J Wood Sci (2005) 51:549–553
DOI 10.1007/s10086-004-0688-1

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ORIGINAL ARTICLE

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Dielectric relaxation due to heterogeneous structure in moist wood

Received: September 22, 2004 / Accepted: November 30, 2004

Abstract Dielectric properties in three main directions for hinoki wood (*Chamaecyparis obtusa*) specimens conditioned at various levels of relative humidity were measured in the frequency range from 20 Hz to 10 MHz over the temperature range from −150°C to 20°C. Three relaxations were observed in the specimens conditioned at high levels of relative humidity. The relaxation in the highest frequency range was ascribed to the motions of adsorbed water molecules. The relaxation in the middle frequency range remained unchanged by the ethanol–benzene extraction of specimens. The relaxation location was independent of measuring directions. The relaxation in the lowest frequency range was not detected in the specimens impregnated with methyl methacrylate (MMA). This result suggested that the relaxation was due to electrode polarization. The Cole-Cole circular arc law applied well to two relaxations recognized in the specimens impregnated with MMA. The relaxation magnitude in the middle frequency range was extremely large, and the distribution of relaxation times was very narrow. These characteristics suggested relaxation of the Maxwell-Wagner type resulting from the interfacial polarization in the heterogeneous structure, which included adsorbed water with large electrical conductivity within the insulating cell walls.

Key words Dielectric relaxation · Heterogeneous structure · Adsorbed water · Cole-Cole circular arc law · Methyl methacrylate

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Introduction

Relaxation has been observed in dielectric measurements of moist wood at around 100 kHz in the temperature range between −100°C and −60°C.[1–4] The cause of this relaxation has been assigned to the motions of adsorbed water in the cell walls.[5] On the other hand, Maxwell-Wagner type relaxation of moist wood has been recognized in the temperature range between −20°C and 80°C over the frequency range from 30 Hz to 5 MHz.[6] There have been few reported studies of this type of relaxation.[6,7]

Moist wood has an extremely high electrical conductivity due to the movements of ions in the cell walls. An electrode polarization at the interface between electrodes and a moist specimen is occasionally observed. Even if Maxwell-Wagner type relaxation due to the interfacial polarization in a heterogeneous structure, including portions with high conductivity in an insulator exists in moist wood, it is buried by the large dielectric loss due to the electrode polarization. Accordingly, to detect the relaxation, it is necessary to remove ions from the specimen and to reduce the dielectric loss due to the electrode polarization.

To investigate Maxwell-Wagner type relaxation, we measured the dielectric properties of the wood specimens extracted with a mixed solvent of ethanol and benzene to remove ions and impregnated with methyl methacrylate to reduce the electrode polarization. The results obtained provide important information to clarify the state of adsorbed water in the wood cell walls.

Materials and methods

Materials and chemical treatments

Hinoki (*Chamaecyparis obtusa*) heartwood cut in three directions [longitudinal (L), radial (R), tangential (T) with regard to the electric field] was used. The dimensions of specimens were 5 × 50 × 50 mm. Some of the specimens were extracted with a mixed solvent of ethanol and benzene (volume ratio 1:2) for 24 h using a Soxhlet extractor and then boiled in water for 3 h. The weight loss of specimens by the extraction was about 4%. Some of the absolutely dried extracted specimens were impregnated with a solution of methyl methacrylate (MMA) containing 1% α,α'-azobisisobutyronitrile as an initiator under reduced pressure, wrapped in aluminum foil, and polymerized for 2 h at 80°C. The untreated, extracted, and MMA-treated specimens were absolutely dried by heating at 60°C for 2 h under reduced pressure and then conditioned at 60%, 80%, 90%, and 97% relative humidity (RH). The moisture contents of the untreated specimens were 10.0%, 15.1%, 17.4%, and 25.3% at the respective RH values. Those of the extracted specimens were 10.4%, 15.1%, 17.4%, and 25.8%, respectively. Those of the specimens impregnated with MMA were 4.2%, 5.6%, 6.8%, and 9.5%, respectively, and the reduced moisture contents (moisture contents calculated based on the weight of specimens before MMA impregnation) were 11.0%, 14.7%, 17.8%, and 24.9%, respectively.

