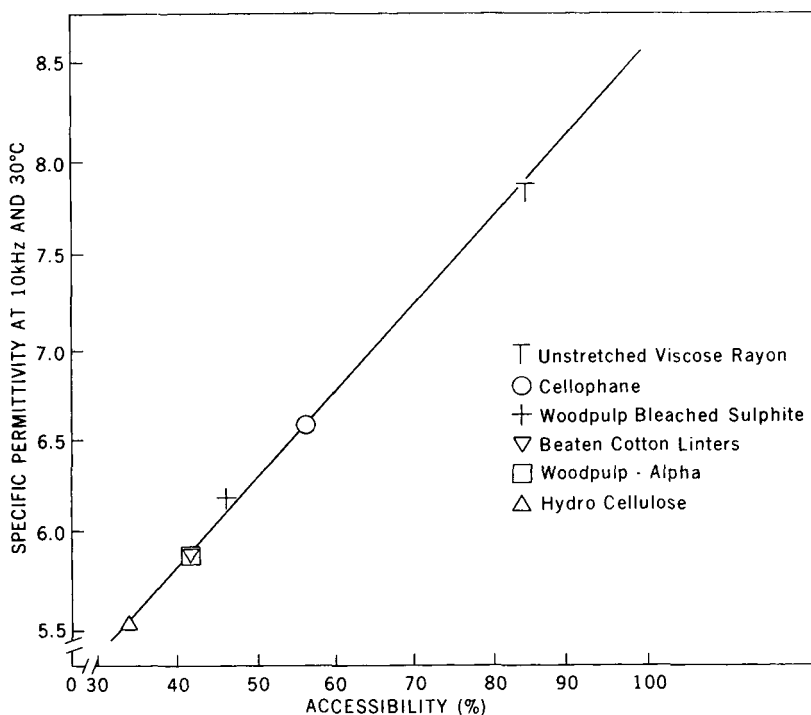
Fig. 3. Specific permittivity for several cellulosic materials (obtained by liquid-mixture
    technique at 30°C and at 10 kHz) versus accessibility.   (From Kane.[6])

activities were equated to their mole fractions.   The validity of these
assumptions has been questioned by Tarkow and others,[27,28] but the equa-
tion appears to yield estimates of crystallinity which are consistent with
the estimates obtained from other techniques.

Relationship Between Permittivity and Crystalline Content Estimated by X-Ray Diffraction

The x-ray diffraction technique for the determination of crystalline
content is based on the interpretation that the crystalline regions in a
cellulosic material give rise to Bragg reflections while the noncrystalline
regions scatter x-rays in a diffuse fashion.   The intensities of the diffracted
rays from various planes of randomly oriented crystals give rise to a series
of concentric rings about the axis of the x-ray beam.   The sample used
for analysis is usually in a pellet or powder form.[29]   But it has been found[8]
that powdering the sample and subjecting it to the compressive stress
used to make a pellet progressively diminished the intensity of the peaks
(Table I), while the x-ray diffractogram retained the pattern of cellulose I.
From this it is inferred that the mechanical procedures reduced the crys-
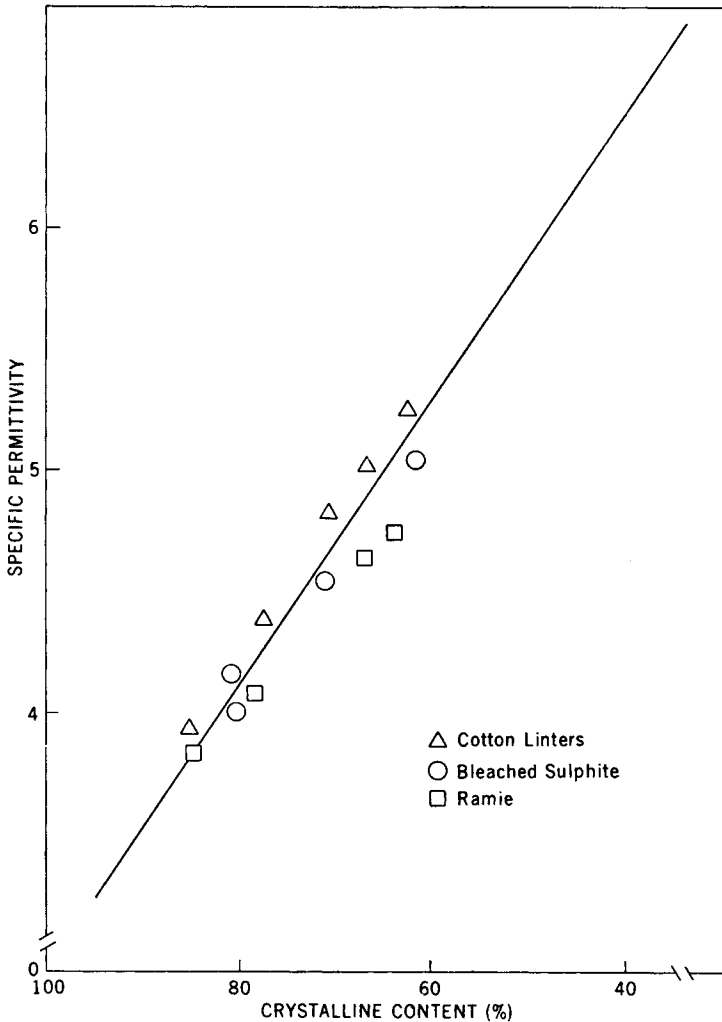talline content of the fiber.

