

On Relationship between Dielectric Properties and Crystallinity of Cellulose*

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Abstract—In the present paper, the dielectric properties for nine dry celluloses were studied over the frequency range from 3×10^2 to 3×10^5 Hz and at -32°C , and compared with their crystallinity estimated by moisture regain. Furthermore, using the theory of FUOSS-KIRKWOOD, a relationship between the dielectric property and the noncrystalline content was derived, and its validity was examined experimentally.

Introduction

The dielectric behaviors of cellulose have already been investigated by many authors. And it has been reported that only one dielectric relaxation in dry state is observed in high frequency range at room temperature.¹⁾ Recently, MIKHAILOV et al.,²⁾ and NORIMOTO and YAMADA³⁾ suggested that this relaxation process is associated with the orientational polarization of methylol groups in the noncrystalline region. If this assignment is correct, then it may be expected that the extent of dielectric dispersion is directly related to the quantity of noncrystalline fraction.

To make clear the correlation between the dielectric properties and the noncrystalline content for celluloses, the several studies have been performed. CALKINS measured the dielectric constant as a function of moisture regain for regenerated celluloses and found a linear relationship between them.⁴⁾ VERSEPUT measured the dielectric constant at 1×10^3 Hz and 30°C for several cellulose fibers to examine the relationship between the dielectric constant and the crystallinity, and showed that, although the amount of the polarization is not necessarily entirely dependent upon the quantity of amorphous region, a certain amount of the polarization seems to be due to the rotational vibration of cellulose chains in the amorphous phase since the dielectric constant of cellulose is profoundly influenced by the crystallinity.⁵⁾ KANE studied the relationship between the intrinsic dielectric constant and the water vapor accessibility of six celluloses, and obtained the following linear equation between them.⁶⁾

$$\epsilon' = 8.60\theta_2 + 3.88\theta_1 \quad \text{at } 10 \text{ kHz and } 30^\circ\text{C},$$

where ϵ' is the intrinsic dielectric constant of cellulose, and θ_1 and θ_2 are the inaccessible and the accessible fractions, respectively. According to this equation, the dielectric constants of the accessible and the inaccessible celluloses are 8.60 and 3.88, respectively. ISHIDA et al. measured the dielectric constant and loss factor for three cellulose fibers in dry condition over the frequency range from 5×10^2 to 3×10^6 Hz and the temperature range from -60 to 20°C , and showed that the values of $(\epsilon_0' - \epsilon_\infty')$ determined from Cole-Cole plots, which are proportional to the concentration of dipoles contributing to the orientational polarization, increase with increasing accessibility of the samples.⁷⁾ VENKATESWARAN et al. investigated the relationship between

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the intrinsic dielectric constant and crystallinity index calculated from X-ray measurements for cotton linters, bleached sulphite pulp and ramie treated with various concentrations of ethylamine, and found that there is an excellent linear correlation between them at any frequency.^{8,9)} NORIMOTO et al. measured the dielectric loss factor for cellulose powders in very low frequency range at high temperature and found a linear relationship between the dielectric loss factor and the degree of crystallinity estimated from X-ray measurements.¹⁰⁾ Thus, the dielectric constant of cellulose can be thought as that of a two component system, i.e. one component the crystalline region and the other the amorphous region, then the two phase structure of cellulose may be assumed.

According to the phenomenological theory of dielectrics, the dispersion magnitude ($\epsilon_0' - \epsilon_\infty'$) can be written as

$$\epsilon_0' - \epsilon_\infty' = \frac{2}{\pi} \int_{-\infty}^{\infty} \epsilon''(\omega) d \ln \omega, \quad (1)$$

where ϵ_0' and ϵ_∞' are the static dielectric constant and the dielectric constant at very high frequency at which the orientational polarization of dipoles is impossible, respectively, and $\epsilon''(\omega)$ is the dielectric loss factor as a function of angular frequency ω . SILLARS derived the following relation by generalizing DEBYE formula.¹¹⁾

$$\begin{aligned} \int_{-\infty}^{\infty} \epsilon'' d \ln \omega &= \int_{-\infty}^{\infty} \left\{ c \int \frac{\omega \tau}{1 + \omega^2 \tau^2} \cdot G(\tau) d\tau \right\} d \ln \omega \\ &= \frac{c\pi}{2} \cdot n, \quad c = \frac{4\pi}{3} \cdot \frac{(\epsilon_0' + 2)^2}{3} \cdot \frac{\mu^2}{3kT}, \end{aligned} \quad (2)$$

where n the number of polar molecules per c.c., μ the dipole moment, k Boltzmann constant, T the absolute temperature, τ the relaxation time, $G(\tau) d\tau = dn$, respectively. This equation shows that if $\epsilon''(\omega)$ is plotted against $\ln \omega$ the total area under the curve is proportional to the total concentration of dipoles. Employing this method, NAKAJIMA and SAITO found a linear relationship between the area under ϵ'' vs. $\log \frac{\omega}{2\pi}$ curve and the amount of amorphous region estimated from density for the low temperature dispersion of polymonochlorotrifluoroethylene.¹²⁾ Furthermore, they discussed the correlation between ($\epsilon_0' - \epsilon_\infty'$) determined from Cole-Cole plots and the crystallinity for α and β absorptions of polyethylene terephthalate.¹³⁾

