

Effect of Bound Water on Piezoelectric, Dielectric, and Elastic Properties of Wood

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Synopsis

The interaction of water with wood, such as bamboo and cedar, is investigated by measuring their complex piezoelectric, dielectric, and elastic constants between -150 and 150°C at 10 Hz .

Bamboo and cedar are found to have two hydration-dependent elastic loss peaks; one is observed at about -100°C and the other at about -40°C . The former loss peak is due to the adsorbed water in the hydration range between 0 and 4% moisture content (MC) and the latter to the adsorbed water above 4% MC.

These two types of water are considered bound on different sites in the regions around crystalline cellulose, where molecules of one type associate with each other and molecules of the other are unassociated.

We consider that the piezoelectric polarization of wood is attributed to the rotation of hydroxyl groups in the crystal lattice of cellulose. The piezoelectric constants are observed to decrease but the elastic and dielectric constants to increase with increasing hydration.

The effect of adsorbed water on elastic losses in bamboo and cedar are found to be similar to that in collagenous substances.

INTRODUCTION

Investigation of the interaction between water and biologic macromolecules is very important for understanding life processes. For wood, water molecules are considered to be located in their cell wall. The cell wall is composed of cellulose microfibrils embedded in an amorphous lignin-hemi cellulose matrix.¹ A model for the physical arrangement of cellulose, lignin, and hemicellulose has been proposed by Kerr and Goring.²

The interaction of water with wood has been studied with various methods, such as nuclear magnetic resonance (nmr), infrared (ir) spectrometry, calorimetry, dielectric studies, and dynamic mechanical measurements by many workers. Among them we are particularly interested in the dynamic mechanical, dielectric, and piezoelectric studies.

From dielectric and mechanical loss factors, the molecular motions of polar or nonpolar groups or segments of the macromolecules, which may be altered by interaction of water, can be investigated. The effect of water on the dielectric constants of wood was investigated by Trapp and Pungs³ (from 40 to $3.5 \times 10^8\text{ Hz}$), Tsutsumi and Watanabe⁴ (30 Hz to 5 MHz), Skaar⁵ (1.5 – 2 MHz), Hearmon and Burchan⁶ (2 – 500 kHz), Takeda⁷ (200 kHz to 300 GHz), Nanassy⁸ (0.1 – 100 kHz), and Norimoto et al.^{9,10} (300 Hz to 1 MHz). The effect of water on the elastic constants was investigated by Becker and Noack¹¹ (0.48 – 1.46 Hz), Bernier and Kline¹² (2 – 2.6 kHz), Kitahara and

Matoumoto¹³ (3.5–110 Hz), and Kline et al.¹⁴ (0.8–2.5 kHz). Further, Handa et al.¹⁵ measured both dielectric (30 Hz to 1 MHz) and elastic (3.5–110 Hz) constants of wood with various hydration levels. These investigators found the hydration-dependent dielectric or elastic loss peaks and discussed the possible molecular assignment of the loss peaks.

The piezoelectric effect has been observed not only in inorganic crystals but also in many biologic tissues. Piezoelectric measurements can provide information about the electrical and mechanical properties of crystalline regions in tissues but dynamic mechanical and dielectrical measurements give only information about the averaged such properties of tissues. Fukada et al.^{16,17} and Maeda et al.^{18,19} measured not only the dielectric and elastic constants but also the piezoelectric constants of hydrated wood at 10 Hz and observed hydration-dependent loss peaks in each constant. Hirai and Yamaguchi²⁰ also measured the piezoelectric constants of wood at 20 and 110 Hz and found two types of piezoelectric loss peaks below 0°C.

In this paper, the interaction of water with wood, e.g., the adsorption sites of water and the behavior of water therein, has been studied by measuring the complex dielectric, elastic, and piezoelectric constants of bamboo and Japan cedar with various hydration levels between –150 and 150°C at 10 Hz.

