Dielectric Studies on Cellulose Fibers

Yoichi Ishida, Masatsugu Yoshino, and Motowo Takayanagi

Department of Applied Chemistry, Faculty of Engineering, Kyushu University, Fukuoka, Japan

Fujio Irie

Department of Electrical Engineering, Faculty of Engineering, Kyushu University, Fukuoka, Japan

INTRODUCTION

In dielectric measurements on cellulose fibers it is difficult to obtain intrinsic dielectric constant and loss factor values because of their undefined state between two electrodes.[1] For such a case the immersion method is generally adopted.[2,3] This method is, however, not only inapplicable to the measurement of dielectric loss, but very troublesome to follow, since it is trial-and-error procedure.

Therefore, another method was developed for obtaining the intrinsic dielectric constant and loss factor along the fiber axis; this method makes it possible to study dielectric properties over a wide range of frequency and temperature.

EXPERIMENTS

The Preparation of Samples

Viscose rayon, Bemberg (cuprammonium rayon), and cotton slivers were used as samples. Fibers were aligned parallel to one another on polyethylene film, after which the film was rolled into a cylinder which was sealed by using a hot flatiron and was then cut into small disks 4.5 mm. thick. Each such disk was dried over the phosphorus pentoxide *in vacuo* at 100°C. for 24 hours before measurement of its dielectric properties.

Apparatus and Measurement

The dielectric measurements were made over the frequency range of from 500 cycles/sec. to 3 Mcycles/sec. and over the temperature range of −60°C. to +20°C. The measuring system is shown in the block diagram (Fig. 1). The mutual inductance bridge used here is of the same type as that developed originally by Cole and Gross.[4] This bridge can facilitate rapid measurement, and, since it allows the usage of three-terminal electrodes, the data obtained are free from errors caused by edge effect, surface effect or stray capacity.

The cell used is illustrated by the simplified cross section shown in Figure 2. Each of the electrodes is fixed through insulators (4) and (5) to the shield case (12) and (13). The temperature of samples is measured by a thermocouple attached to one electrode (2).

The samples in contact with one another are inserted between two electrodes (1) and (2), which are kept at a distance of 4.5 mm. from each other by a rigid insulator ring. Fiber axes are, therefore, parallel to the direction of the electric field, and the results measured may be considered to be dielectric properties in the direction of fiber axis.
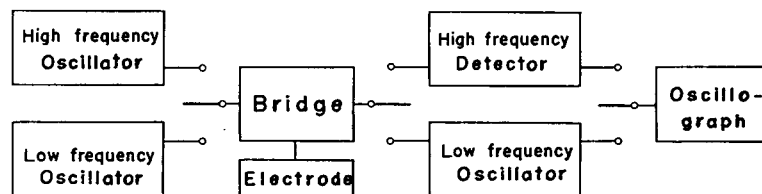
Since the samples are very hygroscopic, the

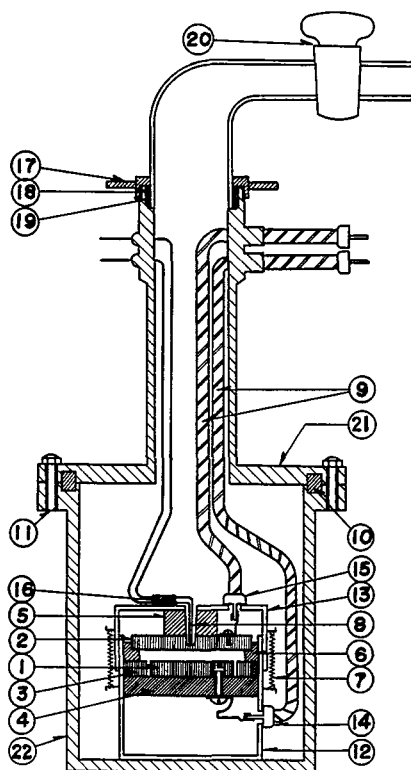Fig. 1. Block diagram of circuit.

Fig. 2. The measuring cell and the air-tight vessel: (1) guarded electrode; (2) unguarded electrode; (3) guarded electrode; (4, 5) insulators; (6) insulator ring; (7) spring; (8) thermocouple; (9) shield wires; (10, 19) packing; (11) nut; (12, 13) shield case; (14, 15) connectors for shield wire; (16) connector for thermocouple; (17) retainer nut; (18) retainer ring; (20) vacuum cock; (21) upper part of airtight vessel; (22) lower part of airtight vessel.

makes it possible to carry out the measurement quickly.

The Calculation of ϵ' and ϵ'' of the Fiber Alone

The values of ϵ' and ϵ'' obtained by the measurement are those of a mixed system, i.e., fiber, polyethylene film, and air. The intrinsic values of the fiber itself, therefore, must be calculated from the values of the system by the following method.

As mentioned above, the sample disks are set between electrodes in such a way that every fiber and the polyethylene film are kept as much as possible parallel to the electrical field.

