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ORIGINAL ARTICLE

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Dielectric relaxation due to the heterogeneous structure of wood charcoal

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Abstract Delignified hinoki wood and cellulose as well as hinoki and lauan woods were carbonized at 590°C for 1 h. The dielectric properties of these specimens were measured at 20°C in a frequency range of 20 Hz to 1 MHz. Inflection points in the dielectric constant (ε') versus the logarithm of frequency ($\log f$) curves as well as in the logarithm of the electric conductivity ($\log \sigma$) versus $\log f$ curves for all specimens prepared were recognized. Peaks in the dielectric loss and the imaginary part of the complex conductivity versus the $\log f$ curves were detected in the frequency location corresponding to the inflection point in the ε' and $\log \sigma$ versus $\log f$ curves. It was considered that this relaxation was responsible for the interfacial polarization observed in heterogeneous materials because no permanent dipoles existed in the specimens carbonized above 500°C. The Cole–Cole circular arc law was applied to account for this relaxation. Similar average relaxation times were obtained for all specimens. These results suggested that the observed relaxation was ascribed to interfacial polarization at microscopic levels in the cell walls.

Key words Dielectric relaxation · Heterogeneous materials · Cole-Cole circular arc law · Interfacial polarization · Charcoal

Introduction

The electric properties of the charcoal from wood and fiberboards have been studied in order to explore the potential utility of materials for electrodes,[1] fuel cell separators,[2] and electromagnetic shielding.[3] However, these electric properties have not been thoroughly clarified, because the properties of charcoal samples prepared from wood depend strongly on treatment conditions such as temperature, time, and atmosphere, and such charcoal is known to have an extremely complicated structure. The electric properties of wood charcoal drastically change depending on the treatment temperature.[4–7] It has been reported[8] that wood charcoal carbonized below 300°C, between 300°C and 800°C, and above 800°C acts as an insulator, a semiconductor, and a conductor, respectively. In our previous reports,[9,10] the dielectric properties of wood charcoal prepared at temperatures below 800°C were investigated. A substantial relaxation was detected in charcoal samples prepared at temperatures between 500° and 600°C. No permanent dipoles existed in specimens treated above 500°C, and the electric conductivity of these specimens began to increase remarkably starting at 500°C, such that it was speculated that this type of relaxation could not be ascribed to dipole polarization, but instead was due to the interfacial polarization observed in heterogeneous materials (a Maxwell-Wagner type of relaxation).[11] In this study, the dielectric properties of charcoal prepared from untreated hinoki and lauan woods, delignified hinoki wood, and cellulose powder carbonized at 590°C were investigated in order to clarify what levels of heterogeneous structure were responsible for the observed dielectric relaxation.

Materials and methods

Specimens of hinoki wood (*Chamaecyparis obtusa*, 60 × 60 × 5 mm) cut in three directions [longitudinal (L), radial (R), and tangential (T) directions with regard to the electric field] and lauan wood (*Shorea* sp.) specimens (L direction) were used. Some of the hinoki wood specimens examined here were delignified by the chlorite method. The weight loss of treated specimens was approximately 16%. Cellulose powder (CF11, Whatman) was also used in the current series of experiments. After the specimens were dried under

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evacuation at 105°C for 1 day and their weight was measured under completely dried conditions, they were subjected to heat treatment in an electric oven. The temperature was raised by 4°C/min up to the prescribed temperature of 590°C, which was maintained for 1 h. Nitrogen gas flowed into the electric oven during the treatment. After treatment, the weight and dimensions of treated specimens were measured. The yield of untreated hinoki and lauan wood specimens, the delignified hinoki wood specimens, and the cellulose powder were 25%–28%, 28%, 28%, and 27%, respectively. Their densities (i.e., the density of the carbonized powder packed in the electrode) were 0.26, 0.30, 0.28, and 0.47 g/cm^3, respectively. An LCR meter (Japan Hewlett-Packard, HP4284A), an electrode (Ando Electric, SE-3O, effective diameter: 16.9 and 38 mm) and a bath (Ando Electric, TO-3) were used for the dielectric measurements. The dielectric constant (ε'), dielectric loss (ε''), and electric conductivity (σ) of the carbonized blocks and powder specimens under absolutely dry conditions were measured at 20°C in the frequency range from 20 Hz to 1 MHz.

