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

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Synopsis

Investigations have been made on the influence of (1) beating on the dielectric properties of cellulose, (2) beating before and after ethylamine treatment of cellulose, (3) compressive stress and moisture on the crystallinity of cellulose, (4) pelletizing cellulose for measurement of crystallinity, and (5) employing different methods of drying the cellulose on the crystallinity of cellulose. It was found that existing formulas involving the 002 peak intensity for estimating the crystallinity index seem to be inadequate. It is suspected that ethylamine treatment does not "decrystallize" cellulose but causes swelling of cellulose, resulting in an alteration in the lateral order structure of the so-called "amorphous content" of cellulose. It is suggested that the moisture regain method is more suitable for comparing the dielectric constant and accessibility of cellulose.

A study¹ of the effect of density due to electrode pressure and due to beating has involved use of the equations:

$$[(\epsilon - 1)/(\epsilon + 2)](1/d_0) = k$$
 (1)

$$\epsilon_1 = (\epsilon - 1) (d_c/d_0) + 1 \tag{2}$$

where ϵ = dielectric constant of cellulose at sheet density d_0 , d_c = reference density (1.0 g./cc. in the previous study¹ and 1.59 g./cc. in the present work), ϵ_1 = intrinsic dielectric constant of cellulose, k = constant.

Use of eqs. (1) and (2) led to the result that beating increased the dielectric constant. The effect of ethylamine treatment on dielectric properties and crystallinity of cellulose was also investigated. The results for unbeaten pulps have been reported.² Several other interesting studies, viz., the influence of beating on pulps before and after ethylamine treatment, the effect of compressive stress and moisture on crystallinity of cellulose, the effect of pelletizing cellulose for crystallinity measurements, have been made. The results of these investigations are reported in the present paper.

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Fig. 2. Frequency-loss factor relationship of unbeaten and beaten cotton linters.

EFFECT OF BEATING ON DIELECTRIC PROPERTIES AND **CRYSTALLINITY OF CELLULOSE**

Several years ago Bergman and Johnson³ studied the effect of beating on the accessibility of wood pulps using the moisture regain method. They reported that beating had either no effect on the ratio of the accessible to the nonaccessible cellulose in wood pulps or that, if such changes did occur, they would be masked by the variation inherent in the procedure

	Beating time, min.	Crystallinity index, C.I. = $100[I_{max} - I_{am}]I_{max}$, %
Bleached sulfite pulp	0	76.0
	5	75.0
	35	74.2
	50	75.0
Cotton linters	0	86.0
	75	86.0
	140	85.2
	215	86.0

TABLE I					
Effect of Beating of Pulp	on Crystallinity by X-Ray Diffraction				

used. It should be noted that the samples used by these investigators were only moderately beaten, and, consequently, it is not surprising that no change was detected. In the present study, bleached sulfite pulp and cotton linters were beaten over a wide range.

To study the effect of beating on the dielectric properties, the sulfite pulp was beaten for 0, 5, 35, 50, and 75 min. and the cotton linters for

Besting time			
min.	Density, g./cc.		
0	1.562		
75	1.560		
140	1,561		
215	1,558		

TABLE II

The samples were beaten in a Jokro mill. 0, 75, 140, and 215 min. The preparation of handsheets and method of measuring dielectric properties were reported earlier.¹ The intrinsic dielectric constants of pulps were calculated by using eq. (2). The results, given in Figure 1, may be expressed by observing that 75 min. of beating caused the dielectric constant of the bleached sulfite pulp to increase 9% while a beating interval of 215 min. produced a 12% increase in the dielectric constant of the cotton linters. This could be due to the fact that beating increases the accessible portion of cellulose, the dielectric constant of which is higher than that of the inaccessible portion.⁴⁻⁶

The effect of beating on loss factor is given in Figure 2. It is seen that the loss factor of the fiber decreases as the level of beating increases.

The previous investigation² showed that there could be a relationship between dielectric constant and crystallinity determined by x-ray diffraction. As the crystallinity decreased, the dielectric constant increased.



Fig. 3. Frequency dependence of dielectric constant on untreated and treated cotton linters.

Since this is true, then beating should decrease the crystallinity. But results from the x-ray diffractograms of beaten and unbeaten sulfite pulp and cotton linters did not show that beating altered the crystallinity. This could be due to the fact that x-ray diffraction is insensitive to small changes in crystallinity. Table I gives the beating time and crystallinity index measured by x-ray diffraction.

