

The Effect of Moisture on the Dielectric Relaxations in Wood

TAKASHI HANDA, MASAYOSHI FUKUOKA, SHUJI YOSHIKAWA, and TETSUO KANAMOTO, *Department of Applied Chemistry, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo 162, Japan*

Synopsis

The dielectric constant ϵ' and the loss factor ϵ'' of moistened wood were measured over a wide range of moisture content (MC), 0–40 wt %, in the temperature range -196 to 0°C , and in the frequency range 30 Hz to 1 MHz. Three relaxations were observed depending on the MC and frequency. The first ϵ'' peak at -103°C (30 Hz) in oven-dried wood is known to be due to the methylol rotation in the amorphous regions. A new ϵ'' peak (second peak), which appeared for $\text{MC} > 0.6$ wt % at -110 to -40°C (30 Hz) depending on the MC, is assigned to the local mode motions of the complexes between moisture and polar groups in the wood system; it is enhanced as the overall loosening of the initial hydrogen bond network is promoted by the extended hydration due to further sorption of moisture. The peak temperatures and the activation energies for these relaxations changed complexly depending on the MC. At $\text{MC} > 10$ wt %, a novel ϵ'' peak (third peak) was disclosed around -40°C (30 Hz) as a shoulder of the ionic conduction. This novel peak may be attributed to the water frozen in wood on the basis of the peak temperature, relaxation strength vs. MC, the activation energy, and the fact that the peak is not observed for the sorption of various polar organic solvents. This suggests that some of the moisture sorbed by wood may probably exist in a frozen state at low temperatures, even at a MC well below the commonly accepted fiber saturation point.

INTRODUCTION

Wood is a semicrystalline polymer composite consisting mainly of cellulose, hemicellulose, and lignin with a ratio of 2:1:1 on average.¹ The properties of dry and moistened wood have been often discussed with reference to specific compositions^{2,3} and complex morphology.^{4,5} It is generally accepted that moisture is sorbed preferentially by the amorphous phase of wood and does not go into the crystalline phase.⁶ On moistening, wood exhibits marked dimensional elongation particularly along the tangential direction, with a ratio along tangential, radial, and longitudinal directions of 10:5:1 approximately.⁷

A large number of studies have been made on the dielectric properties of the moistened wood, and various results and explanations for the relaxation mechanisms have been presented.^{8–10} Those studies, however, were limited primarily to a relatively higher temperature range, from -60 to 20°C , and in a relatively narrow MC range below the fiber saturation point ($\text{MC} = 25\text{--}35$ wt %).¹¹

In this article, the dielectric constant ϵ' and the loss factor ϵ'' of moistened wood were measured along the radial and the longitudinal directions over a wide MC range, 0–40 wt %, in the temperature range -196 to 0°C , and in the frequency range 30 Hz to 1 MHz. Under the present experimental conditions, three dielectric relaxations were observed depending on the wood MC and temperature. These relaxations were remarkably affected by the amount of sorbed moisture. The origin of the multiple relaxations in moistened wood are discussed on the

basis of the dielectric properties of wood sample sorbed moisture and various polar organic solvents. The dynamic viscoelasticity (E' , E'') of moistened wood provided supplementary information on the origins of the relaxations at the molecular level.

EXPERIMENTAL

Materials

The base materials (34 mm \times 34 mm) for the radial (R) direction were from the rotary-cut beech veneers with a thickness of 0.65 mm and those for the longitudinal (L) direction were cut out from beech with a saw to a thickness of 1.0 mm. All samples were dried in vacuo at 80°C for 30 h.

The MC of the specimens was controlled in desiccators over two weeks at room temperature under different standardized relative humidity using aqueous solution of several inorganic salts. The MC of the samples was kept almost constant during measurements at lower temperatures, but a small change in MC sometimes occurred at temperatures near 0°C for samples with an extremely low or high MC. Therefore, only data obtained with samples that exhibited an MC change less than 0.2 wt % were adopted. An average MC value before and after the measurements was used in specifying the MC of a sample.

Sorption of organic solvents such as methanol, acetone, pyridine, and diethylamine was carried out by exposing wood samples to various vapor pressures at room temperature.

The MC and moisture fraction (MF) were defined as grams of sorbed moisture per 1 gram of dried wood and grams of sorbed moisture per 1 gram of moistened wood, respectively.

Measurements

The dielectric constant ϵ' and the loss factor ϵ'' along the L and R directions of the wood were measured by a transformer bridge-type TRS-10C (Ando Electric Co., Ltd.) in the temperature range -196 to 0°C and in the frequency range 30 Hz to 1 MHz. The dynamic storage modulus E' and the loss modulus E'' of the specimens were measured by a Vibron DDV-II (Toyo Measuring Instruments Co., Ltd.) in the temperature range -196 to 0°C and at a frequency of 110 Hz.

RESULTS AND DISCUSSION

General Behavior

The dielectric constant ϵ' and the loss factor ϵ'' of oven-dried wood specimens were measured along the L and R directions over the MC range 0 to 40 wt % (above the fiber saturation point), the frequency range 30 Hz to 1 MHz, and the temperature range -196 to 0°C . The ϵ' and ϵ'' along the L and R directions are expressed by ϵ'_L , ϵ''_L , ϵ'_R , and ϵ''_R , respectively, hereafter. Figure 1 shows the variation of ϵ'_L and ϵ''_L with frequency and temperature for the oven-dried wood. The ϵ' value increased with elevation of the measurement temperature in the

