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## Mechanical properties of wood in an unstable state due to temperature changes, and analysis of the relevant mechanism VI: dielectric relaxation of quenched wood

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**Abstract** To analyze the effects of lignin on the destabilization of wood due to quenching, we examined the dielectric properties of untreated and delignified wood before and after quenching at 20°C from 50 Hz to 100 MHz. For untreated wood, the inflection points of  $\log \epsilon'$  and  $\log \sigma$  vs  $\log f$  and the peak of  $\log(\tan \delta)$  vs  $\log f$  were attributed to interfacial polarization before quenching, and the location of the inflection point shifted to a higher frequency with increasing moisture content because of changes in the water cluster. After quenching, the inflection points of  $\log \epsilon'$  and  $\log \sigma$  and the peak of  $\log(\tan \delta)$  shifted to higher frequency; however, the values of  $\log \epsilon'$ ,  $\log \sigma$  recovered to those before quenching with the passage of time. For delignified wood, dielectric relaxation was observed at a higher frequency than for untreated wood irrespective of quenching. It was inferred that the mobility of water molecules was influenced by the cluster surroundings because of increased number of adsorption sites in hemicellulose. Moreover, after quenching, the recovery process did not change greatly over time; it was shown that the matrix structure was affected more by quenching with the loss of lignin.

**Key words** Dielectric relaxation · Delignification · Quenching · Adsorbed water

### Introduction

In previous studies, we found that the amount of adsorbed water controls the destabilization of wood when moist wood is subjected to a sudden change in temperature or relative humidity. We speculated that the mobility of water molecules accompanied with the redistribution of energy is the main reason for the destabilization of wood.<sup>1–3</sup>

However, the mobility of water molecules is not only limited to their own rotation, but also is influenced by the effects of cell-wall substances such as bonding between the substances and clusters of water molecules.<sup>4</sup> Furthermore, among the chemical components of the cell-wall substance, lignin has to change from the rubbery state to the glassy state due to quenching. It is suggested that the mobility of water molecules would be changed with the structural change of lignin. Therefore, it is necessary to clarify the relationship between the wood substance and the clusters of adsorbed water.

As an effective method, dielectric measurement was used because it can provide useful data from hydrated material through interfacial polarization, dipole polarization, and so on. According to recent research,<sup>5–7</sup> three dielectric relaxations of moist wood were observed depending on frequency. These three relaxation types result from the reorientation of  $\text{CH}_2\text{OH}$  in the amorphous region, the Maxwell-Wagner effect, and the rotation of adsorbed water.

In this study, we focused on the Maxwell-Wagner type relaxation (interfacial polarization) recognized in the temperature range of  $-20^\circ$  to  $80^\circ\text{C}$  over the frequency range from 30 Hz to 5 MHz<sup>8</sup> for moist wood because it is associated with the relationship between cell-wall substance and the clusters of adsorbed water. To analyze the effect of chemical components on the destabilization of wood, especially lignin, we examined the dielectric properties of delignified wood before and after quenching at each MC level, and discussed the changes in interfacial polarization.

### Materials and methods

#### Materials

Wood samples [50 (T) × 50 (R) × 4 mm (L)] were cut from the heartwood of hinoki (*Chamaecyparis obtusa* Endl.). Extraction was carried out with ethanol–benzene (v/v = 1:2) for 8 h and then with ethanol for 8 h.

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## Delignification

Delignification was carried out according to Klauditz's method and treatment time was 6 h at 45°C. The selective and uniform removal of chemical components from wood blocks was verified in a previous report.<sup>9</sup> These samples were named "delignified wood."

After dielectric measurement, the weight loss (WL) of delignified wood was calculated on the basis of the oven-dried weight before and after delignification, and WL was in the range of 6%–9%. It can be considered that the degree of delignification does not influence the structure of hemicellulose and cellulose,<sup>10</sup> and the removed component is proportionate to the weight loss.

