

Effect of Ethylamine Treatment on the Dielectric Properties and Crystallinity of Cellulose. I*

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Synopsis

A study of dielectric properties and crystallinity by x-ray diffraction was made of ramie, cotton linters, bleached sulfite pulp, and cellophane. These cellulosic materials were treated with various concentrations of ethylamine in water. A linear relationship was found to exist between dielectric constant and crystallinity. The results also indicated that both dielectric constant and loss factor of ethylamine-treated cellulose obeyed anomalous dispersion and absorption. The difference in density of untreated and treated samples was not significant for the range of crystallinity change observed by ethylamine treatment. In calculating the intrinsic dielectric constants of cellulose of different crystallinities the density of crystalline cellulose was used for the purposes of comparison.

INTRODUCTION

The arrangement of molecules in polymers has been of considerable interest for a number of years and has been the subject of numerous investigations. Several theories explaining the state of solid polymers have been proposed in the literature. According to the presently accepted "fringe-micelle" theory, polymers consist of molecular chains varying from the state of perfect three-dimensional order to completely randomly oriented chains. Very recently, experimental evidence has been reported in support of the hypothesis that the structure of the monocrystalline lamellae and of the fibrils of numerous linear polymers is composed of bundles of zigzag-folded chain molecules.¹ On the basis of x-ray diffractograms, polymers consist of crystalline and amorphous phases.

The crystalline phase is that part of the polymer giving rise to selective diffraction of x-rays, while the completely random-oriented phase yields diffuse scattering. However, it is well known that small crystallites are not revealed by x-ray diffraction.

Several methods of determining the crystalline-amorphous ratio have been reported in the literature. The important methods are deuterium exchange, acid hydrolysis, moisture regain, density, x-ray diffraction,

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infrared absorption, and nuclear magnetic resonance. Each method has its own merits and shortcomings. A review of some of these methods is given by Gupta and Beevers.²

Baker and Yager³ showed that the interaction between the chains of polymers is related to the dielectric constant. In the case of polydeca-methylene sebacamide, they found that decreased crystallinity and, hence, decreased hydrogen bonding resulted in increased dielectric constant. Thus, the dielectric properties are related to the relative freedom of the polar groups. In this paper an attempt is made to correlate the crystallinity (as determined by x-ray diffraction) and the dielectric properties of cellulose.

REVIEW OF PREVIOUS WORK

According to Hermans,⁴ sorptive power is a function of the amorphous fiber substance, and hence this quantity may be regarded as an approximate relative measure of the amount of amorphous matter in different cellulosic materials. Calkins⁵ observed a relationship between the moisture regain of cellulose and the dielectric constant. From this Calkins concluded that there could be a relationship between the dielectric constant and crystallinity of cellulose. Later, Verseput⁶ investigated this relationship in greater detail. He determined the accessibilities of several cellulosic materials from a number of moisture regain values. He also measured the dielectric constant of these materials and his method of measuring dielectric constant (like Calkins') involved compacting the cellulose samples under elevated compressive stress to decrease the void volume in the condenser. The materials he used for testing were cellophane, cotton linters, cordura, Fortisan wood pulp, and Bemberg. His results showed a good correlation between the dielectric constant and accessibility of cellulose. Kane⁷ further examined this relationship by measuring the dielectric constant and accessibility of beaten cotton linters, hydrocellulose, cellophane, unstretched viscose rayon, wood pulp (alpha), and bleached sulfite pulp. He measured the accessibility by the moisture regain method and the dielectric constant by the liquid mixture technique of DeLuca, Campbell, and Maass.⁸ He also determined by extrapolation that the dielectric constant of the accessible portion of cellulose was about 9, while that of the inaccessible portion was about 4.

It is seen from these investigations that a relationship between the dielectric constant and crystallinity of cellulose could exist. It should be noted that none of these investigations gives a direct verification for the existence of the relationship. Accordingly, it was thought desirable to continue the work on the discovery of Calkins on the sensitive and apparently consistent correlation between the dielectric constant and crystallinity of cellulose. In order that the correlation might be investigated more directly, cellulosic materials were chosen so that samples of varying crystallinity could be obtained from each material by treatment with aqueous ethylamine of various concentrations. The dielectric measurements could then be made

for each specimen while the crystallinity of the corresponding specimen could be obtained by x-ray diffraction.

A search for correlation between these quantities could then be made. It is the purpose of this paper to present the results of the investigation.

EXPERIMENTAL TECHNIQUES AND PROCEDURES

Treatment of Cellulose with Ethylamine

Twenty years ago Davis et al.⁹ reported that cellulose is readily swollen by the lower primary amines, namely, methylamine, ethylamine, and *n*-propylamine, but that it must be preswollen with liquid ammonia before isopropylamine or any of the butylamines will produce a change in the x-ray pattern. Of the various alkylamines, monoethylamine is found to be most effective¹⁰ in altering the lateral order structure of cellulose. Loeb and Segal¹¹ have shown that the extent of this alteration could be controlled if cellulose is treated with aqueous ethylamine of various concentrations. However, they also have found that aqueous ethylamine of concentration below 71% does not bring about appreciable alteration in the lateral order structure of cellulose.

This 71% concentration corresponds to a 1:1 mole ratio of amine and water. It is also reported that most of this alteration taking place during the treatment of cellulose with ethylamine occurs within 15 min., although the maximum effect is reached only in 4 hr.¹²

Segal et al., have further shown that the treatment in ethylamine produces no change in crystalline orientation.¹² Also, if proper precautions are taken to exclude air from the reaction, no appreciable reduction in degree of polymerization is observed. However, the results obtained from a part of the present investigation indicate that such precautions to exclude air from treatment are apparently not necessary. This will be dealt with in greater detail separately.