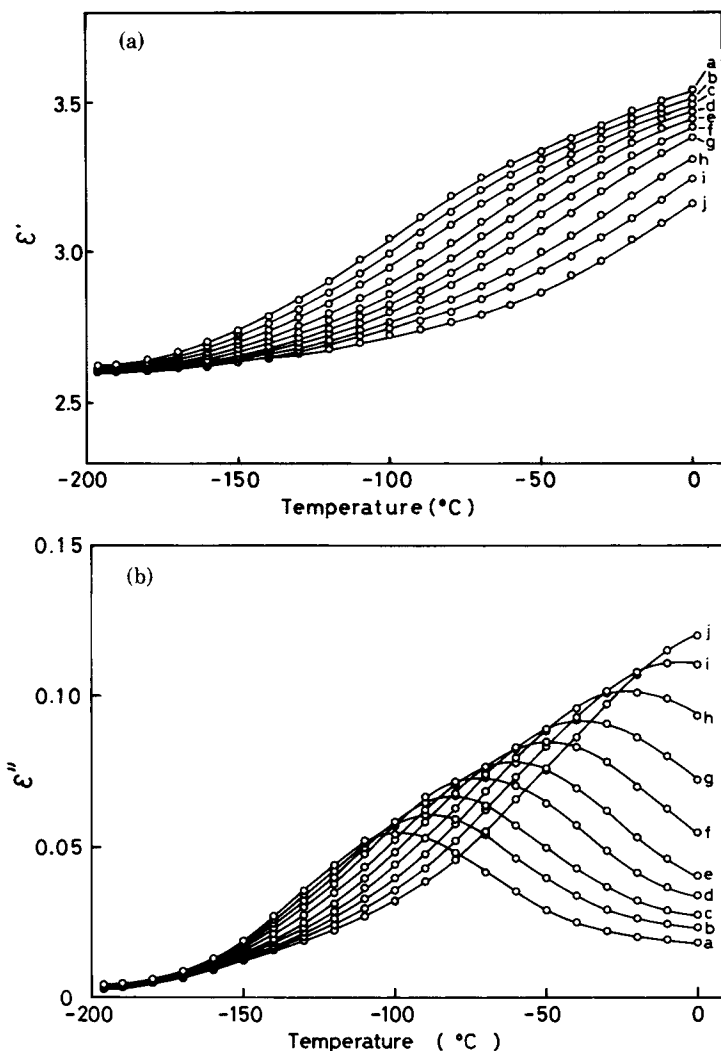


Fig. 1. Dielectric constant ϵ' (a) and loss factor ϵ'' (b) of oven-dried wood (*L* direction) as function of temperature: a, 30 Hz; b, 110 Hz; c, 300 Hz; d, 1 kHz; e, 3 kHz; f, 10 kHz; g, 30 kHz; h, 100 kHz; i, 300 kHz; j, MHz.

range -196 to 0°C and also with lowering the measurement frequency. In the temperature dependence of ϵ'_L in Figure 1(b), a ϵ'' peak at 30 Hz was found at -103°C . This loss peak has been assigned to the rotational motion of methylol groups ($-\text{CH}_2\text{OH}$) in wood systems by Mikhailov et al.¹² and Norimoto et al.¹³

In our recent studies of the wood components isolated from wood systems, this loss peak was observed in filter paper and mannan both having methylol groups, but not in xylan having no methylol groups in chemical repeat unit, confirming the previous assignment of this peak to the methylol rotation. The peak shifted to higher temperatures corresponding to the increase in measurement frequency. The apparent activation energy (ΔE) for the rotational motion of the methylol groups was estimated to be 9.3 kcal/mol from the frequency dependence of the peak temperature, in agreement with the reported value.^{12,13}

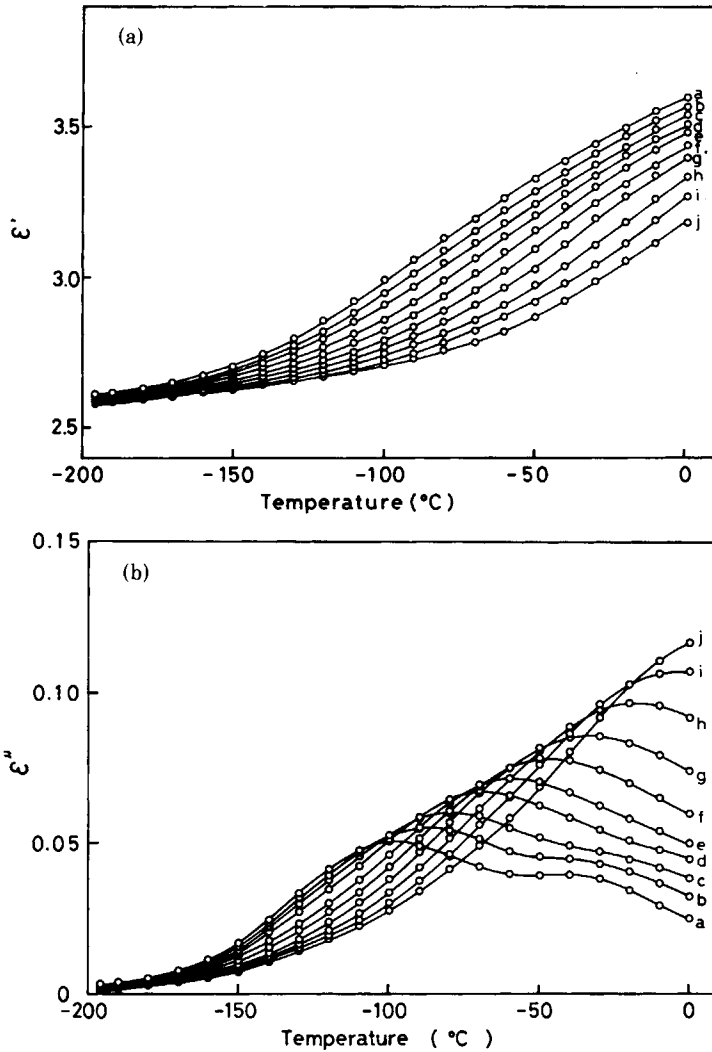


Fig. 2. Temperature dependence of ϵ' (a) and ϵ'' (b) measured at various frequencies for slightly moistened wood (L direction) with MC 0.6 wt %: a, 30 Hz; b, 110 Hz; c, 300 Hz; d, 1 kHz; e, 3 kHz; f, 10 kHz; g, 30 kHz; h, 100 kHz; i, 300 kHz; j, 1 MHz.

