

# Sign Reversal of Piezoelectric Polarization of Hydrated Native Collagenous and Cellulosic Fibers by Addition of Ions

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## SYNOPSIS

Complex piezoelectric constants of native collagenous and cellulosic fibers, which take highly oriented and ordered microfibrillar structures, have been measured at 10 Hz between  $-150$  and  $50^{\circ}\text{C}$ . We have found that piezoelectric polarization of both hydrated fibers, which contain many ions, steeply decrease around  $-60^{\circ}\text{C}$  and subsequently exhibit the sign reversal around  $-40^{\circ}\text{C}$ . These temperatures are found to agree with that at which bound water between the microfibrils begin to get mobile. The steep decrease and sign reversal of the piezoelectric polarization may be explained by actions of ions that reside in piezoelectric and nonpiezoelectric regions of such ordered structures.

## INTRODUCTION

The growth of bone and plant may be considered to significantly relate to piezoelectric polarization. The origin of the polarization seems to be due to the rotation of peptide groups for crystalline proteins<sup>1</sup> and OH groups for crystalline cellulose.<sup>2</sup>

Piezoelectric constants have been measured for many biopolymers and have been known to be greatly influenced by hydration.<sup>3-7</sup> Ueda and Fukada measured piezoelectric constants of a film consisting of three joined layers of gelatin, oriented collagen, and gelatin and found a sign reversal of the piezoelectric constants at  $-35^{\circ}\text{C}$ .<sup>8</sup> They proposed that the mechanism of the sign reversal is a superposition of the following: (1) the Maxwell-Wagner-type dielectric relaxation in the combined films, and (2) the decay of piezoelectric dipoles in piezoelectric phase due to diffusion of counter ions.

The purpose of the present study is to show that the presence of ions is essential for the sign reversal of the piezoelectric polarization, and, thus, the reversal can be induced by increasing the number of the mobile ions.

## SAMPLES AND EXPERIMENTAL

Bovine Achilles' tendon and bamboo were used here as collagenous and cellulosic substances, respectively. The typical dimension of the samples for piezoelectric measurements was  $15 \times 8 \times 0.4$  mm. The direction of the long side of the samples was at  $45^{\circ}$  to the orientation axis of the fibers so as to measure the piezoelectric coefficient  $-d_{14}$ , which indicates the polarization in the  $x$ -direction induced by a shear stress in the  $yz$  plane, where the  $x$ -axis is normal to the sample plane and the  $z$ -axis is parallel to the orientation axis of the microfibrils. (For simplicity, the subscript 14 and negative sign of  $-d_{14}$  is omitted throughout this paper.)

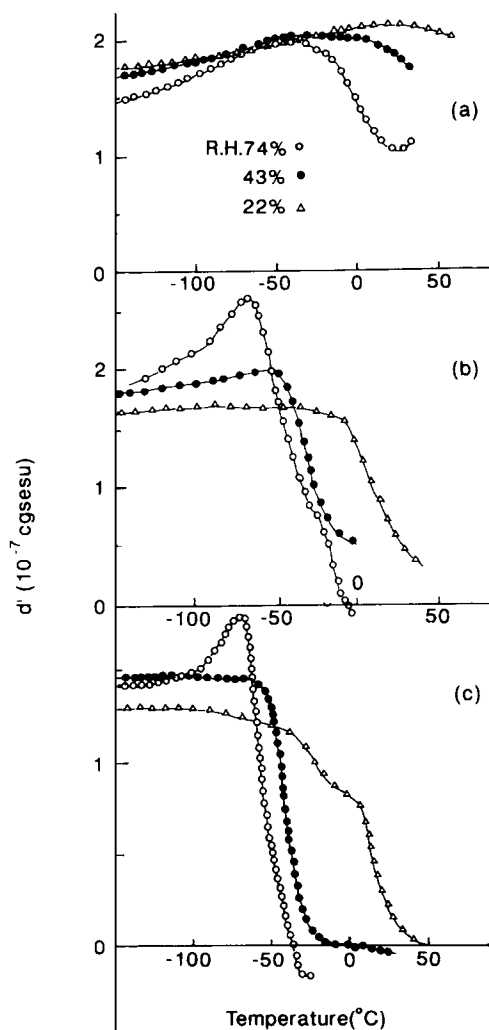
For tendon and bamboo, three kinds of samples, (s1, s2, s3) and (w1, w2, w3) were used, respectively. The sample s1 was obtained by immersing the thin plate of native bovine tendon in distilled water to extract ions contained, and s2 and s3 were, respectively, obtained by immersing s1 in 0.5 and 2 mol NaCl solutions until they were reached at the equilibrium. For bamboo as well, sample w1 was obtained by immersing native bamboo in distilled water, and w2 and w3 were, respectively, obtained by immersing w1 in 0.05 and 0.25 mol NaCl solutions.