Crystallinity Measurement by X-Ray Diffraction

Several methods to estimate the amount of crystalline matter in cellulose are reported in the literature. However, what is to be included in a crystalline state is much more a subject of definition. It was mentioned earlier that, according to the fringe-micelle model, the state of polymers in solid form may vary from the perfect three-dimensional order to the complete and random orientation of the molecular chains. It is to be noted that the noncrystalline part of cellulose may consist of a variety of structures. Hence, the terms "crystalline" and "amorphous" (the terms based on x-ray investigations) should not be taken to mean the absolute values.

The order of crystallinity in samples used in the present work has been calculated by the particular x-ray diffraction method of Segal et al.¹³ In the procedure, a sample of cellulose is subjected to x-rays and the diffraction intensities are scanned from a Bragg angle of about 12 to 24°. This range includes the three main diffraction maxima of the cellulose lattice structure:

the (101), (10 $\bar{1}$), and (002) planes. According to Segal et al.,¹² the percentage crystallinity index is defined by $C.I. = 100[(I_{002} - I_{am})/(I_{002})]$ where I_{002} is the intensity of the diffraction from the (002) plane at $2\theta = 22.6^\circ$ and I_{am} is that of the background scatter measured at $2\theta = 18^\circ$, approximately. The results obtained by using this method have been found to be well correlated with the results from acid hydrolysis, infrared analysis, moisture regain, and density measurements.

Preparation of Samples

In order to study the relationship between the dielectric constant and crystallinity of cellulose, the specimens were tested as far as possible under identical conditions. Usually, in making x-ray measurements, samples are powdered and made into pellet form, following the original powder technique, and the measurements are then made. In the present study, the handsheets used for dielectric measurements were used. From handsheets prepared with the British sheet mold, 44.2 cm.² sheets were cut for dielectric measurements and rectangular sheets of 1.5 \times 1 in. (3.8 \times 2.5 cm.) were used for x-ray diffraction. This will be dealt with in greater detail later.

Apparatus

In this study, a Norelco x-ray diffraction unit operating with parafocusing geometry was employed for the crystallinity measurements. With the use of a copper target and a nickel filter, $K\alpha$ radiation was obtained at 35 kv. and 20 ma. The collimated beam was defined by a divergence slit of 0.5° angular aperture at the x-ray port. The diffracted beam was defined by a 0.006-in. receiving slit and by a 0.5° angular aperture scatter slit. The signal of the diffracted beam was received by a Geiger counter tube and recorded by a Brown recording potentiometer.

Before each test, the performance of the apparatus was checked by measuring the diffraction intensity from a standard brass plate set at a Bragg angle of 42.5° .¹⁴ Slight adjustments of the x-ray tube voltage were made when necessary to return the intensity to the standard value.

The samples to be tested were placed in the holder and mounted in the goniometer. The diffraction intensity was measured from an angle of $2\theta = 10$ – 26° . In order that the error due to misalignment, if any, of the samples in the holder might be eliminated, the samples were tested again after rotating through 90° .

Dielectric Constant Measurements

Apparatus

A conjugate Schering Bridge designed according to ASTM¹⁵ was used in the present study. This equipment was built by Delevanti and Hansen¹⁶ and was described by them. The electrode arrangement used in the present work was built by Calkins.⁶ Briefly, the system consists of a pair of electrodes of 44.2 cm.² area, so mounted that the electrode pressure can be varied over a considerable range. The electrode system is enclosed within a bell jar resting upon a base plate and can be evacuated to 0.1 μ .

Method of Measurement

The dielectric constant and dissipation factor were measured. To measure the dielectric constant of the sample in vacuum, the sample was placed between the electrodes. The test capacitor system was covered with the bell jar and the pressure in the system was reduced to 0.1 μ . It was found that the equilibrium state was reached after 35 hr. Steady indications of the capacitance and loss factor were taken as indications of the equilibrium state. Measurements were made at 1, 2, 5, and 10 kcycle/sec.

The weight of the vacuum-dried sample, needed in the determination of the sheet density, was obtained in the following manner. After measurements were made, dry air was let into the system. This was done by first passing air through a 24-in. long glass tube packed with glass beads and CaSO_4 (Drierite) and then through another tube of the same length packed with glass beads and P_2O_5 . When the system reached atmospheric pressure, the bell jar was raised and the sample was transferred into a tared weighing bottle in a few seconds. Since the CaSO_4 used was of the indicating type (changing color when moisture was absorbed), fresh CaSO_4 was used at suitable intervals.

Calculation of the Dielectric Constant and Loss Factor of the Fiber Alone

If C_2' and C_2 are the readings of the capacitance dial and C_4' and C_4 are the readings of the dissipation factor dial without and with the specimen, respectively, then the dielectric constant ϵ' and dissipation factor D of the specimen are calculated from eqs. (1) and (2), respectively:

$$\epsilon' = 4\pi d(C_2' - C_2)/1.11A \quad (1)$$

$$D = [C_2'/(C_2' - C_2)]2\pi fR(C_4 - C_4')10^{-12} \quad (2)$$

where d = electrode spacing (in centimeters), A = area of the electrodes (in square centimeters), f = frequency (in cycles/second), $R = 10^4$ ohms, in the present case. An edge correction was applied using a formula derived by Scott and Curtis.¹⁵

The values of dielectric constant ϵ' and dissipation factor D obtained from eqs. (1) and (2) are those for a mixture of cellulose and void space. The intrinsic values of dielectric constant and loss factor of cellulose may be calculated from those of the mixture in the following manner.

The dielectric constant and loss factor of a mixture of two components are given by¹⁷

$$\epsilon' = \delta_1\epsilon_1' + \delta_2\epsilon_2' \quad (3)$$

$$\epsilon'' = \delta_1\epsilon_1'' + \delta_2\epsilon_2'' \quad (4)$$

where δ_1 and δ_2 are volume fractions and the subscripts 1 and 2 refer to cellulose and vacuum, respectively. From eqs. (3) and (4) the dielectric constant and loss factor of cellulose can be written as¹⁷

$$\epsilon_1' = (d_1/d_0)(\epsilon_0' - 1) + 1 \quad (5)$$

$$\epsilon_1'' = (d_1/d_0)\epsilon_0'' \quad (6)$$

where d_1 = density of cellulose, d_0 = density of the sheet, ϵ_0' = apparent dielectric constant of the sheet, ϵ_0'' = loss factor of the sheet = $D\epsilon_0''$.