Measurement of dielectric properties

An impedance analyzer (Agilent 4294A Agilent) and an electrode (Agilent 16451B, effective diameter 38 mm) were used in dielectric measurements at 20°C in the frequency range from 40 Hz to 10 MHz. An LCR–meter (HP4284A, Hewlett–Packard), an electrode (SE–3O, Ando Electric, effective diameter 38 mm), and a bath (TO–2, Ando Electric) were used in dielectric measurements with a heating rate of less than 1°C/min in the temperature range from −150°C to 20°C and in the frequency range from 20 Hz to 1 MHz. The dielectric constant ε', loss ε'', and loss tangent $\tan\delta$ of specimens were calculated.

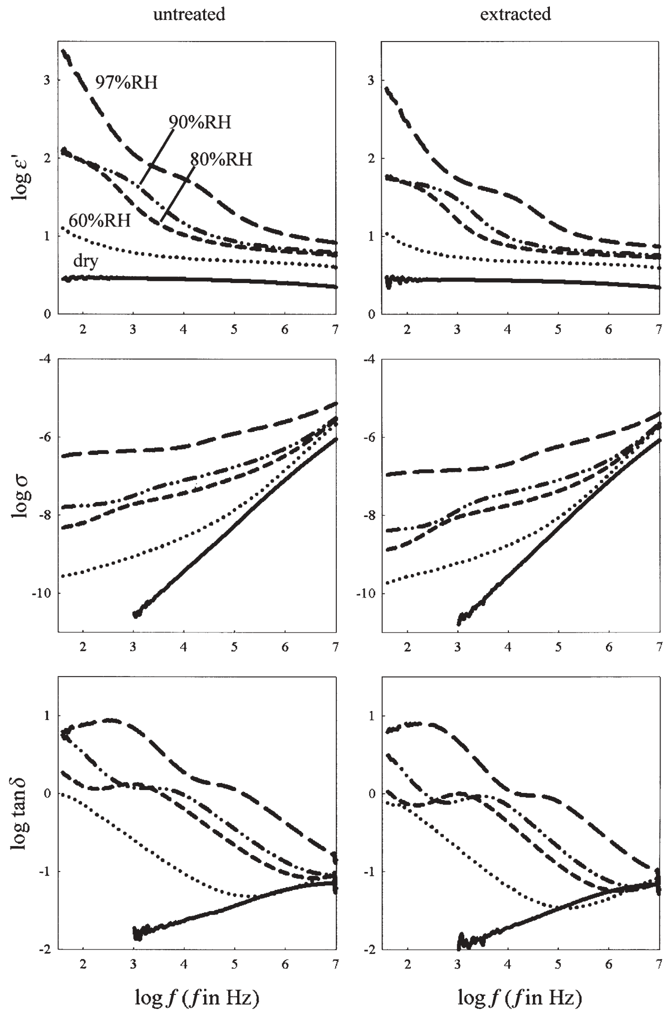

Fig. 1. The logarithm of dielectric constant ($\log\varepsilon'$), the logarithm of electric conductivity ($\log\sigma$), and the logarithm of loss tangent ($\log\tan\delta$) plotted against the logarithm of frequency ($\log f$) at 20°C in the longitudinal direction for the untreated (*left*) and extracted (*right*) hinoki wood specimens conditioned at the indicated relative humidity (*RH*)