With the assumption that all the fiber axes are parallel to the electric field, the following equations hold. Here, we have denoted the dielectric constant and loss factor for the mixed systems by ϵ_m' and ϵ_m'', respectively; for the fibers, by ϵ_f' and ϵ_f'', respectively; for the polyethylene film, by ϵ_p' and ϵ_p'', respectively; and for the air, by ϵ_a' and ϵ_a'', respectively.

$$\epsilon_m' = v_f\epsilon_f'' + v_p\epsilon_p' + (1 - v_f - v_p)\epsilon_a'$$

$$\epsilon_m'' = v_f\epsilon_f'' + v_p\epsilon_p'' + (1 - v_f - v_p)\epsilon_a''$$

Here, the volume fraction occupied by fibers and the polyethylene film between the electrodes are v_f and v_p, respectively. The above equations are modified as follows:

$$\epsilon_f' = [\epsilon_m' - v_p\epsilon_p' - (1 - v_f - v_p)\epsilon_a']/v_f$$

$$\epsilon_f'' = [\epsilon_m'' - v_p\epsilon_p'' - (1 - v_f - v_p)\epsilon_a'']/v_f$$

where, $\epsilon_a' = 1$ and ϵ_p'', $\epsilon_a'' \ll \epsilon_f''$.
Therefore,

$$\epsilon_f' = [\epsilon_m' - \epsilon_p'v_p - (1 - v_f - v_p)]/v_f'' \quad (1)$$

$$\epsilon_f'' = \epsilon_m''/v_f \quad (2)$$

The dielectric constant and loss factor of the fiber itself can be calculated by eqs. (1) and (2). In the above equations, v_f and v_p can be calculated from the volume between electrodes, the density, and the weight of fiber and polyethylene film, respectively.

RESULTS AND ANALYSIS

The frequency characteristics of ϵ' and ϵ'' for viscose rayon, Bemberg and cotton sliver are shown in Figures 3–8.

In the observed range, the behavior of only one dispersion was followed, and the dispersion
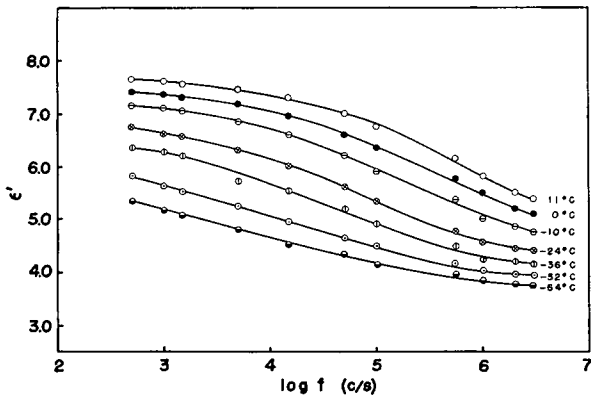
measurements were conducted in an air-tight vessel to eliminate the influence of humidity. The structure of the air-tight vessel is shown by the cross section in Figure 2. By using rubber packing for the drawing out of lead wires and thermocouple and Teflon packing for the connection between the upper (21) and the lower parts (22) of the vessel, the vessel can be kept air tight.

After the cell containing samples has been set in the air-tight vessel, the vessel is evacuated, and dry air is introduced into it through a long tube containing P_2O_5.

The air-tight vessel containing the cell system is cooled in a vacuum bottle containing Dry Ice and alcohol. Temperature is controlled by changing the depth of the vessel dipped in the bottle. The temperature of the sample can be fixed within ±0.5°C. during the measurement, because of the large heat capacity of the measuring cell and vessel and because the mutual inductance bridge

Fig. 3. Frequency dependence of ϵ' at various temperatures for viscose rayon.
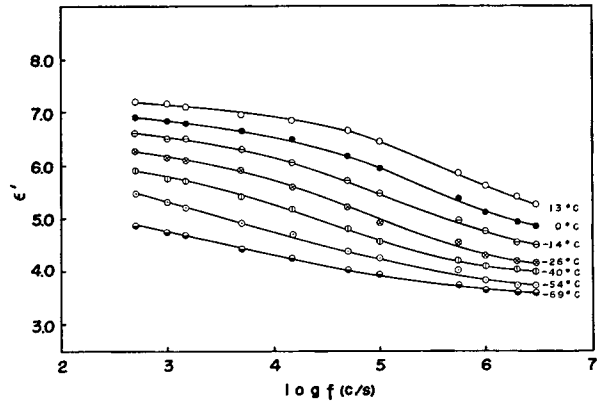

Fig. 4. Frequency dependence of ϵ' at various temperatures for Bemberg.
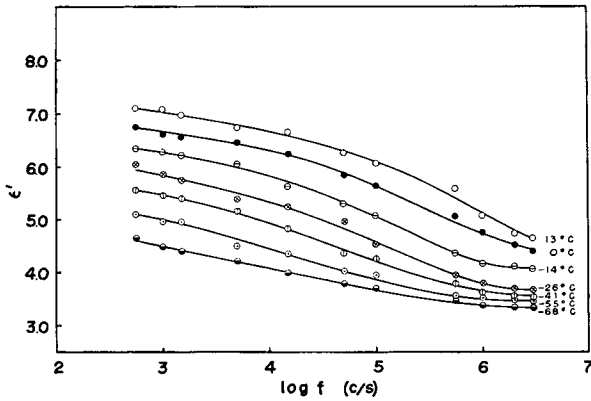