The detail of an apparatus to measure complex piezoelectric constants ( $d = d' - id''$ ) was described

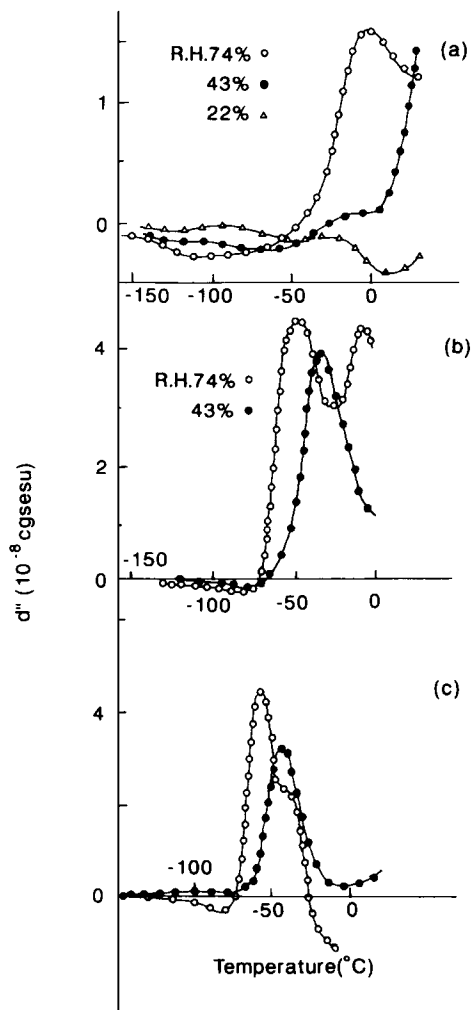
elsewhere.<sup>9</sup> Stress of samples was detected by a piezoelectric ceramic element. Piezoelectric charges on the electrodes of the samples were determined by an operational circuit, which was designated to automatically determine the complex response functions by using a null-balancing system that consists of a null detector, a charge amplifier, integration type-phase sensitive detectors, and sample and hold circuits. Hydration levels of the samples were varied by equilibrating them in desiccators that contain different saturated salt solutions.

## RESULTS

Figures 1(a) and 2(a) show, respectively,  $d'$  and  $d''$  of hydrated deionized tendon s1. At relative humidid-



**Figure 1** Temperature dependence of piezoelectric constants  $d'$  of tendon, s1 (a), s2 (b), and s3 (c), at relative humidities 22, 43, and 73%.