The densities of the beaten cotton linters were measured by a method described earlier.² A slight change in density was observed. The results are given in Table II.

INFLUENCE OF BEATING ON PULPS BEFORE AND AFTER ETHYLAMINE TREATMENT

Influence of Beating After Ethylamine Treatment

It was mentioned above that beating increased the dielectric constant. Hence, it should decrease the crystallinity. It was thought that if cellulose was treated with ethylamine and then beaten the dielectric constant should show a marked increase and, consequently, the crystallinity should show a marked decrease. But this was not the case. Bleached sulfite pulp, cotton linters, and ramie were swollen with ethylamine of various concentrations in water. The method of treatment and apparatus used have been reported earlier.² The treated pulps were washed with distilled water and then beaten. The dielectric constant, loss factor, crystallinity index (C.I.) and density were determined for carefully prepared handsheets. The results are given in Figures 2–5 and Table III.

Typical x-ray diffractograms of ramie and of cotton linters are given in Figures 6 and 7. These x-ray diffractograms show that beating of pulp after ethylamine treatment restores the crystallinity to the original value within the experimental error. The changes in height of the peaks is due to the difference in the mass of the material used.



Fig. 4. Frequency-loss factor relationship of bleached sulfite pulp treated with and without ethylamine.



Fig. 5. Frequency-loss factor relationship of ramie treated with and without ethylamine.

Sample no.	Specifications	Crystal- linity index C.I., %	Density, g./cc.
1	Degummed, bleached, and beaten for 50 min.	81	1.555
2	Degummed, bleached, treated with 5% NaOH, and then beaten for 50 min.	80.7	1.557
3	Degummed, bleached, treated with 5% NaOH, 72% EtNH ₂ , and then beaten for 50 min.	77.3	1.559
4	Degummed, bleached, treated with 5% NaOH, 80% EtNH, and then beaten for 50 min.	76.5	1.560
5	Degummed, bleached, treated with 5% NaOH, 90% EtNHa and then beaten for 50 min.	77 0	1 559
6	Degummed, bleached, treated with 5% NaOH, 99.8% EtNH ₂ , and then beaten for 50 min.	78.0	1.556

TABLE III Density of Ramie Sample Before and After Ethylamine Treatment

Influence of Beating Before Ethylamine Treatment

Cotton linters and ramie were studied in this case. The cotton linters were beaten for 75, 140, and 215 min. and ramie was beaten for 50 min. Both the pulps were treated with 80 and 99.8% ethylamine. After treat-

ment the pulps were washed with distilled water and handsheets were made. The dielectric properties and x-ray crystallinities were also measured. The results are included in Figures 2, 3, and 8. Typical x-ray diffractograms of ramie and cotton linters are given in Figures 9 and 10. The change in height of peaks is due to the change in thickness of the sample used. Modification of the diffractogram produced by further beating is shown in Figure 11. Comparison of Figure 10 with Figure 12 shows that the apparent alteration in lateral order structure caused by the swelling of cellulose by ethylamine is not affected if the pulp is beaten before the ethylamine treatment, whereas beating subsequent to treatment, as shown above, tends to restore the crystallinity.

EFFECT OF COMPRESSIVE STRESS AND MOISTURE ON DIELECTRIC PROPERTIES AND CRYSTALLINITY OF CELLULOSE

It has been reported in the literature⁷ that the pressure (compressive stress) used in the preparation of flat-disk samples for the determination of crystallinity decreases the crystallinity of cellulose. When this effect is to be studied, many factors have to be taken into consideration. This will be dealt with in greater detail in the next section. In the present study, since a correlation between the dielectric constant and crystallinity was under investigation, determination of these two quantities were made as far as possible under identical conditions. Hence, small rectangular portions from the handsheets, used for dielectric measurements, were used for the crystallinity determinations.

Ant-Wuorinen and Visapää⁸ found that the presence of moisture in cellulose affected the crystallinity. However, it was felt desirable to investigate this effect in greater detail, and the following procedure was adopted.