Fig. 5. Frequency dependence of ϵ' at various temperatures for cotton sliver.
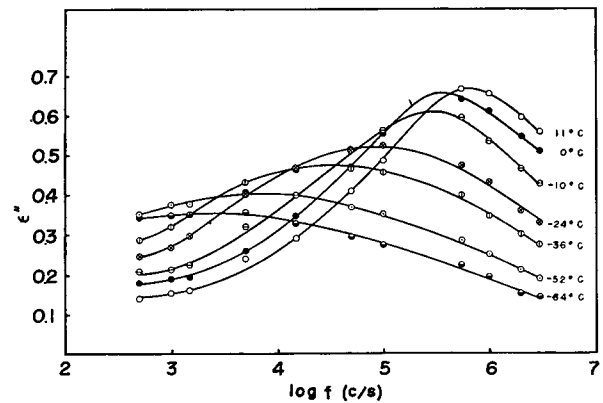

Fig. 6. Frequency dependence of ϵ'' at various temperatures for viscose rayon.
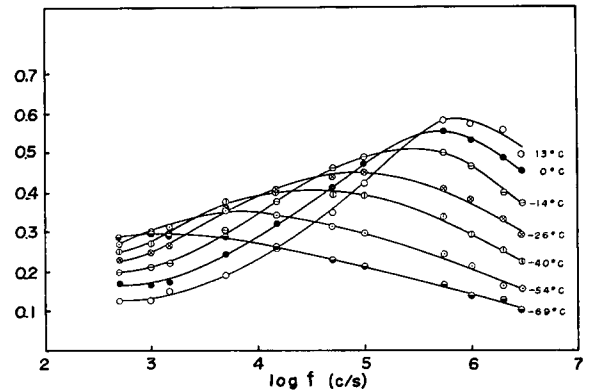

Fig. 7. Frequency dependence of ϵ'' at various temperatures for Bemberg.
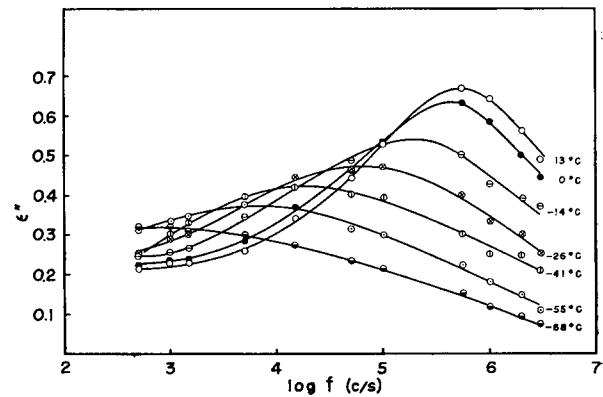

Fig. 8. Frequency dependence of ϵ'' at various temperatures for cotton sliver.

frequency reshifted to a lower value with decreasing temperature.

An analysis was done by Cole and Cole's circular arc laws to discuss these dielectric characteristics obtained.

Cole and Cole's circular arc law is expressed by the following equation:

$$\dot{\epsilon} - \epsilon_\infty = (\epsilon_0 - \epsilon_\infty)/[1 + (i\omega\tau_0)^\beta] \qquad (3)$$

The complex dielectric constant $\dot{\epsilon}$ is given by $\dot{\epsilon} = \epsilon' - i\epsilon''$, and $(\epsilon_0 - \epsilon_\infty)$ corresponds to the length of the chord of Cole-Cole's arc, where ϵ_0 is the dielectric constant for the zero frequency and ϵ_∞ is that for the infinite frequency, and this term is the parameter relating to the magnitude
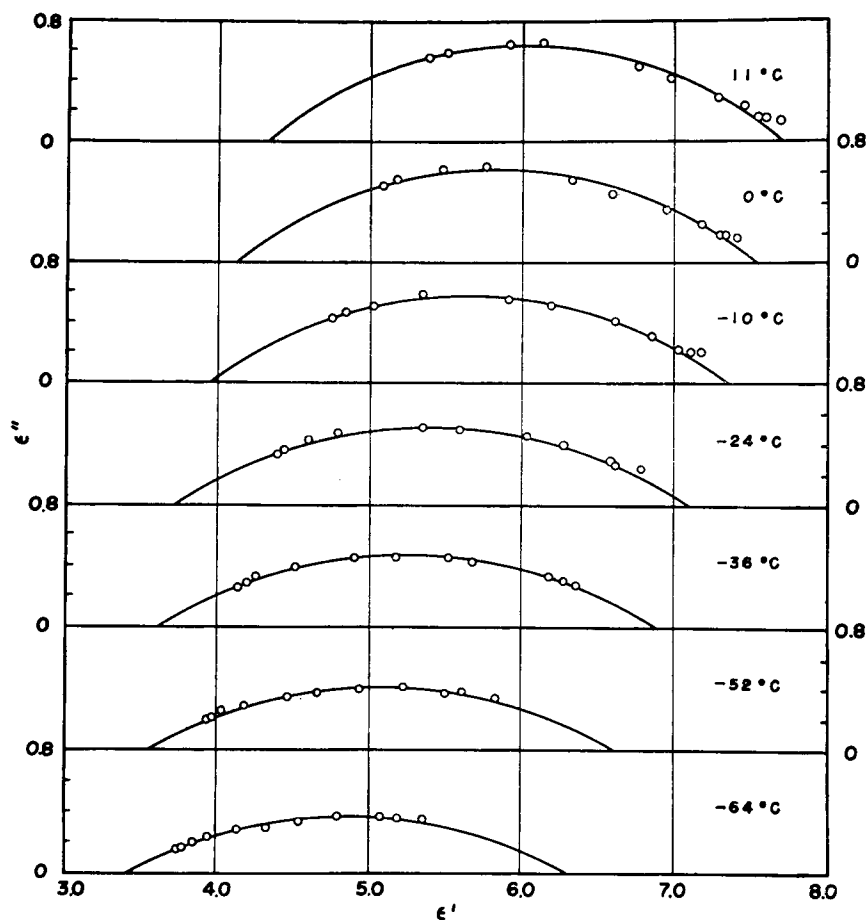
Fig. 9. Cole-Cole plot at various temperatures for viscose rayon.