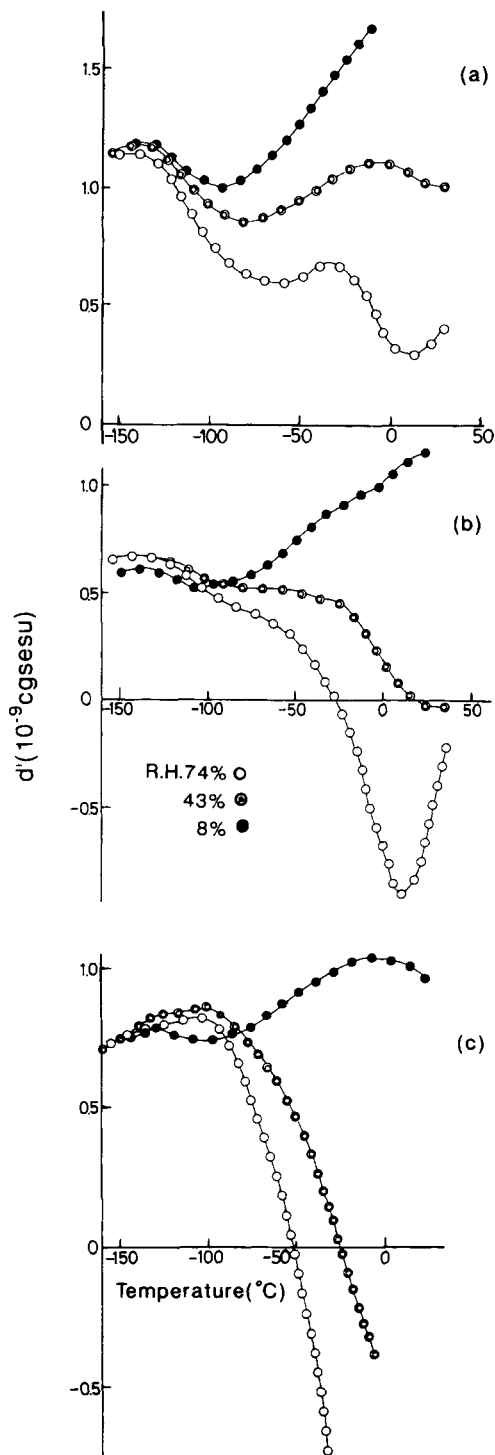
**Figure 2** Temperature dependence of piezoelectric losses  $d''$  of tendon, s1 (a), s2 (b), and s3 (c), at relative humidities 43 and 73%.

ity (r.h.) 22%, the constants  $d'$  gradually decrease around 20°C. With increasing hydration, the temperature shifts toward lower ones, e.g., 0°C at r.h. 43% and -40°C at r.h. 74%. The loss  $d''$  has a peak around -5°C at r.h. 74%.

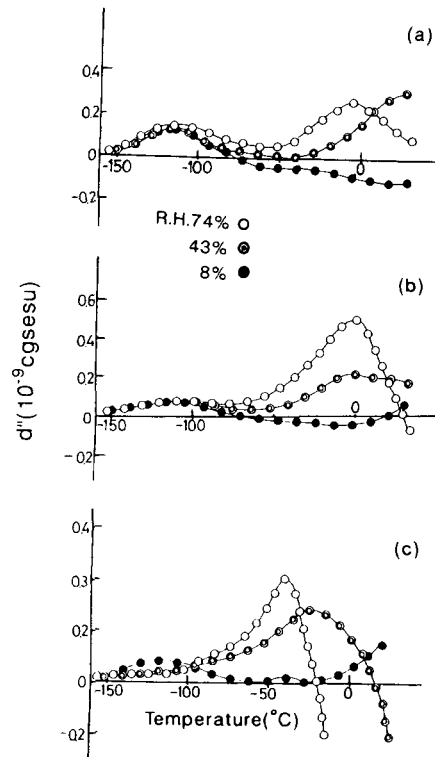
Figures 1(b) and 2(b) show, respectively,  $d'$  and  $d''$  of hydrated sample s2. At r.h. 22 and 43%, the constants  $d'$  begin to steeply decrease around -50 and 0°C, respectively, and the loss  $d''$  (r.h. 43%) has a peak at -40°C. With further increasing hydration, new behavior of  $d'$  appears; e.g., at r.h. 74%,  $d'$  increases up to -60°C and steeply decreases in two steps, at -60 and -25°C, and subsequently changes the sign at -5°C. The corresponding loss  $d''$  has two peaks at -50 and -10°C.