Figure 2 shows the temperature dependence of ϵ'_L and ϵ''_L for moistened wood with a MC of 0.6 wt %. The value of ϵ' for this sample stayed always higher than that for the oven-dried wood throughout the covered ranges of frequency and temperature. Besides the ϵ''_L peak at -103°C (30 Hz) due to the rotation of the methylol groups (first peak), another peak appeared at around -40°C (second peak), which was more clearly seen at lower frequencies [Fig. 2(b)]. This new peak, induced by a small amount of moisture, showed a relaxation strength lower than that of the first peak and had a significantly high ΔE of 25 kcal/mol. As will be discussed later (Fig. 14), the dynamic mechanical data on a sample with MC < 1 wt % also exhibited a loss peak at around -50°C as well as an E'' peak at -125°C , the latter being assigned to the same origin as the first dielectric loss at -103°C (30 Hz).¹⁴

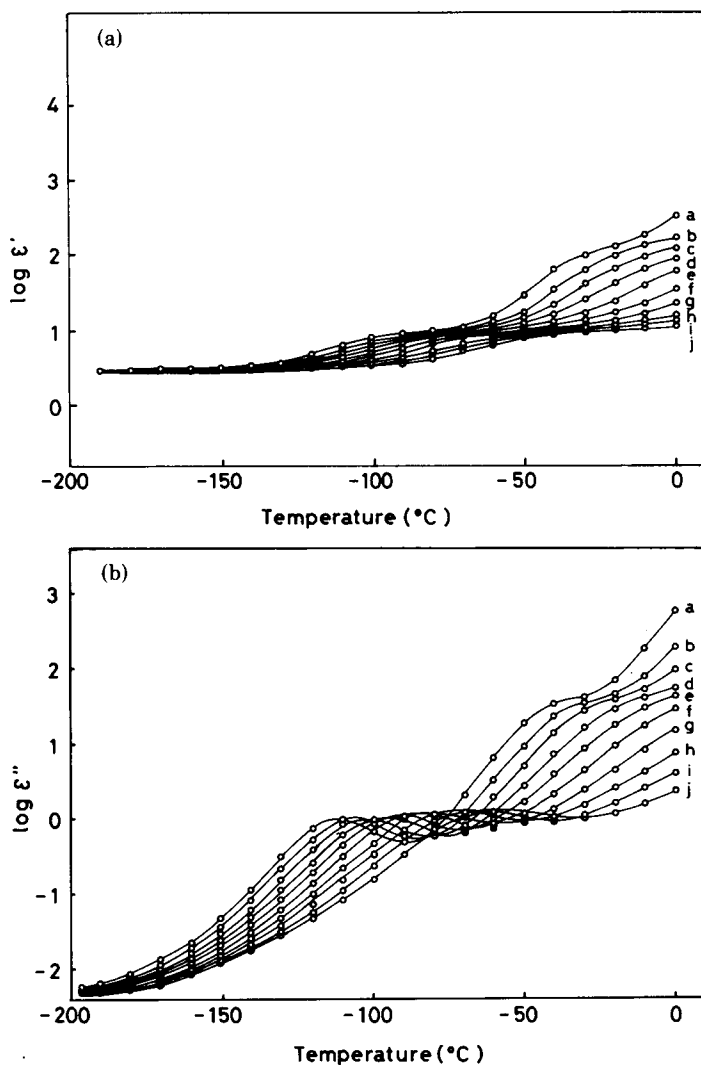


Fig. 3. Temperature dependence of ϵ'_L (a) and ϵ''_L (b) at various frequencies for highly moistened wood (L direction) with MC 16.1 wt %: a, 30 Hz; b, 110 Hz; c, 300 Hz; d, 1 kHz; e, 3 kHz; f, 10 kHz; g, 30 kHz; h, 100 kHz; i, 300 kHz; j, 1 MHz.

Figure 3 shows the temperature dependence of ϵ'_L and ϵ''_L for the moistened wood with a relatively higher MC of 16 wt %. The ϵ'_L and ϵ''_L of the system were extremely enhanced by moistening in the temperature range -70 to 0°C and these values were plotted on logarithmic scales. The ϵ'_L and ϵ''_L vs. temperature curves in Figure 3 exhibited patterns quite different from those at lower MC (Fig. 2) independent of the difference due to their scales. For the sample with a high MC, the intensity of the ϵ''_L peak at -113°C (30 Hz) which was formed by merging of the first and the second peaks increased markedly, and a novel loss peak (third peak) was induced at -40°C (30 Hz) as a low-temperature shoulder superimposed on a dc ionic conduction. This novel peak has a molecular origin obviously different from that of the second peak at -40°C (30 Hz) observed for the lower MC around 1 wt % (Fig. 2), as is discussed later.

To summarize the variation of the dielectric loss with MC, the ϵ'' values measured at 30 Hz along the L and R directions are plotted as a function of temperature in Figures 4(a) and 4(b), respectively. No significant anisotropy in the effect of moistening was noted for the L and R directions. Both figures exhibit apparently four ϵ'' peaks which, at 30 Hz, rise at -103°C (the first peak, observed for dry and slightly moistened wood with $\text{MC} < 1.7$ wt %), -40°C (the second peak, for $\text{MC} 0.6$ – 1.7 wt %), -70 to -113°C (the fourth peak, occurred by merging of the first and the second peaks for $\text{MC} > 2.3$ wt %), and -40°C (the third peak, for highly moistened wood for $\text{MC} > 8$ wt %). With increasing MC, the first loss peak at -103°C (30 Hz) for dry wood moved to higher temperatures, while the second peak at -40°C (30 Hz) for slightly moistened wood shifted to lower temperatures. As a result, these two peaks merged to form apparently the fourth peak at -70°C (30 Hz) at $\text{MC} 2.3$ wt %. With increasing MC, the merged peak (fourth peak) gradually shifted to lower temperatures and reached a limiting temperature of -113°C at $\text{MC} > 10$ wt %. The apparent activation energy for this peak also showed a change similar to that in the peak temperature with respect to the effect of MC. This is discussed further in the next section on the basis of the decomposition of the fourth peak into the first and the second peaks.