## Moisture adsorption measurement

For untreated wood, which was not treated by delignification, the samples were oven-dried at 103°C to a constant weight and then were equilibrated at relative humidities (RH) of 22.8% ( $\text{CH}_3\text{COOK}$ ), 42.6% ( $\text{K}_2\text{CO}_3 \cdot 2\text{H}_2\text{O}$ ), 75.4% ( $\text{NaCl}$ ), and 93.0% ( $\text{KNO}_3$ ) over saturated salt solutions in a desiccator and 65.0% (climatic chamber) at 20°C, respectively. For delignified wood, the samples were air-dried at 65% RH for 2 weeks, and then were equilibrated at 84% RH or 93.0% RH to avoid abnormal deformation of the cell wall. All samples were allowed to equilibrate for more than 3 weeks.

## Quenching treatment

After equilibration to RH, the dielectric properties of the sample were measured at each MC level (control sample). The same sample was then preheated at 80°C in a humidity-controlled chamber for 3 h, plastic bag, sealed in and cooled to 20°C by immersion in a water bath (quenched sample). After 3 min, the sample was removed from the water and the plastic bag, and the dielectric properties of quenched sample were measured.<sup>11</sup> The MC of the sample was measured, then the sample was placed back in a desiccator that had the corresponding RH to the MC of the

sample. After 30 min or 6 h, the same dielectric measurement was repeated and MC was measured again. The difference in MC between the measurements was small and can be disregarded.

## Measurement of dielectric properties

A dielectric meter (Hewlett-Packard, HP4284A) and plate electrodes (16451B) with a diameter of 38 mm were used to determine the dielectric constant  $\epsilon'$  and dielectric loss factor  $\epsilon''$  at 20°C. The frequency range was 50 Hz to 100 MHz. The measurement can be completed in seconds.

Recently, it was reported that the adsorption of water molecules, especially in the swelling of wood, was influenced slightly by temperature.<sup>12</sup> Thus, it is suggested that the distribution of water molecules in the sample after quenching for 3 min does not affect the dielectric polarization.

## Results and discussion

### Dielectric relaxation of untreated wood before and after quenching

The dielectric constant ( $\epsilon'$ ) and loss factor ( $\epsilon''$ ) of wood before quenching were measured over a wide range of MC (8%–24%) at 20°C. Figure 1 shows the frequency dependence of the logarithms of  $\epsilon'$  ( $\log \epsilon'$ ), electrical conductivity ( $\log \sigma$ ), and dielectric loss tangent [ $\log(\tan \delta)$ ] at each MC level. The value of  $\log \epsilon'$  for low MC was very small and changed slightly, while for MC over 13%, the values of  $\log \epsilon'$  increased and an inflection point was observed. The inflection point shifted to a higher frequency with increasing MC. These observations suggest that dielectric relaxation occurred. Moreover, in  $\log \sigma$  vs  $\log f$  curves and  $\log(\tan \delta)$  vs  $\log f$  curves, inflection points and peaks were observed and the locations did not change compared with  $\log \epsilon'$  vs  $\log f$  curves. These results accorded with a previous literature report.<sup>13</sup> Below 21% MC, this dielectric relaxation was attributed to Maxwell-Wagner relaxation; that is, interfacial polarization.<sup>8</sup> For MC over 21%, two clear peaks were