EXPERIMENTAL

Samples used in this work are bamboo and Japan cedar. Their complex piezoelectric ($d = d' - id''$), dielectric ($\epsilon = \epsilon' - i\epsilon''$), and elastic ($c = c' + ic''$) constants with various hydration levels are measured at 10 Hz between –150 and 150°C. The measuring method is described elsewhere in detail.²¹

The long sides of the samples are cut at 45° to their fiber axis in order to measure the piezoelectric constant d_{14} , which is the coefficient between a polarization in the x direction and a shear stress T_{yz} in the yz plane (Fig. 1). The typical size of the samples is 20 × 10 × 0.2 mm. These dimensions are also used for dielectric measurement. For determination of the elastic constant, the long sides of the samples are parallel to their fiber axis and the typical size is 20 × 1 × 0.1 mm.

Water content in the samples is controlled in the desiccators, each of which has a different kind of saturated salt solution. Samples are dried by heating in a measuring cell at 120°C for about 2 h.

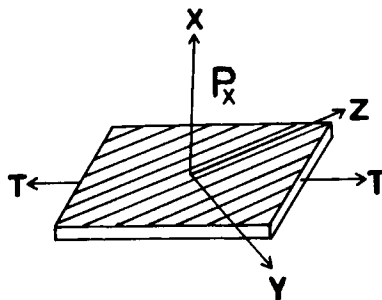


Fig. 1. Orthogonal coordinates assigned to specimen. The z axis is the orientation axis of fibers, P_x is the polarization, and T_{yz} is the stress.

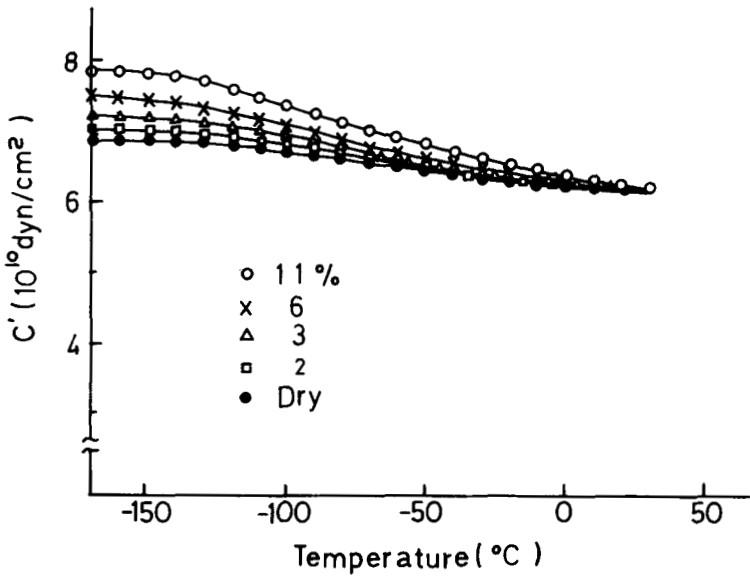


Fig. 2. Temperature dependence of the elastic constant c' of bamboo with various hydration levels (11, 6, 3, 2% MC and dry).

RESULTS

Figure 2 shows the temperature dependence of the elastic constant c' of bamboo at various hydration levels 11, 6, 3, 2% MC and oven dry. Below 40°C, c' increases with increasing hydration levels and decreases with increasing temperature. (A similar hydration and temperature dependence of c' is also obtained for Japan cedar.)

Figure 3 shows the temperature dependence of the elastic loss c'' of bamboo corresponding to the elastic constant c' in Figure 2. For a sample with 11%

