EFFECT OF WATER ON PIEZOELECTRICITY IN BONE AND COLLAGEN

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ABSTRACT Interferometric measurements of bovine bone and tendon show that the values of the piezoelectric strain constant d_{14} decrease with hydration from the dry values of 0.2×10^{-14} and 2.0×10^{-14} m/V, respectively. The decrease of piezoelectricity in tendon is exponential with a characteristic hydration of 7% by weight from which an upper limit of the average molecular weight of the responsible electric dipole moments is deduced. The piezoelectricity in bone decreases relatively slowly with hydration indicating that the electric dipoles in bone collagen are subject to a different cancelling mechanism.

INTRODUCTION

Although piezoelectric phenomena in bone and native collagen have been studied (1–5) no experiment as yet identifies the dipoles responsible for the piezoelectric effect. Since the electrical polarizability of bone and collagen increases with water content (6), the question of the role of water in piezoelectricity arises. Starting with samples of bovine femur and achilles tendon from recently butchered animals, the deformation $S = \Delta L/L$ is measured along an axis 45° from the growth axis following application of an electric field in the perpendicular direction (see Fig. 1). Electrodes were deposited by metal evaporation and by painting metal powder suspensions.

METHOD

The deformation was measured by a differential Perot-Fabry interferometer developed for the study of cyclical dimensional changes. Fig. 2 shows a block diagram of the interferometer and its associated circuitry applied to the measurements of inverse piezoelectric coefficients. The sample S is subjected to a 50 Hz sinusoidally varying electric field which causes mirror M_2 to oscillate with an amplitude proportional to the transverse piezoelectric coefficient. A linear photo detector D transforms the light transmitted by the interferometer to a voltage signal whose amplitude is analyzed by a synchronous amplifier and displayed on an xy-recorder. The x-axis of the recorder is slowly varied by a linearly increasing voltage also applied to a piezoelectric translator PZ on the otherwise fixed mirror M_1. Whenever the mirror separation is near an integral number of half wavelengths of laser light, there is a synchronous signal proportional to the sample movements, as well as to the laser intensity and to the Perot-Fabry finesse.

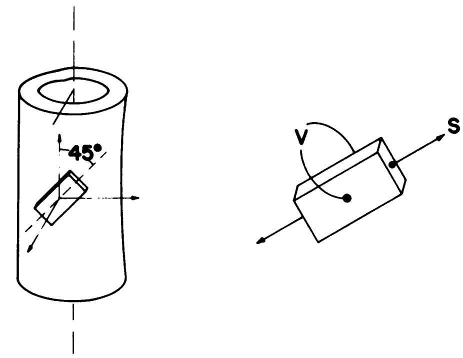

FIGURE 1 Orientation of samples cut from bone and tendon. The deformation S was observed interferometrically when an electrical potential V was applied as shown. The piezoelectric constant is $d = St/V$ were t is the sample thickness.

Calibration is accomplished by connecting the oscillator to the piezoelectric translator whose deflection factor is independently determined by measuring the voltage necessary to increase the mirror separation by precisely one half wavelength.

Differential deformations have been measured to a precision better than 0.1 Å with Perot-Fabry plates whose finesse is about 10, where all thermal and vibrational effects are eliminated by the nature of the synchronous method.

Room temperature measurements were continued with a given sample, initially dried in vacuum at 60°C, over a period of several days during which water from the atmosphere entered the sample. Concurrent measurements of weight and conductivity were used to monitor the water content. Since large changes of the elastic constants and of the electric conductivity and dielectric constant take place, the method was rigorously developed (observations of deformation at zero stress for an applied electric field) to observe only the effects on the piezoelectric coefficient.