Argue and Maass¹⁸ calculated the dielectric constant of cellulose using eq. (3). In their work, Ishida et al.¹⁹ used the same method and equation for calculation of intrinsic dielectric constant of cellulose. While they claimed that this method of calculating the intrinsic dielectric constant of cellulose was developed by them, the method was, in fact, employed by Argue and Maass about 30 years ago.

Preparation of Pulps

Materials Used

Four cellulosic materials were chosen in the present study. These were: (1) ramie, (2) cotton linters, (3) bleached sulfite, (4) cellophane. The reason for choosing these materials was that they cover a wide range of crystallinity.

For the present study, ramie was obtained from the Everglades Experimental Station, Belle Glade, Florida. These fibers were obtained in the decorticated form. The degumming and bleaching methods of ramie employed so as to get pulp suitable for papermaking are reported separately.²⁰ The cotton linters used were of acetate grade. Microscopic analysis of the fiber showed that the bleached sulfite was from western hemlock. The cellophane film was obtained from the Visking Company, Chicago. It was prepared from cotton linters; there was glycerin plasticizer in the film, which was thoroughly removed by washing with water.

It is reported¹² that oxidative degradation of the pulp takes place during ethylamine treatment. In order that this could be minimized, a suitable vessel similar in construction to that used by Parker²¹ was made. This allowed not only treatment of the pulp in a nitrogen atmosphere, but also washing in the same atmosphere. The vessel was first made of Plexiglas. The thickness of the wall of the vessel was 0.63 cm., while that of top and bottom was 2.54 cm. Both the top and bottom were sealed with O-rings. The treated pulp was retained on a 250-mesh stainless steel wire cloth which was supported by a 16-mesh stainless steel screen. Both of these were held tight by the bottom O-ring. The vessel used in the present study was approximately 16 cm. high and had an internal diameter of 19 cm. so that the volume of working space was over four liters.

It should be mentioned that a Plexiglas vessel was constructed first for the ethylamine treatment. After a few treatments it was observed that Plexiglas particles were present on the samples. This was clearly visible on samples treated with 99.8% ethylamine. In order to study this in more detail the Plexiglas vessel was abandoned and a vessel of stainless steel was made. Dielectric measurements were made on samples treated with ethylamine in the Plexiglas vessel and in the stainless steel vessel. It was found that the pulp treated with ethylamine in a Plexiglas vessel had a lower value of dielectric constant than the pulp treated with ethylamine in a stainless steel vessel.

In order to study the effect of treatment on the dielectric constant, the following pulps were prepared: (1) beaten and unbeaten, (2) ethylamine treated and then beaten and unbeaten, (3) beaten and then ethylamine treated. The results of beaten pulps will be treated separately. The aqueous ethylamine concentrations chosen in the present study were approximately 74, 80, 90, and 99.8%.

Preparation of Handsheets

The pulps treated with ethylamine at the four concentrations were washed thoroughly with distilled water until the wash water was neutral. The pulps were then dried in a room conditioned at 73°F. and 10% R.H. Handsheets were made in a British sheet mold with the use of deionized water. In order to prepare sheets of better formation, a sheet mold 92 cm. high giving 200 cm.² sheets was used. The consistency of slurry used was approximately 0.05%. Sheets of excellent formation were made from beaten pulps. Immediately after forming, the sheets were subjected to a pressure of 50 psi for 5 min. and then for 3 min., after changing the blotters. They were dried between rings in a room conditioned at 73°F. and 50% R.H.

To prepare sheets at various levels of beating, each pulp was beaten in a Jokro mill at 6% consistency. Sulfite pulp was beaten for 5 and 35 min. Cotton linters were beaten for 75, 140, and 215 min. Ramie was beaten for 50 min.

In order to know the effect of consistency in a Jokro mill, sulfite pulp was beaten for 35 and 50 min. at 3, 4.5, and 6% consistencies. The densities of sheets and dielectric constants were measured. The results are given in Table I. It is seen from Table I that the apparent dielectric constant increases as the consistency is decreased and that the sheet density reaches a maximum value for an intermediate consistency of the pulp. Possibly the increase in the apparent dielectric constant could be due to the change in crystallinity of the pulp.

TABLE I
Effect of Pulp Consistency in a Jokro Mill on Dielectric
Constant and Density of Cellulose (Bleached Sulfite Pulp)

Consistency of pulp slurry	Beating time, min.	Density d_4 , g./cc.	Apparent dielectric constant at various frequencies	
			5 kcycle/ sec.	10 kcycle/ sec.
6.0	35	0.8945	3.240	3.211
4.5	35	0.9318	3.427	3.410
3.0	35	0.8720	3.467	2.439
6.0	50	0.9536	3.734	3.711
4.5	50	0.9842	3.762	3.752
3.0	50	0.9272	3.951	3.930

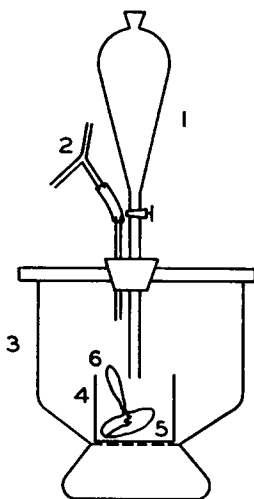


Fig. 1. Density determination apparatus: (1) separatory funnel for pouring liquid in vessel 4; (2) Y-shaped tube, one part of which is connected to the vacuum desiccator 3, a second part to the pump, and the third to a pressure gage; (3) vacuum desiccator, with a rubber stopper having two holes, one allowing the passage of a glass tube connected in turn to the Y-tube and the second for a separatory funnel; (4) vessel in which the sample is kept; (5) circular wire of copper, with several hooks along the circumference (not shown) and a hook at the center to keep the paper sample parallel to the surface of the liquid; (6) wire loop to connect the circular wire specimen holder to the hook of the balance. The diameter of the wire is about 4 mils.