Results and discussion

The ε' and $\log\sigma$ of the hinoki wood charcoal in the three principal directions are plotted against $\log f$ in Fig. 1a,b. An inflection point suggesting a relaxation was observed in both curves. Because an increase in ε' below 100 Hz was considered to be due to the electrode polarization, the limiting dielectric constant values of the relaxation on the low-frequency side (ε_h) were determined as shown in Fig. 1a,b. The $\log\sigma$ remained at a constant value below 1 kHz, and this value was denoted by $\log\sigma_l$. The dielectric loss ($\Delta\varepsilon''$) and the imaginary part of the complex electric conductivity ($\Delta\sigma''$) due to this relaxation were calculated using ε_h and σ_l and the following equations:

$$\Delta\varepsilon'' = \varepsilon'' - \frac{\sigma_l}{\omega\varepsilon_v},$$

$$\Delta\sigma'' = (\varepsilon' - \varepsilon_h)\omega\varepsilon_v,$$

where σ_l is the electric conductivity at the limiting low frequency, ω is the angular frequency ($\omega = 2\pi f$), ε_v is the dielectric constant of free space, ε_h is the dielectric constant at the limiting high frequency. The results are shown in Fig. 1c,d. A peak in each of the $\Delta\varepsilon''$ versus $\log f$ and $\Delta\sigma''$ versus $\log f$ curves was recognized in the frequency corresponding to the inflection point in ε' versus $\log f$ and $\log\sigma$ versus $\log f$ curves.

The values of ε', $\Delta\varepsilon''$, $\log\sigma$, and $\Delta\sigma''$ were the largest in the L direction over the frequency range tested. On the other hand, the values in the R direction were larger than those in the T direction. It is well known that the cellular structure of wood is maintained even with treatment at 1600°C.[12] It is reported that the same trend in dielectric anisotropy is observed in absolutely dry untreated wood.[13] The electric anisotropy of wood can be explained by the arrangement of cell lumens (air) and cell walls. The arrangement of cell lumens and carbonized cell walls for the carbonized wood in the L direction was almost parallel, such that the respective values of the dielectric properties were the largest. On the other hand, a mixture of series and parallel arrangements was observed in the R and T directions. Because the specimens in the R direction contained a larger parallel fraction than did the specimens cut in the T direction, the obtained dielectric property values were larger in the R direction than in the T direction.

Figure 2 shows the relationships between ε', $\log\sigma$, $\Delta\varepsilon''$, and $\Delta\sigma''$ in the L direction and $\log f$ for the lauan wood charcoal. The same relaxation observed in the hinoki wood charcoal was detected in the lauan wood charcoal. The $\log\sigma_l$ of the lauan wood charcoal was very small compared with that of the hinoki wood charcoal.

The results for the delignified hinoki charcoal are shown in Fig. 3. The relaxation also observed in the hinoki and lauan wood charcoal was detected, but the frequency location shifted to a slightly higher frequency range. The $\log\sigma_l$ values of the delignified wood charcoal were larger than those of the hinoki and lauan wood charcoal. A large increase in ε' due to electrode polarization was recognized in the low-frequency range.

There are two main relaxation mechanisms due to dipole polarization and interfacial polarization. Maxwell-Wagner theory predicts that dielectric relaxation due to the interfacial polarization occurs when a material consists of two parts with different sets of ε' and σ.[11] Because no permanent

