INDUCED PIEZOELECTRICITY
IN ISOTROPIC BIOMATERIAL

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ABSTRACT   Isotropic material can be made to exhibit piezoelectric effects by the application of a constant electric field. For insulators, the piezoelectric strain constant is proportional to the applied electric field and for semiconductors, an additional out-of-phase component of piezoelectricity is proportional to the electric current density in the sample. The two induced coefficients are proportional to the strain-dependent dielectric constant $(d\epsilon/dS + \epsilon)$ and resistivity $(d\rho/dS - \rho)$, respectively. The latter is more important at frequencies such that $\rho\epsilon\omega < 1$, often the case in biopolymers. Signals from induced piezoelectricity in nature may be larger than those from true piezoelectricity.

INTRODUCTION

Materials with no permanent dipole moments, and amorphous materials in which the dipole moments have random orientations, have no true piezoelectricity. Mechanical deformation can cause no first order separation of charge, and conversely, an electric field is not coupled to elastic deformations. However, all materials exhibit an apparent piezoelectricity related to second order effects induced by a fixed external electric field (1).

These induced effects are superposed on the inherent piezoelectricity. In an isotropic material in which there is no inherent piezoelectricity, nor polarization proportional to E^2, one can write the electric polarization P and the mechanical deformation S as functions of the electric field E and the mechanical stress T,

$$P = \eta E + 2\gamma ET, \tag{1}$$

$$S = sT + \gamma E^2, \tag{2}$$

where η, s, and γ are the electric susceptibility at zero stress, the mechanical compliance at zero electric field, and the electrostriction constant, respectively. By regrouping Eq. 1, γ may be interpreted as the stress-dependent electric susceptibility and may be measured that way. However, to demonstrate the apparent piezoelectricity, either one measures the polarization with a constant electric field E and a variable stress T, or one measures the deformation with zero stress and a superposition of a bias field E_o and a smaller variable electric field E, such that the quadratic term γE^2 is linearized $\gamma(E + E_o)^2 \cong E_o^2 + 2\gamma E_o E$. Regrouping Eqs. 1 and 2, we have

$$P = P_o + dT, \tag{3}$$

$$S = S_o + dE, \tag{4}$$

where the constant $P_o = \eta E_o$ and $S_o = \gamma E_o^2$ are caused by the constant bias field. The linear variable terms are characteristic of piezoelectricity. The coefficient of T and E is the coefficient of electric field-induced piezoelectricity and is linearly proportional to the bias field E_o

$$d = 2\gamma E_o. \tag{5}$$

This result appears in classical textbooks (2).

There is an alternate point of view, important in interpreting apparent piezoelectric effects in biopolymers, partially developed in ref. 1. When a sample in film form is stretched, the change in dimensions and the change in the dielectric constant alter the capacitance. The change in capacitance C may be written

$$\partial C / \partial S = C[(1/\epsilon)(\partial\epsilon/\partial S) + 1 - \tau_1 + \tau_2],$$

where ϵ is the dielectric constant. The area increases by a fraction $(1 - \tau_1)S$ and the thickness of the sample decreases by a fraction $\tau_2 S$, with appropriate Poisson's ratios τ_1 and τ_2. The variance in capacitance becomes

$$\partial C / \partial S = C[(1/\epsilon)(\partial\epsilon/\partial S) + 1], \tag{6}$$

using the fact that amorphous materials have $\tau_1 = \tau_2$. When a constant potential V is applied across the film of area A, the apparent piezoelectric strain constant e is

$$e \equiv \partial P / \partial S = (1/A)(\partial/\partial S)(CV) = E_o[(\partial\epsilon/\partial S) + \epsilon], \tag{7}$$

and the induced piezoelectric stress constant d is expressed

$$d \equiv es = E_o[(\partial\epsilon/\partial S) + \epsilon]s, \tag{8}$$

where s is the elastic compliance and E_o is the constant applied field from the constant potential V. The apparent piezoelectric constant varies linearly with the applied field, with a slope larger for polar materials for which the dielectric constant is larger. Comparing Eq. 5 with Eq. 8

$$2\gamma = [(\partial\epsilon/\partial S) + \epsilon]s. \tag{9}$$

An additional effect is expected when the material conducts electricity. We may include the conductivity in Eq. 8 as the imaginary part of the dielectric constant, but it is simpler according to the equivalent point of view that the deformation S changes the resistance across the film by changing the dimensions and by changing the resistivity. The change in electrical resistance R can be written

$$\delta R / \delta S = R[1/\rho)(\delta\rho/\delta S) - 1 + \tau_1 - \tau_2],$$

where the changes in the resistance with strain are owing to the resistivity change, the area increase, and the thickness decrease. For an amorphous material $\tau_1 = \tau_2$

and

$$\delta R/\delta S = R[(1/\rho)(\delta\rho/\delta S) - 1].$$ (10)

Eq. 10 somewhat resembles the strain gauge equation which treats the resistance change of metal alloys in the same direction as the strain, and so involves a Poisson's ratio.