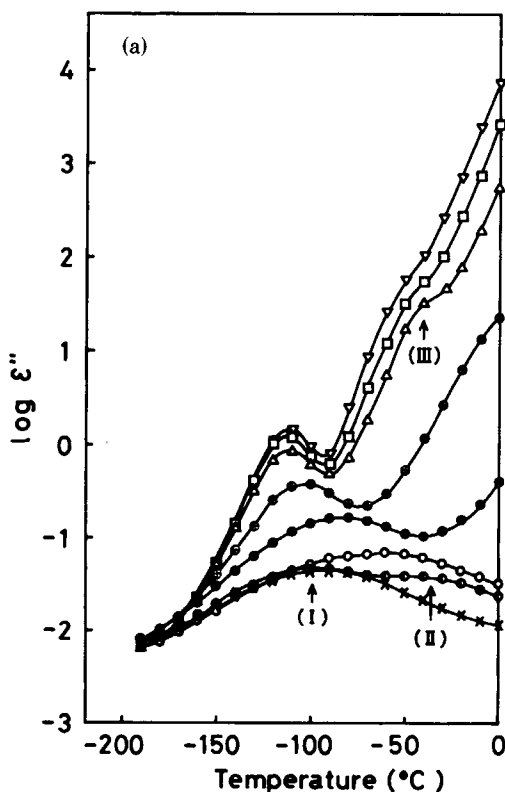


Fig. 4. Temperature dependence of $\log \epsilon''$ at 30 Hz for wood measured along L direction (a) and R direction (b) containing various amounts of moisture. (a) (X) Oven-dried; (●) 0.6 wt %; (○) 1.7 wt %; (●) 4.5 wt %; (⊕) 10.5 wt %; (Δ) 16.1 wt %; (□) 19.0 wt %; (▽) 23.0 wt %. (b) (X) Oven-dried; (●) 0.7 wt %; (○) 4.2 wt %; (●) 8.7 wt %; (⊕) 13.5 wt %; (Δ) 18.5 wt %; (□) 24.7 wt %.

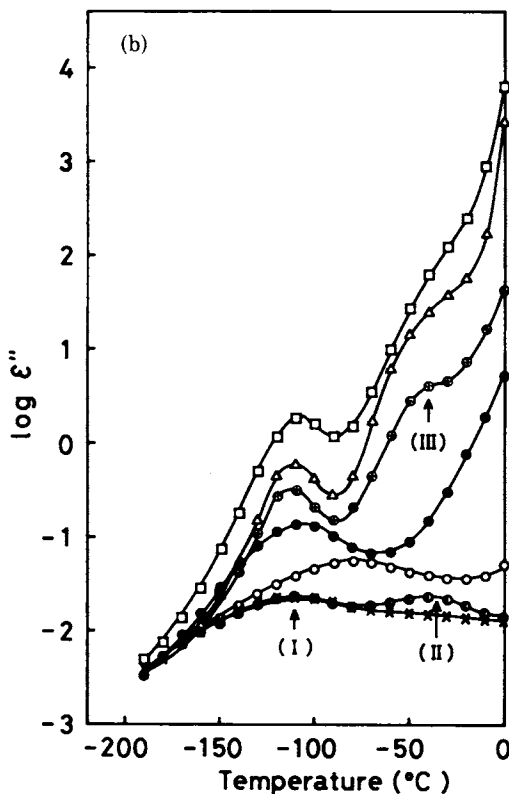


Fig. 4. (Continued from previous page.)

Second Peak

Christenzen et al.¹⁵ studied the contribution and role of each component of wood to the moisture sorption by wood. Norimoto et al.¹⁶ reported that the ϵ'' peak around -40°C (30 Hz) was also observed in moistened lignin with MC < 1 wt %. In this respect, it is important to study whether the ϵ'' peak at -40°C (30 Hz) comes intrinsically from the moistened lignin or whether it includes the contribution from the moistened cellulosic system. To clarify this point, we have studied the dielectric behavior of moistened cellulose using filter paper.

Figure 5 shows the dielectric loss ϵ'' for filter papers with various MC values measured as a function of temperature at 30 Hz. At a MC of 0.7 wt %, a second peak appeared at -40°C as a feasible shoulder on the high-temperature side of the main peak at -110°C which is due to the rotational motion of the methylol groups (first peak). The filter paper as well as the wood samples showed a Gaussian-type dispersion in the ϵ'' -vs.- $1/T$ diagram, except at the higher temperature skirt. When the ϵ'' -vs.- $1/T$ curve indicated an overlapping of multiple relaxations, each ϵ'' peak was isolated by initially subtracting the dc ionic conduction¹⁷ and then decomposing the curve on a computer assuming Gaussian-type dispersions and constant half-widths characteristic for the first and the third peaks, utilizing the least-squares error method in the fitting.

Figure 6 compares the decomposed peaks of the filter paper and wood for dry [Fig. 6(a)] and slightly moistened [Fig. 6(b)] samples. The first loss peak in the dry filter paper appeared at a significantly higher temperature (-90°C) and had

