The Dielectric Properties of Wood IV*,**

On Dielectric Dispersions of Oven-dried Wood

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Abstract——In this paper, the dielectric absorptions of oven-dried wood were investigated. There existed three dielectric absorptions in wood. The position of dielectric absorption in high frequency range at low temperature coincided with that of viscoelastic one, and the relaxation process may be associated with the motion of CH_2OH groups in the disordered region of wood substances. The absorption of oven-dried KUSUNOKI appeared in low frequency range at room temperature may be due to the existence of the conductive material and was influenced by the shape of the material in wood. The absorption in very low frequency range at high temperature may be associated with the segmental motion of molecules in the amorphous region accompanied by thermal degradation.

Introduction

Although many investigations on dielectric properties of wood have been done, there are a few reports which intend to clarify the relation between dielectric and viscoelastic relaxation. The aim of this study is to investigate the dielectric and the viscoelastic properties of wood over the wide ranges of frequency and temperature and to clarify the mode of molecular motion concerned with the relaxations.

It has been reported that a dielectric dispersion of oven-dried wood exists in the frequency range of 10^7 to 10^8 Hz at room temperature and is associated with the orientation of OH groups in the amorphous phase. However, it has not been discussed whether other dispersions do occur or not at very low frequency range.

In this paper, the following three points are discussed.

(1) The dielectric and the viscoelastic dispersion in high frequency range at low temperature.

(2) The dispersions of oven-dried KUSUNOKI (*Cinnamomum camphora* SIEB.) in low frequency range at room temperature.

(3) The dispersion of oven-dried wood and cellulose in very low frequency at high temperature.

Experimental

The samples for the dielectric experiment are shown in Table 1. The measurement was made over the frequency range of 0.3 to 10^6 Hz and the temperature range of -70 to 140°C. The inductive and the resistive ratio arm bridges were used for the frequency range of 30 to 10^6 and 0.3 to 10 Hz, respectively.

Table 1. Samples used for the dielectric measurement.

Material			Treatment
Glucose			
Cellobiose			
Cotton			treated with 3% HCl for several hours at 90°C
Avicel	Powder (200 mesh)		
Whatmann cellulose			
Beeech xylan			
KUSUNOKI			hot water and alcohol-benzene extraction
SUGI	Block	L*, 5 mm**	
HOONOKI			
HINOKI		L, 1.5 mm	
		L, 1 mm	hot water and alcohol-benzene extraction
		L, 5 mm	alcohol-benzene extraction
KUSUNOKI		L, 2.5 mm	
		T, 2 mm	
		L, 5 mm	hot water extraction
			hot water and alcohol-benzene extraction

* Direction of electric field.
** Thickness of sample.

The sample for the viscoelastic experiment was oven-dried HOONOKI (*Magnolia obovata* THUNB.) in longitudinal direction ($5 \times 5 \times 50$ mm). The measurement was made over the temperature range of -70 to 30°C at 60 KHz and the composite osillator method was employed.

Before the measurement, wood samples were dried at 105°C and other samples were dried over the phosphorus pentoxide in vacuo (10^{-2} mmHg) at room temperature.

Results and Discussion

The dielectric and the viscoelastic dispersion in high frequency range at low temperature

KRÖNER and TRAPP et al. reported that a dispersion for oven-dried wood occured in the frequency range of 10^7 to 10^8 Hz at room temperature[1]. The same result about various cellulose fibers was also reported by ISHIDA et al. and it was explained that the relaxation process was related to the movement of local parts[2]. MIKHAILOV et al. reported that a dielectric temperature dispersion of dry cellulose existed in low temperature range at 10 KHz and was associated with the movement of CH_2OH groups in the less ordered zones[3]. The value of activation energy in the relaxation process was about $10\sim13$ Kcal/mol[4].

On the other hand, BERNIER et al. investigated the mechanical temperature dispersions for oven-dry wood in the temperature range of 90 to 475°K at about $2\sim3$ KHz. They considered that the relaxation in low temperature range was associated with the motion of rather small molecular segments and that the one in high temperature range was due to the cooperative movement of rather large segments of molecule[5]. FUKADA examined the temperature dependence of piezoelectric, viscoelastic and dielectric properties of dry wood at low frequency and considered that the relaxation occurred at about $-100°C$ was associated with the tortional vibrations of cellulose molecules[6].

The relationship between dielectric loss factor and frequency for glucose, cellobiose, cotton and dextrin is shown in Fig. 1. The value of ϵ'' for glucose and cellobiose was small and no peak occured. On the other hand, the value of ϵ''
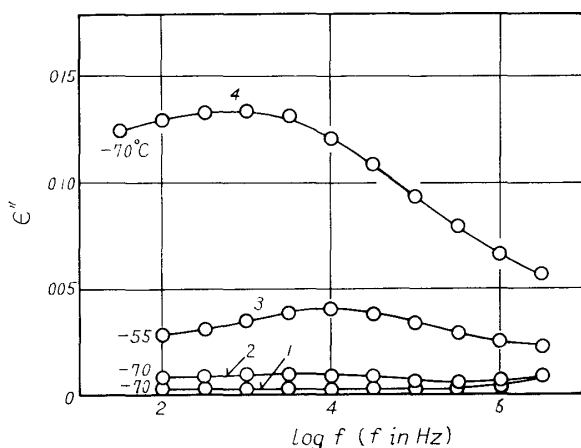