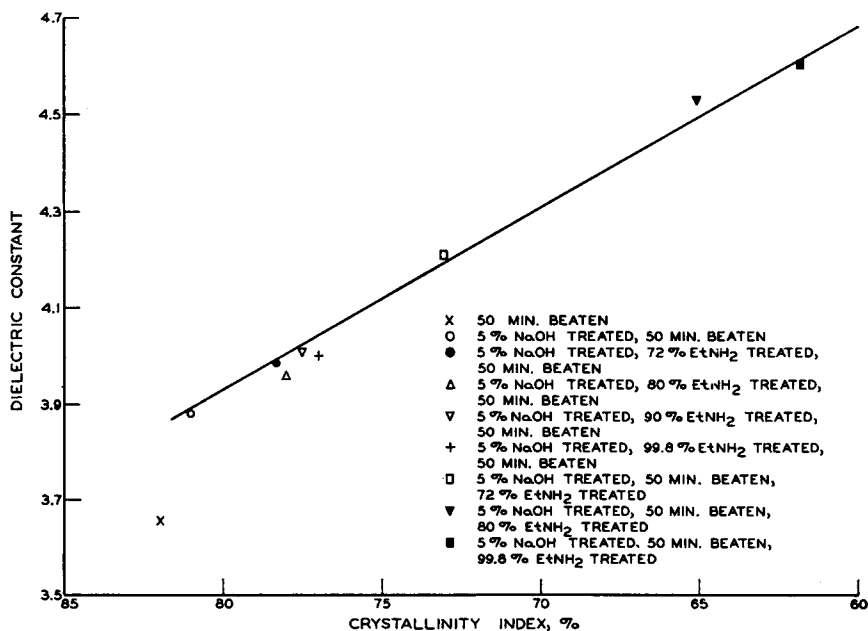


Fig. 2. Dielectric constant-crystallinity index relation for ramie fibers.

Measurement of Density of Samples

Several methods, viz., the floating method, the modified floating method,⁴ and the gradient column method, to determine the density of cellulose are reported in the literature. However, in the present study, a method based on Archimede's principle is employed. If W_1 and W_2 are the weights of a sample of cellulose in two nonpolar liquids and d_1 and d_2 are the densities of the liquids, then it can be shown that the density of the cellulose sample is given by:

$$d = (W_1d_2 - W_2d_1)/(W_1 - W_2)$$

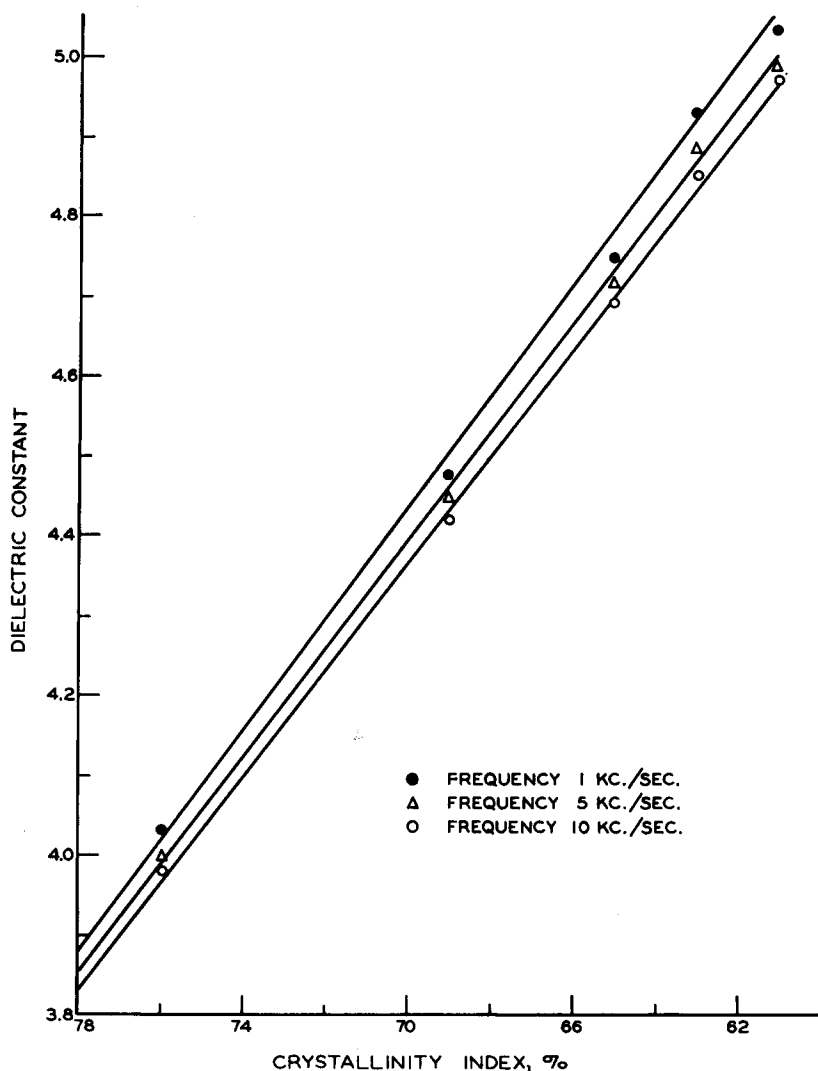


Fig. 3. Dielectric constant-crystallinity index relation for unbeaten bleached sulfite pulp.