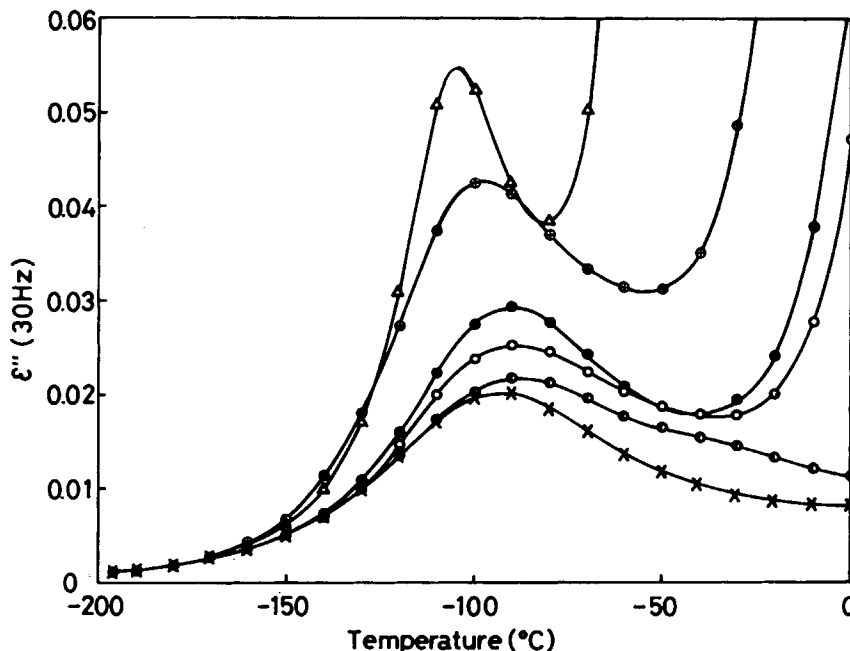


Fig. 5. Temperature dependence of ϵ'' at 30 Hz for filter paper containing various amounts of moisture: (X) oven-dried; (●) 0.7 wt %; (○) 1.6 wt %; (●) 2.1 wt %; (⊕) 2.9 wt %; (Δ) 5.4 wt %.

a narrower half-width (3.5×10^{-4}) than those (-103°C and 2.2×10^{-3}) of the dry wood. This indicates that the mobility of the methylol groups is less restricted in the wood system than in a pure cellulosic system and also that the relaxation in wood includes the contributions from various components.

The second peak at -40°C (30 Hz) induced by sorption of a very small amount of moisture is clearly isolated in Figure 4(b). At lower MC, this peak was revealed more clearly in the moistened wood than in the filter paper, probably because of the greater amorphous content in wood than in filter paper and/or an extra contribution from the moistened lignin for the wood specimens.

The effect of MC on the dielectric properties was more remarkable for the filter paper than for wood. The peak temperatures at 30 Hz and apparent activation energies for the first and second dielectric losses in both filter paper and wood samples were determined based on the decomposed peaks and plotted against MC in Figures 7 and 8, respectively. No appreciable dielectric anisotropy was observed for the *L* and *R* directions of wood. At low MC, the marked difference between filter paper and wood samples is seen in the peak temperature-vs.-MC curves for both peaks (Fig. 7). With increasing MC, the first peak commonly increased gradually until it reached a maximum temperature of -80°C at MC 2 wt % for the filter paper and -95°C at MC 5 wt % for wood, and then slightly decreased again in both materials.

In contrast, the second peak decreased rapidly, approaching to limiting temperature of -110°C . As a result, the first and the second peaks merged at a characteristics MC which varied depending on the materials (MC \approx 2 wt % for filter paper and MC \approx 8 wt % for wood). The crystallinity index (*CI*) of the samples was measured by wide-angle x-ray diffraction according to the method

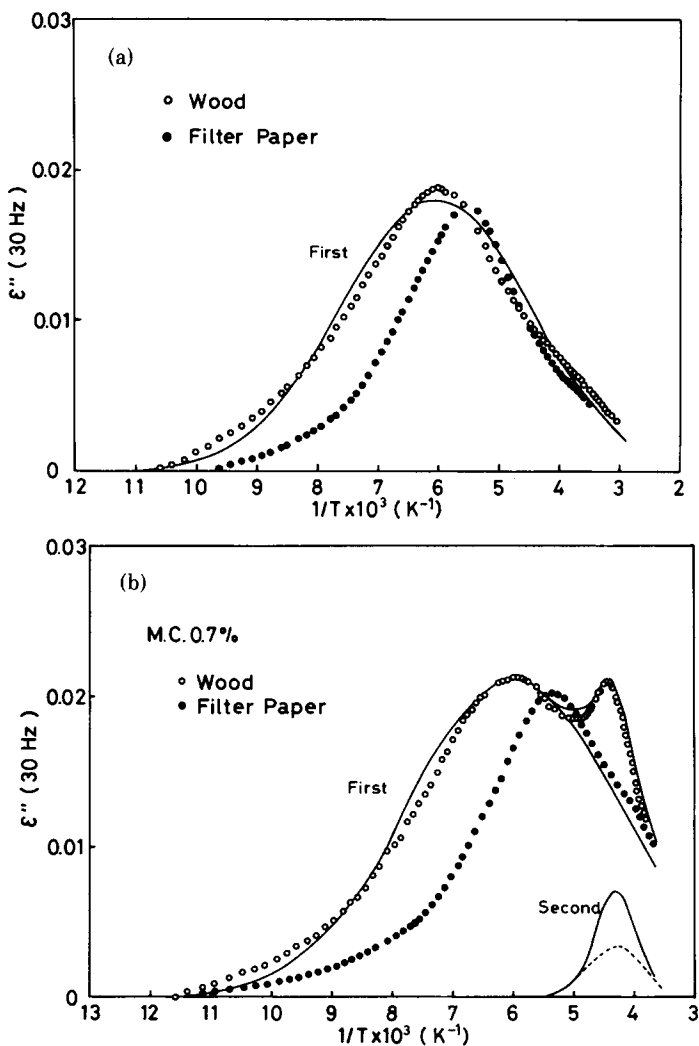


Fig. 6. Comparison of ϵ'' plotted as function of $1/T$ for wood and filter paper, at MC = 0 (a) and MC = 0.7 wt % (b): (—) computer simulation in wood; (-----) computer simulation in filter paper.

proposed by Segal et al.¹⁸ and found to be 45 and 80% for the wood and filter paper, respectively.¹⁹ The ratio of the moisture sorbed by the wood to that by the filter paper at each critical MC is about 4 and is fairly larger than 2.7, the ratio of the amorphous contents of the wood to filter paper.