Fig. 1. The relationship between dielectric loss factor and frequency for (1) glucose, (2) cellobiose, (3) cotton and (4) dextrin.
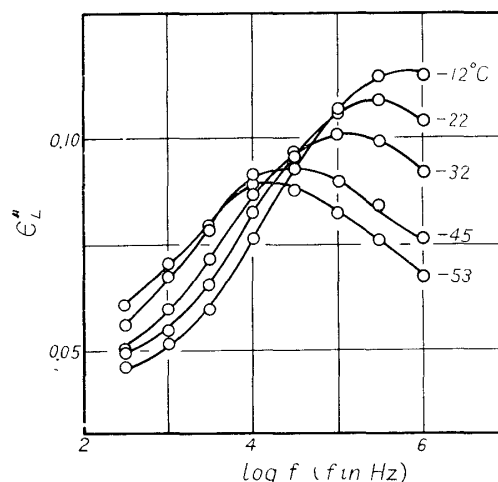
Fig. 2. The dielectric loss factor of oven dried HOONOKI as a function of frequency at respective temperatures.

for cotton and dextrin was large and a clear peak appeared.

In the case of glucose and cellobiose powder almost all CH_2OH group on glucose residues may form a hydrogen bond with a neighbouring molecule, though other OH groups do not always form hydrogen bond, because CH_2OH group is more flexible than other OH groups. On the other hand, it can be considered that many CH_2OH groups in cotton and dextrin can not form hydrogen bonds because of steric hindrance. If free CH_2OH groups contribute to the orientation polarization,
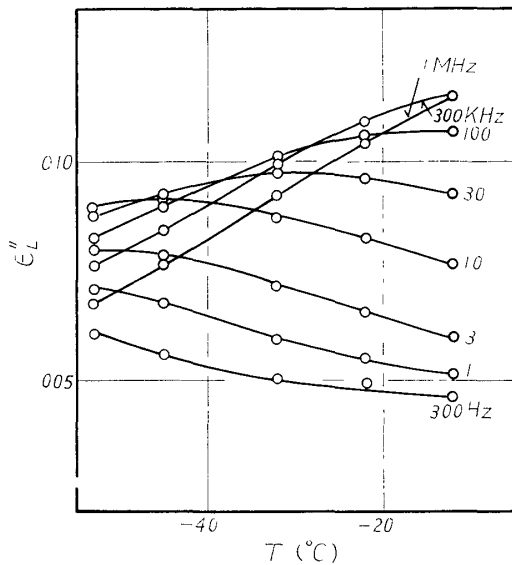
Fig. 3. The dielectric loss factor of oven dried HOONOKI as a function of temperature at respective frequencies.
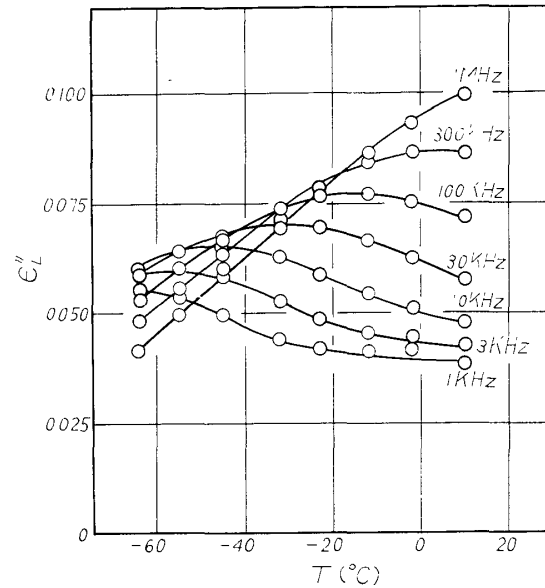
Fig. 4. The dielectric loss factor of oven dried SUGI as a function of temperature at respective frequencies.
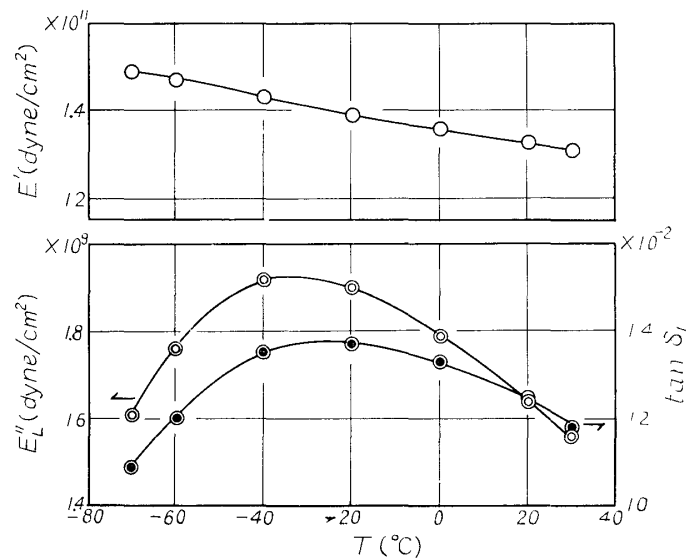

Fig. 5 The dynamic modulus, the loss modulus and the loss tangent of oven-dried HOONOKI as a function of temperature at 60 KHz

the above results can be explained. Moreover, since the absorption in high frequency range did not occur in beech xylan which has not CH_2OH group, as shown in Fig. 18, it is reasonable to consider that only CH_2OH group can contribute to the orientation polarization.