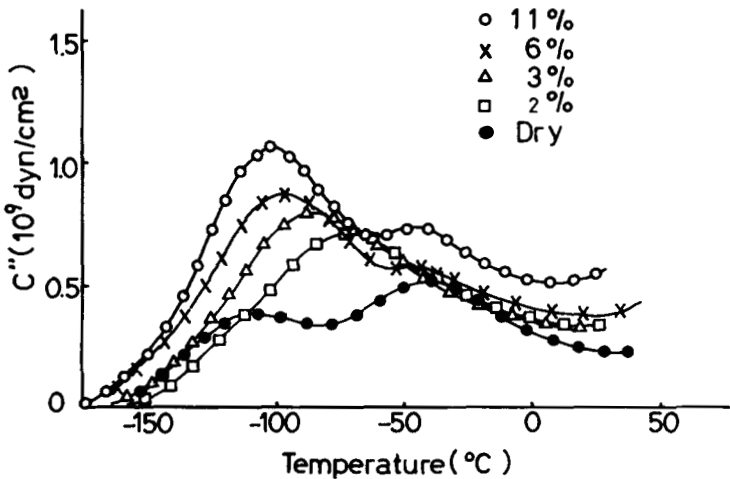


Fig. 3. Temperature dependence of the elastic loss c'' of bamboo with various hydration levels corresponding to Fig. 2.

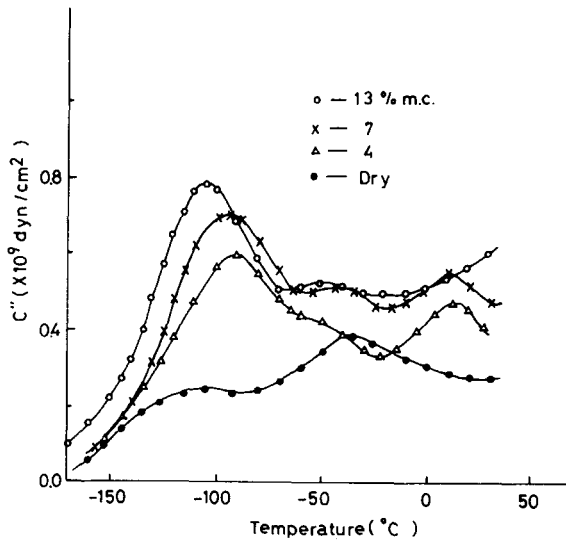


Fig. 4. Temperature dependence of the elastic loss c'' of Japan cedar with various hydration levels.

MC, two loss peaks are observed at -100 and -40°C , respectively. The peak at -100°C shifts toward a higher temperature and the intensity of the peak decreases with decreasing hydration levels. Further, another loss peak appears around -110°C in the dry state.

Figure 4 shows the elastic loss c'' of Japan cedar. Below 0°C , a hydrated sample with 13% MC has two loss peaks at -105 and -45°C , whose intensity decreases with decreasing hydration. The dry sample has two loss peaks at -110° and -40°C .

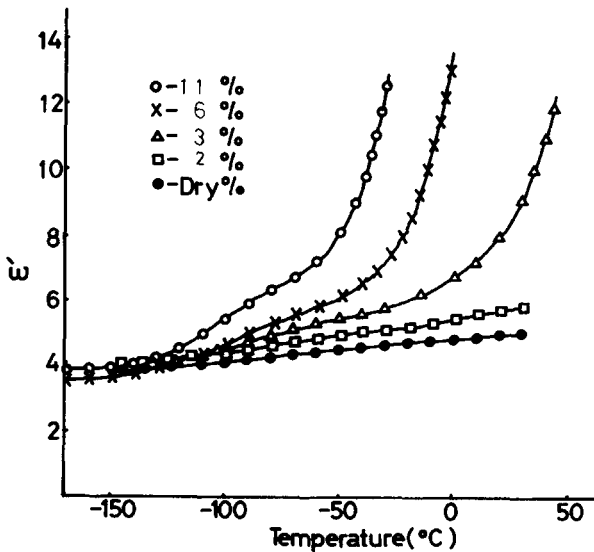


Fig. 5. Temperature dependence of the dielectric constant ϵ' of bamboo with various hydration levels (11, 6, 3, 2% MC and dry).