of dipole orientation. The angle between the radii of the arc drawn to the points ϵ_∞ and ϵ_0 from the center of the circle is given by $\beta\pi$, and β is the parameter relating to the distribution of relaxation times. The broader the distribution of relaxation times becomes, the smaller the β value. In the single relaxation system, β is unity. The generalized relaxation time τ_0 is given by $\tau_0 = 1/2\pi f_m$, where f_m is the dispersion frequency.

The results of Cole-Cole's plots are shown in Figures 9–11. As can be seen from these figures, each locus becomes almost a circular arc, having a slight deviation in the lower frequency region. Except for those few deviating points belonging to some other relaxation mechanism, the parameters of the circular arc ($\epsilon_0 - \epsilon_\infty$) and β, are determined. Plots of ($\epsilon_0 - \epsilon_\infty$) and β versus temperature are shown in Figures 12 and 13, respectively.

In order to calculate the apparent activation energy for the dielectric response, $\Delta H^\ddagger$, log f_m is

plotted for reciprocal temperatures such as shown in Figure 14, where f_m is the frequency corresponding to the loss factor maximum. $\Delta H^\ddagger$ can be calculated by the following formula:

$$\Delta H^\ddagger = 2.303\ Rd \log f_m/d(1/T)$$

The results are shown in Figure 15. When the shape of the distribution is broad, this method to determine f_m directly from the ϵ' vs. log f curve can give only an inaccurate value. The following method was therefore adopted. At first, the value of the dielectric constant corresponding to the mid point of the chord of the arc is calculated by ($\epsilon_0 + \epsilon_\infty$)/2, where ϵ_0 and ϵ_∞ can be easily obtained from Cole-Cole's arc. The frequency corresponding to ($\epsilon_0 + \epsilon_\infty$)/2 is the dispersion frequency, for ϵ'' takes maximum when ϵ' equals ($\epsilon_0 + \epsilon_\infty$)/2 as shown in Cole-Cole's arc. The desired f_m, therefore, can be uniquely read as the frequency corresponding to ($\epsilon_0 + \epsilon_\infty$)/2 in the ϵ vs. log f curve.
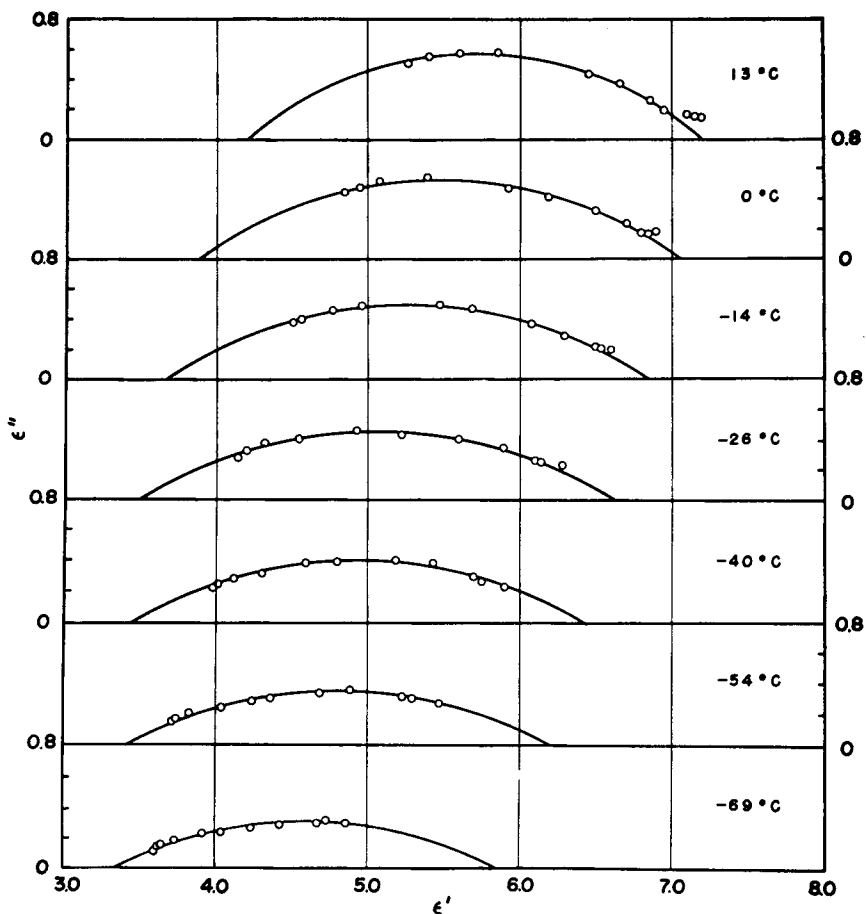
Fig. 10. Cole-Cole plot at various temperatures for Bemberg.