Fig. 2 shows the relationship between ϵ'' and frequency for oven-dried HOONO-KI at respective temperatures. A frequency dispersion occurred at low temperature and the position of peak shifted to higher frequency region with increasing temperature. Figs. 3 and 4 show dielectric loss factor ϵ'' for oven-dried HOONOKI and SUGI at respective frequencies as a function of temperature. The position of the peak shifted to higher temperature range with increasing frequency. The values of activation energy for the relaxation process were 10.2 Kcal/mol for HOONOKI and 9.6 Kcal/mol for SUGI.

The dynamic modulus E', the loss modulus E'' and the loss tangent $\tan \delta$ for oven-dried HOONOKI in longitudinal direction at 60 KHz as a function of temperature are shown in Fig. 5. A temperature dispersion occurred at about $-20 \sim$ $\sim -30°C$. ϵ'' for SUGI (Cryptomeria japonica D. DON.) and HOONOKI at 30 and 100 KHz and E'' for HOONOKI at 60 KHz as a function of temperature are shown in Fig. 6. The position of dielectric absorption coincided with that of viscoelastic one, and it may be suggested that the both relaxation processes are associated with the same molecular motion and are due to the local motion of CH_2OH groups in the disordered region of wood substance. In this paper, the absorption is called r.
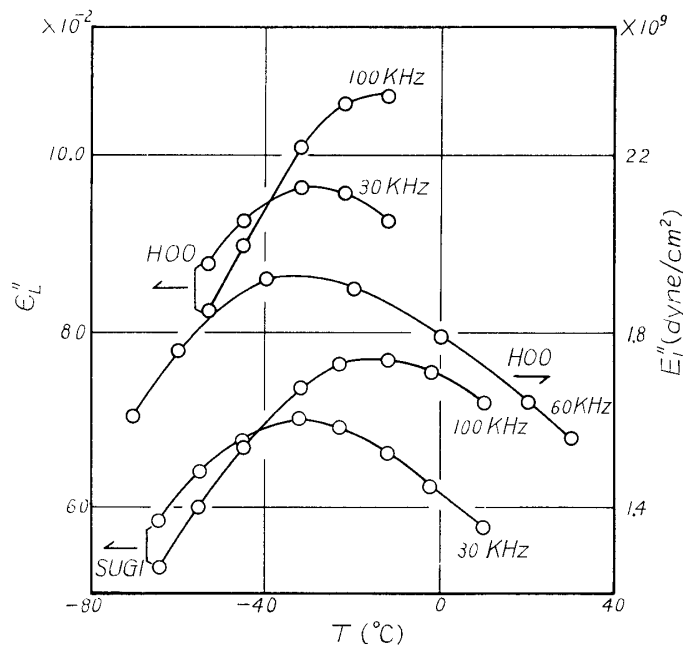

Fig. 6 The comparison of the data for a dielectric and a mechanical relaxation process

The dispersions of oven-dried KUSUNOKI in very low frequency range at room temperature

It was reported by TRAPP et al. that there was another dielectric dispersion in air-dried wood in low frequency range and that the dispersion was due to the interfacial polarization[1]. However, the dispersion did not occur in oven-dried wood.
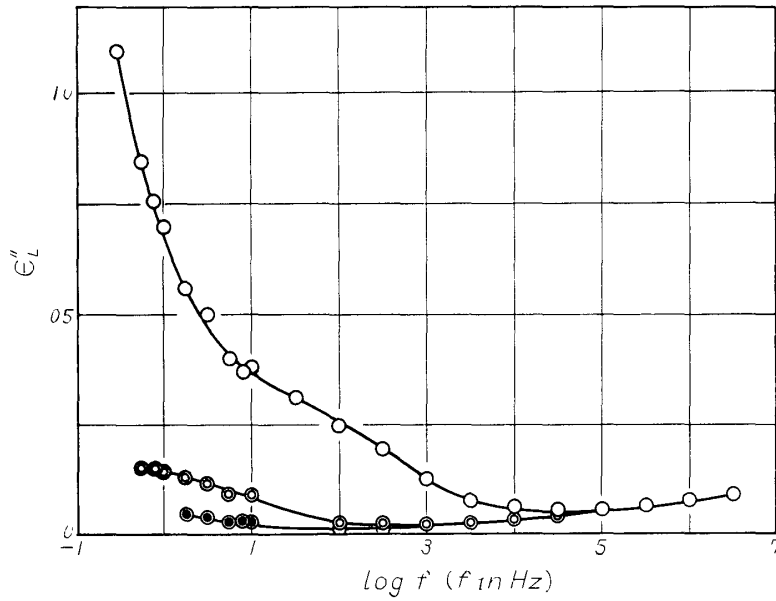