Unbeaten cotton linters treated with 99.8% ethylamine were used for the following experiment. Immediately after the formation of a sheet in the British sheet mold, the former was covered with one thickness of blotter and was couch-rolled a few times to remove the excess water. Small rectangular pieces of the handsheets were cut, and x-ray diffractograms were taken. Then x-ray diffractograms of these were again taken at partially dried (again by couch-rolling between blotters a few times) and completely dried (finally in air) stages. The x-ray diffractogram at each stage is given in Figure 12. It is seen from this figure that the x-ray diffractogram changes to its original pattern (cellulose I) when water is completely removed.

In order to determine whether the presence of water in the sample caused a real change in the crystallinity index, corrections for the dead time of the Geiger tube and the statistical distribution of the x-ray intensity were applied.⁹

As a further means for testing the effect of water on crystallinity, halfwidths were determined. With reference to Figure 14, obtained for a





Fig. 6. X-ray diffractograms of degummed, bleached, and 5% sodium hydroxidetreated ramie: (a) beaten for 50 min.; (b) treated with 72% ethylamine and then beaten for 50 min.; (c) treated with 99.8% ethylamine and then beaten for 50 min.

handsheet prepared from cotton linters first beaten for 140 min. and then treated with 99.8% ethylamine, the values of N at P_n , P_n' give intensities of the background and maximum at any value of 2θ . These values are calculated using the data from x-ray measurements.⁹ A graph is drawn of $(I_{\max} - I_{back})$ against 2θ for the dry sample. A second graph is drawn for the same sample, but wet. The half widths are measured in each case. If half widths are denoted by B_{dry} and B_{wet} , then B_{dry} could be equal to, greater than, or less than B_{wet} . If B_{dry} is equal to B_{wet} , then the presence of water causes no change in the crystallinity. On the other hand, if B_{dry} is less than B_{wet} a decrease in the crystallinity is indicated for the wet cellulose. Typical diffractograms are given in Figures 13 and 14. Figure 15 shows the half widths for dry, wet, and rewet samples.

X-ray diffractograms for wet, dry, and rewet samples were obtained as follows. A sheet obtained from the British sheet mold was couch-rolled a few times to remove excess water. A few rectangular pieces of wet sheet were cut to take x-ray diffractograms. The remaining part of the sheet was dried at 200 psi in a Williams press. The x-ray diffractograms were



taken. To rewet the dried sample, the sheets were soaked in water for 30 min. These were then pressed between blotters and the x-ray diffractograms were again taken.

It was determined from Figure 15 that the half widths are 4.7, 4.1, and 4.2 arbitrary units, respectively, for wet, dry, and rewet samples. This shows that in the wet sample, there may be a decrease in the lateral order structure due to the swelling of the fibers. On the other hand, the half widths of the same sample in the dry and rewet condition have almost the same value. This shows that in the rewet sample, there may not be any change in the lateral order structure. Ant-Wuorinen and Visapää^s reported that increasing the relative humidity lowered the crystallinity.



Fig. 7. X-ray diffractograms of cotton linters: (a) cotton linters untreated and unbeaten; (b) cotton linters untreated and beaten 215 min.; (c) cotton linters treated with 80% ethylamine and beaten 215 min.; (d) cotton linters treated with 99.8% ethylamine and beaten 215 min.;



Fig. 8. Crystallinity index-dielectric constant relationship of cotton linters, beaten and treated with and without ethylamine.

They found that when the relative humidity was increased from 0 to 53.5%, the crystallinity was lowered by 4.5% for cotton linters, 4.2% for bleached sulfite pulp, and 8.5% for viscose staple rayon. This change was reversible when the relative humidity was returned to zero.

The effect of moisture on dielectric constant and loss factor of a bleached sulfite sample, treated with and without ethylamine are given in Figure 16. It is seen that both dielectric constant and loss factor increase as the moisture content is increased.

EFFECT OF USING PELLETS FOR DETERMINATION OF X-RAY CRYSTALLINITY

Debye and Scherrer¹⁰ developed the powder technique for analysis of crystals by x-ray diffraction. Using this technique, many investigators have powdered cellulose, compressed it in pellet form, and then measured the crystallinity by x-ray diffraction. However, as mentioned earlier, since the purpose of the present investigation was to study the correlation between dielectric constant and crystallinity, the powder technique was evaluated and then abandoned. The main factors influencing the apparent crystallinity of powdered cellulose would be the fineness of the screen, time of pressing, and magnitude of the compressive stress applied. Effects of compressive stress and fineness of the screen were investigated in the present work, and the results are given in Table IV. The dry cotton linters were treated in a Wiley mill, in one case using a 20-mesh screen and in another an 80-mesh screen. (Only the material passing the screen was used.)