Furthermore, the apparent activation energy ΔE for the second peak of the wood is notably higher than that of the filter paper. These facts indicate that not only the amorphous content but also the composition of the samples play an important role in the moisture sorption and its effect on the dielectric properties. The effect of moistening on the apparent activation energy for the first and the second loss peaks (Fig. 8) is very similar to that observed on the peak temperature (Fig. 7). These facts indicate that the mobility of the methylol rotation (first peak) is suppressed as a result of the moisture sorption in the lower

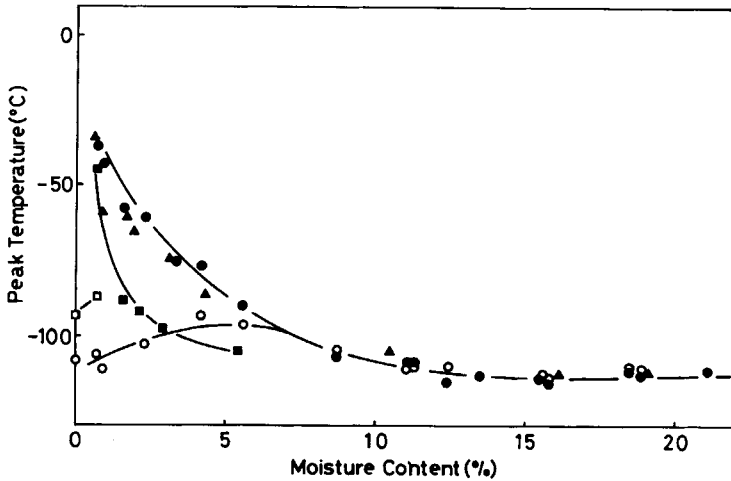


Fig. 7. Changes of ϵ'' peak temperatures at 30 Hz with MC for wood and filter paper: (○) first and (●) second peaks for *R* direction wood; (▲) second peak for *L* direction wood; (□) first and (■) second peaks for filter paper.

range of MC < 5 wt % but increases again approaching a limiting high mobility at higher MC. In contrast, the constraint imposed on the molecular motion responsible for the second peak rapidly decreases with moistening in the MC lower range again reaching a limiting low magnitude of the restriction at higher MC. On the basis of these facts, it is assumed that the second peak in moistened wood may be related to the molecular motion of moisture itself¹⁶ or the local mode motions of the complexes formed by the hydrogen bondings between moisture and the total components of wood system including lignin and cellulosic systems.

To pursue the nature of the second peak, the relaxation strength was estimated

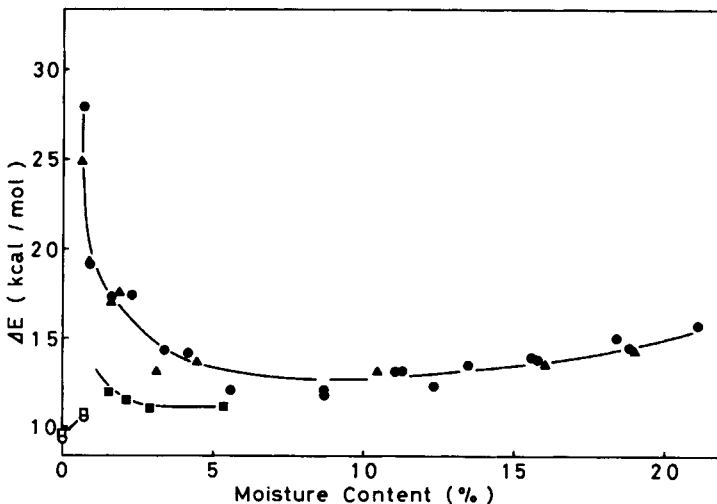


Fig. 8. Apparent activation energy (ΔE) vs. MC for wood and filter paper: (○) first and (●) second peaks for *R* direction wood; (▲) second peak for *L* direction wood; (□) first and (■) second peaks for filter paper.

from the ϵ'' -vs.- $1/T$ curves, which were also obtained by decomposing the observed curves on a computer, and is plotted as a function of MC in Figure 9. The relaxation strength increased only slightly at MC < 5 wt % and rapidly at MC 5–20 wt %, where the dimension of wood also increased rapidly along the tangential direction due to swelling. At MC 20 wt %, where the dimension reached a limiting length, the relaxation strength also approached a limiting magnitude. It is noted that there are significant correlations with respect to the effects of MC on the relaxation strength, the apparent activation energy, and the loss peak temperature in wood, and all these quantities are greatly changed at the critical MC of 5 and 20 wt %, where the transitions occurred in the dimensional change of wood.²⁰

As shown in Figure 10, the temperature dependence of the dynamic loss modulus E'' at 110 Hz for moistened wood exhibited two loss peaks at around -125 and -50°C which corresponded to the dielectric loss at the first and the second peaks, respectively. With increasing MC, the first mechanical loss peak shifted to higher temperatures, whereas the second peak moved to lower temperatures in accordance with the dielectric behavior.

To clarify the origin of the second peak, i.e., whether it comes from the molecular motion of the moisture itself¹⁶ or from other factors,²¹ the dielectric

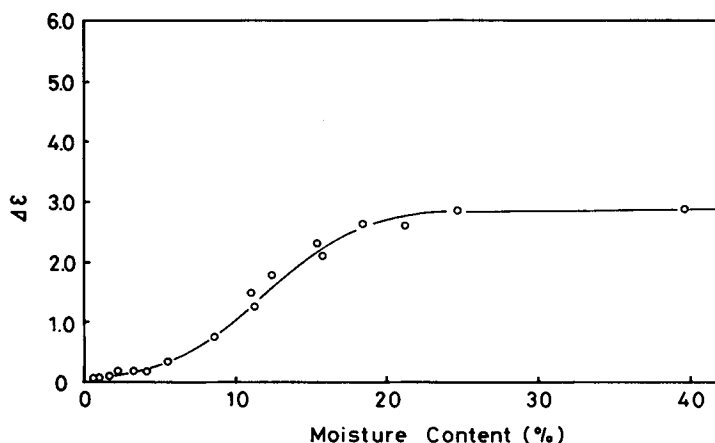


Fig. 9. Relaxation strength ($\Delta\epsilon$) of the second peak for wood (*R* direction) vs. MC.