Results and discussion

Figure 1 shows the relationship between the logarithm of the dielectric constant ($\log\varepsilon'$), the logarithm of electrical conductivity ($\log\sigma$), and that of the logarithm of loss tangent ($\log\tan\delta$) and the logarithm of frequency ($\log f$) in the longitudinal direction at 20°C for the untreated (left row) and extracted (right row) specimens conditioned at various levels of RH. The values of $\log\varepsilon'$ in the absolutely dried condition for the untreated specimens were very small and almost constant, while those in the moist condition increased with increasing RH. An inflection point suggesting a dielectric relaxation was detected in the specimens conditioned at RH above 80%. The inflection point moved to a higher frequency range with increasing RH. The values of $\log\varepsilon'$ for the untreated specimens conditioned at 97%. RH increased linearly with decreasing frequency below 1 kHz. No remarkable changes in $\log\varepsilon'$ vs $\log f$ curves above 1 kHz were recognized by the extraction of specimens. The values of $\log\sigma$ in the absolutely dried condition for the untreated specimens increased linearly with increasing $\log f$ and increased greatly with increasing RH. An inflection point was observed in $\log\sigma$ vs $\log f$ curves for the specimens conditioned at RH above 80%. Although the extraction induced no significant changes in the absolutely dried specimens, the values of $\log\sigma$ in the specimens conditioned at higher RH decreased in the low frequency range. On the other hand, the location of the inflection point remained unchanged. The values of $\log\tan\delta$ for both the untreated and extracted specimens were very small in the absolutely dried condition, but increased greatly with increasing RH. The values in the low frequency range were decreased by the extraction. A clear peak was detected in $\log\tan\delta$ vs $\log f$ curves for the specimens conditioned at both 80% and 90% RH. The peak's location was close to that of the inflection point in the curves of $\log\varepsilon'$ and $\log\sigma$ plotted against $\log f$. Two peaks were recognized in the specimen conditioned at 97% RH, and the peak value in the lower frequency side was extremely large.

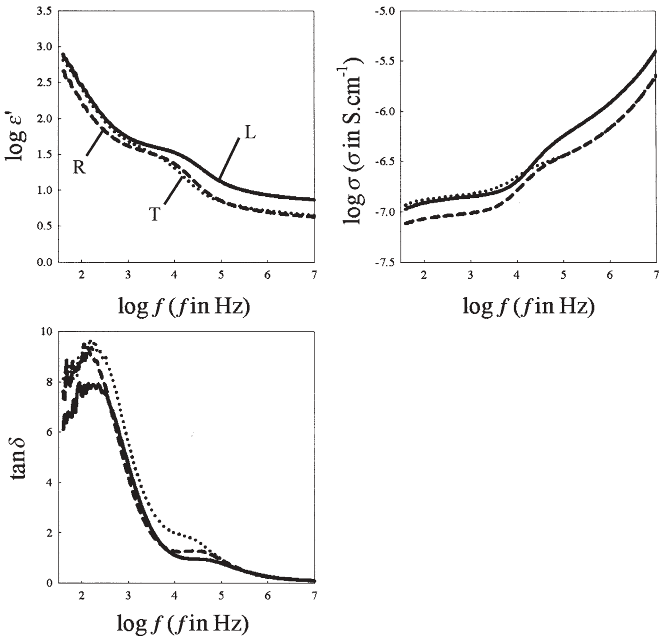

Fig. 2. The logarithm of dielectric constant ($\log \varepsilon'$), the logarithm of electric conductivity ($\log \sigma$), and the loss tangent ($\tan \delta$) plotted against the logarithm of frequency ($\log f$) at 20°C in the longitudinal (L), radial (R), and tangential (T) directions for the extracted hinoki wood specimens conditioned at 97% RH

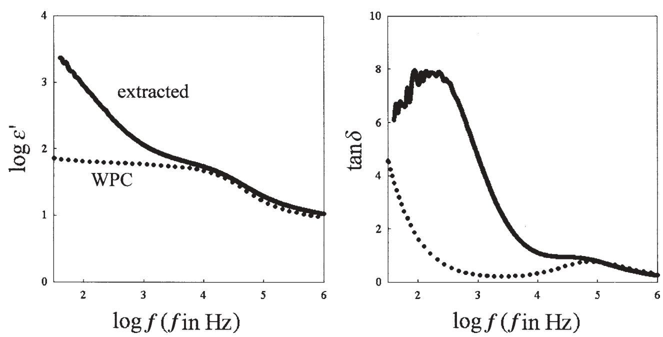

Fig. 3. The logarithm of dielectric constant ($\log \varepsilon'$) and the loss tangent ($\tan \delta$) plotted against the logarithm of frequency ($\log f$) at 20°C in the longitudinal direction for the extracted and methyl methacrylate-impregnated (*WPC*) hinoki wood specimens conditioned at 97% RH