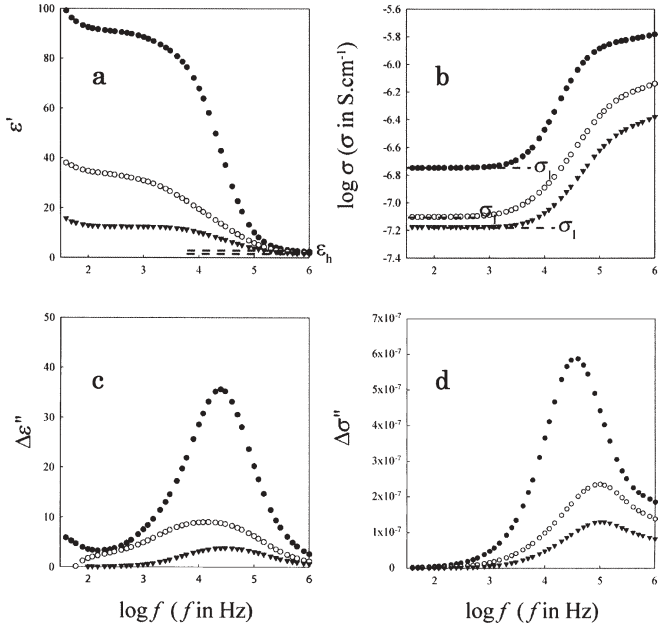

Fig. 1a–d. The dielectric properties observed at 20°C for hinoki wood charcoal specimens carbonized at 590°C. **a** Dielectric constant (ε') versus the logarithm of frequency ($\log f$) curves, **b** the logarithm of electric conductivity ($\log\sigma$) versus $\log f$ curves, **c** dielectric loss minus electric conduction ($\Delta\varepsilon'' = \varepsilon'' - \sigma_l/\omega\varepsilon_v$) versus $\log f$ curves, and **d** the imaginary part of complex electric conductivity [$\Delta\sigma'' = (\varepsilon - \varepsilon_h)\ \omega\varepsilon_v$] versus $\log f$ curves. *Filled circles*, longitudinal direction; *open circles*, radial direction; *triangles*, tangential direction

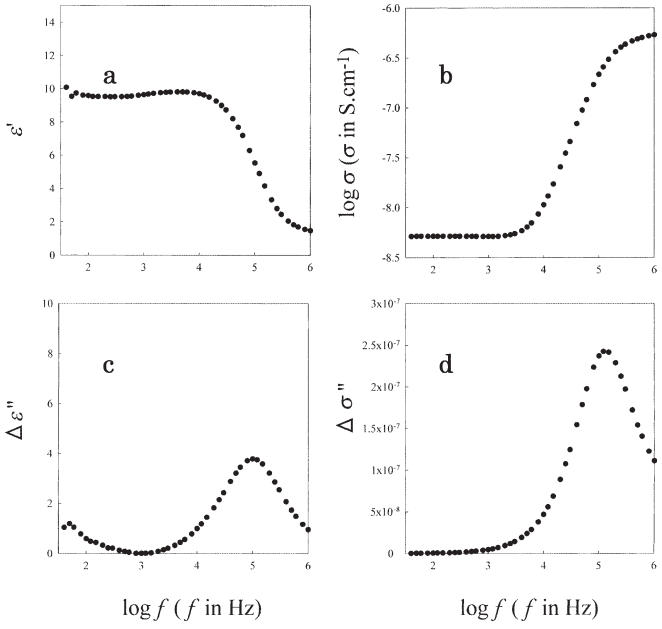

Fig. 2a–d. The dielectric properties in the longitudinal direction at 20°C for lauan wood charcoal samples carbonized at 590°C. **a** Dielectric constant (ε') versus the logarithm of frequency ($\log f$) curve, **b** the logarithm of electric conductivity ($\log \sigma$) versus $\log f$ curve, **c** dielectric loss minus electric conduction ($\Delta\varepsilon'' = \varepsilon'' - \sigma_l/\omega\varepsilon_v$) versus $\log f$ curve, and **d** the imaginary part of complex electric conductivity [$\Delta\sigma'' = (\varepsilon - \varepsilon_h)\ \omega\varepsilon_v$] versus $\log f$ curve