DISCUSSION

The Relationship between $(\epsilon_0 - \epsilon_\infty)$ and Crystallinity

As shown in Figure 12, the values of $(\epsilon_0 - \epsilon_\infty)$ which are proportional to the concentration of the dipoles contributing to the orientation, decrease in the order, viscose rayon > Bemberg > cotton sliver over the observed temperature range; and this order parallels that of the accessibility of the three samples. This fact can be explained in accord with the view that the dipoles in the amorphous region and the surface of crystallites make a great contribution to this dielectric dispersion. A similar view is also held by Kane.[3]

Cause of the Dispersion

In recent studies on the dielectric properties of high polymers, it has been brought to light that there are generally two dispersions, primary and secondary. Typical examples are found in

the dielectric studies of polyethylene terephthalate[6] and some substituted acrylic ester polymers[7] by Reddish and others. Reddish interpreted the mechanism of two dispersions in polyethylene terephthalate as follows: the primary dispersion with $\Delta H^\ddagger = 90$ kcal./mole is due to the relaxation of the ester groups in the main chains; the secondary dispersion, for which $\Delta H^\ddagger = 12$ kcal./mole, is due to the presence of the OH endgroups.

Summarizing the data of Reddish and others, Würstlin[8] considers the primary dispersion with $\Delta H^\ddagger$ from 70 to 100 kcal./mole to be dependent on the orientation of dipoles related to the segmental movement of the main chains and the secondary dispersion, with $\Delta H^\ddagger$ from 10 to 20 kcal./mole, to be caused by the orientation of the dipoles of the local parts, such as side chains.

However, it is rather rare that two dispersions are caught clearly, as reported by Reddish. Usually only one dispersion can be observed, the other being outside of the range of usual measurement. Cellulose belongs to the latter case. Stoops[9]
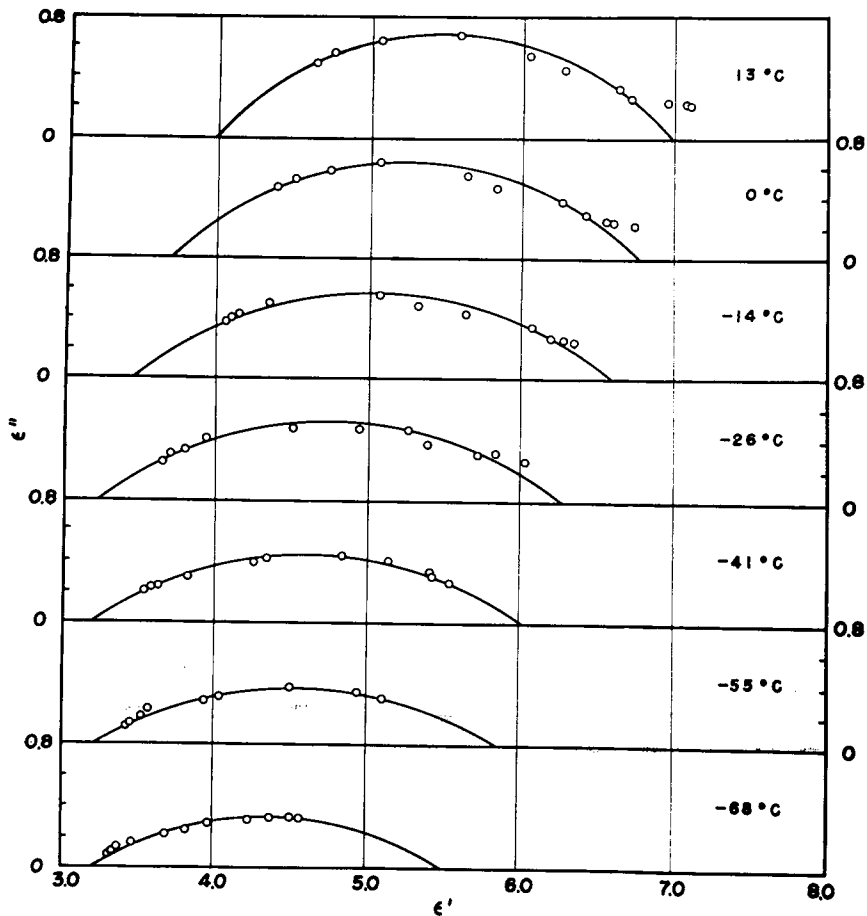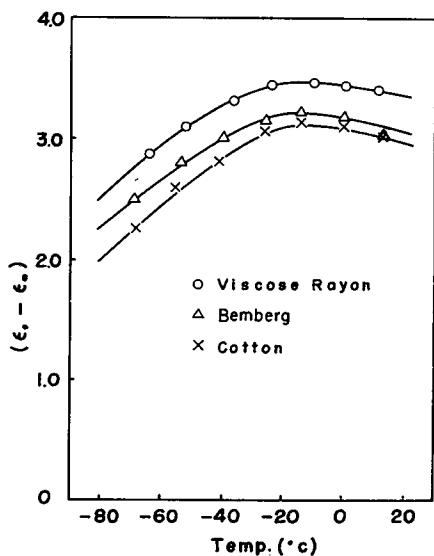
Fig. 11. Cole-Cole plot at various temperatures for cotton sliver.