Fig. 7   The dielectric loss factor of the untreated and the extracted
KUSUNOKI as a function of frequency at 41°C
○ : the untreated,   ◎ : the hot water extracted,
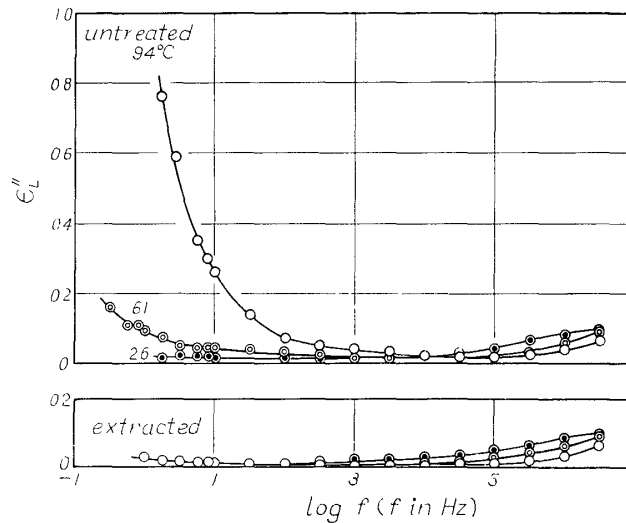● : the hot water and alcohol-benzene extracted.

Fig. 8.   The dielectric loss factor of the untreated and the extracted oven
dried HINOKI at 26, 61 and 94°C.

Fig. 7 shows the relationship between the dielectric loss factor and the frequency for oven-dried KUSUNOKI in longitudinal direction at 41°C. The value of ϵ'' for untreated KUSUNOKI increased rapidly in very low frequency range. However, the value of ϵ'' decreased by hot water extraction and the absorption disappeared completely by alcohol-benzene extraction. Therefore, the absorption appeared in oven-dried KUSUNOKI in very low frequency range may be associated with the conductive impurities like camphor.

ϵ'' of oven-dried HINOKI (*Chamaecyparis obtusa* ENDL.) in longitudinal direction as a function of frequency at 26, 61 and 94°C is shown in Fig. 8. At high temperature, the value of ϵ'' for the untreated HINOKI increased rapidly in very
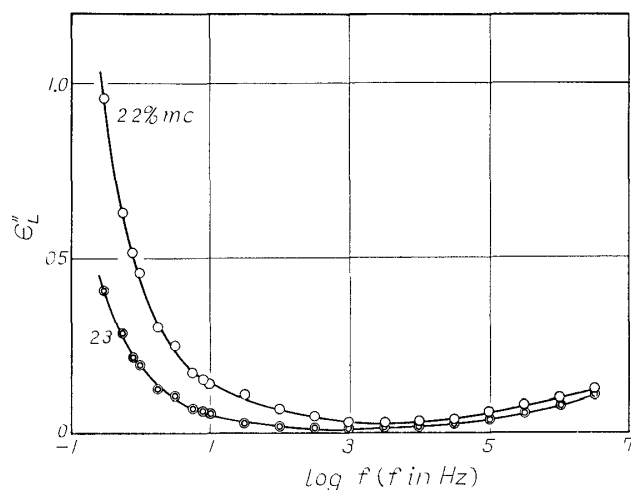

Fig. 9. The dielectric loss factor of the untreated and the extracted HINOKI at 2.2-2.3 % m. c. as a function of frequency.
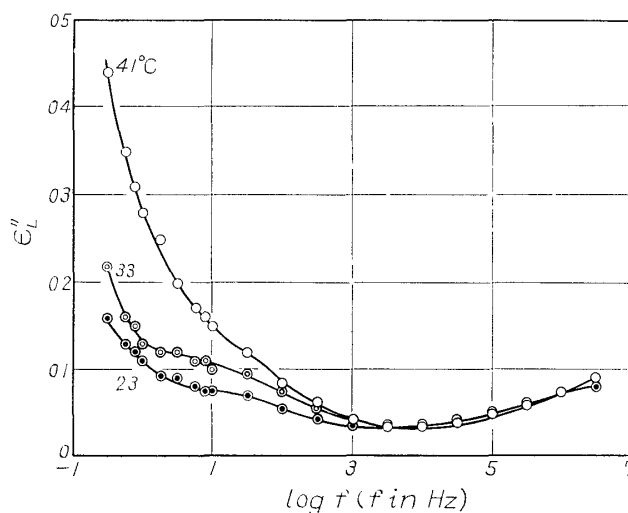○ : the untreated, ◎ the extracted

Fig. 10 The dielectric loss factor of oven dried KUSUNOKI as a function of frequency at respective temperatures

low frequency range and the absorption disappeared by hot water and alcohol-benzene extraction. ϵ'' of HINOKI of about 2 % moisture content at 41°C as a function of frequency is shown in Fig. 9. An absorption also appeared in very low frequency range and ϵ'' value for the untreated was larger than that of the extracted.