Figure 2 shows the curves of $\log \varepsilon'$, $\log \sigma$, and $\tan \delta$ plotted against $\log f$ at 20°C in the longitudinal, radial, and tangential directions for the specimens conditioned at 97% RH. The values of $\log \varepsilon'$ were the largest in the longitudinal direction, while those in the radial and tangential directions were almost the same. The inflection points between 10kHz and 100kHz in the $\log \varepsilon'$ and $\log \sigma$ curves coincided in the three measuring directions. The locations of two peaks observed in the $\tan \delta$ curves coincided in the three directions. These results suggested that the relaxation in the high frequency side was related to the structure inside the cell walls.

Figure 3 shows the curves of $\log \varepsilon'$ and $\tan \delta$ plotted against $\log f$ at 20°C in the longitudinal direction for the extracted and MMA-impregnated specimens conditioned

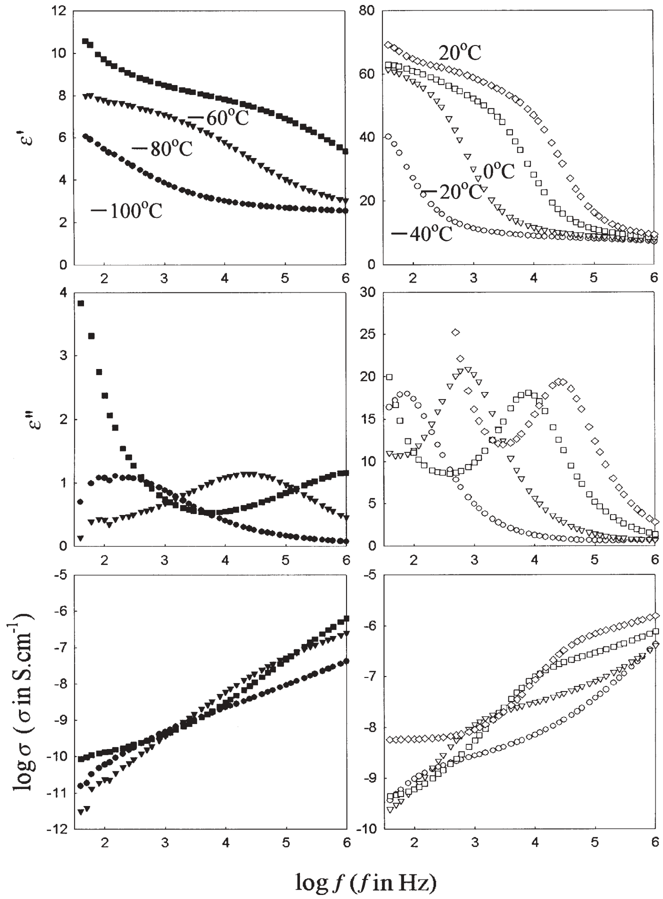

Fig. 4. The dielectric constant (ε'), the dielectric loss (ε''), and the logarithm of electrical conductivity ($\log \sigma$) plotted against the logarithm of frequency ($\log f$) at the indicated temperatures in the longitudinal direction for the methyl methacrylate-impregnated hinoki wood specimens conditioned at 97% RH

at 97% RH. The values of $\log \varepsilon'$ were decreased to almost a constant value below 10kHz by the MMA impregnation. However, no significant changes were recognized above 10kHz. The values of $\tan \delta$ were also decreased in the low frequency range, and a large peak observed in the extracted specimens disappeared. Our previous study[8] showed that the relaxation due to the motions of methylol groups in the cell walls remained unchanged by MMA impregnation. The moisture contents of the untreated specimens and the reduced moisture contents of the MMA-impregnated specimens were almost the same. The reduced moisture content means the moisture content calculated based on the weight of the specimen before the treatment. These results suggested that MMA was deposited selectively in the cell lumens. The electrical conductivity due to the movements of ions in the specimen appears to have been reduced considerably by the treatment. The large values of $\tan \delta$ in the low frequency side for the untreated specimen could be ascribed to electrode polarization. On the other hand, the $\tan \delta$ peak in the high frequency range for the extracted and MMA-impregnated specimens could be ascribed to relaxation inside the cell walls.