Fig. 9. X-ray diffractograms of degummed, bleached, and 5% sodium hydroxidetreated ramie: (a) beaten for 50 min. and then treated with 80% ethylamine; (b) beaten for 50 min. and then treated with 99.8% ethylamine.

The weight of each pellet was 0.5 g. The time of pressing was 1 min. in each case. It is seen that the crystallinity index of cellulose is reduced by powdering it in a Wiley mill, passing it through a screen, and then making a pellet at a high compressive stress.



Fig. 10. X-ray diffractograms of cotton linters: (a) cotton linters beaten 75 min. and then treated with 99.8% ethylamine; (b) cotton linters beaten 215 min. and then treated with 99.8% ethylamine.

Since rectangular sheets were used for crystallinity measurements in the present study, the effect of the thickness of the samples was investigated. To study this and the reproducibility of the results, the following procedure

Effects of Pelletizing on the Crystallinity Index of Cotton Linters						
Untreated cotton linters			EtNH ₂ -treated cotton linters			
		Crysta inde	allinity x, %	Treatment	Crystallinity index, %	
Sample	Pressure, psi	20 mesh	80 mesh		Paper (50 psi)	Pellet (7650 psi, 20 mesh)
Pellet	7,650 20,600 30,600	78 77 79		Beaten 140 min. after 99.8% EtNH ₂ treat- ment	83	74
Paper	50ª	86		Beaten 140 min. before 99.8% EtNH₂ treat- ment	68	62

TABLE IV ts of Pelletizing on the Crystallinity Index of Cotton Lin

* Pressed for 8 min. after formation.

was adopted. First, the x-ray diffractogram was obtained on a single sheet. The specimen was then replaced after rotating it through 90° , and the diffractogram was again recorded. The number of specimens was then gradually increased until the x-ray diagram reached its saturation. Although the heights of the peaks in the x-ray diffractograms gradually increased as the thickness of the specimen was increased to saturation, the crystallinity index remained unaltered.

While studying the x-ray diffractograms of cotton, Nelson and Schultz¹¹ recently investigated the effect of sample size, use of cement, and the kind of metal in the sample holder. According to them, an appropriate standard sample weight for a 1×2 cm. rectangular x-ray specimen (pellet) of cotton



Fig. 11. X-ray diffractograms of cotton linters first beaten for 215 min., then treated with 99.8% ethylamine, and then further beaten for 140 min.



cellulose is 100 mg. From the present work, it is clear that if small rectangular pieces of handsheets $(3.8 \times 2.54 \text{ cm.})$ are used as samples, saturation in the x-ray diffractogram occurs at and above a certain thickness, depending on the density of the material and possibly other factors. When handsheets can be used as samples, then it is preferable to prepare sheets



Fig. 12. X-ray diffractograms of 99.8% ethylamine treated and unbeaten cotton linters handsheets: (a) handsheet saturated with water; (b) same handsheet, partly dried; (c) same handsheet, dried more than in Fig. 12b; (d) same handsheet, completely dried.



1184



Fig. 14. X-ray diffractogram of sample used in Figure 13 dried completely.



Fig. 15. Curves showing half widths for wet, dry, and rewet handsheets from cotton linters.

of larger thickness and to use two or three pieces (as many as needed for saturation). After inserting the sample (without a holder) into the goniometer, it is then possible to keep the sample in position by means of a flat paper clip. This procedure eliminates any error due to cement and holder. Although Nelson and Schultz found that use of a mixture of 10 ml. Duco cement and 100 ml. amyl acetate to prevent bulging of the specimen does not affect the diffractogram, the present procedure is direct and simple.



Fig. 16. Effect of moisture content on dielectric constant and loss factor of unbeaten and ethylamine-treated bleached sulfite pulp: (a) effect of moisture content on dielectric constant of unbeaten bleached sulfite pulp; (b) effect of moisture content on dielectric constant of unbeaten and 72% ethylamine-treated bleached sulfite pulp; (c) effect of moisture content on dielectric constant of unbeaten and 99.8% ethylamine-treated bleached sulfite pulp; (d) effect of moisture content on loss factor of unbeaten 72 and 99.8% ethylamine-treated bleached sulfite pulp.