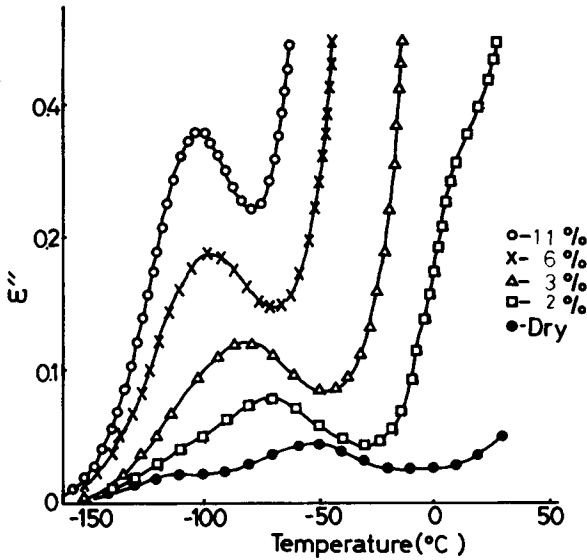


Fig. 6. Temperature dependence of the dielectric loss ϵ'' of bamboo with various hydration levels corresponding to Fig. 5.

Figure 5 shows the temperature dependence of the dielectric constant ϵ' of bamboo with various hydration levels (11, 6, 3, and 2% MC and oven dry). For a sample with 11% MC, ϵ' increases in two steps around -100° and -50°C . These temperatures shift toward higher temperatures with decreasing hydration levels. (A similar hydration and temperature dependence of ϵ' is also obtained for Japan cedar, but its dielectric constants are smaller than those of bamboo, particularly beyond -40°C and 4% MC).

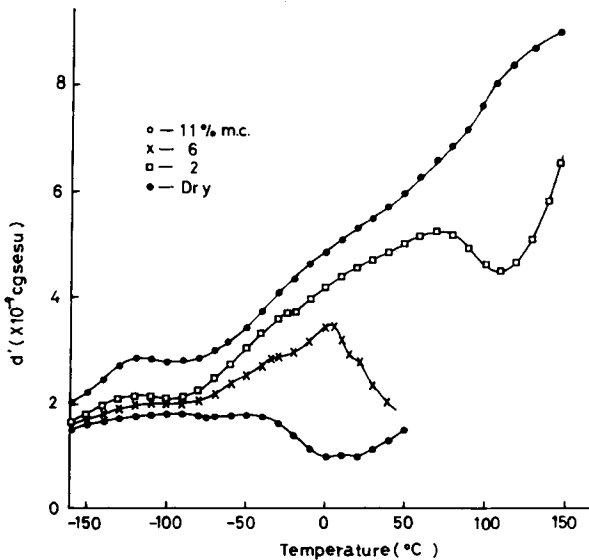


Fig. 7. Temperature dependence of the piezoelectric constant d' of bamboo with various hydration levels (11, 6, 2% MC and dry).

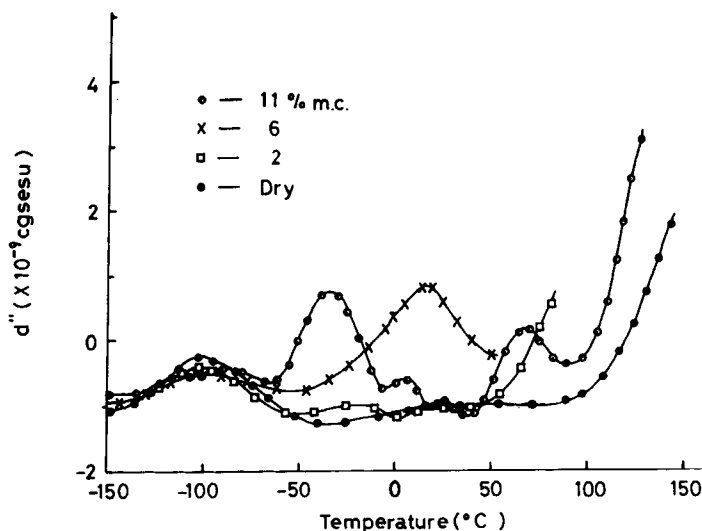


Fig. 8. Temperature dependence of the piezoelectric loss d'' of bamboo with various hydration levels corresponding to Fig. 7.

Figure 6 shows the temperature dependence of the dielectric loss ϵ'' corresponding to the dielectric constants in Figure 5. For a sample with 11% MC, a loss peak is observed at -100°C , which shifts toward higher temperatures and whose intensity decreases with decreasing hydration levels. Further, another loss peak appears at -110°C in the dry state. (Similar loss peaks are also found for Japan cedar.)