Fig. 4. Specific permittivity for three cellulosic materials versus crystalline content. (From Venkateswaran and Van den Akker.[7])

   A comparison of dielectric properties and crystallinity determined by x-ray diffraction was made on ramie, cotton linters, bleached sulfite pulp, and cellophane.[7] To avoid the difficulties created by powdering and pelletizing the fibers, the specimens for x-ray measurements were made in sheet form. The per cent of crystallinity of these materials was varied by treating the samples with various concentrations of ethylamine in water. The x-ray crystallinity was calculated from a formula[11] which uses the intensity of the peak corresponding to the 002 plane. The permittivities of various cellulosic materials, measured at several frequencies up to 10 kHz, were corrected to the common density of crystalline cellulose (1.59).

Figure 4 shows the corrected permittivity values, measured at 10 kHz and at 20°C, plotted against the x-ray crystallinity values. There is an excellent correlation between the permittivity at any frequency and the x-ray crystallinity of ramie, cotton linters, and bleached sulfite pulp.

TABLE I
Effect of Particle Size and Pelletizing Pressure on Per cent Crystallinity[8]
of Cotton Linters

Pressure, psi	Crystallinity index, %		
	Sheet form	20-mesh	80-mesh
50	86	—	—
7,650	—	78	71.2
20,600	—	77	70.2
30,600	—	79	68.6

However, cellophane gave very different x-ray patterns for different orientations[30] and it was not possible to assign a unique value of x-ray crystallinity to cellophane for comparison with the dielectric measurements.

Relative Merits of the Different Techniques for Estimating Crystalline Content in Cellulosic Materials

It is seen from the examples cited that relationships exist between dielectric properties of both native and regenerated cellulosic materials and: (a) density and (b) the noncrystalline content determined by moisture regain. Although a negative correlation between permittivity and crystallinity by x-ray diffraction has been established for native fibers,[8] a correlation could not be extended to cellophane. In general, wherever a correlation exists, the results support the hypothesis that polarization is a measure of the noncrystalline content of polymers.

Density measurement is the simplest method for estimating the noncrystalline portion in cellulose. A widely used expression involving the specific volume of a polymer is

$$V = xV_c + (1 - x)V_a \qquad (4)$$

where V_c and V_a are specific volumes of the crystalline and noncrystalline regions, respectively, and x is the fractional crystalline content.[31] This relation assumes that the crystalline and noncrystalline phases are well defined in the polymer matrix, which assumption is not in agreement with any modern theory of molecular structure. There is also inadequate knowledge concerning the values of V_b and V_a.

Density measurements on oriented fibers seem to be unreliable for the determination of crystallinity. Using x-ray data to define the density of the crystalline phase, Farrow and Ward[32] found that the calculated density of the noncrystalline content of polyethylene terephthalate increased with

orientation. Therefore, the density method, based on the assumption of constant density for the noncrystalline regions, is not equally applicable to samples having differing amounts of orientation.

The absorption of water vapor by cellulosic materials at a given relative humidity would be expected to increase as the ratio between the crystalline and noncrystalline regions decreases, and there is a fair amount of experimental support for this expectation. Experimentally, the water sorption method for estimating crystalline content is reproducible and simple, but it is very slow.

The x-ray diffraction technique for estimating crystalline content is rapid and simple. A negative correlation between dielectric constant and crystalline content in native cellulose has been established.[7] However, when this technique is applied to polymers in general, one cannot arrive at a simple definition of crystallinity because of the difficulty in interpretation of the diffraction patterns. This difficulty has been encountered in native cellulose,[33,34] regenerated cellulose,[30,35] and other polymers.[36] In all such cases, application of general procedures for estimating the crystalline content yield varying and incomplete results. For reasons which have been detailed in another report,[30] it is concluded that the estimation of crystalline content in cellulosic materials from x-ray diffractograms is not yet a clearly defined technique.