ϵ'' for KUSUNOKI in longitudinal and tangential direction as a function of frequency is shown in Figs. 10 and 11. In tangential direction, a clear peak occurred at low frequency range, whereas a shoulder occurred in longitudinal direction. The comparison of both results is shown in Fig. 12. The value of ϵ'' in longitudinal direction was larger than that in tangential direction. $\epsilon''-\log f$ curve for oven-dried KUSUNOKI in tangential direction can be divided into the three relaxation processes by the method of ALGIE[9], as shown in Fig. 13. In this paper, the relaxations are called α_1', α_2' and γ in order of increasing frequency.
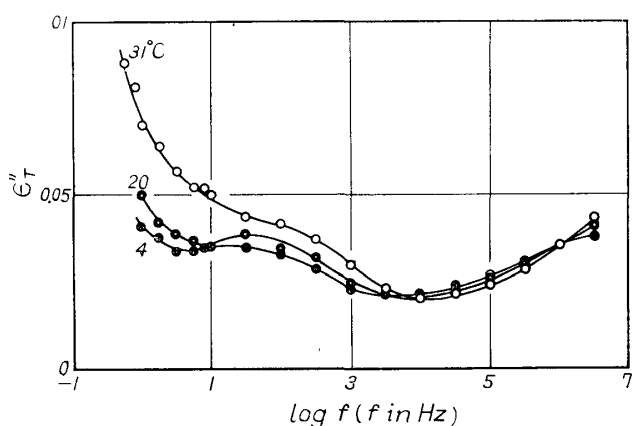

Fig. 11 The dielectric loss factor of oven-dried KUSUNOKI in tangential direction as a function of frequency at 4, 20 and 31°C
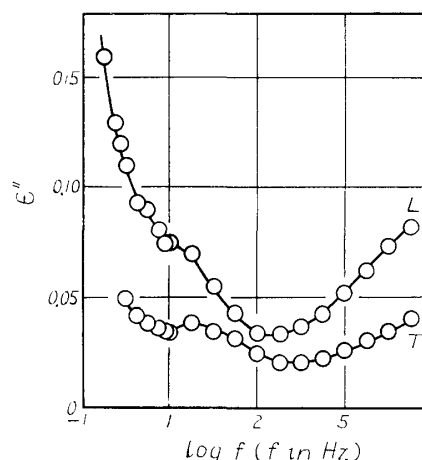

Fig. 12 The dielectric loss factor vs. frequency curve of KUSUNOKI in longitudinal and tangential direction at 20-23°C
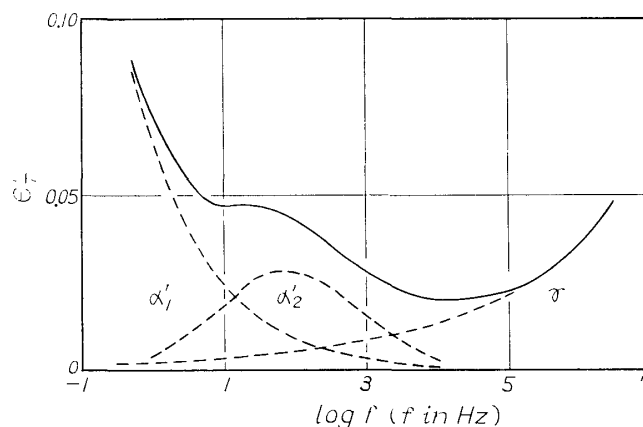

Fig. 13. The overlap of three dielectric relaxation processes for KUSUNOKI in tragential direction.
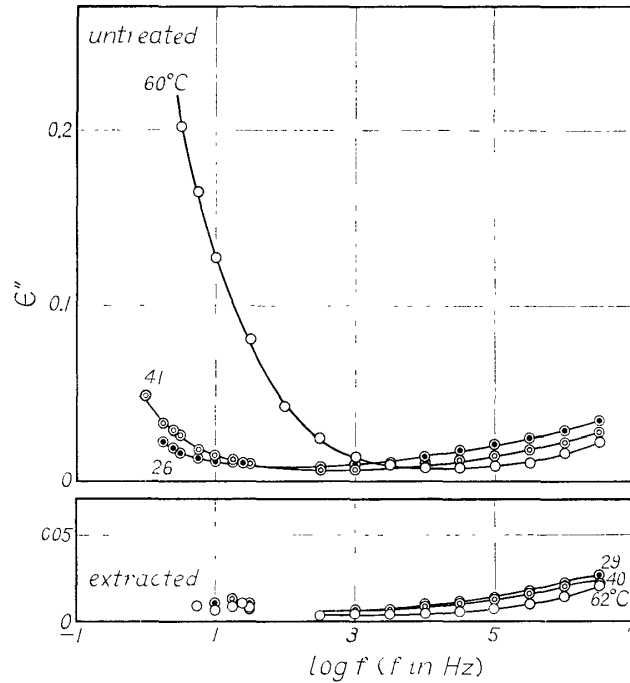
Fig. 14. The dielectric loss factor of the untreated and the extracted KUSUNOKI (powder) as a function of frequency at respective temperatures.