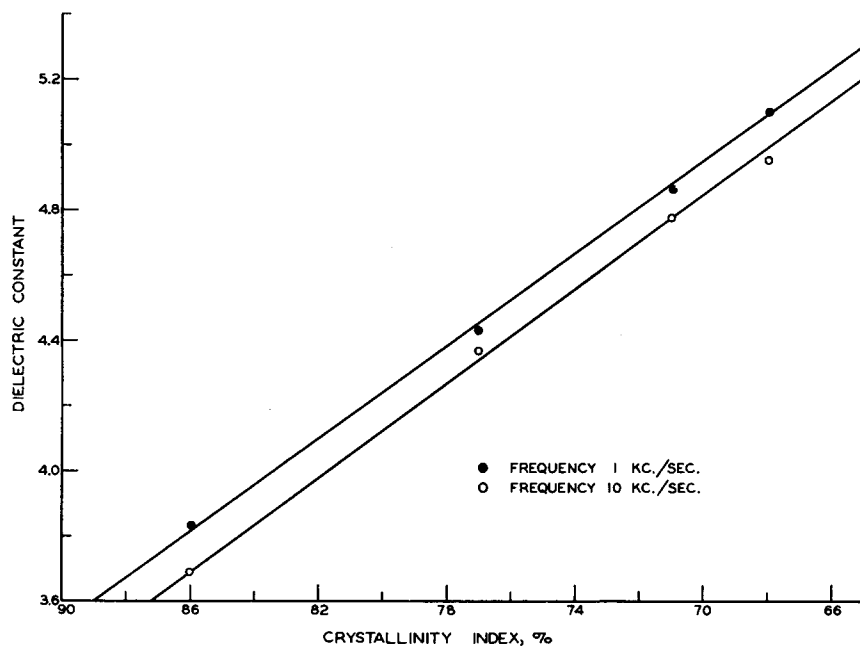


Fig. 4. Dielectric constant-crystallinity index relation for unbeaten cotton linters.

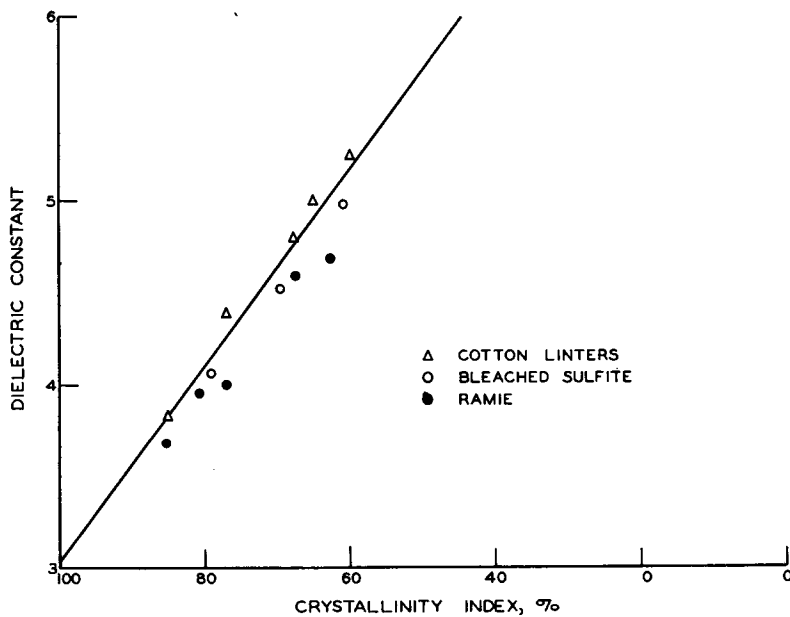


Fig. 5. Dielectric constant-crystallinity index relation for cotton linters, bleached sulfite pulp, and ramie fibers.

The apparatus used for density determination (Fig. 1) is somewhat similar to that used by Kane.⁷ The weight of each sample used for the density determination varied from 1.5 to 2.5 g. in air. Samples were water dried. Each sample was subjected to a vacuum for over 40 hr. The

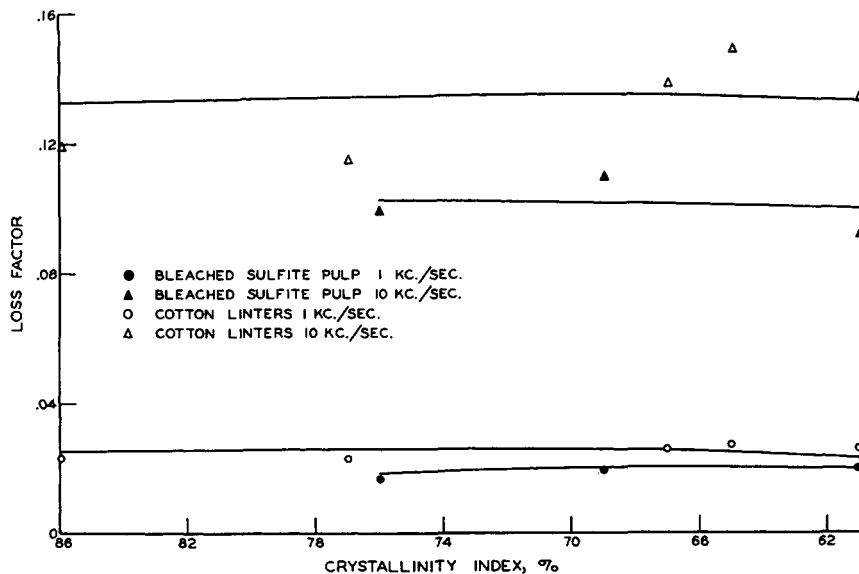


Fig. 6. Loss factor-crystallinity index relation for untreated and treated bleached sulfite and cotton linters.