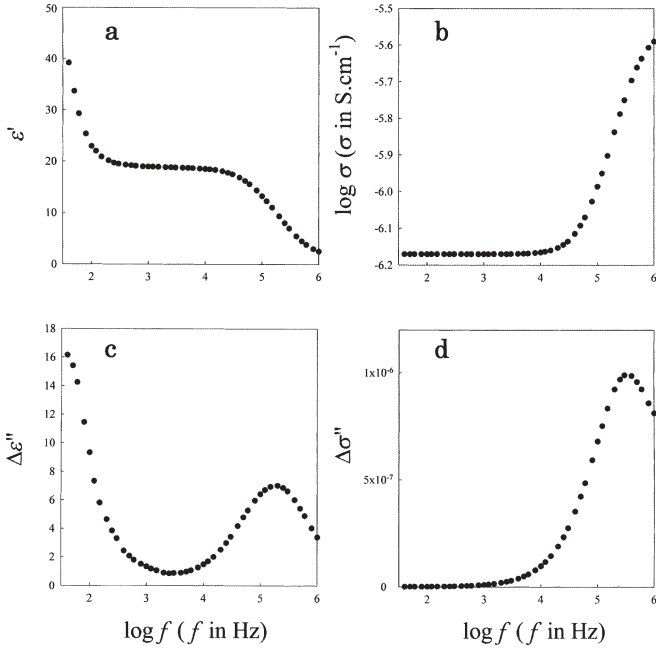

Fig. 3a–d. The dielectric properties in the longitudinal direction at 20°C for delignified hinoki wood charcoal specimens carbonized at 590°C. **a** Dielectric constant (ε') versus the logarithm of frequency ($\log f$) curve, **b** the logarithm of electric conductivity ($\log \sigma$) versus $\log f$ curve, **c** dielectric loss minus electric conduction ($\Delta\varepsilon'' = \varepsilon'' - \sigma_l/\omega\varepsilon_v$) versus $\log f$ curve, and **d** the imaginary part of complex electric conductivity [$\Delta\sigma'' = (\varepsilon - \varepsilon_h)\ \omega\varepsilon_v$] versus $\log f$ curve

dipoles were found in specimens treated above 500°C, it is possible that the relaxation observed at 590°C cannot be ascribed to dipole polarization. The conductance of the specimens began to increase remarkably starting at a temperature of 500°C. Therefore, the relaxation observed in specimens treated at 590°C is speculated to be a Maxwell-Wagner type of relaxation.

Relaxation was observed in both the charcoal from lauan wood with no annual rings and in the charcoal from hinoki wood with distinct annual rings. This finding suggested that the heterogeneous structure responsible for the interfacial polarization is not that at a macroscopic level (e.g., such as in earlywood and latewood structure), but instead is the heterogeneous structure found at the microscopic level in the cell walls. Moreover, relaxation was also observed in the delignified hinoki wood charcoal specimens.

In order to characterize the dielectric relaxation occurring in these charcoal specimens carbonized at 590°C, the Cole–Cole circular arc law[14] was applied to the results of $\Delta\varepsilon''$ versus ε' and $\Delta\sigma''$ versus σ for the hinoki, lauan, and delignified hinoki charcoal samples. The law is expressed by the following equations:

$$\varepsilon^* - \varepsilon_h = (\varepsilon_l - \varepsilon_h) \cdot \frac{1}{1 + (i\omega\tau_m)^{\beta}},$$

$$\sigma^* - \sigma_l = (\sigma_h - \sigma_l) \cdot \frac{1}{1 + (i\omega\tau_m)^{-\beta}},$$

where ε^* and σ^* are the complex dielectric constant ($\varepsilon^* = \varepsilon' - i\varepsilon''$) and electric conductivity ($\sigma^* = \sigma - i\sigma''$), ε_l is the dielectric constant at the limiting low frequency, σ_h is the electric conductivity at the limiting high frequency, ω is the angular frequency ($\omega = 2\pi f$), τ_m is the generalized relaxation time, and β ($0 \leqq \beta \leqq 1$) is the parameter relating to the distribution of relaxation times. The terms ($\varepsilon_l - \varepsilon_h$) and ($\sigma_h - \sigma_l$) are called the relaxation magnitudes of dielectric constant and electric conductivity, respectively. These equations predict that the locus of $\Delta\varepsilon''$ versus ε' or $\Delta\sigma''$ versus σ gives a circular arc. The values intersecting the abscissa are ε_h and ε_l or σ_l and σ_h, respectively.