From equations (1) and (2), the following relation is derived.

$$\epsilon_0' - \epsilon_\infty' = Cn. \quad (3)$$

Assuming that ϵ_∞' is constant regardless of the degree of crystallinity, then ϵ' is proportional to the concentration of the dipole contributing to the orientational polarization, i.e. the quantity of noncrystalline fraction, since it is considered that ϵ_0' is nearly equal to ϵ' in low frequency range and that the dipoles in the noncrystalline region make a substantial contribution to the orientational polarization.

On the other hand, PANDE derived theoretically the following linear relationship between ϵ' and the volume fraction of crystallinity δ for cellulose from MAXWELL relation and GLADSTONE-DALES law.¹⁴⁾

$$\begin{aligned} \epsilon' &\simeq c_1 \delta + c_2, \\ c_1 &= 2(\rho_c - \rho_a) \frac{\eta - 1}{\rho} \left(1 + \frac{\eta - 1}{\rho} \cdot \rho_a \right), \\ c_2 &= \left(1 + \frac{\eta - 1}{\rho} \cdot \rho_a \right)^2, \end{aligned} \quad (4)$$

where η the average refractive index, ρ_a and ρ_c the density of crystalline and amorphous regions, ρ the average density of the substance, respectively.

It was the purpose of the present paper to derive the relationship between the dielectric properties and the degree of crystallinity for celluloses independent of equations (2) through (4), and to examine it experimentally.

Experimental

Specimen Preparation— Nine cellulose powders shown in Table 1 were used as the samples. After the powders passed a 200-mesh screen they were dried over the phosphorus pentoxide *in vacuo* at room temperature, discs 20 mm in diameter and about 1 mm in thickness were prepared by compressing of the powders under a pressure. The density were about 1.2 g/cm³. These discs were used for both dielectric and X-ray measurements. On the other hand, for the measurement of sorption ratio the dry powders passed a 200 mesh screen were used.

Table 1. The cellulose samples used.

No.	Samples
1	Cotton treated with 3% HCl for several hrs.
2	Untreated Whatman cellulose
3	Whatman cellulose ground in a vibratory ball mill for 15 mins.
4	Whatman cellulose ground for 30 mins.
5	Avicel
6	Merck cellulose
7	Whatman cellulose ground for 1 hr.
8	Whatman cellulose treated with 17.5% NaOH (cellulose II)
9	Cotton treated with 3% HCl and then with 17.5% NaOH (cellulose II)

Dielectric Measurement— The inductive-ratio-arm bridge was employed as the measuring device. The instruments and the methods of measurement were all the same to the ones described in the previous papers.^{3,15)} The measurements were made in dry condition over the frequency range from 300 Hz to 300 kHz and at -32°C .

X-ray Measurement— The X-ray measurements were performed by the focusing technique. The samples were scanned over the range of $2\theta=8$ to 32 degree. Crystallinity index defined by SEGAL,¹⁶⁾ which expresses the relative degree of crystallinity, was calculated from the following equation.

$$CI = \frac{(I_{002} - I_{am})}{I_{002}} \times 100,$$

where I_{002} is the maximum intensity of the 002 lattice diffraction and I_{am} is the intensity of diffraction in the same units at $2\theta=18$ degree. On the other hand, the crystalline width was calculated from the 002 diffraction by using the following SCHERRER equation.¹⁷⁾

$$D = \frac{K\lambda}{\cos \theta \cdot B},$$

where B the peak breadth of the 002 diffraction at half maximum intensity, θ the Bragg angle, λ the wave length of X-ray, K the crystalline shape constant, and D the mean crystallite dimension normal to the diffracting planes, respectively. As X-ray diffractometer, Rota flex (Rotating anode X-ray generator, Rigaku Denki Co. Ltd.) was used.

Sorption Measurement— The sorption ratio of the samples was calculated as a measure for the quantity of noncrystalline fraction, since it is reported that the sorption ratio is independent of temperature and relative humidity over a wide range of the conditions and can be related with the quantity of noncrystalline fraction for cellulose by equation (15).¹⁸⁾ Here, the sorption ratio is defined as the ratio of sorption of a cellulose to that of cotton under the same conditions.¹⁹⁾ The sorption ratio was determined at 63.5% R.H. and 20°C, since it is reported that humidity of 60 to 85% would be suitable for the determination of crystallinity.¹⁸⁾