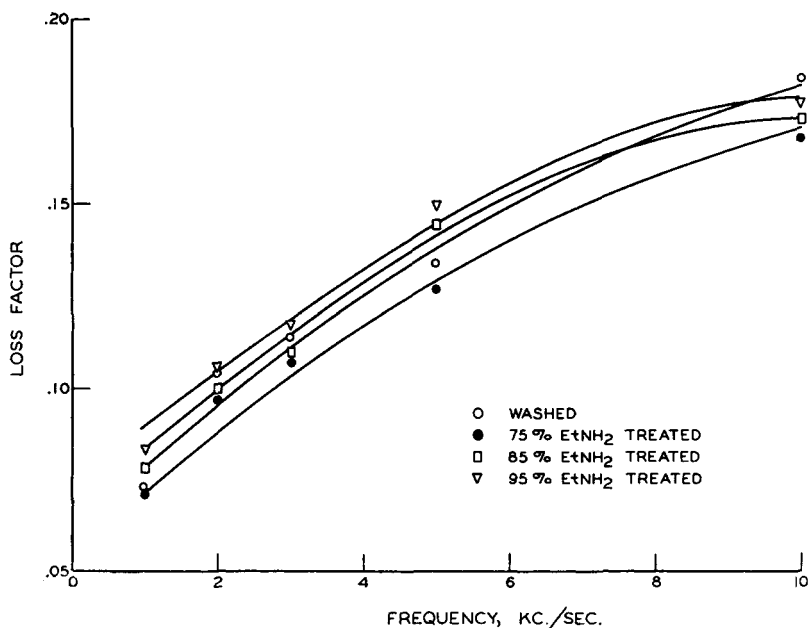


Fig. 7. Loss factor-frequency relation for cellophane.

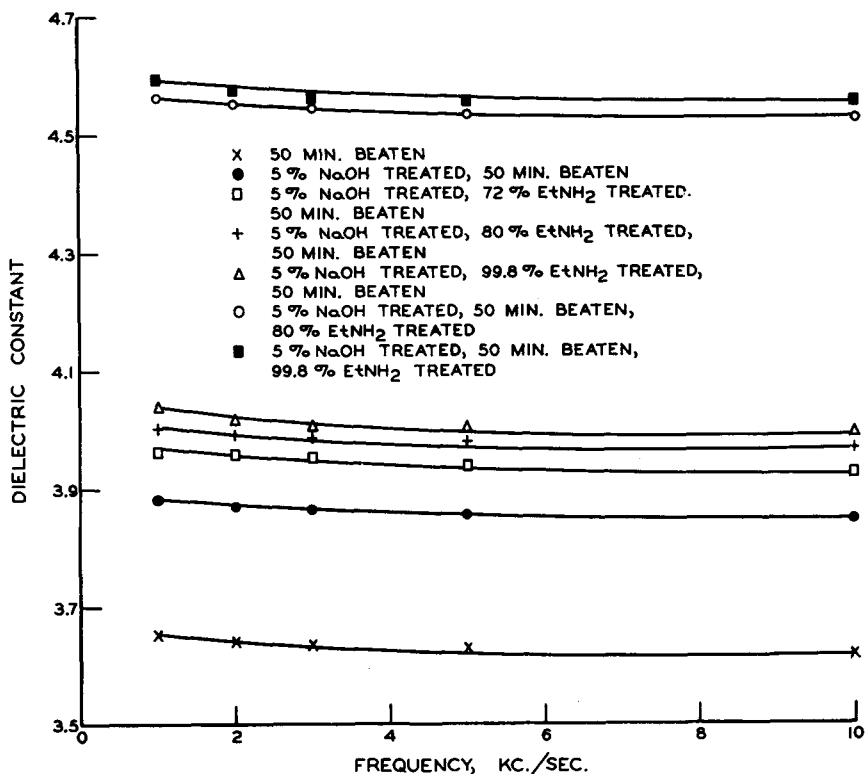


Fig. 8. Frequency dependence of dielectric constant for ramie fibers.

pressure in the system was of the order of 5μ . After the pump was turned off, the liquid was allowed to fall into the vessel. The sample was kept immersed in the liquid for 30 min. The system was then brought to atmospheric pressure and to room temperature (73°F). The vessel was then covered with a plate of glass with a hole at the center, allowing the passage of the straight suspension of the wire to the hook of the balance.

The arms of the balance were counterpoised and the weight required for balance was noted. This was done at several intervals until there was a steady equilibrium. At the end, the paper sample was carefully removed

TABLE II
Density of Kenaf Fiber

Sample	Density, g./cc. ^a
Ethylene chloride with dissolved air	1.2492
Ethylene chloride after vacuum treatment	1.2553
Benzene with dissolved air	0.8738
Benzene after vacuum treatment	0.8786
Kenaf fiber (using liquids with dissolved air)	1.5485
Kenaf fiber (second determination)	1.5482
Kenaf fiber (using vacuum-treated liquids)	1.5610

^a At R.H. = 20%, temperature = 73°F .

and the suspension system without the sample was weighed. The difference in weight of the suspension system with and without the sample gave the weight of the sample in the liquid. The sample was again subjected to vacuum treatment for the same period as before and the procedure was repeated with the second liquid. The entire procedure was repeated for both the liquids for reproducibility of results.

In order to determine whether or not the dissolved air in the liquids would make a difference in the value of the density, the whole experiment was once again performed with the use of vacuum-treated liquids. For this purpose a water aspirator pump was used. The pressure was measured with a mercury manometer and was found to be 12 mm. The liquid was subjected to a vacuum for 40 min. There was bubbling at first, but this stopped completely after 20 min. The liquid was stirred by shaking the flask.

The two liquids used in the present study are ethylene chloride and benzene. Their densities are determined by a specific gravity bottle, before and after vacuum treatment. The results are given in Table II.