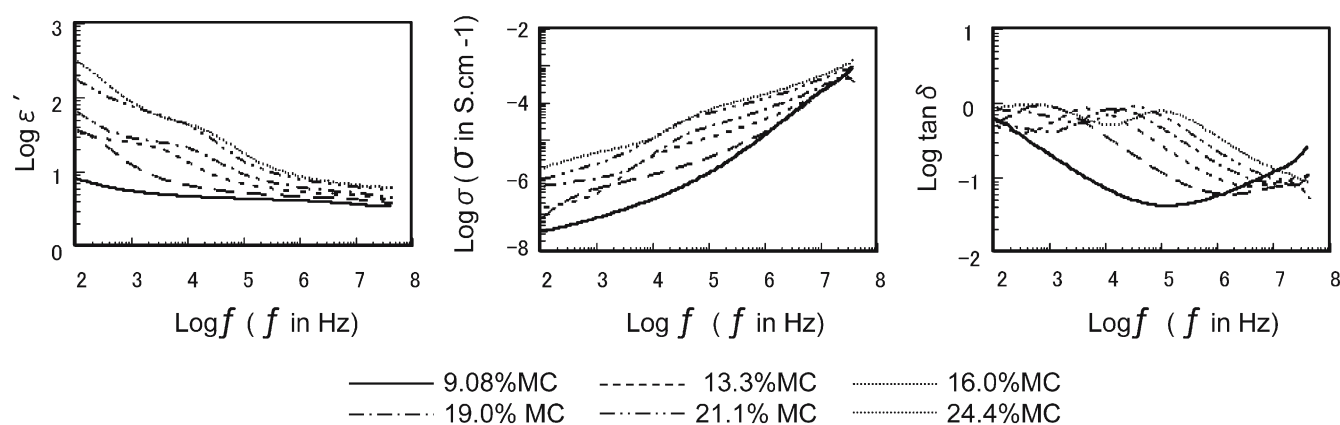
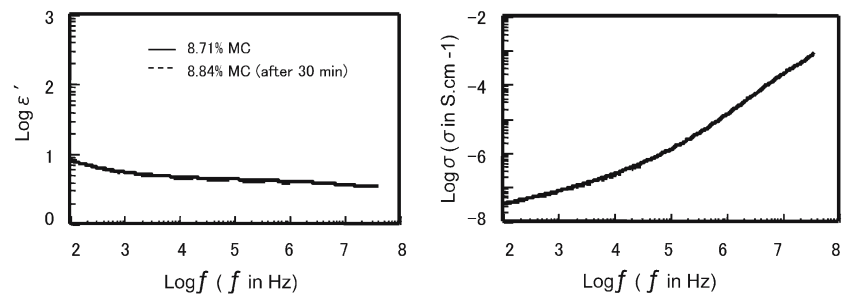
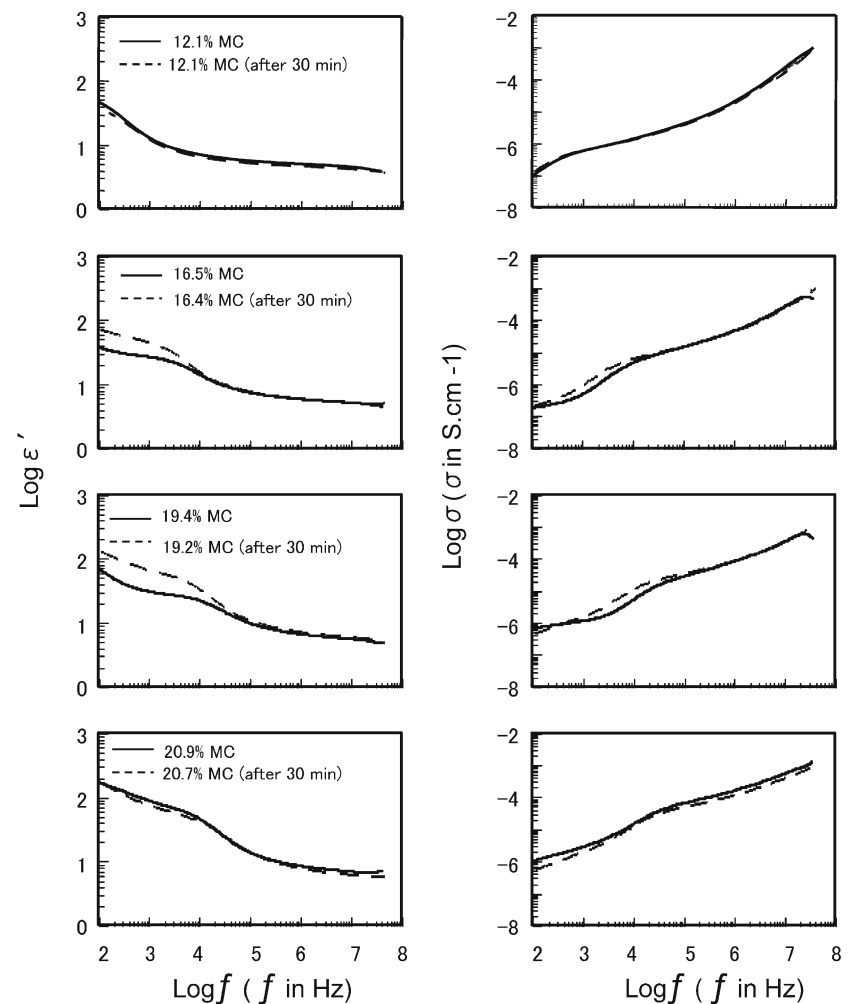