Results and Discussion

Independent of equations (2) through (4), we shall derive the equation correlating the dielectric property with the degree of crystallinity for cellulose by applying the molecular theory of FUOSS-KIRKWOOD.^{20,21)} Let us now consider a glucose residue as the unit and assume that the glucose residues in the crystalline region contribute to the dielectric constant only by the deformation polarization, while the ones in the amorphous region contribute to it by the orientational polarization in addition to the deformation polarization. Thus, using FUOSS-KIRKWOOD theory,²¹⁾ the molecular polarization is related to the quantity of amorphous region of cellulose by the following equation.

$$\varphi(\epsilon^*) \frac{\sum_{i=1}^2 M_i \theta_i}{\rho} = \sum_{i=1}^2 P_i \theta_i, \quad (5)$$

$$\varphi(\epsilon^*) = \frac{(\epsilon^* - 1)(2\epsilon^* + 1)}{9\epsilon^*}, \quad (6)$$

where $\epsilon^*(=\epsilon' - i\epsilon'')$ the complex dielectric constant, M_i and θ_i the molecular weight and the mole fraction of the i -th unit, ρ the average density of cellulose, P_i and α_i the molecular and electronic polarizability of the i -th unit, respectively. Considering that $i=1$ and 2 represent the glucose residues in crystalline and amorphous regions, respectively,

$$P_1 = \frac{4\pi N}{3} \cdot \alpha_1,$$

$$P_2 = \frac{4\pi N}{3} \left(\alpha_2 + \frac{\langle \vec{\mu} \cdot \vec{\mu} \rangle_{AV}}{3kT} \right),$$

where N the AVOGADRO'S number, $\vec{\mu}$ the dipole moment per a glucose residue in amorphous region, $\vec{\mu}$ the vector sum of μ and the moment induced by the molecule in its environment, and $\langle \vec{\mu} \cdot \vec{\mu} \rangle_{AV}$ the average value of the product $(\vec{\mu} \cdot \vec{\mu})$ taking into account all possible configurations and weighing them according to the probability of finding the unit in such a configuration, respectively. In this case, $\alpha_1 \approx \alpha_2 = \alpha_0$, $M_1 = M_2 = M$ and $\theta_1 + \theta_2 = 1$, then equation (5) becomes

$$U \equiv \varphi(\epsilon^*) - \varphi(\epsilon'_{\infty}) = \frac{\rho}{M} \cdot p_3 \cdot \theta_2, \quad (7)$$

$$\varphi(\epsilon'_{\infty}) = \frac{\rho}{M} \cdot \frac{4\pi N}{3} \cdot \alpha_0,$$

$$P_3 = \frac{4\pi N}{3} \cdot \frac{\langle (\vec{\mu} \cdot \vec{\mu}) \rangle_{AV}}{3kT}$$

Writing $P_3(\omega)$ and $P_3(0)$ as P_3 at the angular frequency $\omega = \omega$ and 0 respectively, the ratio $P_3(\omega)$ to $P_3(0)$ is represented as

$$\frac{P_3(\omega)}{P_3(0)} = \frac{\varphi(\epsilon^*) - \varphi(\epsilon'_{\infty})}{\varphi(\epsilon'_0) - \varphi(\epsilon'_{\infty})} = \int_0^{\infty} \frac{G(\tau)}{1+i\omega\tau} \cdot d\tau, \quad (8)$$

$$\int_0^{\infty} G(\tau) d\tau = 1.$$

Separating equation (8) into real and imaginary parts, the imaginary part becomes

$$H(x) = \int_{-\infty}^{\infty} \frac{e^{s-x} \cdot \Phi(s) ds}{1+e^{2(s-x)}} \simeq \frac{\epsilon'' \left(2 + \frac{1}{\epsilon'^2}\right)}{9U_0}, \quad (9)$$

$$s = \ln \frac{\tau}{\tau_0}, \quad x = \ln \frac{\omega_0}{\omega},$$

$$\tau G(\tau) = \Phi(s), \quad \int_{-\infty}^{\infty} \Phi(s) ds = 1,$$

where U_0 represents U at $\omega = 0$, τ_0 and ω_0 are τ and ω corresponding to ϵ'' maximum respectively. If $H(x)$ can be approximated by the following equation, then the distribution function for relaxation times $\Phi(s)$ is calculated from equation (11).

$$\frac{H(x)}{H(0)} = \sec h \alpha x \simeq \frac{\epsilon'' \left(2 + \frac{1}{\epsilon'^2}\right)}{\epsilon''_m \left(2 + \frac{1}{\epsilon'^2_m}\right)}. \quad (10)$$

$$\Phi(s) = \frac{2H(0)}{\pi} \cdot \frac{\cos\left(\frac{\alpha\pi}{2}\right) \cos \alpha s}{\cos^2\left(\frac{\alpha\pi}{2}\right) + \sin^2 \alpha s}, \quad (11)$$

where $H(0) = \frac{\alpha}{2}$ from the condition of $\int_{-\infty}^{\infty} \Phi(s) ds = 1$. Then, equation (7) can be written as

$$9U_0 \equiv \Delta = \frac{2\epsilon''_m \left(2 + \frac{1}{\epsilon'^2_m}\right)}{\alpha} = \frac{4\pi N \rho}{M} \cdot \frac{\langle (\vec{\mu} \cdot \vec{\mu}) \rangle_{AV}}{kT} \cdot \theta_2 \quad (12)$$