The Cole–Cole plots of the complex dielectric constants and electric conductivities in three principal directions for the hinoki charcoal are shown in Fig. 4. The circular arc law well described the results of the complex dielectric constant in the L direction. However, the locus of the experimental values in the R and T directions deviated from the circular arc, because an increment in the dielectric constant was large due to electrode polarization. On the other hand, a slight deviation in the experimental values from the circular arc at higher frequencies of the complex electric conductivity was observed in all three directions.

Figure 5 shows the Cole–Cole plots of the complex dielectric constants and electric conductivities for the lauan charcoal. The electric conductivities for the lauan charcoal were very small and no electrode polarization was recognized. The circular arc law applied well to the results for the lauan charcoal. Figure 6 shows the Cole–Cole plots of the complex dielectric constants and electric conductivities for

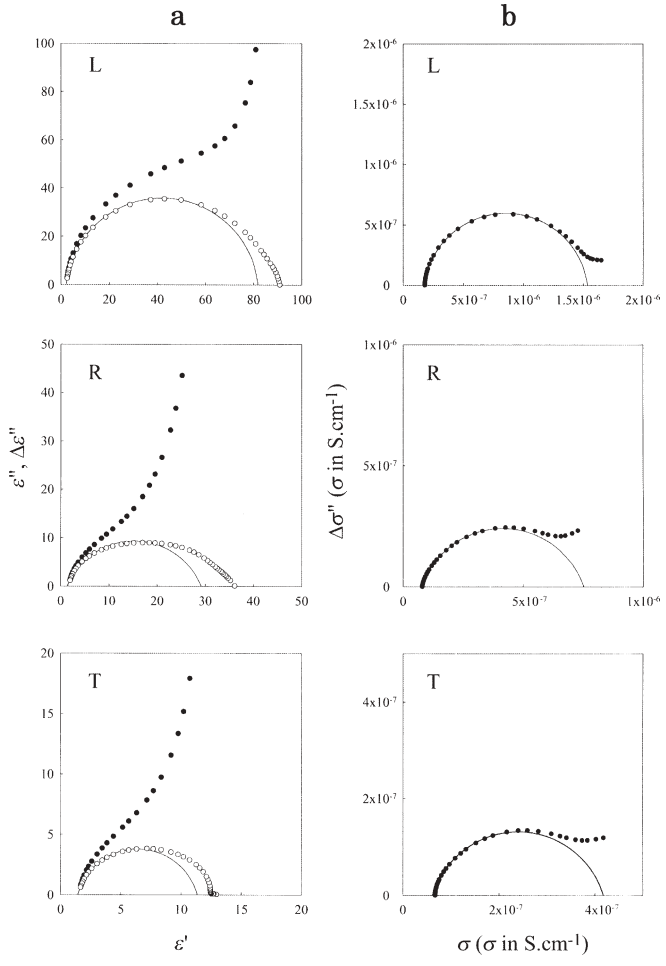

Fig. 4a,b. Cole–Cole plots in three principal directions [longitudinal (*L*), radial (*R*), and tangential (*T*) directions to the electric field] for hinoki wood charcoal specimens carbonized at 590°C. **a** Dielectric loss (*filled circles*, ε''; *open circles*, $\Delta\varepsilon''$) versus dielectric constant (ε'), and **b** the imaginary part of conductivity ($\Delta\sigma''$) versus electric conductivity (σ) at 20°C

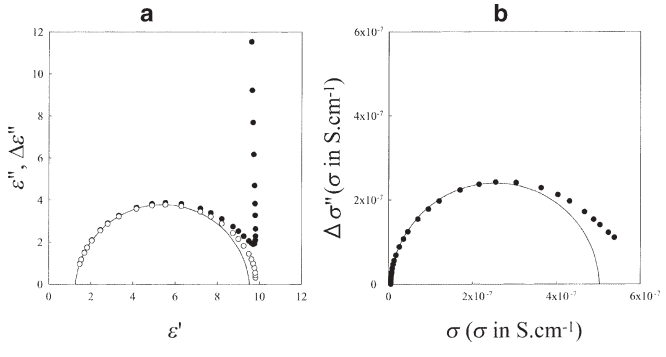

Fig. 5a,b. Cole–Cole plots in the longitudinal direction for lauan wood charcoal specimens carbonized at 590°C. **a** Dielectric loss (ε'', $\Delta\varepsilon''$) versus dielectric constant (ε'), and **b** the imaginary part of conductivity ($\Delta\sigma''$) versus electric conductivity (σ) at 20°C