Fig. 1. Frequency dependence of  $\log \epsilon'$ ,  $\log \sigma$ , and  $\log(\tan \delta)$  for untreated wood before quenching

**Fig. 2.** Frequency dependence of  $\log \epsilon'$  and  $\log \sigma$  for untreated wood after quenching at low moisture content (MC)



**Fig. 3.** Frequency dependence of  $\log \epsilon'$  and  $\log \sigma$  for untreated wood after quenching



observed: one peak at low frequency was ascribed to electrode polarization;<sup>13</sup> the other at high frequency was ascribed to interfacial polarization.

Figure 2 shows the frequency dependence of  $\log \epsilon'$  and  $\log \sigma$  at 20°C for quenched wood at low MC. The values of  $\log \epsilon'$  and  $\log \sigma$  of quenched wood changed slightly and the values did not change over time. It was considered that the water molecules were adsorbed by a cellulose chain with strong bonding energy<sup>14</sup> so that the adsorbed water could not move with sudden changes in temperature; therefore, no relaxation phenomenon was recognized below 9% MC. However, with increasing MC, an inflection point was observed in each curve (Fig. 3). The values of  $\log \epsilon'$  and  $\log \sigma$

of quenched wood after 30 min became larger than those just after quenching, and the location of the inflection point shifted to a lower frequency. These results showed that the interfacial polarization of quenched wood varied with the relationship between water molecules and wood substance, and this relationship would change over time.

In order to compare changes in dielectric relaxation for control and quenched wood, the frequency ( $f_m$ ) at maximum  $\tan \delta$  for each MC is presented in Fig. 4, in which the MC dependence of  $\tan \delta$  is shown. The value of  $f_m$  for both control and quenched wood increased with increasing MC. This means that interfacial polarization became easy irrespective of quenching; however, at the same MC level, the

values of  $f_m$  for quenched wood were larger than those for control wood. Changes in the value of  $f_m$  show that interfacial polarization of quenched wood was easier than for control wood. Over time, the value of  $f_m$  tended to recover to the value of the control wood. This behavior was similar to stress relaxation of quenched wood,<sup>1</sup> and recovery to the control wood level needed more time. These behaviors show that changes in the relationship between the adsorbed water and cell-wall substance were temporary.

From the above results, the state of adsorbed water in wood and changes in cell-wall substance should be discussed separately. According to past research,<sup>15,16</sup> for the control wood, when water molecules are added to wood, a cluster of adsorbed water was formed by dimers, trimers, and other formations. Because the shape of the cluster is an important factor for dielectric relaxation,<sup>17</sup> as a result, the location of the inflection point and the peak of  $\log(\tan \delta)$  for control wood shifted to a higher frequency with increasing MC; that is, interfacial polarization became easy, which related closely with adsorbed water.<sup>13</sup> For quenched wood, although it is difficult to conclude that the changes of water cluster are due to temperature change, it can be considered that the adsorbed water state changed and the proton transfer of adsorbed water in the dielectric field would differ from the control wood.<sup>18</sup> As a result, even though the MC values before and after quenching were similar, the location of the

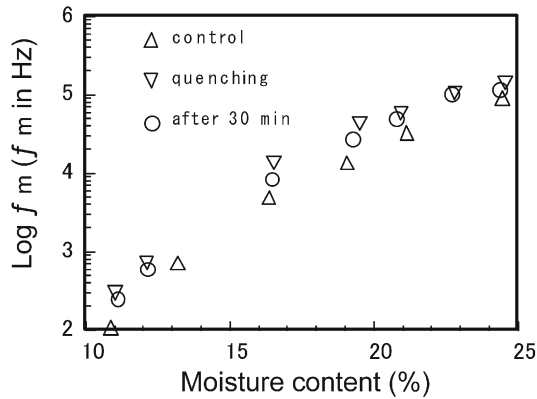
inflection point and the peak of  $\log(\tan \delta)$  for quenched wood shifted to a higher frequency.