From this equation, if $\langle (\vec{\mu} \cdot \vec{\mu}) \rangle_{AV}$ is regarded as a constant for celluloses, Δ is proportional to $\rho\theta_2$. Putting $M=162$, $k=1.4 \times 10^{-16}$, $N=6.0 \times 10^{23}$, $T=2.4 \times 10^2$, $\alpha=0.30$, $\rho \simeq 1.6$, $\theta_2=0.26$ and 0.35 , $(\epsilon''_m)_{1.6}=0.17$ and 0.24 , $(\epsilon'_m)_{1.6}=3.3$ and 3.7 for cotton and Avicel respectively, the average dipole moment per glucose residue in amorphous region, $\bar{\mu} (= \sqrt{\langle (\vec{\mu} \cdot \vec{\mu}) \rangle_{AV}})$, become 2.1 DEBYE for cotton and Avicel. Then, the value of $\langle (\vec{\mu} \cdot \vec{\mu}) \rangle_{AV}$ can be regarded as a constant for celluloses used in this paper.

In Figs 1a and 1b the dielectric loss factor $\epsilon''_{1.2}$ at -32°C computed to standard density $\rho=1.2$ as a function of $\log f$ is illustrated. The data showed that the dielectric loss factor of cellulose I goes through a maximum at 1×10^5 Hz. The same trend was also observed in cellulose II. The value of $\epsilon''_{1.2}$ for Whatman celluloses increased in magnitude with increasing prolonged grinding in a ball mill.

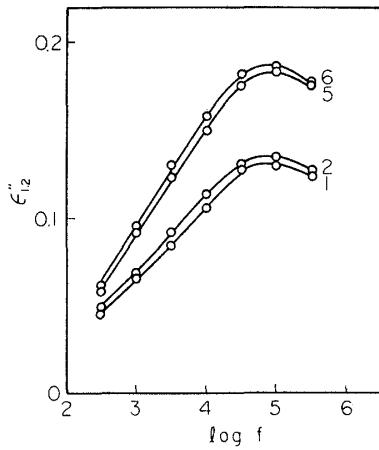


Fig. 1a. Dielectric loss factor vs. $\log f$ curves for celluloses, 1: Cotton, 2: Whatman cellulose, 5: Avicel, 6: Merck cellulose.

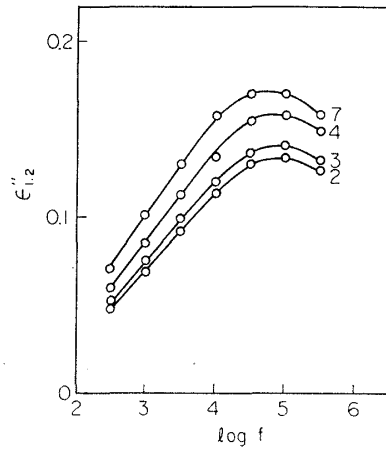


Fig. 1b. Dielectric loss factor vs. $\log f$ curves for Whatman cellulose, 2: untreated, 3: ground in a ball mill for 15 mins., 4: ground for 30 mins., 7: ground for 1 hr.

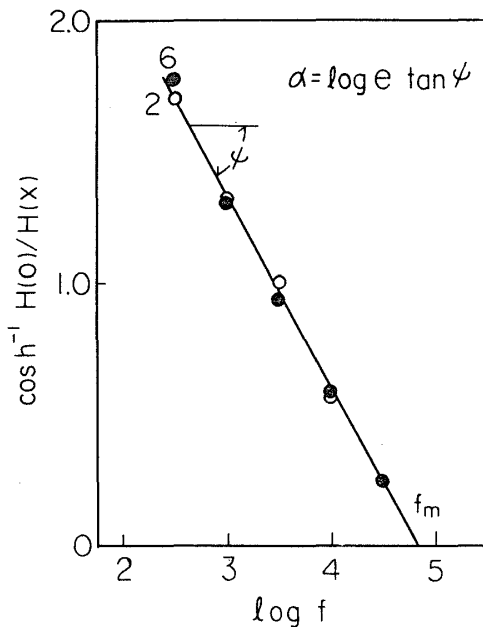


Fig. 2. $\cosh^{-1} H(0)/H(x)$ vs. $\log f$ curves at -32°C for Whatman cellulose (2) and Merck cellulose (6), α : measure of distribution for relaxation times, f_m : frequency at ϵ'' maximum.