Figure 7 shows the temperature dependence of the piezoelectric constant d' of bamboo with various hydration levels (11, 6, 2% MC and oven dry). The constant d' of dry bamboo is larger than those of hydrated bamboo. It increases with increasing temperature. There are regions of temperature where its slope decreases, roughly at -110 to -80°C , -20 to 70°C , and over 100°C . For a sample with 11% MC d' decreases at about -35°C and the temperature shifts toward higher temperatures with decreasing hydration levels.

Figure 8 shows the temperature dependence of the piezoelectric loss d'' of bamboo corresponding to the piezoelectric constant d' in Figure 7. A hydrated bamboo with 11% MC has loss peaks at -100 , -35 , 5 , 25 , and 70°C . The peak at -35°C corresponds to the decrease of d' at about -35°C . Dry bamboo has a loss peak at around -100°C , which corresponds to the decrease in slope between -110 and -80°C . Dry bamboo also has a large loss peak above 100°C .

Figure 9 shows the temperature dependence of the piezoelectric constant d' of Japan cedar with various hydration levels (13, 7, and 4% MC and oven dry). The constant d' increases with decreasing hydration levels. In the dry state, d' increases with increasing temperature and its slope decreases at temperature regions at about -110 to -70°C and -20 to 70°C . At 13% MC, d' decreases between 0 and 25°C with increasing temperature.

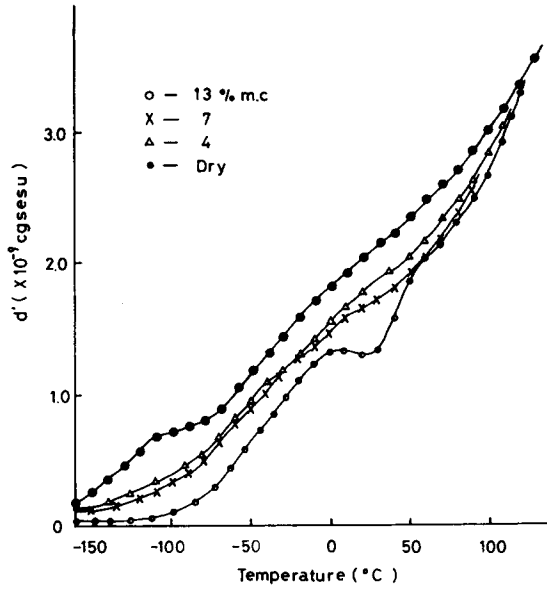


Fig. 9. Temperature dependence of the piezoelectric constant d' of Japan cedar with various hydration levels (13, 7, 4% MC and dry).

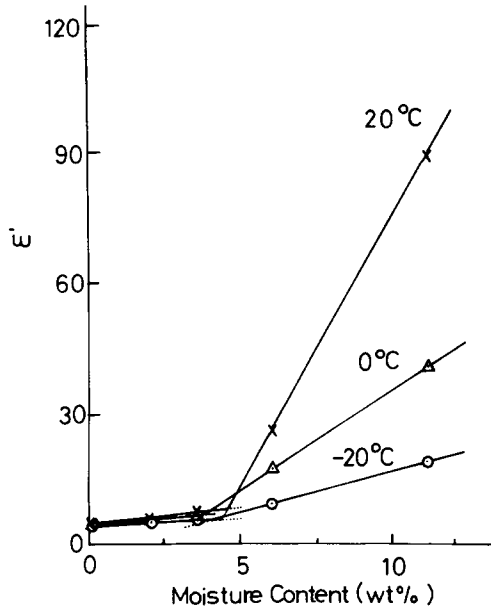


Fig. 10. Moisture dependence of the dielectric constant ϵ' of bamboo at various temperatures (20, 0, and -20°C).