Fig. 12. Temperature dependence of $(\epsilon_0 - \epsilon_\infty)$ for viscose rayon, Bemberg, and cotton sliver.

served by the authors, in view of the temperature and the frequency at which it appears is the same as that observed by Stoops, but its apparent activation energy is lower, as shown in Figure 15. Therefore, it is reasonable to consider that this dispersion is due to the orientation of the OH groups, as suggesed by Würstlin.[8]

Moreover, the log f_m vs. $1/T$ curves of natural

observed only one dispersion in cellophane and suggested the possibility that the chain rotation is the cause of the dispersion. The dispersion ob-
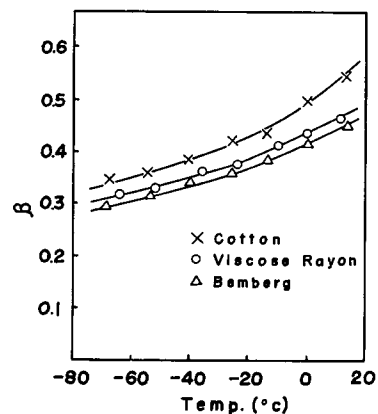
Fig. 13. Temperature dependence of β for viscose rayon, Bemberg, and cotton sliver.

cellulose (cotton sliver) and regenerated cellulose (viscose rayon and Bemberg) almost coincide with each other, despite the differences in the fine structures and the degree of polymerization of these samples. The fact above mentioned could be understood from considering that this dispersion is caused by the orientation of local parts such as side chains, especially methlyol groups on glucose residues, which will hardly be affected by the configurations of the main chains.

Dielectric Transition

Considering that $(\epsilon_0 - \epsilon_\infty)$ is proportional to the concentration of the dipoles contributing to the orientation and that β is the parameter showing the width of the distribution of relaxation times,
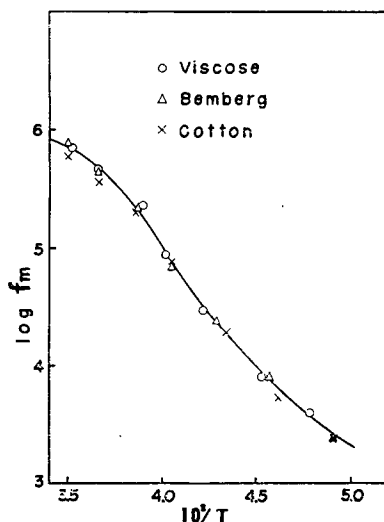
Fig. 14. Plot of logarithmic dispersion frequency against reciprocal of absolute temperature.

it is understood from Figures 12 and 13 that the frozen-in dipoles are gradually freed, and the number of dipoles contributing to the orientation increases with the rise in temperature, while the distribution of relaxation times becomes more narrow. With a rise in temperature to nearly $-20°C.$, $(\epsilon_0 - \epsilon_\infty)$ tends to a limiting value, and then, at a higher temperature, tends to drop to some degree. The degree of increase of β concurrently tends to increase somewhat at temperatures above $-20°C.$ It should be noted that the apparent activation energy for dielectric response reaches a maximum around $-20°C.$, as seen in Figure 15. All these facts suggest that some transition takes place in the neighborhood of $-20°C.$
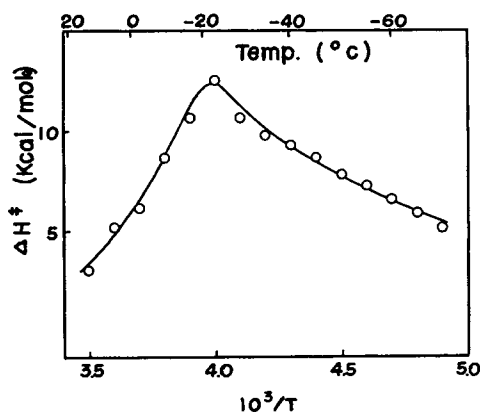
Fig. 15. Temperature dependence of apparent activation energy for dielectric response.