Figures 1(c) and 2(c) show, respectively,  $d'$  and  $d''$  of hydrated sample s3. At r.h. 22%,  $d'$  begins to

steeply decrease in two steps: at  $-35$  and  $10^{\circ}\text{C}$ . With increasing hydration, these temperatures shift toward lower ones, e.g.,  $-60$  and  $-50^{\circ}\text{C}$  at r.h. 74%,



**Figure 3** Temperature dependence of piezoelectric constants  $d'$  of bamboo, w1 (a), w2 (b), and w3 (c), at relative humidities 22, 43, and 73%.



**Figure 4** Temperature dependence of piezoelectric losses  $d''$  of bamboo, w1 (a), w2 (b), and w3 (c), at relative humidities 22, 43, and 73%.

respectively. In addition, at r.h. 74%, the sign of  $d'$  changes at  $-35^{\circ}\text{C}$  and  $d''$  has two peaks at  $-60$  and  $-30^{\circ}\text{C}$ .

Figures 3(a) and 4(a) show, respectively,  $d'$  and  $d''$  of hydrated sample w1. At r.h. 8%,  $d'$  decreases between  $-120$  and  $-90^{\circ}\text{C}$  and begins to increase above that. With increasing hydration, e.g., at r.h. 43 and 74%, this decrease of  $d'$  becomes larger and another one appears around  $0$  and  $-30^{\circ}\text{C}$ , respectively. At all hydration levels, the losses  $d''$  have peaks around  $-110^{\circ}\text{C}$ , and at r.h. 74%,  $d''$  has another peak at  $0^{\circ}\text{C}$ .

Figures 3(b) and 4(b) show, respectively,  $d'$  and  $d''$  of hydrated sample w2. At all hydration levels, the decrease of  $d'$  around  $-100^{\circ}\text{C}$  becomes smaller, whereas the decreases at higher temperatures (between  $-50$  and  $0^{\circ}\text{C}$ ) are amplified, as compared with those of w1. At r.h. 43 and 74%, the sign of  $d'$  changes at  $20$  and  $-30^{\circ}\text{C}$ , respectively. It should be noted that the value of the latter reversed  $d'$  is fairly larger than that of the former and, further, that the maximum absolute value is comparable to the values at lower temperatures below  $-120^{\circ}\text{C}$ . At all hydration levels, the losses  $d''$  have peaks around  $-110^{\circ}\text{C}$ , and at r.h. 43 and 74%,  $d''$  has other peaks around  $0^{\circ}\text{C}$ .

Figures 3(c) and 4(c) show, respectively,  $d'$  and  $d''$  of hydrated sample w3. At r.h. 8%, the decrease of  $d'$  appears at 0°C, in addition to one around -110°C. At r.h. 43 and 74%, the constants  $d'$  increase up to -110°C and subsequently decrease to reverse the sign at -40 and -25°C, respectively. It should be noted that, at r.h. 43 and 73%, the temperature coefficients of  $d'$  change at -40 and -50°C, respectively. The losses  $d''$  at r.h. 43 and 73% have peaks at -40 and -25°C, respectively.

## DISCUSSION

We thought that ions in both piezoelectric and nonpiezoelectric regions play an essential role for the sign reversal and thus carried out piezoelectric experiments for hydrated tendon and bamboo with various ion contents; as a result, we have found that the piezoelectric polarization for both reverses the sign as the number of the ions increases [Figs. 1(b) and (c), 3(b) and (c)]. The sign reversal of the piezoelectric polarization may be due to both of the following two effects, (1) and (2).