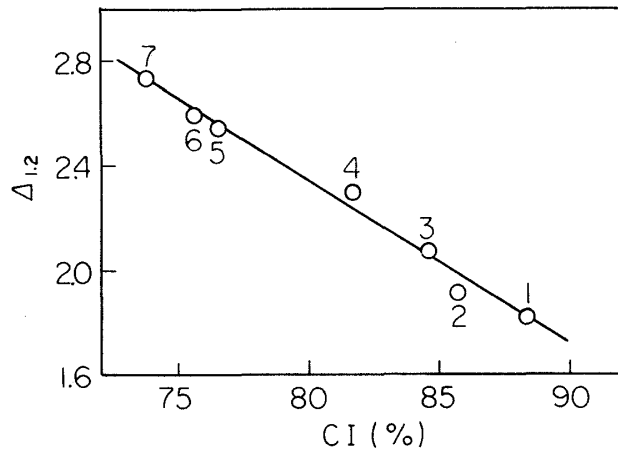


Fig. 3. $\Delta_{1.2}$ vs. crystallinity index curve for celluloses.

In Fig. 2, $\cosh^{-1} H(0)/H(x)$ is plotted against $\log f$ for Whatman cellulose and Merck cellulose as an example. There is an excellent linear correlation between them and this relation holds also for other samples used. Then, it is clear that the assumption of equation (10) is satisfied. Here, α , which is a parameter determining the measure of the distribution for relaxation times, is calculated from the slope ϕ of the straight line in Fig. 2 using the following equation.

$$\alpha = \log e \tan \phi,$$

where e is base of natural logarithm. The values of α calculated are shown in Table 2.

In Fig. 3 the relationship between $\Delta_{1.2}$ at $\rho=1.2$ and crystallinity index for cellulose I is shown. From equation (12),

$$\Delta \approx \frac{4\epsilon''_m}{\alpha} = \frac{\rho}{1.2} \Delta_{1.2} \quad \text{if} \quad \frac{1}{(\epsilon'_m)^{2.1.2}}, \frac{1}{(\epsilon'_m)^2} \ll 2,$$

where

$$\epsilon''_m \approx \frac{\rho}{1.2} (\epsilon''_m)_{1.2}.$$

Then, it can be considered that $\Delta_{1.2}$ is proportional to Δ . There is an excellent linear correlation between them, and the equation is written as

$$\Delta_{1.2} = -6.33 \times 10^{-2} CI + 7.40, \quad |r| = 0.992,$$

where r is the correlation coefficient,

From equations (6) and (7),

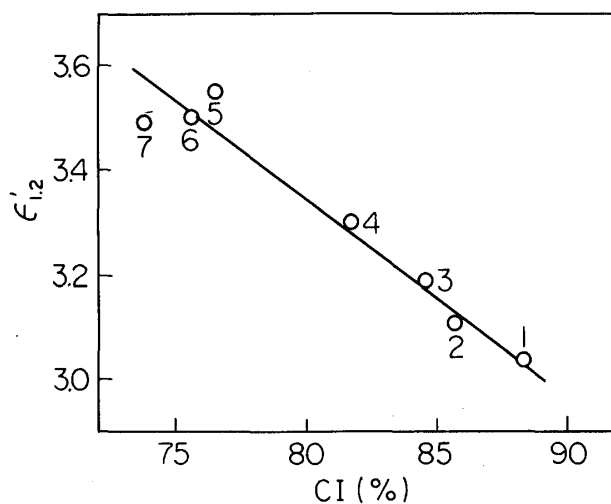


Fig. 4. $\epsilon'_{1.2}$ vs. crystallinity index curve for celluloses.

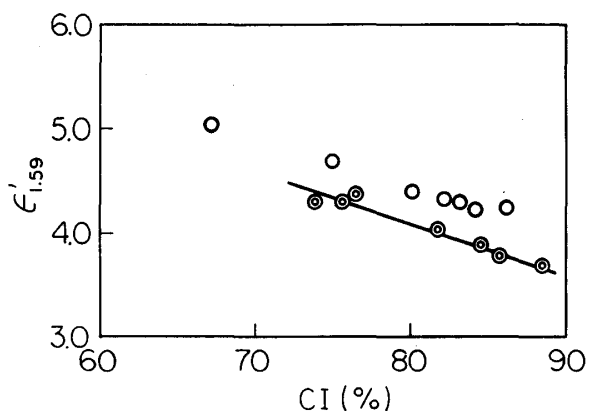


Fig. 5. Intrinsic dielectric constant vs. crystallinity index for celluloses, ⊙: author's results (-32°C , 1 kHz), O: VENKATESWARAN's results (20°C , 1 kHz).

$$\varphi(\epsilon_0') - \varphi(\epsilon_\infty') = \frac{1}{9} \left(2\epsilon_0' - 2\epsilon_\infty' - \frac{1}{\epsilon_0'} - \frac{1}{\epsilon_\infty'} \right) \approx \frac{2}{9} (\epsilon_0' - \epsilon_\infty') = K\theta_2.$$

Thus, $\epsilon_0' = (9K/2)\theta_2 + \epsilon_\infty'$, $K = (\rho/M)P_3$.

Hence, it can be derived that ϵ' is a linear function of crystallinity, independent of equations (3) and (4), regarding as $\epsilon_0' \approx \epsilon'$ at low frequency range.