Phenomena which are indicative of the apparent activation energy maximum have not yet been reported in dielectric studies conducted on high polymers. By a careful analysis of the data, we have also found the same behavior in the case of polyvinyl chloride.[10] Analogous phenomena have already been found in the temperature dependence of viscoelastic properties of high polymers. Tobolsky and Castiff[11] and Bueche[12] have discovered that the apparent activation energy for elastic response reaches a maximum near the glass temperature (the temperature of the primary transition).

The transition temperature of $-20°C.$ which we have observed for dry cellulose is considered not to be the glass temperature of dry cellulose, since T_g of stiff molecules such as dry cellulose is supposed to be at a higher temperature and the observed value of the apparent activation energy for dielectric response is too small to activate the segmental movement of the main chains. It might be possible to expect that some secondary transition, probably thermodynamical in nature, relating to the movement of local parts such as side chains, especially methylol groups on glucose residue, would take place around $-20°C.$, though there is no other support for this expectation.

References

1. J. W. S. Hearle, *Textile Research J.*, **24**, 307 (1954).
2. H. A. De Luca, W. B. Campbell, and O. Maass, *Can. J. Research*, **16**, 273 (1938).
3. D. E. Kane, *J. Polymer Sci.*, **18**, 405 (1955).
4. R. H. Cole and P. M. Gross, *Rev. Sci. Instr.*, **20**, 252 (1949).
5. K. S. Cole and R. H. Cole, *J. Chem. Phys.*, **9**, 341 (1941).
6. W. Reddish, *Trans. Faraday Soc.*, **46**, 459 (1950).
7. K. Deutsch, E. A. W. Hoff, and W. Reddish, *J. Polymer Sci.*, **13**, 565 (1954).
8. H. Thurn and F. Würstlin, *Kolloid Z.*, **145**, 133 (1956).
9. W. N. Stoops, *J. Am. Chem. Soc.*, **56**, 1480 (1934).
10. Y. Ishida, Y. Takada, M. Takayanagi, and F. Irie, to be published.
11. E. Castiff and A. V. Tobolsky, *J. Appl. Phys.*, **25**, 1092 (1954).
12. F. Bueche, *J. Appl. Phys.*, **26**, 738 (1955).

Synopsis

A method for obtaining the intrinsic dielectric constant and loss factor of dry cellulose fiber along the fiber axis was developed, and the dielectric properties of viscose rayon, Bemberg (cuprammonium rayon), and cotton sliver were measured over the frequency range from 500 cycles/sec. to 3 Mcycles/sec. and the temperature range from −60 to +20°C. by using the mutual inductance bridge. Only one dispersion could be observed in this temperature and frequency range. Cole-Cole's circular arc law could be satisfactorily applied to the data obtained, and the parameters of the arc ($\epsilon_0 - \epsilon_\infty$) and β for the three samples could be determined at each temperature. The value of ($\epsilon_0 - \epsilon_\infty$), which is proportional to concentration of the dipoles contributing to the orientation, increased with rising temperature and reached a limiting value at about −20°C. The value of β relating to the width of the distribution of relaxation times also increased with rising temperature, showing a little rise in the degree of increase at temperatures above −20°C. On the other hand, the apparent activation energy for dipole orientation, as calculated from the temperature dependence of the dispersion frequency, reached a maximum around −20°C. All these facts suggest that some transition will take place in the neighborhood of −20°C. This temperature is not considered to be likely to be the glass transition temperature for dry cellulose, since −20°C. is too low for a primary transition in stiff molecules such as cellulose, and since the observed value of the apparent activation energy is too small to activate the segmental movement of the main chains. It might be possible to expect some secondary transition, probably of a thermodynamical nature, relating to the movement of local parts such as side chains, especially methylol groups on glucose residue, at about −20°C., though there is no other support for this expectation. Moreover, the effect of the fine structures on the dielectric properties is that the magnitude of ($\epsilon_0 - \epsilon_\infty$) at each temperature decreases in the order, viscose rayon > Bemberg > cotton sliver, and this order parallels that of the accessibility of the three samples. This fact suggests that the dipoles in the amorphous region and on the surface of the crystallite provide the chief contribution to this dispersion.