On the other hand, when wood underwent sudden changes in temperature or relative humidity, the matrix microstructure in the vicinity of the adsorbed water could not reach the new stable state immediately and the mobility of adsorbed water in the wood changed.<sup>2,3</sup> This indicated that the cell-wall substance influences the relation to the water cluster and the incitement of interfacial polarization would differ from that of control wood. In previous reports,<sup>1,3</sup> it was found that the wood destabilization increased with increased temperature range and the destabilization also occurred above the glass transition temperature, which is closely related to softened lignin. At high temperature, lignin in the wood was softened, and when the wood was quenched, the softened lignin had to change to the glassy state to adapt to the low temperature, suggesting that the network structure of lignin changed greatly. Consequently, the structure of the substance was frozen and the adsorbed water state was changed to easily respond to the electric field in a larger space than in the control wood, causing a larger value of  $f_m$  for quenched wood.

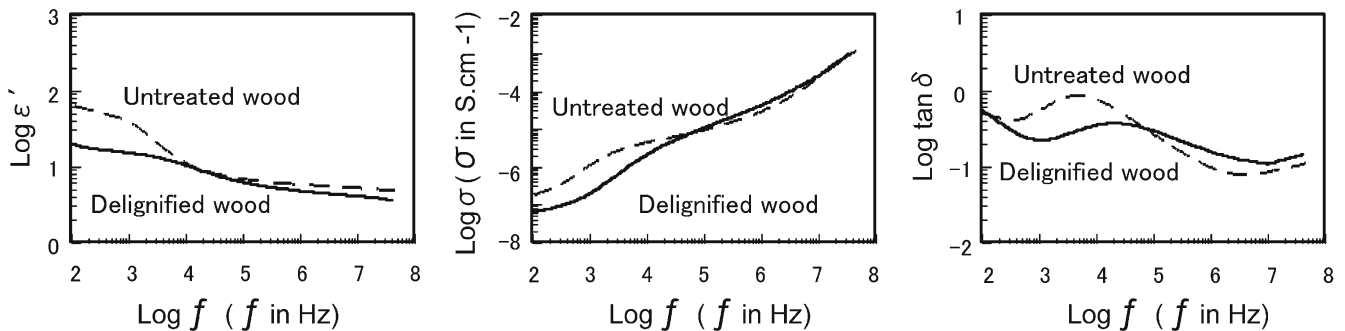
#### Dielectric relaxation of delignified wood before and after quenching

To define the effects of lignin on the control and quenched wood, the dielectric relaxation of delignified wood was measured at the same MC under control (before quenching) and quenching conditions. The frequency dependencies of  $\log \epsilon'$ ,  $\log \sigma$ , and  $\log(\tan \delta)$  at 16.3% MC and 20°C before quenching are shown in Fig. 5. The inflection points in  $\log \epsilon'$  and  $\log \sigma$  curves and the peak of  $\log(\tan \delta)$  for delignified wood are clear. Interfacial polarization can be recognized although the interface was changed by delignification. Furthermore, the location of inflection points and the peak shifted to a higher frequency. The value of  $f_m$  at maximum  $\log(\tan \delta)$  for delignified wood was similar to that of untreated wood with 19.1% MC. It was shown that the interfacial polarization of delignified wood became easier than in untreated wood.

Although more adsorption sites of hemicellulose were exposed with a decrease in lignin content, the cluster form