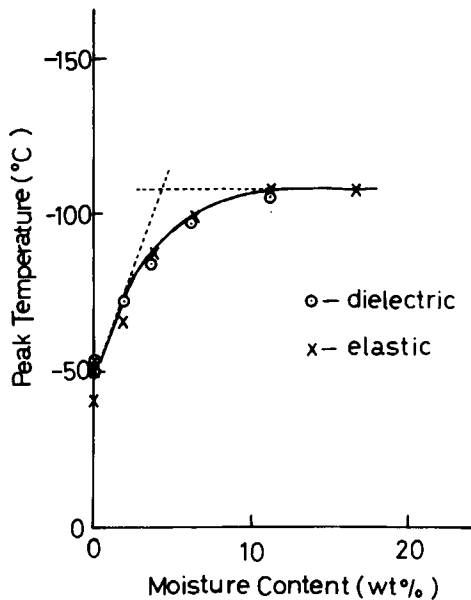


Fig. 11. Moisture dependence of the elastic and dielectric loss peaks at around -100°C of bamboo.

Figure 10 shows the hydration dependence of the dielectric constant ϵ' at various temperatures (20 , 0 , and -20°C) for bamboo. The curves have deflection points, which are called the crytical hydration, at 3.8 – 4.5% MC. (The deflection points nearly agree with those of Japan cedar, but the slopes of ϵ' for Japan cedar are larger than those for bamboo, particularly beyond 4% MC.)

Figure 11 shows the hydration dependence of the peak temperatures of the elastic and dielectric losses around -100°C for bamboo. They both agree well, and the curve has a deflection point at around 3.9% MC. (Such a deflection point is found to be 3.8% MC for Japan cedar.)

DISCUSSION

As seen from Figures 3 and 4, three mechanical loss peaks are found in bamboo and Japan cedar: two of them depend on hydration and the rest can be seen at about -110°C only at very low hydration levels. The hydration-dependent loss peaks are observed at -100 and -40°C for bamboo with 11% MC and at -105 and -45°C for Japan cedar with 13% MC. The loss peaks at about -100°C are considered to correspond to those observed by Kitahara and Matoumoto¹³ and Handa et al.¹⁵

The hydration-dependent dielectric loss peaks are also observed at about -100°C (Figure 6) and they are considered to correspond to those for wood observed by Trapp and Pungs,³ Hearmon and Burcham,⁶ Tsutsumi and Watanabe,⁴ Maeda and Fukada,¹⁸ and Handa et al.¹⁵

We found that the hydration dependence of these dielectric and elastic loss peaks at around -100°C agrees well with each other (Figure 11). The same is found to be true of Japan cedar. The temperature of the loss peaks does not

depend on the measuring method. From such behavior, we suggest that the relaxing units are well localized. We suppose that the relaxing units are water molecules, which form hydrogen bonds with hydroxyl groups in the interfibril regions. In addition, Figure 11 shows the deflection point at about 3.9% MC. Below this point, the peak temperatures shift lower with increasing hydration level, but above this point they depend very little on the hydration level. Thus, we consider that the dielectric and elastic loss peaks at about -100°C are assigned to adsorbed water below the deflection point, which is called critical hydration. Figure 11 also suggests that the adsorbed water molecules below and above the critical hydration are hardly interrelated; in other words, these two types of water adsorb on different sites in the interfibril regions.

On the other hand, Kline et al.¹⁴ reported the hydration dependence of the elastic loss peaks for white ash at around 2 kHz. Their curve has a deflection point at 6% MC and the loss peak temperature hardly shifted below this point; it shifted toward lower temperatures above this point with increasing hydration. This is, however, quite different from the behavior we observed (Figure 11), probably because Klein et al. used frequencies different (about 2 kHz) from ours, which give information about different relaxing units.

At high hydration levels, the elastic loss peaks appear at about -40°C (Figures 3 and 4). We think that the loss peak is due to the adsorbed water above the critical hydration, since it can be hardly seen below 3% MC (Figure 3). The peak temperature has little hydration dependence, but the peak at about -100°C shows a rather large shift with hydration. Taking into account that loss peak temperature generally depends on the size of a relaxing unit, the relaxing unit at -40°C is considered larger than that at -100°C . Thus, we assume that the adsorbed water molecules above 4% MC are associated with each other, but those below 4% MC are unassociated or isolated.