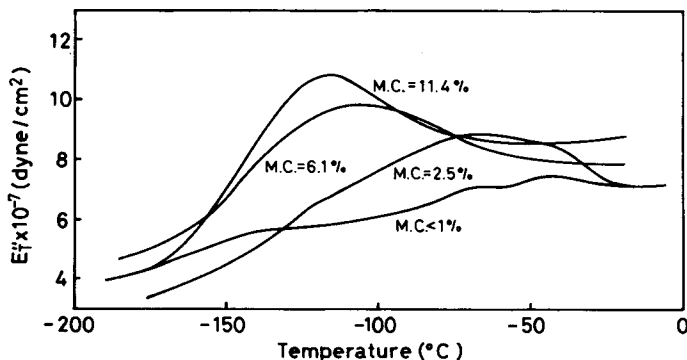


Fig. 10. Temperature dependence of dynamic mechanical loss modulus E'' at 110 Hz for wood containing various amounts of moisture.

properties of wood containing various polar organic solvents such as methanol, acetone, pyridine, and diethylamine were measured. Wood samples containing various organic solvents exhibited ϵ'' -vs.-temperature curves similar to those observed on moistened wood, with regard to the loss peak temperature and the apparent activation energy for the second peak. The fact that the second loss was also activated by the sorption of various polar organic solvents clearly indicates that the loss is not attributed to the motion of moisture itself but to the complexes formed between sorbed molecules and wood components such as cellulose, hemicellulose, and lignin. No difference was observed in the peak intensity normalized on the basis of the mole number of sorbed molecules per gram wood, irrespective of the fairly large variety in dipole moment and molecular size of these sorbates. The similarity in performance of these organic solvents and moisture are well reflected in the features of the ϵ'' peak temperature and the apparent activation energy plotted as a function of mole number of sorbed molecules per gram of wood system, as shown in Figures 11(a) and 11(b), respectively. The second relaxation observed for the wood samples containing polar organic solvents may have a similar molecular mechanism to that for the moistened wood.

Therefore, it is concluded that the second dielectric loss peak is not due to the molecular motion of moisture itself but to the local mode motions of the complexes formed by sorbed moisture and hydrophobic parts in the amorphous regions of cellulose, hemicellulose, and lignin. This motion is gradually enhanced as the overall loosening of the initial hydrogen bond network is promoted by the extended hydration due to the further sorption of moisture.

Third Peak

A novel peak (third peak) was observed at around -40°C only in highly moistened wood with $\text{MC} > 8 \text{ wt } \%$ as a shoulder on the dc ionic conduction, as shown in Figure 4 for the L and R directions of wood. The growth of the third peak with increasing MF is striking. Figure 12 shows the relation between the relaxation strength ($\Delta\epsilon$) of the third peak isolated on the computer and the fraction of sorbed moisture. The $\Delta\epsilon$ for pure ice was estimated on the basis of the data presented in the literature.²² The plots of the $\Delta\epsilon$ for wood with MF from 0.080 to 0.284 were laid slightly below the line connecting the origin and the pure ice value. The apparent activation energy for the third peak was around 13 kcal/mol independent of the variation in MF. This activation energy and the peak temperature for the third peak are very close to those of ice ($\Delta E = 13.25$ kcal/mol, and around -40°C at 110 Hz).²² Furthermore, the methanol-sorbed wood showed no trace of the third dielectric loss (around -40°C) up to the highest methanol content of 12 wt % achieved in the present experimental conditions. Hsi et al.²³ carried out NMR measurements on moistened wood and reported that no frozen water was detected at MC below 38 wt %. However, the dielectric method is very sensitive for the detection of a small amount of polar materials (Fig. 12), whereas the pulsed NMR is commonly useful only when the fraction exceeds 5 or 10 wt % in the system.²⁴ Ice is known to take various structures depending on the crystallization conditions. Although some of the present dielectric results can be explained by assuming the ice I structure in highly moistened wood samples, there is no definite evidence concerning the structure of

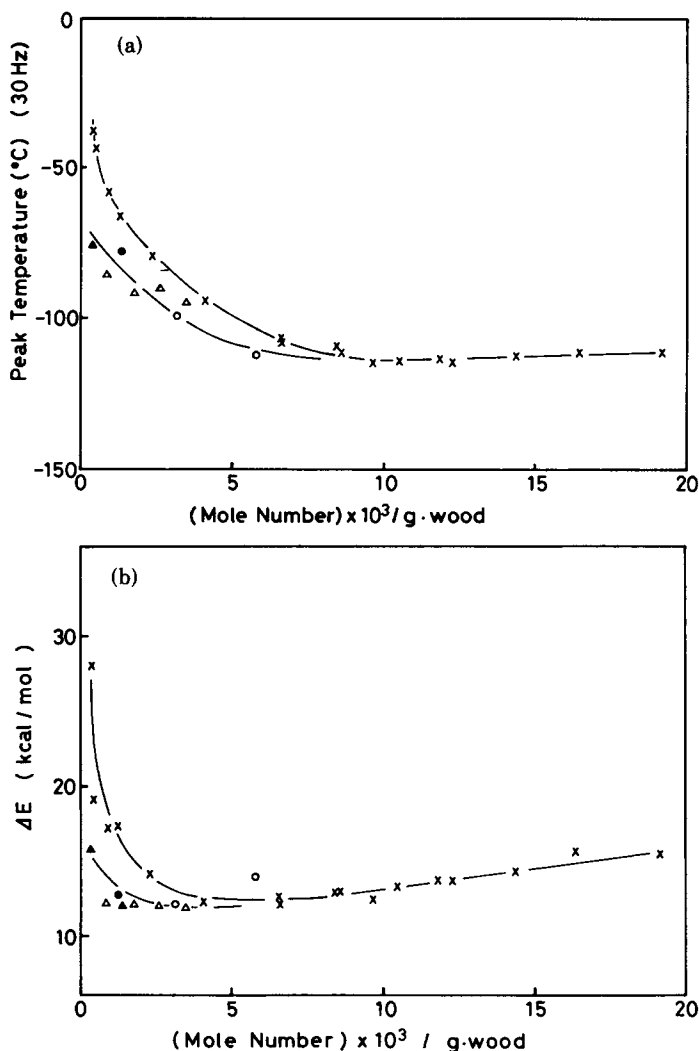


Fig. 11. Peak temperature (a) and ΔE (b) vs. mole number of sorbed molecules per gram of dry wood: (X) moisture; (O) methanol; (Δ) acetone; (\bullet) pyridine; (\blacktriangle) diethylamine.

the water frozen in wood. The structure and properties of this frozen water must be studied in more detail.