In Fig. 4, $\epsilon'_{1.2}$ computed to standard density $\rho=1.2$ as a function of CI for cellulose I is shown. As expected from equation (13), there is a linear relationship between them. The equation determined by the statistical analysis of the experimental results is shown as

$$\epsilon'_{1.2} = -3.75 \times 10^{-2} CI + 6.33 \text{ at } 1 \text{ kHz and } -32^\circ\text{C, } |r|=0.973.$$

In Fig. 5 the intrinsic dielectric constant $\epsilon'_{1.59}$ for cellulose I is presented as a function of CI , and compared with that obtained by VENKATESWARAN et al.⁸⁾ The values of the intrinsic dielectric constant were calculated by the extrapolation according to the following equation.²²⁾

$$\epsilon'_{1.59} = \frac{1.59}{1.20} (\epsilon'_{1.2} - 1) + 1.$$

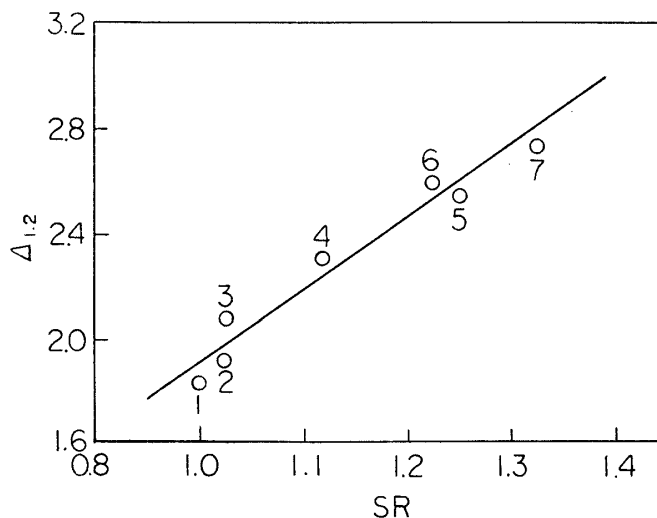


Fig. 6. $\Delta_{1.2}$ vs. sorption ratio curve for celluloses.

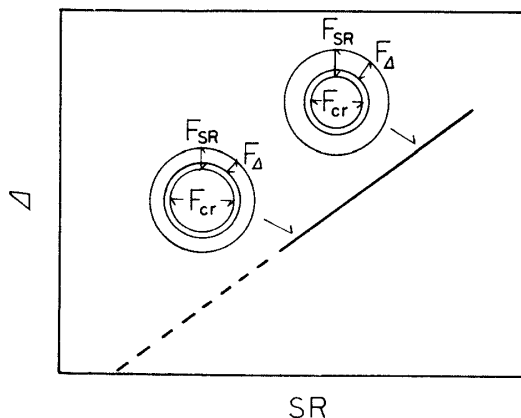


Fig. 7. Schematic diagram for Δ - SR relation, F_{cr} : crystalline fraction, F_{SR} : fraction which contributes to water sorption, F_{Δ} : fraction which contributes to dielectric loss factor.

The values obtained by VENKATESWARAN et al. are slightly greater in magnitude than the authors'. This discrepancy may be due to the difference in temperature conditions for both experiments.

In Fig. 6 the relation of $\Delta_{1,2}$ to SR is shown. A linear relationship is observed between them, and the equation is written as

$$\Delta_{1,2} = 2.82SR - 0.93, \quad r = 0.976.$$

According to this equation, the value of SR at $\Delta_{1,2} = 0$ is 0.33. This fact suggests that all methylol groups contributing to moisture adsorption does not necessarily contribute to the orientational polarization, so that there is so called paracrystalline region in which water vapor can be adsorbed but the orientation of dipoles is not permitted. Fig. 7 shows a schematic model of cellulose crystallite, in which the cross section of the crystallite is simply represented by the circle. In the figure, F_{cr} , F_{SR} and F_d represent the crystalline region, the region contributing to the adsorption, and the region in which the dipoles can orientate by the applied field, respectively. Thus, it can be explained qualitatively that equation (14) does not pass the origin.

In Fig. 8 $\epsilon'_{1,2}$ as a function of SR for cellulose I is shown. The regression line is written as