ϵ'' for powder of oven-dried KUSUNOKI as a function of frequency is shown in Fig. 14. In this case, an absorption, which is called α', appeared in very low frequency range, but no peak or shoulder occurred and the absorption also disappeared by the extraction. From the results it can be concluded that the absorption in very low frequency range is due to the existence of the conductive materials and is influenced by the shape of the material in wood. The results may be explained qualitatively by the theory of Sillars.

In the mixture, consisting of the spheroid whose dielectric constant and conductivity are ϵ_2 and σ_2, and the homogeneous medium whose dielectric constant and conductivity are ϵ_1 and σ_1, the complex dielectric constant of the mixture ϵ^* is expressed by the following equation.

$$\epsilon^* = \epsilon_1^* \left\{ 1 + q \frac{n(\epsilon_2^* - \epsilon_1^*)}{(n-1)\epsilon_1^* + \epsilon_2^*} \right\}$$

$$\epsilon^* - \epsilon_1^* \ll \epsilon_1^*$$

where ϵ_1^* and ϵ_2^* are the complex dielectric constant of the components, and n and q are the shape factor and the volume fraction of the spheroid. When σ_1 is equal to 0, the dielectric loss factor of the mixture ϵ'' is written as follows:

$$\epsilon'' = \frac{kw\tau}{1 + w^2\tau^2}$$

where,

$$k = n^2 q \frac{\epsilon_1}{(n-1)\epsilon_1 + \epsilon_2}, \qquad \tau = \frac{(n-1)\epsilon_1 + \epsilon_2}{4\pi\sigma_2}$$

(1) In case of sphere

$$\epsilon'' = \frac{9q\epsilon_1^2 w \cdot 4\pi\sigma_2}{(4\pi\sigma_2)^2 + w^2(2\epsilon_1 + \epsilon_2)^2}, \quad \epsilon''_{max} = \frac{9q\epsilon_1^2}{2(2\epsilon_1 + \epsilon_2)} \quad \text{at} \quad w = \frac{4\pi\sigma_2}{2\epsilon_1 + \epsilon_2}$$
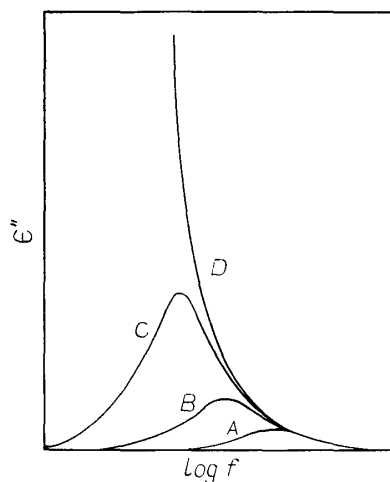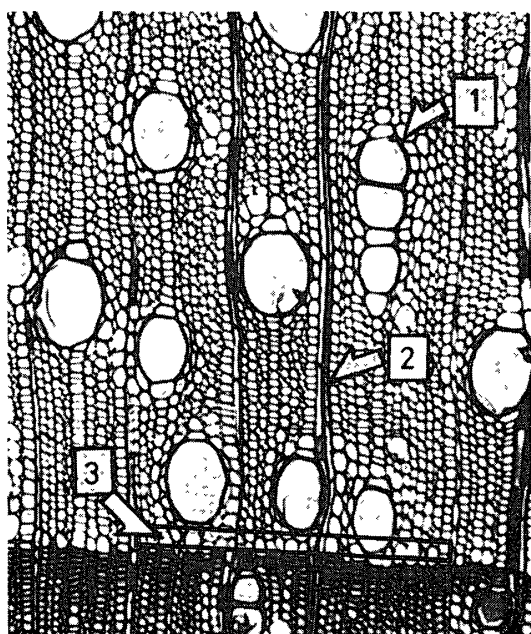
(2) In case of oblate spheroid

Fig. 15. ϵ'' vs. $\log f$ (schematic curve).
A : lamella, B : sphere, C : prolate spheroid, D : cylinder

Phot. 1 Cross section of KUSUNOKI (ca ×80)
1) Parenchyma cell, 2) Ray cell, 3) when electric field applies to tangential direction, parenchyma exists as a flat plate parallel to the field

Phot. 2 Tangential section of KUSUNOKI (ca ×80)
1) Parenchyma cell, 2) Ray cell

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$$\epsilon'' = \frac{q\epsilon_1{}^2 w \cdot 4\pi\sigma_2}{\{(4\pi\sigma_2)^2 + w^2\epsilon_2{}^2\}}, \quad \epsilon''_{max} = \frac{q\epsilon_1{}^2}{2\epsilon_2} \quad at \quad w = \frac{4\pi\sigma_2}{\epsilon_2}$$

(3) In case of prolate spheroid

$$\epsilon'' = \frac{4\pi\sigma_2 q}{w}$$

From the above equations, the value of ϵ'' decreases in the order, case (3) $>$case (1) $>$case (2) and the position of frequency corresponding to ϵ'' maximum decreases in the order, case (2) $>$case (1) $>$case (3). The schmatic curve of ϵ'' as a function of frequency for the mixture is shown in Fig. 15.