These two kinds of adsorbed water are also observed from the hydration dependence of ϵ' . In Figure 10 the deflection points, which suggest the existence of the two types of adsorbed water, are found at around 3.8–4.5% MC (average, 4.1% MC). It is very significant that such deflection points agree well with those obtained from the hydration dependence of the dielectric or elastic loss peak temperatures (Figure 11). From measurements of the dielectric constant of wood, Skaar⁵ and Trapp and Pungs³ found the critical hydration to be 3 and 5% MC, respectively, and from dynamic mechanical measurements, Kline et al.¹⁴ and Kitahara and Matoumoto¹³ found it to be 6% MC. Such values agree well with our values.

A steep increase in ϵ' is seen above the critical hydration in Figure 10. The increase is considered to be attributed to Maxwell-Wagner kind of interfacial or space charge polarization, which is induced by the increase in the number of mobile ions from adsorbed water. Below the critical hydration, adsorbed water has no effect on the mobility of the ions, as ϵ' hardly increases with increasing hydration (Figure 10). Thus, we suggest that there are two kinds of adsorption sites; (1) isolated sites, such as methylol groups of noncrystalline cellulose, hemicellulose, or lignin, where the water molecules below 4% MC are tightly bound; and (2) interstices with regularly arranged adsorption sites around crystalline cellulose, where the water molecules beyond 4% MC can be associated with each other. Impurity ions are trapped on the surfaces of such interstices and they can be dissociated by water molecules above 4% MC.

Additionally, we found these two types of adsorbed water act as a filler in the interfibril regions, since the elastic constants increase in ranges both below and above critical hydration (Figure 2). This behavior can be explained by the effect of the "water bridge" between adsorption sites.

Keylwerth²² found deflection points around 5% MC in curves of the hydration dependence of volumetric hygro-expansion for various woods. This behavior can also be explained by the existence of the two types of adsorption sites mentioned above.

To explain temperature and hydration dependence of the piezoelectric constants for bamboo and Japan cedar, it is very helpful to use a two-phase model such that the piezoelectric phase is dispersed in the nonpiezoelectric phase.²³ In fact, bamboo and Japan cedar are approximately considered to consist of the piezoelectric phase or crystalline regions of cellulose and the nonpiezoelectric phase or the noncrystalline regions, composed of cellulose, hemicellulose, and lignin. The piezoelectric polarization of bamboo and Japan cedar is considered to be generated by the internal rotation of the hydroxyl groups that form hydrogen bonds in the crystal lattice of cellulose.

The piezoelectric constant d is generally defined as an electric polarization P induced by an external stress S applied to specimens as follows²³:

$$d = \frac{P}{S} = \phi d_2 \cdot \frac{5c_2}{3c_1 + 2c_2} \frac{3\epsilon_1}{2\epsilon_1 + \epsilon_2} \quad (1)$$

where ϕ indicates the volume fraction of the crystalline phase, the suffixes 1 and 2 the piezoelectric and nonpiezoelectric phases, respectively, d_2 the piezoelectric constant of the phase 2, c_1 and c_2 the elastic constants of the phases 1 and 2, respectively, and ϵ_1 and ϵ_2 the dielectric constants of the phases 1 and 2, respectively. The physical meaning of eq. (1) is as follows. First, the stress to the piezoelectric phase (internal stress) is not equal to the external stress itself, but depends on the elastic constants of both phases c_1 and c_2 . Second, the actually observed piezoelectric polarization is not the polarization of the piezoelectric phase itself but depends on the dielectric constants of both phases ϵ_1 and ϵ_2 . Thus, we can gather information on the electrical and mechanical properties of the piezoelectric phase if the dielectric and elastic constants are given in addition to the piezoelectric constants.