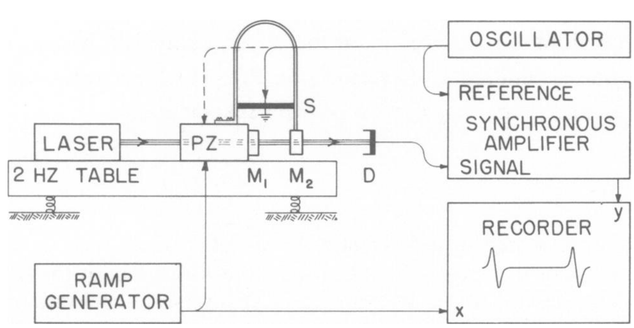

FIGURE 2 Differential Perot-Fabry interferometer $M_1 M_2$ for measuring small piezoelectrically induced deformations in sample S. The synchronous amplifier rectifies the signal from the photodetector D in synchronism with the sinusoidal voltage from the oscillator. The piezoelectric translator PZ slowly moves mirror M_1 through conditions for interference (two such conditions shown on the recorder). The translator is also used to calibrate the sensitivity of the system (substitutional connection shown by dashed line).

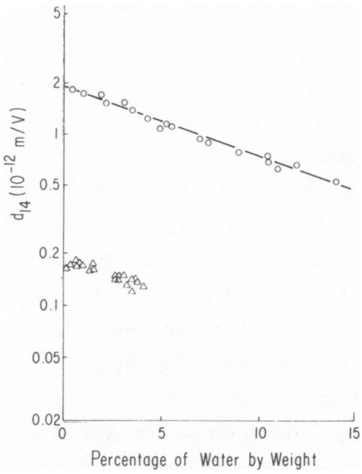

FIGURE 3 The piezoelectric constant of bovine tendon (upper points) and bone (lower points). The perfect exponential decrease signifies a random transitory cancellation of electric dipoles by water molecules. The slope of the upper line may place limits on the average molecular weight of the amino acid residual responsible for piezoelectricity in collagen.

RESULTS AND DISCUSSION

The results are shown in Fig. 3, where the piezoelectric coefficient d_{14} for both bone and tendon are displayed as a function of water content as a percentage of the weight of each sample. The fact that piezoelectricity decreases with water content suggests that the piezoelectric polarization is effectively cancelled by binding of the water to the polar residues responsible for piezoelectricity in collagen. Separate measurements show a small nonexponential resistivity decrease, ruling out changes in conductivity as a possible cause for the decrease in d_{14}.

The fact that the decrease of piezoelectricity is exponential, rather than linear, supports the idea of cancellation by transitory water binding: for small concentrations of water, the decrease is linear, but for higher concentrations, a unit increase in concentration is less effective owing to the decreased probability of finding an uncancelled site. At a given hydration, the differential decrease in piezoelectricity for unit hydration increase is proportional to the number of uncancelled sites, exactly the mathematical expression for a down-going exponential. This interpretation is not in conflict with recent work in this laboratory, which reveals that the electric polarization of collagen increases with water content. The water molecules, being polar, contribute positively to the electret, even though symmetrically bound, while such symmetry reduces piezoelectricity.

Finally, the fact that the piezoelectricity in tendon decreases $1/e$ for approximately each 7% water concentration increase is quantitatively significant. As usual, the decay characteristic of an exponential is interpreted as follows: if the initially linear decrease were continued, the piezoelectricity would be totally cancelled at 7% water concentration. In that hypothesis, the average molecular weight for the cancelled dipole would be about 15 times that of water, or 280. That this is consistent with an amino-acid residue (7) origin of piezoelectricity, even though their weights are less, may be accepted because the cancelling of dipoles is accomplished by water which is shared also with other nonpiezoelectric sites.

Fig. 3 shows that bone piezoelectricity, whose dry value is about 10 times less than dry tendon, also decreases with water content. Although the trend for bone is not well established, Fig. 3 shows that the piezoelectricity of bone probably is higher than that of tendon at the in vivo water concentrations (12% for bone, 50% for tendon).

Unlike tendon the situation is less clear for bone. However, we can offer the following considerations: the ratio of 10 between the value of d_{14} for dry bone and dry tendon is almost entirely owing to the larger mechanical rigidity of the inert mineral component in bone. However, a given weight percentage of water should reduce the piezoelectricity in bone three times as fast as in tendon owing to the known weight fraction of the inert component. Fig. 3 shows that bone piezoelectricity decreases much more slowly, a fact at present not understood.

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