The photographs for cross and tangential section of KUSUNOKI are shown in Phots. 1 and 2. When the electric field applies to longitudinal direction, parenchyma cell exists as a cylindrical shape parallel to electric field and ray cell exists as a cylindrical shape perpendicular to electric field. On the other hand, when electric field applies to tangential direction, ray cell exists as a flat plate perpendicular to electric field and parenchyma cell exists as a cylindrical shape perpendicular to electric field or as a flat plate parallel to the field.

In case of powder, the conductive material exists as a granulate shape. From these results, it may be considered that α_2' and α_1' are associated with the conductive material existing as the cylindrical or flat plate shapes perpendicular and parallel to the electric field respectively and α' is associated with the conductive material existing as the granulate shape.

The dispersion of oven-dried wood and cellulose in very low frequency at high temperature

BERNIER et al. reported that there was a large mechanical relaxation beginning beyond 400°K and that the relaxation might be associated with cooperative motion of large segments of molecules[5]. MIKHAILOV et al. reported that the value of dielectric loss tangent of cellulose increased with increasing temperature in high temperature range[3].

On the other hand, KANE investigated that there was a linear relationship between dielectric constant and water-vapor accessibility of cellulose[7]. VERSEPUT studied on the relation between dielectric constant and crystallinity of cellulose and found that dielectric constant increased with decreasing the degree of crystallinity[8].

The frequency dependence of ϵ'' for the untreated and the extracted HINOKI at 105°C is shown in Fig. 16. Even if wood was extracted, the absorption still existed. Then the following three points may be considered as the main reasons of the absorption.

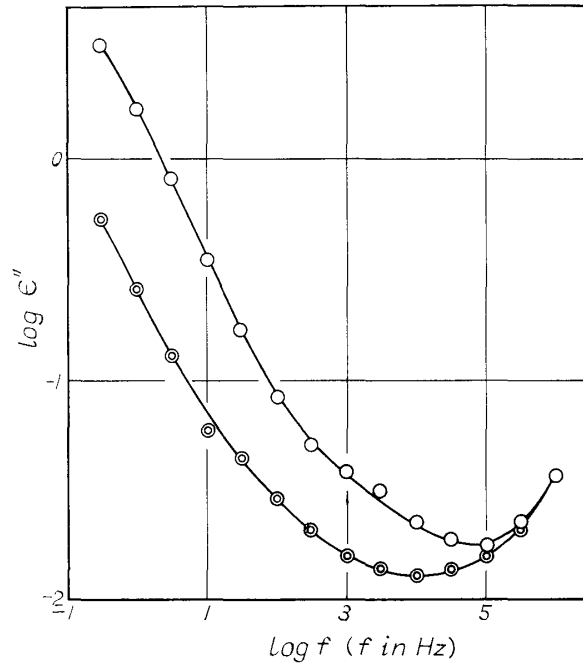(1) The orientation polarization by segmental motion of molecules, namely

Fig. 16. log ϵ'' vs. log f for HINOKI at 105°C. The open and the double circles represent the untreated and the extracted, respectively.
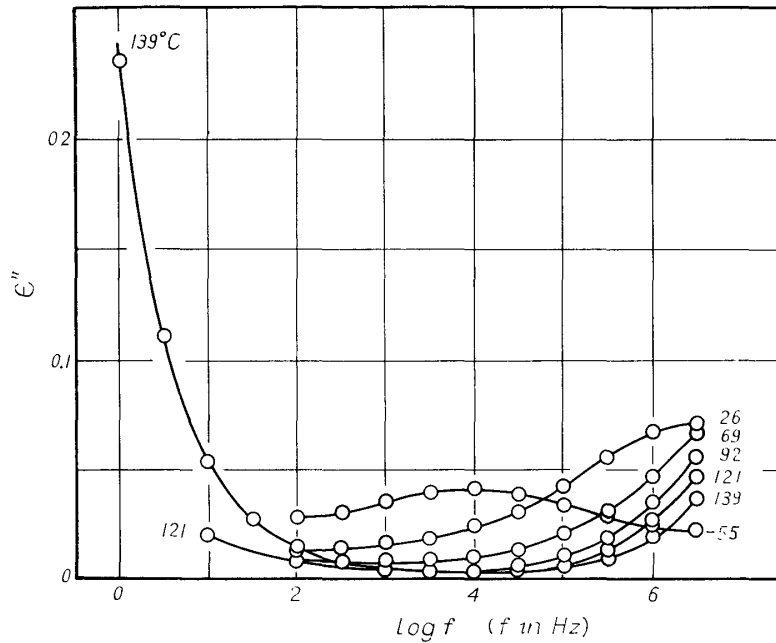

Fig. 17. The dielectric loss factor of oven-dried cotton as a function of frequency at respective temperatures.

cellulose, hemicellulose and lignin.

(2) The interfacial polarization at the boundary between amorphous and crystalline region of cellulose.