The dielectric technique for estimating crystallinity in cellulosic materials is free from the theoretical uncertainties which cloud other techniques. Permittivity measurements yield estimates of crystallinity which may be slightly different from the estimates obtained from density, accessibility (moisture regain), and x-ray diffraction techniques. For example, in the density and moisture regain methods, it is conceivable that some noncrystalline regions may be surrounded by crystalline zones so as to be inaccessible to liquids. It is also well known[37] that x-ray diffraction is insensitive to small crystallized regions. Again, since x-ray diffraction patterns of synthetic and regenerated polymer films and fibers have been found to depend on orientation and the variables of preparation, varying values for crystallinity are found with this technique.[8,37,38,39] In all such cases, in the presence of an external field the entire dielectric, as well as its individual molecules, will be polarized. Therefore, the dielectric method should yield more consistent and meaningful values for crystallinity since every type of submicroscopic structure makes its characteristic contribution to the observed permittivity, i.e., polarization is determined uniquely by the structure of the system.

It is likely that Bragg reflection of x-rays can be obtained from orientation in noncrystalline as well as from orientation in crystalline regions. In other words, x-ray diffraction cannot differentiate between these two types of orientations. Conversely, dielectric measurements for estimating crystalline regions should successfully distinguish between these two types of orientation since polarization is determined by the freedom of movement of the various components of the system.

The reported studies of the permittivity of cellulosic materials[6,7,8,24] have shown that the permittivity is strongly related to crystalline–noncrystalline ratio estimated by other techniques. The exception was that a meaningful value of crystalline content in cellophane (regenerated cellulose) could not be obtained from x-ray studies[8,30] to correlate with its permittivity, while Kane[6] showed that the permittivity of cellophane was well correlated with the accessibility measured by moisture regain.

The permittivities of completely crystalline and completely noncrystalline celluloses are not directly measurable. However, extrapolation of the relationship between dielectric constant and accessibility (moisture regain) for natural and regenerated fibers (Fig. 3), and also of the relationship between permittivity and x-ray crystallinity of native fibers (Fig. 4), yields similar estimates of the specific permittivities of completely crystalline and completely noncrystalline celluloses of about 3 and 9, respectively. Using these values, it is possible to assign a percentage crystallinity to a given material from a single permittivity measurement. If we arbitrarily choose three materials having specific permittivities of 5, 6, and 8, we can obtain from Figures 3 and 4 two estimates of per cent crystallinity for each material (Table II). The agreement between these estimates is well within the experimental error, including the uncertainty in the x-ray measurement of crystallinity. Thus, determination of permittivity provides an estimation of per cent crystallinity from a single measurement.

TABLE II
Crystallinity Values for Three Materials of Arbitrary Specific Permittivity Determined from Figures 3 and 4

| Sample no. | Specific permittivity | Crystallinity, % | |
		Fig. 3	Fig. 4
1	8	14.0	14.0
2	6	53.0	50.0
3	5	72.0	68.0

The dielectric procedure for determining the crystalline content in a cellulosic material could also be usefully applied when a knowledge of the endpoints is not required. Since capacitance measurements are very sensitive and rapid, the dielectric method is capable of following small and rapid changes in crystalline content arising from mechanical, thermal, or chemical treatments. For example, the dielectric technique could be applied in a study of rate of crystallization. In such a study any *change* produced could be measured rapidly and accurately.

An illustration of the sensitivity of the dielectric technique is its ability to detect the small but measurable changes in permittivity which result from mechanical treatment of cellulose pulp (beating).[8] This would be interpreted to mean that beating increases the noncrystalline content of

cellulose, remembering that the permittivity of the noncrystalline regions is higher than that of the crystalline portion.[6,19,24] However, moisture regain,[40] density, and x-ray diffraction methods[8] have failed to detect this change.

CONCLUSIONS

Over the past 30 years a considerable body of evidence has been accumulated on the various techniques of estimating the percentage of crystallinity in cellulosic materials. The available information permits comparisons between data from the dielectric method and from density, moisture regain, and x-ray diffraction techniques. The estimates of crystallinity in cellulosic materials obtained from the dielectric method correlate well with those obtained from moisture regain and density methods (and *vice versa*).

The permittivities of various native celluloses correlate with the crystallinity calculated from x-ray diffractograms. This correlation does not extend to regenerated cellulose (cellophane) because of the difficulties in interpreting the x-ray diffractograms of this material.

Wherever correlations exist, the relationships are essentially linear in nature. Therefore, it appears reasonable to continue to represent the fine structure of a cellulosic material by a simple model of a mixture of two hypothetical components—"crystalline" and "noncrystalline" cellulose —and to retain the concept of "percentage crystallinity" in its present form.

Of these various techniques, the dielectric method offers some distinct advantages, either as a method of estimating the percentage crystallinity of a cellulosic material or even more as a precise and rapid method of following small changes in crystallinity resulting from mechanical, chemical, or thermal treatments.

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