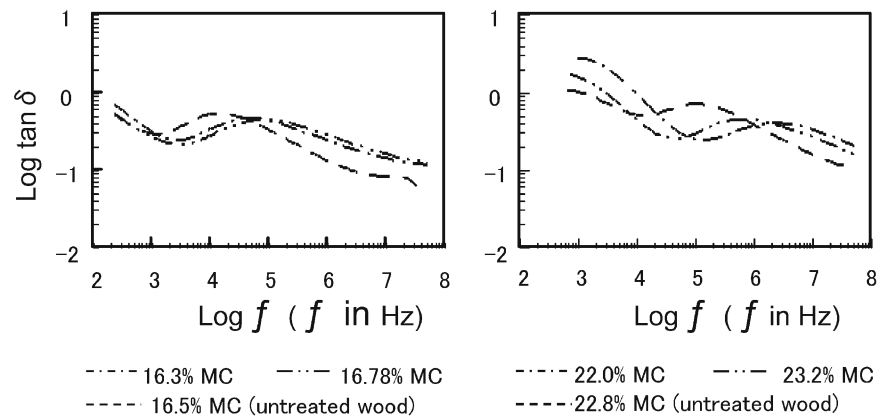


**Fig. 4.** Moisture content dependence of frequency at the maximum  $\tan \delta$  for untreated wood



**Fig. 5.** Frequency dependence of  $\log \epsilon'$ ,  $\log \sigma$ , and  $\log(\tan \delta)$  for delignified wood (16.0% MC) and untreated wood (16.3% MC) before quenching. The *solid lines* show the results for delignified wood before quenching

**Fig. 6.** Frequency dependence of  $\log(\tan \delta)$  for delignified wood after quenching



**Table 1.** Changes over time in frequency ( $f_m$ ) at maximum  $\tan \delta$  for delignified wood

Sample	MC (%)	$f_m$ (Hz)		
		Quenching	After 30 min	After 6 h
1	16.30	$7.61 \times 10^4$	$7.61 \times 10^4$	$8.81 \times 10^4$
	23.40	$1.65 \times 10^6$	$1.65 \times 10^6$	$1.43 \times 10^6$
2	15.10	$2.03 \times 10^4$	$2.03 \times 10^4$	$3.66 \times 10^4$
	23.20	$6.86 \times 10^5$	$6.86 \times 10^5$	$5.93 \times 10^5$
3	15.30	$1.52 \times 10^4$	$1.52 \times 10^4$	$2.36 \times 10^4$
	20.20	$2.46 \times 10^5$	$2.46 \times 10^5$	$2.12 \times 10^5$

MC, Moisture content

would differ from the untreated wood, and it was thought that the influence of loose substance structure was more important. This would allow the water molecules to easily respond to the electric field.

The dielectric relaxation of delignified wood after quenching was then measured. Figure 6 shows the frequency dependence of  $\log(\tan \delta)$  at about 16% and 22% MC at 20°C just after quenching. For comparison with delignified wood,  $\log(\tan \delta)$  for untreated wood after quenching is shown by broken lines. The peak of  $\log(\tan \delta)$  curves for delignified wood shifted to a higher frequency. This result proved that the changes of cell-wall substance and the state of adsorbed water greatly influence the interfacial polarization. At a higher MC, the shift of the peak was clearer.

However, changes in the relaxation of delignified wood were not clear with the passage of time. Table 1 shows the values of  $f_m$  for delignified wood after quenching. After 30 min, the values of  $f_m$  did not differ from those just after quenching. After 6 h, the values of  $f_m$  increased or decreased slightly. This result shows that the mobility of water molecules was not only influenced by the surroundings of the cluster because recovery to the control condition (before quenching) was very slow. This suggests that after quenching, the loose matrix structure had difficulty recovering because the frame of the cell wall was weakened after the loss of lignin. Consequently, interfacial polarization did not change. As a result, after quenching, the dielectric relaxation of delignified wood did not change greatly with time. Conversely, for untreated wood, lignin plays an important role

in the recovery of substance structure, and cluster mobility was also influenced.

## Conclusions

For untreated wood, dielectric relaxation was influenced by moisture content. As a result, interfacial polarization was observed at a higher frequency with increasing MC, relating with the water cluster. After quenching, the water molecules easily respond to electric field. For delignified wood, the location of the inflection point shifts to a higher frequency. This means that the mobility of water molecules increased under the loose structure and interfacial polarization occurred easily irrespective of quenching. Moreover, after quenching, the dielectric relaxation of delignified wood did not change over time. After delignification, the loose matrix structure was difficult to recover over time. These results show that wood destabilization was greatly influenced by the state of adsorbed water and changes of matrix structure.

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