Figure 4 shows the curves of ε', ε'', and $\log \sigma$ plotted against $\log f$ in the longitudinal direction at various temperatures for the MMA-impregnated specimens conditioned at 97% RH. Two relaxations were observed in the temperature range between −100°C and 20°C. The three plots on the left of Fig. 4 show the results of the relaxation at low temperature. In our previous reports, we ascribed this relaxation to the motion of adsorbed water.[1–5] The three plots on the right of Fig. 4 show the results of the relaxation above −40°C. This relaxation is the same as that in the high frequency range in Fig. 3. This large relaxation appeared in the specimen conditioned at high RH.

There are two main relaxation mechanisms, which are due to dipole polarization and interfacial polarization. The Maxwell-Wagner theory predicts that a dielectric relaxation due to interfacial polarization occurs when a material consists of two parts with different sets of ε' and σ.[9] Micro-Brownian motions of chemical constituents of the cell walls may be considered as a mechanism of the relaxation in the high temperature range; however, according to this mechanism, it is difficult to explain the extremely high relaxation magnitude of about 50 shown in Fig. 4. On the other hand, it is well known that the relaxation due to the interfacial polarization generally shows a very large relaxation magnitude.[10] The adsorbed water molecules in the cell walls at high moisture contents appear to aggregate and form clusters. Electrical conductivity in the clusters of the adsorbed water is made possible by proton transfer through hydrogen bonds.[11] Therefore, we speculate that two phases consisting of the cell wall substance and the clusters of the adsorbed water molecules are formed in the cell walls. The cell wall substance has low values of ε' and σ, while the clusters of the adsorbed water have high ε' and σ values. Thus, Maxwell-Wagner's type relaxation can be expected to occur in the cell walls.

With respect to two relaxations observed in the MMA-impregnated specimens, the Cole-Cole circular arc law was applied to the sets of ε' and ε''. The law is expressed by the following equation:[12]

$$\varepsilon^* - \varepsilon_\infty = \left(\varepsilon_0 - \varepsilon_\infty\right) \cdot \frac{1}{1 + \left(i\omega\tau_m\right)^\beta},$$

where ε^* is the complex dielectric constant ($\varepsilon^* = \varepsilon' - i\varepsilon''$), ε_0 is the dielectric constant at the limiting low frequency, ε_∞ is the dielectric constant 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 value of ($\varepsilon_0 - \varepsilon_\infty$) is called the relaxation magnitude. This equation predicts that the values of ε'' give a circular arc when plotted against those of ε'. The values intersecting the abscissa are ε_0 and ε_∞, respectively.

Figure 5 shows the Cole-Cole plots for the relaxation due to the motions of the adsorbed water at −80°C and −100°C. The circular arc law applied well to the results. The values of ε_0, ε_∞, ($\varepsilon_0 - \varepsilon_\infty$), β, and $\log f_m$ are shown in Table 1. When the values of $\log f_m$ were plotted against the reciprocal of absolute temperature, a straight line was obtained. The value of apparent activation energy calculated from the slope of the straight line was 69.3 kJ/mol. The details of this relaxation have been described in our previous work.[2]

Table 1. Parameters calculated from Cole-Cole plots at various temperatures for relaxation due to adsorbed water and heterogeneous structure in methyl methacrylate-impregnated hinoki wood specimens conditioned at 97% RH

Temperature (°C)	ε_0	ε_∞	$\varepsilon_0 - \varepsilon_\infty$	β	$\log f_m$
Relaxation due to adsorbed water					
−100	7.6	2.6	5.0	0.5	2.24
−90	7.8	2.6	5.2	0.5	3.29
−80	7.9	2.5	5.4	0.5	4.32
−70	7.9	2.4	5.4	0.5	5.27
Relaxation due to heterogeneous structure					
−50	55.5	9.0	46.5	0.8	1.10
−40	56.5	9.8	46.7	0.8	1.83
−30	59.8	10.8	49.1	0.8	2.35
−20	61.8	10.3	51.5	0.8	2.85
−10	61.8	10.1	51.7	0.8	3.41
0	55.5	9.7	45.8	0.8	3.87
10	55.4	9.7	45.6	0.8	4.18
20	57.7	9.5	48.1	0.8	4.43