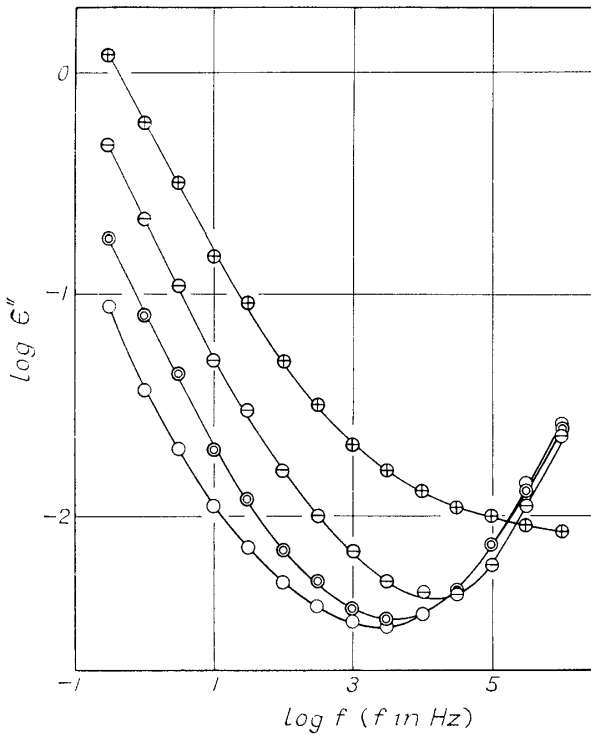(3) The interfacial polarization by the submicroscopic heterogeneous structures

Fig. 18. $\log \epsilon''$ vs. $\log f$ for cotton (○), Whatmann cellulose (◎), Avicel (⊖) and beech xylan (⊕) at 105°C.
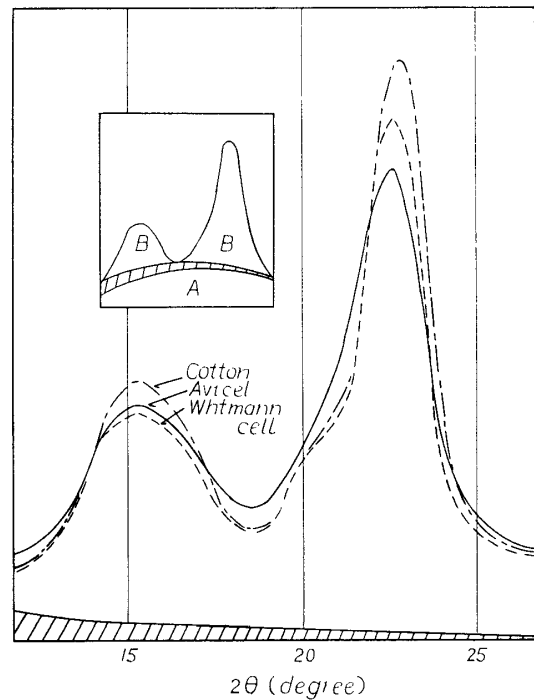
Fig. 19. The X-ray diagram for cotton. Avicel and Whatmann cellulose. Hatched area is the radiation scattered by air.
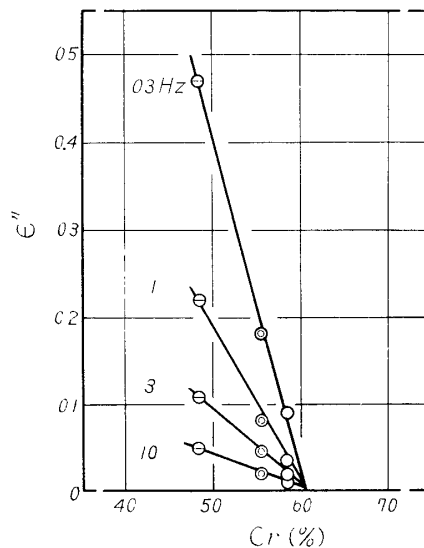
Fig. 20 The relationship between the dielectric loss factor of cotton, Avicel and Whatmann cellulose and crystallinity at respective frequencies.

of wood such as lamellar structures.

In order to clarify the reason of the residual absorption, the frequency dependence of ϵ'' for pure celluloses and wood hemicellulose were examined. The relationship between ϵ'' and frequency for dry cotton powder at respective temperatures is shown in Fig. 17. The value of ϵ'' increased rapidly in very low frequency at over 120°C and no peak appeared. The relationship between ϵ'' and frequency for cellulose and hemicellulose powder is shown in Fig. 18. And X-ray diagram for cellulose powders is also shown in Fig. 19. The degree of crystallinity decreased in the order, cotton>Whatmann cellulose>Avicel. The relationship between ϵ'' and Cr for dry cellulose at respective frequencies is shown in Fig. 20. In this paper, Cr was defined by the ratio of the area B to the area A+B in X-ray diagram of Fig. 18. There was a linear relationship between ϵ'' and Cr and the value of ϵ'' increased with decreasing the degree of crystallinity. Considering these results, the absorption in very low frequency range at high temperature may be associated with the segmental motions of molecules in the amorphous region accompanied by the thermal degradation. If the absorption is caused by the interfacial polarization at the boundary between amorphous and crystalline region of polysaccharides, the value of ϵ'' for amorphous polysaccharides must be small like high crystalline cellulose. On the contrary, the value of ϵ'' for amorphous wood hemicelluloses (beech xylan) was very large as shown in Fig. 18.

Acknowledgement

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