Résumé

Une méthode d'obtention des constantes diélectriques intrinsèques et du facteur de perte de fibres sèches de cellulose le long de l'axe de la fibre a été inventée et les propriétés dielectriques de morceaux de rayonne viscose, de Bemberg (rayonne cuprammonique) et de coton ont été mesurées sur une échelle de fréquences allant de 500 cycles/sec à 3 mégacycles/sec et à des températures allant de-60 à +20°C. en utilisant le pont d'inductance mutuel. Une dispersion seulement peut être observée à ces températures et à ces fréquences. La loi de Cole-Cole relative à l'aro circulaire pourrait être appliquée d'une façon satisfaisante aux données obtenues et les paramètres de l'arc, ($\epsilon_0 - \epsilon_\infty$) et β des trois échantillons peuvent être déterminés pour chaque température. Les valeurs de ($\epsilon_0 - \epsilon_\infty$), qui sont proportionnelles à la concentration des dipôles contribuent à l'orientation augmentent par élévation de température et sont saturées vers −20°C. Les valeurs de β en relation avec la largeur de la distribution des temps de relaxation augmentent aussi avec l'élévation de température, montrant une légère augmentation pour les températures supérieures à −20°C. D autre part l'énergie d'activation apparente de l'orientation des dipôles, calculée à partir de la dépendance de la température des fréquences de dispersion atteint un maximum vers −20°C. Tous ces faits suggèrent qu'une certaine transition aurait lieu vers −20°C. Evidemment, la température observée pour la cellulose sèche n'est pas la température de passage de l'état vitreux à l'état élastique, puisque −20°C. est trop bas pour la transition primaire de molécules rigides, telle la cellulose, et les valeurs observées de l'énergie d'activation apparente sont trop petites pour activer le mouvement des segments de la chaîne principale. Il est probable qu'il y a une transition secondaire de nature thermodynamique en relation avec le mouvement de parties locales telles des chaînes latérales et spécialement des groupes méthyloliques sur les résidus de glucose et qui aurait lieu vers −20°C. quoique les auteurs n'aient d'autres preuves supplémentaires pour cette prévision. De plus, les résultats obtenus quant aux effects de la structure fine sur les propriétés diélectriques indiquent que les valeurs de ($\epsilon_0 - \epsilon_\infty$) à chaque température diminuent dans l'ordre suivant morceaux de rayonne viscose > morceaux de Bemberg > morceaux de coton, et cet ordre est en relation parallèle à l'accessibilite des trois echantillons. Ce fait suggère que les dipôles dans la région amorphe et la surface du cristallite contribueront grandement à la dispersion.

Zusammenfassung

Es wurde eine Methode zur Ermittlung der wahren Dielektrizitätskonstanten und des Verlustfaktors trockener Cellulosefasern längs der Faserachse entwickelt und die dielektrischen Eigenschaften von Viskoserayon-, Bemberg- (Cuprammonrayon) und Baumwollfasern im Frequenzbereich von 500 Hertz bis 3 Megahertz und im Temperaturbereich von −60° bis +20°C mit der Brückenmethode (gegenseitige Induktanz) gemessen. In diesem Temperatur- und Frequenzbereich konnte nur ein Dispersionsgebiet beobachtet werden. Das Gesetz des kreisförmigen Bogens von Cole-Cole konnte in befriedigender Weise auf die erhaltenen Daten angewendet und die Parameter des Bogens, ($\epsilon_0 - \epsilon_\infty$) und β, für die drei Proben bei jeder Temperatur bestimmt

werden. Der Wert von ($\epsilon_0 - \epsilon_\infty$) der der Konzentration der zur Orientierung beitragenden Dipole proportional ist, nahm mit steigender Temperatur zu und erreicht um etwa −20°C einen Sättigungswert. Der Wert von β, der zur Verteilungsbreite der Relaxationszeiten in Beziehung steht, nahm ebenfalls mit steigender Temperatur zur und zeigte bei Temperaturen über −20°C eine kleine Zunahme dieses Anstiegs. Andrerseits hatte die aus der Temperaturabhängigkeit der Dispersionsfrequenz berechnete, scheinbare Aktivierungsenergie der Dipolorientierung bei etwa −20°C einen Maximalwert. Alle diese Tatsachen sprechen dafür, daß in der Nähe von −20°C eine Art von Umwandlung stattfindet. Natürlich ist die an trockener Cellulose beobachtete Temperatur nicht die Umwandlungstemperatur für den Übergang vom Blaszustand in den kautschukartigen Zustand, da −20°C zu niedrig für die primäre Umwandlung so steifer Moleküle, wie die der Cellulose und der beobachtete Wert der Scheinbaren Aktivierungsenergie zu klein für eine Aktivierung der Segmentbewegung der Hauptketten ist. Es erscheint möglich, dass der Eintritt einer Art sekundärer Umwandlung, wahrscheinlich thermodynamischer Natur, die mit der Bewegung lokaler Teile wie etwa Seitengruppen, besonders Methylolgruppen an Glukoseresten, verknüpft ist, in der Gegend von −20°C zu erwarten ist; die Autoren können aber nichts weiteres zur Unterstützung dieser Erwartung beibringen. Weiters zeigen die Ergebnisse, die bezüglich des Einflusses der Feinstruktur auf die dielektrischen Eigenschaften erhalten wurden, dass die Grösse von ($\epsilon_0 - \epsilon_\infty$) bei jeder Temperatur für die drei Proben in der Reihenfolge Viskoserayon- > Bemberg- > Baumwollfäden abnimmt und diese Reihenfolge stimmt mit der der Angreifbarkeit der drei Proben überein. Dieser Umstand spricht dafür, daß die Dipole im amorphen Bereich und in der Oberfläche der Kristallite den Hauptbeitrag zur Dispersion liefern.