Also, since the saturation thickness is used, variation in the x-ray diffractogram arising in thickness fluctuation is eliminated. If the sample under test is in the powder form, a moderate compressive stress, say 2000 lb./in.², is applied to form a pellet. The applied compressive stress may be altered so that the pellet may not break during insertion in the sample holder. In this case, also, the saturation thickness of the pellet should first be investigated. An aluminum holder is recommended for inserting the pellet.



Fig. 17. Diffraction patterns of celluloses I, II, III, and IV.¹⁴

EFFECT OF DIFFERENT METHODS OF DRYING ON THE CRYSTALLINITY OF CELLULOSE

In the present study, all samples used were washed with water and dried in air. The water from a water-swollen sheet can also be removed by the solvent replacement technique, e.g., washing the wet sheet with methyl alcohol, acetone, and finally with benzene. In a similar manner, the ethylamine from an ethylamine-swollen fiber can be removed by washing with water or pyridine or by distilling with chloroform. The effects of such treatments will be treated separately. It has been reported that the properties of the fiber depend upon the method of water removal. If the solvent replacement technique is used to dry the fiber, it will have increased dielectric constant⁶ and decreased crystallinity compared to those of waterdried samples.¹² If cellulose is treated with ethylamine which is then removed by chloroform, a still lower value of crystallinity than that obtained by solvent replacement drying occurs.¹³

This could be due to the fact that the liquids such as benzene, acetone, chloroform, etc., being nonswelling agents, help in retaining the change produced by aqueous swelling in the lateral order structure of cellulose.



Further disorder in lateral order structure is effected by ethylamine treatment since ethylamine has a greater swelling capacity than water. It is worth mentioning that the change in lateral order structure need not be in the crystalline region but probably occurs in the so-called amorphous portion of the cellulose.

CELLOPHANE

In the present study, one of the samples used was cellophane because of its low value of crystallinity and, consequently, high value of dielectric The chemical analysis of the cellophane film is given in Table V. constant. The dielectric measurements showed that the cellophane had a dielectric constant of about 8 at 1 kcycle/sec. for the glycerin-plasticizer-removed sample and about 8.8 at the same frequency for the 95% ethylaminetreated sample. X-ray diffractograms were taken to calculate the crystallinity. Cellophane is cellulose II. In the case of cellulose II and III, the molecules are displaced relative to one another along the a axis and in cellulose IV the group of chains are displaced relative to one another in the b axis. In all the cases, the intensity of the peak corresponding to the 002 plane is predominant. The x-ray diffractograms of celluloses I, II, III, and IV¹⁴ are given in Figure 17. The x-ray diffractograms of cellophane, unwashed, washed, and 75, 85, and 95% ethylamine-treated, obtained from the present study are shown in Figure 18. It is seen that in addition to the shift of $10\overline{1}$ peak toward 002, a reversal of intensity also is observed.

Onennear marysis of	Cenophane	
Glucan, % ^b	96.9	
Xylan, % ^b	<0.5	
Mannan, % ^b	<0.5	
Araban, % ^b	<0.5	
Galactan, % ^b	<0.5	
Ash, %°	0.1	

TABLE V Chemical Analysis of Cellophane^a

* Basis of report: sugars, ovendry (water-washed); ash, ovendry.

^b Method of Saeman et al.¹⁷

• Method of TAPPI T 15 m-58.

The crystallinity index in all cases has been calculated by using the formula,¹⁵ C.I. = $100(I_{max} - I_{min})/I_{max}$. This formula appears to be inapplicable to cellophane (cellulose II).¹⁶ In using this formula, the peak corresponding to the 002 plane is considered and the corresponding value of crystallinity index is regarded as the state of order in the sample. Despite the fact that the 101 and 101 peaks also contribute to the order in the system, they are not taken into consideration. In cellophane, the 101 peak is very sharp. If this peak were used in calculating the crystallinity index, then the crystallinity index of cellophane would be approximately the same as that of cotton linters. Consequently, it seems that further work is to

be done to estimate the crystallinity of cellophane from x-ray diffractograms.