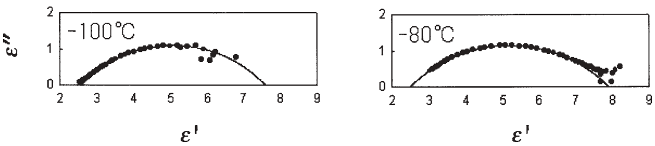

Fig. 5. Cole-Cole plots at −80°C and −100°C for relaxation due to motion of water adsorbed on methyl methacrylate-impregnated hinoki wood specimens conditioned at 97% RH

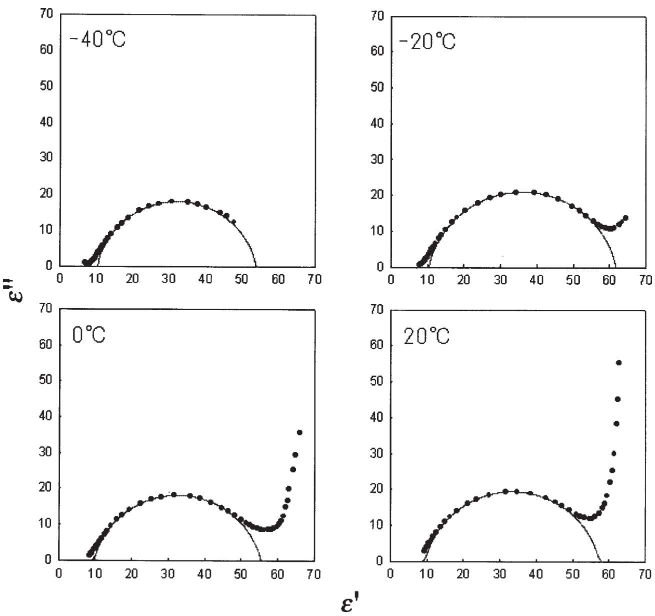

Fig. 6. Cole-Cole plots at −40°C, −20°C, 0°C, and 20°C for relaxation due to heterogeneous structure in methyl methacrylate-impregnated hinoki wood specimens conditioned at 97% RH

Figure 6 shows the Cole-Cole plots at −40°C, −20°C, 0°C, and 20°C. The circular arc law applied well to the results. The parameters obtained from the plots are shown in Table 1. The values of ($\varepsilon_0 - \varepsilon_\infty$) were very high values of about 46 to 52. The values of β were 0.8, showing a very narrow distribution of relaxation times. The heterogeneous structure of the cell walls in which the clusters of the adsorbed water were distributed in the cell wall substance suggests that this is Maxwell-Wagner type relaxation.

Conclusions

The dielectric constant, dielectric loss, and electric conductivity for untreated and extracted hinoki wood (*Chamaecyparis obtusa*) specimens conditioned at various levels of relative humidity were measured in the frequency range from 20 Hz to 10 MHz over the temperature range from $-150°C$ to $20°C$. The measurements were also conducted for specimens impregnated with methyl methacrylate (MMA). The results obtained are as follows:

1. The untreated specimens showed three relaxations. The relaxation in the highest frequency range was ascribed to the motions of the adsorbed water. The relaxation in the middle frequency range was not affected by extraction with a mixed solvent of ethanol and benzene. The location was independent of the measuring directions.
2. The MMA-impregnated specimens did not show relaxation in the lowest frequency range for the untreated specimen. This suggested that the relaxation was due to electrode polarization.
3. The Cole-Cole circular arc law applied well to the relaxations recognized in the MMA-impregnated specimens. The relaxation magnitude in the lower frequency side was about 50, and the distribution of relaxation times was very narrow. This relaxation was considered to be due to the heterogeneous structure consisting of the clusters of adsorbed water and the cell wall substance.

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