From such a standpoint, we may consider the possible mechanism by which the piezoelectric constants, particularly in the dry state, steeply increase with increasing temperature (Figures 7 and 9). Following eq. (1), we may consider two possible causes for the increase of the piezoelectric constant; one is due to the temperature change of the dielectric and/or elastic constants of the nonpiezoelectric regions and the other to the temperature change of the piezoelectric constant of the piezoelectric regions. Eq. (1) shows that the decrease in the elastic constant c_1 or the increase in the dielectric constant ϵ_1 in the nonpiezoelectric phase results in an increase in d . The decrease in c_1 increases the internal stress applied to the piezoelectric phase to increase its polarization, and the increase in ϵ_1 more effectively transmits polarization in the piezoelectric phase to the electrodes on the surface of the specimens. For bamboo and Japan cedar, however, it is readily recognized that such a

temperature change of the elastic or dielectric constants in the nonpiezoelectric phase contributes little to the increase in the piezoelectric constants because the slopes of d' are much larger than those of c' and ϵ' , particularly in the dry state (compare Figures 7 and 9 with Figures 2 and 5). Thus, as the possible cause for the increase in the piezoelectric constants of bamboo and Japan cedar, we suggest that there is a thermal change of the piezoelectric constant for the cellulose crystal d_2 such that the piezoelectric dipole moments in the crystal lattice of cellulose become easier to reorient under stress with increasing temperature.

We further suggest that there is relaxation of the atomic groups in the piezoelectric phase which has a specific effect on the piezoelectric constant but little effect on either the dielectric or the elastic. First, at low hydration levels, the slopes of d' versus temperature decrease at around -100°C , but such clear changes cannot be found in the slopes of c' and ϵ' (Figures 7, 9, 2, and 5). Second, as hydration increases, the peaks of c'' and ϵ'' shift from -40 to -100°C , but those of d'' show only a small shift at around -100°C . However, it may be better to expand the definition of the piezoelectric phase to include the regions of cellulose that have the piezoelectric effect but do not form ideal crystalline structures. We need further investigation of this.

For bamboo with 11% MC, the piezoelectric constant d' decreases and the loss d'' has a peak at around -35°C (Figures 7 and 8). The temperature shifts toward higher with decreasing hydration levels. Such a decrease in d' is considered to be caused by the mobile ions just around the crystalline regions of cellulose, the number of which is increased by adsorbed water above 4% MC. This is verified by the observation that temperatures at which d' decreases are the same temperatures at which ϵ' and ϵ'' steeply increase or the Maxwell-Wagner effect takes place.

We will see the difference between the electromechanical properties of bamboo and Japan cedar. The dielectric constants of bamboo are found to be more sensitive to changes in temperature and hydration than those of Japan cedar. That is, the slopes of ϵ' and ϵ'' versus hydration and temperature, particularly beyond about 4% MC and -40°C for bamboo, are rather larger than those for Japan cedar. The piezoelectric constant of bamboo with 11% MC decreases at -35°C , but the constant of Japan cedar with 13% MC decreases at higher temperature or about 0°C . Further, the decrease in the constant of bamboo is larger than that of Japan cedar (Figures 7 and 9). This behavior suggests that bamboo has more mobile ions than Japan cedar. We found further that the piezoelectric constant of dry bamboo is two or three times larger than that of dry Japan cedar. This is considered to be attributed to the difference in morphology between bamboo and Japan cedar.

Last, we will see the similarities between the elastic properties of cellulosic substances, such as bamboo and Japan cedar, and those of collagenous substances, such as tendon and decalcified bone. As already shown, both bamboo and Japan cedar have two types of hydration-dependent elastic loss peaks at around -100 and -40°C at high hydration levels. For tendon and bone collagen, elastic loss peaks have been also observed at -110 and -60°C ²⁴ and the hydration dependence of the loss peaks is found to resemble that of bamboo and Japan cedar. The loss peak at about -100°C is frequently observed in hydrated macromolecules, but the same is not true of the

loss peaks at about -40°C . We actually observed only one loss peak at about -100°C for hydrated gelatin²⁵ and poly(N-isopropyl)acrylamide films.²⁶ Thus, we consider that the elastic loss peaks at about -40°C for wood and at about -60°C for collagenous substances are both related to the associated water molecules, which reside in the interstices, probably with regularly arranged adsorption sites, in the interfibril regions.

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