EXPERIMENTAL RESULTS

Effect of Crystallinity on the Dielectric Constant and Loss Factor of Cellulose

The results of the study on the effect of crystallinity on dielectric constant and loss factor of bleached sulfite pulp, cotton linters, cellophane, and

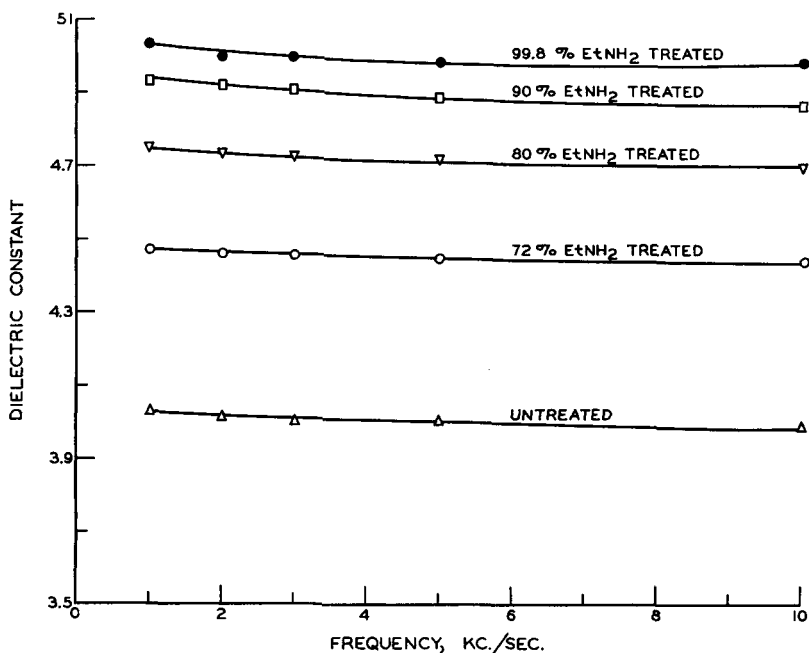


Fig. 9. Frequency dependence of dielectric constant for unbeaten bleached sulfite.

TABLE III
Dielectric Constant of Ramie Calculated at the Density of 1.59 g./cc.

Sample and treatment	Electrode pressure, psi	Sheet density, d_0 , g./cc.	Apparent dielectric constant at various frequencies					Intrinsic dielectric constant calculated to the density of cellulose (1.59 g./cc.) at various frequencies				
			1	2	3	5	10	1	.2	3	5	10
			keycycle/ sec.	keycycle/ sec.	keycycle/ sec.	keycycle/ sec.	keycycle/ sec.	keycycle/ sec.	keycycle/ sec.	keycycle/ sec.	keycycle/ sec.	keycycle/ sec.
Ramie fibers beaten for 50 min.	41	0.8364	2.369	2.364	2.361	2.350	2.363	3.601	3.592	3.586	3.565	3.560
	83	0.8433	2.392	2.389	2.386	2.381	2.373	3.623	3.618	3.612	3.600	3.588
Ramie fibers treated with 99.8% ethylamine and then beaten for 50 min.	123	0.8613	2.433	2.429	2.427	2.423	2.418	3.640	3.637	3.634	3.620	3.617
	41	0.7160	2.345	2.337	2.333	2.326	2.320	3.987	3.969	3.961	3.965	3.932
	83	0.7220	2.373	2.370	2.368	2.358	2.351	4.020	4.016	4.012	3.990	3.975
	123	0.7420	2.411	2.408	2.404	2.403	2.394	4.023	4.017	4.009	4.000	3.986

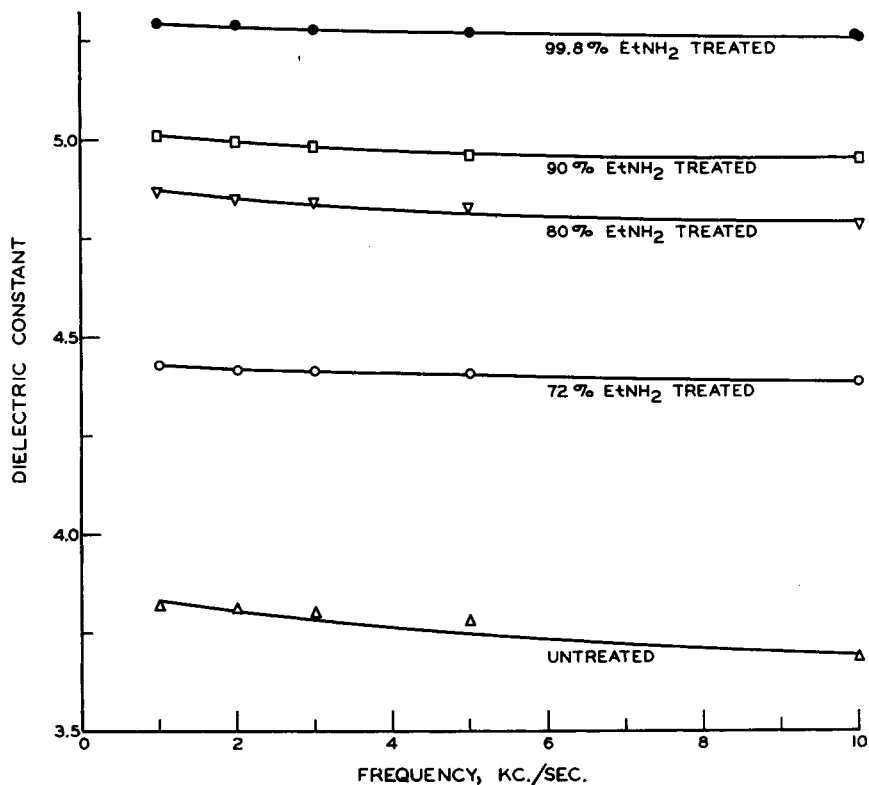


Fig. 10. Frequency dependence of dielectric constant for unbeaten cotton linters.