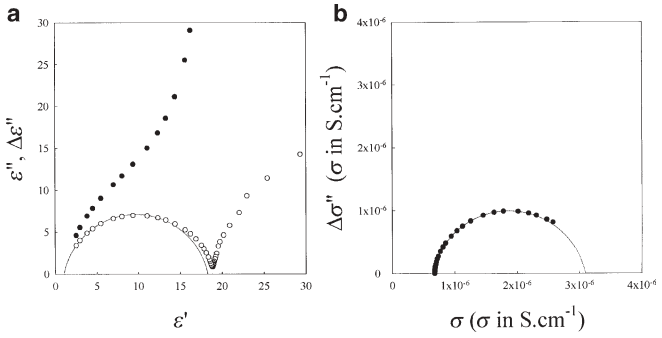

Fig. 6a,b. Cole–Cole plots in the longitudinal direction for delignified hinoki wood charcoal specimens carbonized at 590°C. **a** Dielectric loss (ε'', $\Delta\varepsilon''$) versus dielectric constant (ε'), and **b** the imaginary part of conductivity ($\Delta\sigma''$) versus electric conductivity (σ) at 20°C

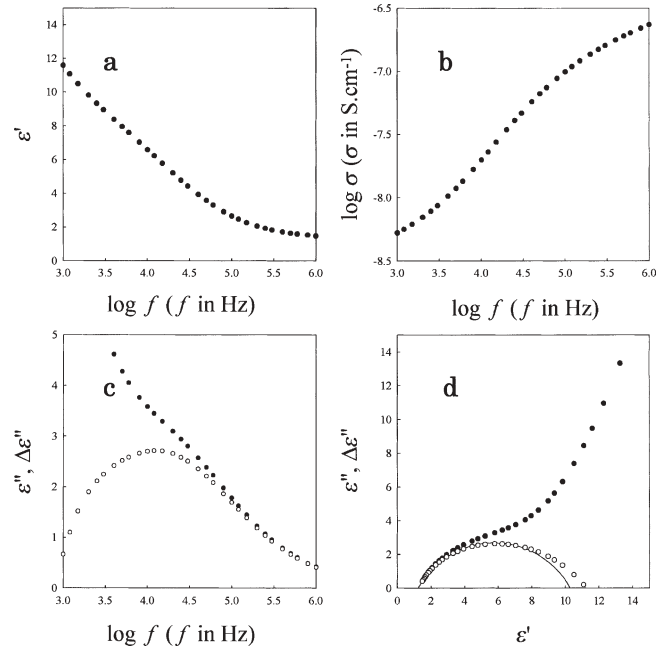

Fig. 7a–d. The dielectric properties at 20°C for cellulose charcoal powder specimens carbonized at 590°C (**a–c**) and the Cole–Cole plots (**d**). **a** Dielectric constant (ε') versus the logarithm of frequency ($\log f$) curve, **b** the logarithm of electric conductivity ($\log\sigma$) versus $\log f$ curve, and **c** dielectric loss (ε'') or dielectric loss minus conduction ($\Delta\varepsilon''$) versus $\log f$ curve

the delignified hinoki wood charcoal specimens. The circular arc law applied well to the results.

The ε', ε'', $\Delta\varepsilon''$, and $\log\sigma$ values for the cellulose charcoal powder are plotted against $\log f$ in Fig. 7. The Cole–Cole plots are also shown in Fig. 7. The same relaxation observed in the wood charcoal was detected in the cellulose charcoal, and the circular arc law agreed well with the results.