### (1) Electrode Polarization and Maxwell-Wagner Effect

To explain the temperature dependence of the piezoelectric constants described above, it is convenient to use a two-phase model,<sup>10</sup> which consists of randomly dispersed piezoelectric spheres and nonpiezoelectric phase around them. The piezoelectric constant  $d'$  for such a model considering high electric conduction is formulated as follows<sup>11</sup>:

$$d = e_2 \cdot \frac{1}{c} \cdot \frac{3\phi\epsilon_1}{(2 + \phi)\epsilon_1 + (1 - \phi)\epsilon_2} \cdot \frac{\epsilon_{el}^*}{\epsilon_{el}^* + \epsilon_s} \quad (1)$$

where  $\phi$  is the volume fraction of piezoelectric phase,  $e_2$  is piezoelectric polarization per unit strain of the spheres,  $\epsilon$  and  $c$  are the dielectric and elastic constants, respectively, and subscripts 1 and 2 indicate nonpiezoelectric and spherical piezoelectric phases, respectively. The last term of the right-hand side in eq. (1) indicates the effect of an electrode polarization, where  $\epsilon_s$  is the dielectric constant of the sample and  $\epsilon_{el}^*$  is an equivalent dielectric constant representing the electrode polarization, and they can be written as<sup>12</sup>

$$\epsilon_{el}^* = \epsilon_{el}(i\omega)^{n-1} (0 \leq n \leq 1)$$

where  $\omega$  is angular frequency, and

$$\epsilon_s = \epsilon_1 \cdot \frac{2(1 - \phi)\epsilon_1 + (1 + 2\phi)\epsilon_2}{(2 + \phi)\epsilon_1 + (1 - \phi)\epsilon_2}$$

where the dielectric constants are usually expressed by use of electric conductivity as follows:  $\epsilon = \epsilon' - i \times \sigma/4\pi\omega$ . In eq. (1), usually  $\epsilon_{el}^* \gg \epsilon_s$ , then  $\epsilon_{el}^*/(\epsilon_{el}^* + \epsilon_s) \sim 1$ , and, hence,

$$d = e_2 \cdot \frac{1}{c} \cdot \frac{3\phi\epsilon_1}{(2 + \phi)\epsilon_1 + (1 - \phi)\epsilon_2} \quad (2)$$

In eq. (2),  $d$  increases as  $\epsilon_1$  increases. Thus, when electrode polarization can be neglected, the increase of  $\epsilon_1$  and/or  $\sigma_1$  of the nonpiezoelectric phase results in the increase of  $d$ . In fact,  $d'$  of tendon (s2 and s3) increases below -60°C with increasing temperature at high salt and water contents. Thus, this increase of  $d'$  seems to be due to the increase of mobile ions in the nonpiezoelectric phase.

On the other hand, in eq. (2), if  $\epsilon_2 \gg \epsilon_1$  or the piezoelectric phase is more conductive than that of the nonpiezoelectric phase,  $d'$  decreases as  $\epsilon_2$  increases. This indicates the Maxwell-Wagner effect, which occurs in the piezoelectric phase to reduce  $d'$ . Further, in eq. (1), if  $\epsilon_1 \gg \epsilon_2$  and electrode polarization cannot be neglected because of high hydration and ion contents in the nonpiezoelectric phase, then

$$d \sim e_2 \cdot \frac{1}{c} \cdot \frac{\epsilon_{el}^*}{\epsilon_{el}^* + Q\epsilon_1} \cdot \frac{3\phi}{2 + \phi},$$

where  $Q = 2(1 - \phi)/(2 + \phi)$  and  $d$  decreases as  $\epsilon_1$  increases.

Thus, there seems to be two types of reduction of  $d'$ , that is, electrode polarization due to mobile ions in the nonpiezoelectric phase and the Maxwell-Wagner effect due to mobile ions in the piezoelectric phase. In fact,  $d'$  of the samples s2, s3, w2, and w3 decreases at about -60°C at r.h. 74% [Figs. 1(b) and (c) and 3(b) and (c)], and these may be explained by two effects mentioned above. These effects, however, cannot inverse the sign of  $d'$ , although they can sufficiently reduce  $d'$ .