TABLE IV
Densities of Ethylamine-Treated Samples

Sample	Approximate concentration of EtNH ₂ in water, %	Density, g./cc.
Unbeaten bleached sulfite	0	1.565
	72	1.555
	80	1.550
	90	1.550
	99.8	1.545
Unbeaten cotton linters	0	1.562
	72	1.560
	80	1.552
	90	1.540
	99.8	...
Cellophane	0	1.534
	75	1.532
	85	1.532
	95	1.531

ramie are presented in Figures 2-11. The frequency dependence of dielectric constant on the samples treated with various percentages of ethylamine is also given. The effect of beating on the dielectric constant and loss factor of these samples beaten under different conditions will be treated separately. Table III gives the apparent dielectric constant, sheet density, and intrinsic dielectric constant of untreated and 99.8% ethylamine-treated ramie fibers at 41, 83, and 123 psi electrode pressures. It is seen that the intrinsic dielectric constant calculated to the density of solid cellulose agrees well within the experimental error, showing that the electrode pressure has no effect on the intrinsic dielectric constant of cellulose. Consequently, the apparent dielectric constant of cellulose measured at 123 psi has been

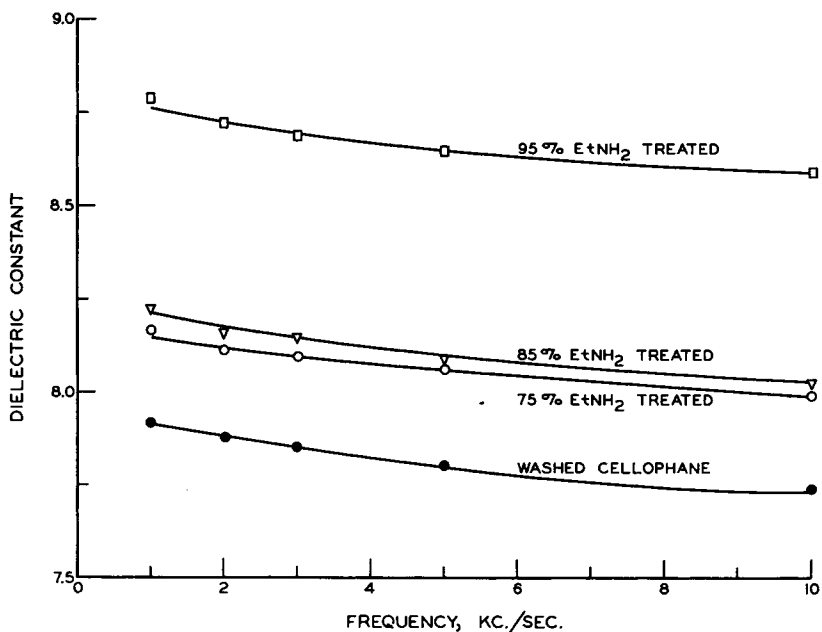


Fig. 11. Frequency dependence of dielectric constant for cellophane.

used for calculating the intrinsic dielectric constant of the other cellulosic samples studied.

The intrinsic dielectric constants and loss factors of cellulose given in Figures 2-11 are calculated from the apparent dielectric constants by using the density of crystalline cellulose at 1.59.⁴ The purpose of doing this was to compare the dielectric constants at a constant density to the crystallinity of cellulose. However, it should be noted that the decrease in density of cellulose by ethylamine treatment is small and the consequent difference between the dielectric constants calculated at density 1.59 and at the density of cellulose under that condition is 1.7% for ramie, 1.8% for bleached sulfite, 1.86% for cotton linters, and 4.5% for cellophane. The density of the untreated and treated samples is given in Table IV.

It is seen from Figures 2-4 that a linear relationship for each sample exists between dielectric constant and crystallinity. Figure 5 gives the dielectric constant-crystallinity curve for ramie, bleached sulfite, and cotton linters. Cellophane is not included, the reasons for which will be given later. Treating cellulose with ethylamine causes swelling, producing more random orientation of molecular chains. In other words, more accessible portions are formed, resulting in an increase in dielectric constant. Figures 6-9 indicate that there is no significant change in the loss factor of untreated and treated samples. The frequency dependence of dielectric constant is given in Figures 8-11 and the absorption is given in Figure 6. It is seen from these figures that samples treated without and with ethylamine obey anomalous dispersion and absorption.

However, it should be noted that a decrease in crystallinity of cellulose occurs for a treatment of ethylamine concentration only between 75 and 100%. If water is used as the washing agent, then the change in crystallinity is only 15-20%. It is found that washing the ethylamine-treated cellulose with ice-cold tap water produces no significant change in crystallinity in comparison to the ethylamine-treated cellulose washed with distilled water at room temperature. It has been reported in the literature²² that if ethylamine is removed from cellulose by chloroform, then a further decrease in crystallinity takes place. A detailed report on the swelling of cellulose with ethylamine will be published separately.²³

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Résumé

On a fait une étude des propriétés diélectriques et de la cristallinité, par la méthode de diffraction aux rayons-X, de ramies, de fibres de coton, de la pulpe blanchie par le sulfite et de la cellophane. Ces matériaux cellulosiques ont été traités par des solutions aqueuses d'éthylamine de diverses concentrations. On trouve une relation linéaire entre la constante diélectrique et la cristallinité. Les résultats montrent aussi que la constante diélectrique et le facteur de perte de la cellulose, traitée par l'éthylamine, obéissent à une dispersion et absorption anormales. La différence de densité des échantillons traités et non traités par l'éthylamine n'est pas significative dans le domaine de changement de cristallinité observé par traitement à l'éthylamine. En vue de calculer les constantes diélectriques intrinsèques de la cellulose de différentes cristallinités, on a employé, comme point de comparaison, la densité de la cellulose cristalline.

Zusammenfassung

Eine Untersuchung der dielektrischen Eigenschaften und der Kristallinität durch Röntgenbeugung wurde an Ramie, Baumwollinters, gebleichtem Sulfitpulp und Zellophan ausgeführt. Diese Zelluloseprodukte wurden mit verschiedenen Konzentrationen an Äthylamin in Wasser behandelt. Zwischen der Dielektrizitätskonstanten und der Kristallinität besteht eine lineare Beziehung. Die Ergebnisse zeigen weiters, dass Dielektrizitätskonstante und Verlustfaktor von Äthylaminbehandelter Zellulose eine anomale Dispersion und Absorption aufweisen. Für den bei Äthylaminbehandlung beobachteten Kristallinitätsbereich besteht kein signifikanter Unterschied in der Dichte der unbehandelten und behandelten Proben. Bei der Berechnung der spezifischen Dielektrizitätskonstanten von Zellulose verschiedener Kristallinität wurde zum Vergleich die Dichte der kristallinen Zellulose verwendet.

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