$$\epsilon'_{1,2} = 1.68SR + 1.40, \quad r = 0.947.$$

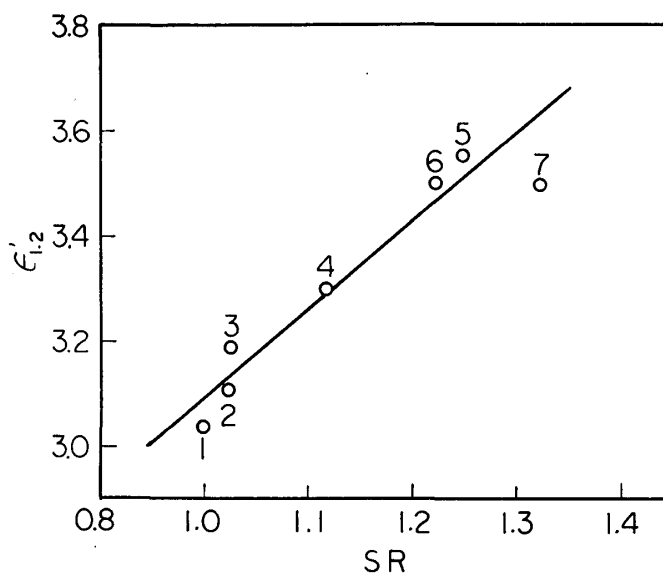


Fig. 8. $\epsilon'_{1,2}$ vs. sorption ratio curve for celluloses.

The quantity of amorphous region F_{am} is related with SR by the following equation.¹⁸⁾

$$F_{am} = \frac{SR}{2.60}. \quad (15)$$

In Fig. 9 the relationship between $\Delta_{1,2}$ and F_{am} calculated by equation (15) is shown. Assuming that $(F_{SR} - F_d)$ is constant in the region from $F_{am} = 0.39$ to 0.51, we obtain 0.13 as the value of F_{am} corresponding to $(F_{SR} - F_d)$ by inserting $SR = 0.33$ into equation (15). As the value of θ_2 , therefore, $(F_{am} - 0.13)$ must be used. The values of θ_2 for cellulose I calculated in this manner are shown in Table 2.

In Fig. 10, $\Delta_{1,2}$ is presented as a function of SR for cellulose I and II. The values of SR

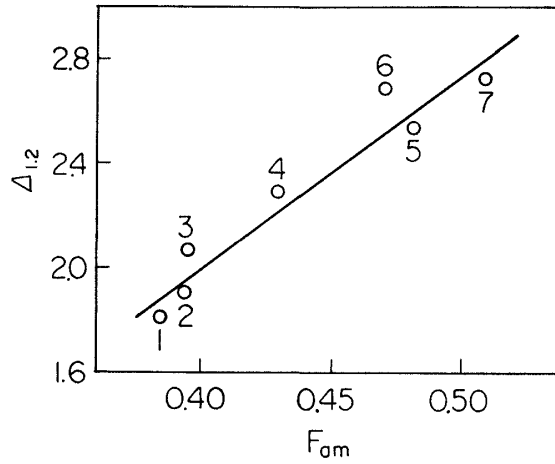


Fig. 9. $\Delta_{1.2}$ vs. noncrystalline fraction curve for celluloses.

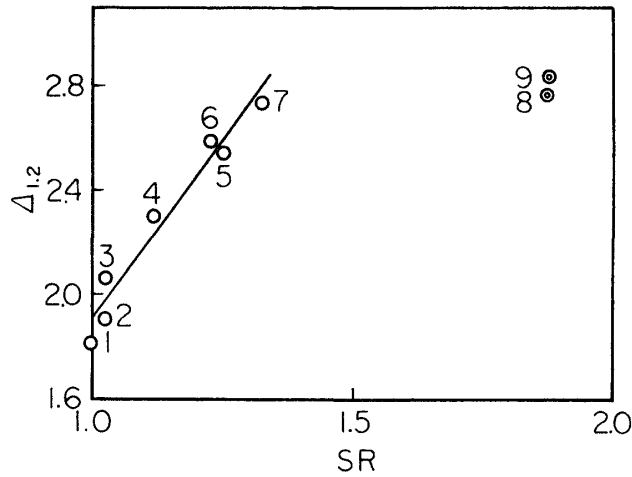


Fig. 10. $\Delta_{1.2}$ vs. sorption ratio curve for celluloses, \circ : cellulose I, \odot : cellulose II.

Table 2. The values of CI , SR , $\Delta_{1.2}$, $(\epsilon'_{1.2})$ 1 kHz, and D for cellulose samples.

No.	Samples	CI (%)	SR	$\Delta_{1.2}$	$(\epsilon'_{1.2})$ 1 kHz	α	D (Å)
1	Cotton treated with 3% HCl	88.4	1.000	1.82	3.04	0.304	69
2	Whatman cellulose	85.7	1.025	1.91	3.11	0.300	66
3	Whatman cellulose ground for 15 mins.	84.6	1.027	2.07	3.19	0.289	66
4	Whatman cellulose ground for 30 mins.	81.7	1.119	2.30	3.30	0.279	64
5	Avicel	76.5	1.252	2.54	3.55	0.302	46
6	Merck cellulose	75.6	1.225	2.59	3.50	0.299	44
7	Whatman cellulose ground for 1 hr.	73.8	1.326	2.73	3.49	0.274	60
8	Whatman cellulose treated with 17.5% NaOH (cellulose II)	—	1.871	2.77	3.67	0.289	—
9	Cotton treated with 3% HCl and then 17.5% NaOH (cellulose II)	—	1.873	2.84	3.68	0.280	—

for cellulose II are extremely greater than those for cellulose I. The same evidence was reported by JEFFRIES²³⁾, who found that the disordered regions of cellulose II absorb slightly more water per unit of disordered region than do cellulose I samples. Furthermore, in the infra-red measurements of celluloses, it is reported that the OD stretching bands in disordered regions for the bacterial cellulose differs significantly from these of the regenerated celluloses.²³⁾ Therefore, it may be considered that the structures of cellulose II in the amorphous region as well as in the crystalline region are different from those of cellulose I.