### (2) Relaxation in Piezoelectric Phase

At r.h. 74%, the constants  $d'$  of s2, s3, w2, and w3 do not only decrease but also change the sign with increasing temperature [Figs. 1(b) and (c) and 3(b) and (c)]. That may be attributed to a relaxation of the piezoelectric phase, which is coupled with an action of ions therein as described below.

In eq. (1), if  $\epsilon_1 \gg \epsilon_2$  and  $n = 0.5$ , then  $d$  is written as follows:

$$d = e_2 \frac{1}{c} \cdot \frac{p}{(p + Q\epsilon_1')^2 + (p + \sigma_1 Q/4\pi\omega)^2} \\ \times \{2p + Q(\epsilon_1' + \sigma_1/4\pi\omega) \\ - i \cdot Q(\epsilon_1' - \sigma_1/4\pi\omega)\},$$

where  $p = \epsilon_{el}/\sqrt{2\omega}$ . If  $e_2$  is a real value in the equation, then  $d'$  is always positive (in other words, the sign of  $d'$  never changes) as follows:

$$d' \propto 2p + Q(\epsilon_1' + \sigma_1/4\pi\omega) > 0$$

However, if  $e_2$  is a complex value or  $e_2' + ie_2''$  as well as  $\epsilon$  and  $c$  and further  $\sigma_1 \gg \epsilon_1'$ , then

$$d' \propto \frac{p}{(p + Q\epsilon_1')^2 + (p + \sigma_1 Q/4\pi\omega)^2} \\ \times \{e_2'(2p + \sigma_1 Q/4\pi\omega) - e_2''\sigma_1 Q/4\pi\omega\}$$

Two conditions, (a)  $e_2' > 0$  and (b)  $e_2''/e_2' > 1 + 8\pi p\omega/\sigma_1 Q$ , can allow us to deduce  $d' < 0$  or the sign reversal of  $d'$  from this equation.

We think that specific structures of tendon and bamboo may be related to the sign reversal of  $d'$ . They both have fibrillar structures consisting of ordered microfibrils, among which water molecules can be associated with each other. For tendon,  $d'$  at r.h. 43% steeply decrease in two steps: at  $-60$  and  $-20^\circ\text{C}$  [Fig. 1(b)] and  $d'$  at r.h. 74% at  $-60$  and  $-50^\circ\text{C}$  [Fig. 1(c)]. Further, for bamboo,  $d'$  at r.h. 43 and 74% have deflections around  $-40$  and  $-50^\circ\text{C}$ , respectively [Figs. 3(b) and (c)]. These temperatures seem to agree well with that at which the associated bound water begins to get mobile.<sup>5,6</sup> Thus, the steep increase of the mobility of the bound water seems to be a trigger of the sign reversal.

Two kinds of relaxations, which correspond to such a two-step decrease of  $d'$ , seem to support an idea that the sign reversal of  $d'$  may be due to two ionic mechanisms already mentioned. It is, however,

difficult to know what type of relaxation due to the ions takes place in the piezoelectric phase. Ueda and Fukada proposed that the decay of the piezoelectric dipoles is due to diffusive ions in the phase.<sup>8</sup> We, however, think that it may be difficult for ions to diffuse into crystalline regions of collagen and cellulose but may be possible into such pseudocrystalline regions so that main chains of collagen and cellulose align uniaxially as an average, but distances between the chains are random. We think that the piezoelectric polarization can generate not only in the crystalline regions but also in such pseudocrystalline ones, and, thus, the decay of piezoelectric dipoles due to diffusive ions would be possible therein to induce the sign reversal of  $d'$ . However, to confirm the molecular mechanism of such relaxation in the piezoelectric phase, more investigation will be needed.

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