The dielectric constant obtained for cellophane is of the expected order. Verseput⁵ and Kane⁶ found a linear relationship for dielectric constant and accessibility by moisture regain for cellulose fibers; in Kane's work the relationship held also for cellophane. This seems to be reasonable because higher amorphous content in cellulose should be associated with both higher moisture regain and dielectric constant. On the other hand, x-ray diffraction gives inconsistent patterns. Consequently, the values of the order of crystallinity of cellophane estimated by any of the methods reported in the literature give unreliable results when compared with the dielectric constant.

DISCUSSION

It is interesting to note that there exists a definite relationship between dielectric constant and lateral order structure of cellulose as determined by x-ray diffraction. The relationship for unbeaten samples is given in an earlier paper. Several factors influencing the dielectric constant and crystallinity are considered and the corresponding dielectric properties and crystallinity indices are reported in this paper. In order to know whether the relationship will hold good for cellulose treated under any condition used in this investigation, dielectric constants of some samples and their crystallinities are chosen at random and are plotted. These values for cotton



Fig. 19. Dielectric constant-crystallinity index relation for cotton linters.

linters and for bleached sulfite pulp are given in Figures 19 and 20, respectively. It is seen from Figure 19 that beating the sample first and then treating it with ethylamine retains the change in lateral order structure.

The moisture regain method may be more suitable than x-ray diffraction for comparison of the dielectric constant and order of cellulose. It should be noted that the moisture regain method has its own shortcomings just as other methods do. It is well known that x-ray diffraction is insensitive to small crystalline regions. But, emphasis should be given to the fact that, in the dielectric method, polarization is uniquely determined by the struc-



Fig. 20. Dielectric constant-crystallinity index relation for bleached sulfite pulp.

ture of the system. All of the molecules within the system make their contribution to the polarization. In other words, each of these types of submicroscopic structure makes its characteristic contribution to the observed dielectric constant. Figures 19 and 20, showing the correlation between dielectric constant and crystallinity, indicate the importance of the freedom of the free hydroxyl groups and of portions of the cellulose molecules in determining the dielectric constant of cellulose. Since such motion is restricted in the crystalline regions, only atomic and electronic polarization might occur, thus explaining the lower value of the observed dielectric constant.

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Résumé

Des résultats sont présentés concernant l'influence (1) du laminage sur les propriétés diélectriques de la cellulose, (2) du laminage avant et après le traitement de la cellulose avec l'éthylamine, (3) de la force de compression et de l'humidité sur la cristallinité de la cellulose, (4) de la création des boulettes de la cellulose pour le mésurement de la cristallinité, et (5) de l'emploi de différentes méthodes de séchage sur la cristallinité de la cellulose. On a trouvé que les formules qui utilisent l'intensité du pic 002 pour estimer l'indice de cristallinité sont inadéquates. On a supposé que le traitement avec l'éthylamine ne décristallise pas la cellulose mais la gonfle seulement, provoquant un changement dans la structure latérale de la "partie amorphe". On a suggéré que la méthode de regain d'humidité est plus favorable pour comparer la constante diélectrique et l'accessibilité de la cellulose.

Zusammenfassung

Eine Untersuchung des Einflusses (1) des Klopfens auf die dielektrischen Eigenschaften von Zellulose, (2) des Klopfens vor und nach der Äthylaminbehandlung von Zellulose, (3) der Kompressionsspannung und der Feuchtigkeit auf die Kristallinität von Zellulose, (4) der Pelletisierung von Zellulose für die Kristallinitätsmessung und (5) der Verwendung verschiedener Trocknugsmethoden für die Zellulose auf die Kristallinität von Zellulose wurde durchgeführt. Die bekannten auf der Intensität des 002-Maximums beruhenden Formeln zur Bestimmung des Kristallinitätsindex scheinen nicht brauchbar zu sein. Es wird vermutet, dass eine Äthylaminbehandlung Zellulose nicht "dekristallisiert," sondern eine zu einer Änderung der seitlichen Ordnungsstruktur des sogenannten "amorphen Anteils" der Zellulose führende Quellung verursacht. Es wird angenommen, dass die Methode der Feuchtigkeitswiederaufnahme zum Vergleich der Dielektrizitätskonstanten und der Zugänglichkeit von Zellulose besser geeignet ist.

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1192