Table 2 shows the values of CI , SR , $\Delta_{1,2}$, $\epsilon'_{1,2}$, α , D , and θ_2 for the cellulose samples used. In Fig. 11, the distribution function for relaxation times calculated from equation (11) for

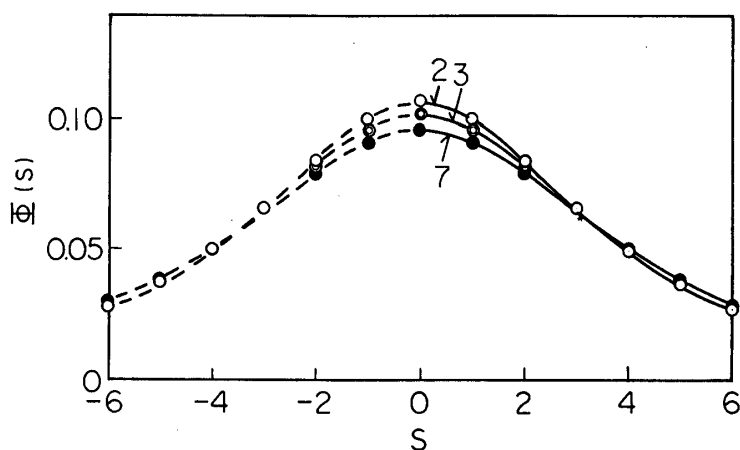


Fig. 11. Distribution function for relaxation times for Whatman celluloses, 2: untreated, 3: ground in a ball mill for 15 mins., 7: ground for 1 hr.

Whatman celluloses is shown. The distribution of relaxation times seems to become slightly wide by prolonged grinding in a ball mill. Furthermore, it is considered that the distribution of relaxation times for cellulose II is generally wide compared with that for cellulose I, since the value of α for cellulose II is smaller than that for cellulose I.

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References

- 1) W. TRAPP und L. PUNGS, *Holzforsch.*, **10**, 144 (1956).
- 2) G. P. MIKHAILOV et al., *Polymer Sci. USSR*, **11**, 628 (1969).
- 3) M. NORIMOTO and T. YAMADA, *Wood Research*, No. 52, 31 (1972).
- 4) C. R. CALKINS, *Tappi*, **33**, 278 (1950).
- 5) H. W. VERSEPUT, *Tappi*, **34**, 573 (1951).
- 6) D. E. KANE, *J. Polymer Sci.*, **18**, 405 (1955).
- 7) Y. ISHIDA et al., *J. Appl. polymer Sci.*, **1**, 227 (1959).
- 8) A. VENKATESWARAN and J. A. Van Den AKKER, *J. Appl. Polymer Sci.*, **9**, 1167 (1965), **9**, 1149 (1965).
- 9) A. VENKATESWARAN, *ibid.*, **13**, 2469 (1969).
- 10) M. NORIMOTO and T. YAMADA, *Wood Research*, No. 50, 36 (1970).
- 11) R. W. SILLARS, *Proc. Phys. Soc., London*, **A169**, 66 (1939).

- 12) T. NAKAJIMA and SAITO, *J. Polymer Sci.*, **31**, 423 (1958).
- 13) S. SAITO and T. NAKAJIMA, *J. Soc. Materials Sci., Japan*, **8**, 315 (1959).
- 14) A. PANDE, *Laboratory Practice*, **18**, 1052.
- 15) M. NORIMOTO and T. YAMADA, *Wood Research*, No. 46, 1 (1969).
- 16) L. SEGAL et al., *Tex. Res. J.*, **29**, 786 (1959).
- 17) T. NOMURA and T. YAMADA, *Wood Research*, No. 52, 1 (1972).
- 18) L. VALENTINE, *J. Polymer Sci.*, **27**, 313 (1958).
- 19) P. H. HERMANS et al., *J. Polymer Sci.*, **1**, 169 (1946).
- 20) J. G. KIRKWOOD, *J. Chem. Phys.*, **7**, 911 (1939).
- 21) R. FUOSS and J. G. KIRKWOOD, *J. Am. Chem. Soc.*, **63**, 385 (1941).
- 22) A. VENKATESWARAN, *J. Appl. Polymer Sci.*, **9**, 1127 (1965).
- 23) N. M. BIKALES and L. SEGAL, *Cellulose and Cellulose Derivatives Part 4 (High Polymer Vol. V)*, 100, Wiley-Interscience, (1971).