Table 1 lists the values of ε_l, ε_h, $(\varepsilon_l - \varepsilon_h)$, σ_l, σ_h, $(\sigma_h - \sigma_l)$, β, and $\log f_m$ obtained from the Cole–Cole plots at 20°C for all of the charcoal specimens. The values of β were smaller in the L direction than in the R and T directions. The values of β and $\log f_m$ obtained from the Cole–Cole plots of complex dielectric constants and electric conductivities were

Table 1. Parameters at 20°C calculated from Cole–Cole plots

Charcoal	$\varepsilon' - \varepsilon''$ relationship					$\sigma - \Delta\sigma''$ relationship				
	ε_l	ε_h	Relaxation magnitude ($\varepsilon_l - \varepsilon_h$)	β	$\log f_m$	σ_h	σ_l	Relaxation magnitude ($\sigma_h - \sigma_l$)	β	$\log f_m$
Hinoki (L)	82.0	2.2	79.8	0.93	4.42	1.53×10^{-6}	1.75×10^{-7}	1.36×10^{-6}	0.93	4.55
Hinoki (R)	29.2	1.7	27.5	0.76	4.31	7.29×10^{-7}	7.62×10^{-8}	6.53×10^{-7}	0.81	4.94
Hinoki (T)	11.4	1.5	9.9	0.82	4.59	4.08×10^{-7}	6.16×10^{-8}	3.46×10^{-7}	0.83	4.97
Lauan (L)	9.5	1.3	8.3	0.92	5.01	5.03×10^{-7}	4.97×10^{-9}	4.98×10^{-7}	0.99	5.04
Delignified hinoki (L)	18.3	1.0	17.2	0.86	5.27	3.10×10^{-6}	6.34×10^{-7}	2.46×10^{-6}	0.87	5.51
Cellulose powder	10.3	1.2	9.1	0.70	4.22	2.30×10^{-7}	2.53×10^{-9}	2.28×10^{-7}	0.74	5.05

almost identical. The relaxation magnitudes of ε' in the L, R, and T directions for the hinoki wood charcoal were 79.8, 23.8, and 9.9, respectively. The dielectric magnitudes were larger in the L direction than in the R and T directions, because the cell lumens (air) and the cell walls of the specimens cut in the L direction were arranged almost in parallel, whereas the arrangement of the specimens in the R and T directions was both in series and in parallel. The value in the R direction was larger than that in the T direction, because the volume fraction of the parallel arrangement of the cell walls and the cell lumens in the R direction was larger than that in the T direction.

Conclusions

The dielectric constant (ε'), dielectric loss (ε''), and electric conductivity (σ) values of absolutely dry charcoal prepared from hinoki wood (*Chamaecyparis obtusa*) in three principal directions, lauan wood (*Shorea* sp.) and delignified hinoki wood in the longitudinal direction, and cellulose powder, all of which were carbonized at 590°C, were measured. The measurements were conducted in the frequency (f) range from 20 Hz to 1 MHz at 20°C. The following results were obtained.

Inflection points in the curves of ε' and $\log\sigma$ versus $\log f$ were detected. A peak in ε'' or in the imaginary part of the complex electric conductivity ($\Delta\sigma''$) versus $\log f$ curves was clearly observed in the frequency location corresponding to the inflection points in the ε' and $\log\sigma$ versus $\log f$ curves. This relaxation was ascribed to the interfacial polarization observed in heterogeneous materials (a Maxwell-Wagner type of relaxation), because no permanent dipoles were found in the wood charcoal specimens treated at temperatures exceeding 500°C.

The Cole–Cole circular arc law could be used to describe the results of all of the charcoal samples prepared. The dielectric constants and electric conductivities at the limiting low and high frequencies, both the relaxation magnitudes of ε' and σ, the logarithm of the generalized relaxation time ($\log f_m$), and the parameter related to the distribution of relaxation times (β) could be calculated from the Cole–Cole plots of both ε' versus ε'' and σ versus $\Delta\sigma''$ for all of the charcoal samples tested. The values of β were smaller in the longitudinal direction than in the radial and tangential directions. The values of β and $\log f_m$ obtained from both the Cole–Cole plots were almost the same. These findings suggest that the observed relaxation was not caused by interfacial polarization at a macroscopic level (i.e., such as that in earlywood and latewood structures), but rather was the result of phenomena occurring at a microscopic level in the cell walls.

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