Thus, it is suggested that the third peak comes from the motion in ice or quasi-ice clusters of water in the wood system. This has a major implication concerning the mechanism of moisture sorption by wood. Some of moisture sorbed by wood exist in a frozen state at low temperatures even at MC as low as 8 wt %, which is well below the commonly accepted fiber saturation point (MC = 25–35 wt %).¹¹

CONCLUSIONS

The effect of moisture sorption on the dielectric properties of wood has been studied over a wide range of MC, 0 to 40 wt %, in the temperature range -196 to 0°C , and in the frequency range 30 Hz to 1 MHz. Three relaxation processes

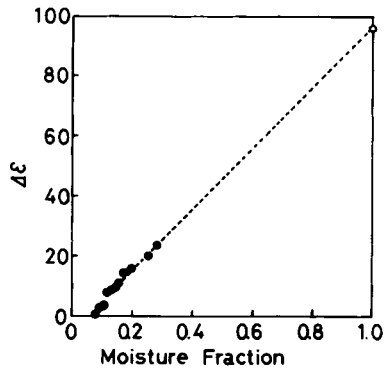


Fig. 12. Relaxation strength $\Delta\epsilon$ of the third peak for wood (R direction) vs. moisture fraction.

were observed depending on MC, frequency, and temperature. The sorbed moisture had complex effects on the loss peak temperatures, the relaxation strengths, and the activation energies for the dielectric relaxations.

The first loss peak observed for all samples at -103 to -96°C (30 Hz) depending on the MC had been previously assigned to the rotational motion of the methylol groups in the amorphous regions of the wood system. The present studies also support this assignment.

The second peak, which appeared for $\text{MC} > 0.6$ wt % at -110 to -40°C (30 Hz), is attributed to the local mode motion of the complexes formed by hydrogen bonding between moisture and polar groups of wood components in the amorphous regions including cellulosic materials and lignin.

A novel (third) loss peak was found only for highly moistened samples ($\text{MC} > 8$ wt %) at about -40°C (30 Hz). The relaxation behavior (the peak temperature, activation energy, and relaxation strength) is well explained by assuming normal ice²² for water highly sorbed by wood samples. The fact that the sorption of organic polar solvents does not induce the dielectric loss supports the above assignment. These results have an important suggestion concerning the mechanism for moisture sorption by wood. Some of the sorbed moisture may be frozen to ice even at MC of 8 wt % ($\text{MF} \approx 0.1$) which is well below the commonly accepted fiber saturation point ($\text{MC} 25\text{--}35$ wt %). However, the structure and properties of this frozen water are not clear and must be studied in more detail.

References

1. N. Migita, Y. Yonezawa, and T. Kondo, *Wood Chemistry*, Vol. I, Kyoritsu Press, Tokyo, Japan, 1968, p. 72.
2. Y. Fushitani, *Mokuzai Gakkaishi*, **14**, 11 (1968).
3. R. A. Stratton, *J. Polym. Sci., Polym. Chem. Ed.*, **11**, 535 (1973).
4. T. Yamada, *Mokuzai Gakkaishi*, **17**, 37 (1971).
5. T. Sado, *Mokuzai Kogyo*, **14**, 537 (1959).
6. K. Kitahara, *Wood Physics*, Morikita Press, Tokyo, Japan, 1967, p. 31.
7. K. Kitahara, *Wood Physics*, Morikita Press, Tokyo, Japan, 1967, p. 49.
8. M. Takeda, *Bull. Chem. Sci. Jpn.*, **24**, 169 (1951).
9. M. Norimoto and T. Yamada, *Mokuzai Gakkaishi*, **15**, 56 (1969).
10. J. Tsutsumi, *Bull. Kyushu Univ. Forests*, No. **41**, 109 (1967).
11. K. Kitahara, *Wood Physics*, Morikita Press, Tokyo, Japan, 1967, p. 32.
12. G. P. Mikhailov, A. I. Artyukhov, and T. I. Borisova, *Polym. Sci. USSR*, **9**, 2713 (1967).

13. M. Norimoto and T. Yamada, *Wood Res.*, **52**, 31 (1972).
14. T. Handa, S. Yoshizawa, and M. Fukuoka, *Kobunshu Ronbunshu*, **35**, 307 (1978).
15. G. N. Christenzen and K. E. Kelseg, *Aust. J. Appl. Sci.*, **9**, 265 (1958).
16. M. Norimoto and T. Yamada, *Mokuzai Gakkaishi*, **22**, 937 (1973).
17. K. Nakagawa and Y. Ishida, *J. Polym. Sci., Polym. Phys. Ed.*, **11**, 1503 (1973).
18. L. Segal, J. J. Greely, A. E. Martin, and C. M. Courad, *Text. Res. J.*, **29**, 786 (1959).
19. T. Handa, S. Yoshizawa, M. Suzuki, and M. Fukuoka, *Proc. 22nd Jpn. Congr. Mater. Res.*, 1978, p. 223.
20. T. Handa, M. Fukuoka, S. Yoshizawa, Y. Hashizume, and M. Suzuki, *Kobunshi Ronbunshu*, **36**, 703 (1979).
21. N. Hirai and A. Yamaguchi, *Mokuzai Gakkaishi*, **25**, 1 (1979).
22. R. P. Auty and R. H. Cole, *J. Chem. Phys.*, **20**, 1309 (1952).
23. E. Hsi, R. Hossfeld, and R. G. Bryant, *J. Colloid Interfac. Sci.*, **62**, 3 (1977).
24. K. Fujimoto and T. Nishi, *Polym. J.*, **3**, 448 (1972).

Received January 8, 1981

Accepted July 27, 1981