When a constant potential V is applied across the film, the conduction current, as well as the stored charge, is modulated by the strain and the apparent piezoelectric strain constant includes both the effect of changing capacitance and of changing resistance:

$$e \equiv e' - je''$$

$$e' = \epsilon E_o[(1/\epsilon)(\delta\epsilon/\delta S) + 1]$$ (11A)

$$e'' = J_o/\omega[(1/\rho)(\delta\rho/\delta S) - 1]$$ (11B)

where $J_o = E_o/\rho$ is the average current density in the sample, and use has been made of a sinusoidally modulated strain with frequency ω. The current density may also include displacement current densities $(J_o + dP/dt)$ following step function changes in E_o, the so-called thermal polarization and depolarization currents (3). The effect in the second term of Eq. 11 can be called the current-induced piezoelectric effect and will be important in materials for which $\rho\epsilon\omega < 1$.

EXPERIMENTAL METHOD

Fig. 1 shows a block diagram of the apparatus for simultaneously measuring the piezoelectric effects and the electrical conductivity of biomaterials, subject to a constant electric field and to a sinusoidal stress at 20 Hz.
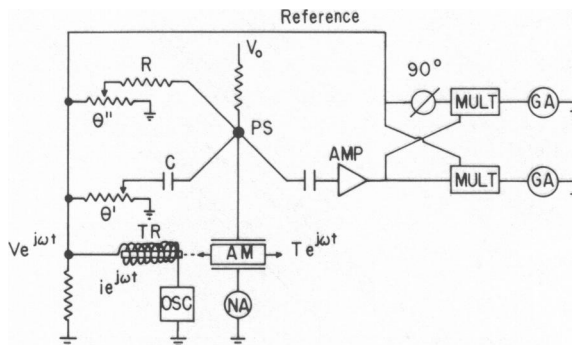

FIGURE 1 Simplified diagram of null method for obtaining the complex piezoelectric stress coefficients $d = d' - jd''$, while simultaneously measuring conduction, polarization, and thermal depolarization currents. Constant, or step-function, voltages are applied at V_o. Currents are read by the nanoperimeter NA. Charge and current at 20 Hz injected through the capacity C and the resistance R, respectively, achieve a null at the summing point PS. Departures from the null are amplified and rectified by the multipliers MULT. The potentiometer fractions θ' and θ'' are adjusted until the galvanometer GA indicate zero.

The nanoamperimeter NA measures the conduction and polarization currents ($J_o + dP/dt$) in a sample film AM subject to a fixed potential V_o. A sinusoidal stress is produced in the film by an electromagnetic transducer TR driven by a 20 Hz oscillator. The piezoelectric voltage across the film is cancelled at the summing point PS by cancelling voltages derived from the transducer driving current and supplied through a capacity C and a resistance R. Any unbalanced 20 Hz voltage on the sample is amplified and led to synchronous detectors whose reference voltages are either in phase, or 90° out of phase, with the transducer driving current. The canceling voltages are determined to null the output of the synchronous detectors by adjusting the potentiometer fractions θ' and θ''.

The experimental values for the real and imaginary parts of the piezoelectric stress coefficient are

$$d = d'' - jd'',$$

$$d' = \theta'(t\omega/A)(\alpha C),$$

$$d'' = \theta''(t\omega/A)(\alpha/\omega R),$$

where t, ω, A are the thickness, width, and electrode area of the sample film, respectively, and the force transducer constant is $\alpha = 2.7 \, \text{V/N}$.

The samples were cut from films typically to dimensions $40 \times 5 \times 0.02$ mm. The gelatin films were made by drying thin layers of aqueous gelatin solution on mercury or aluminum foil. The hydration state could be varied by vacuum drying and by monitoring the weight gain when exposed to room humidity.

The synthetic films are all commercial polymers supplied in the thickness used. For the polar materials the samples were annealed under short circuit at appropriate temperatures
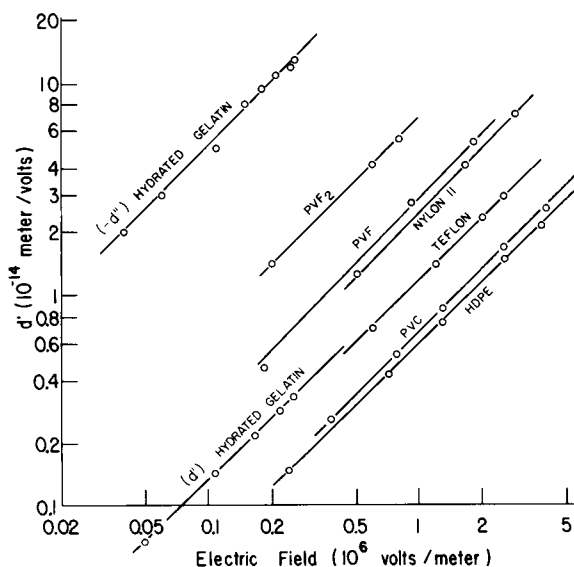

FIGURE 2 The induced piezoelectric stress coefficients in various synthetic polymers and in hydrated gelatin at 20 Hz and 20°C. The large negative imaginary coefficient for hydrated gelatin is caused by the strain modulated conduction current. The field-induced piezoelectricity in the synthetic polymers was reported and analyzed by Zimmerman et al. (1).

to remove intrinsic piezoelectric effects. Electrodes were aluminum deposited on both sides of the films by vacuum evaporation.

RESULTS AND DISCUSSION

Fig. 2 shows the observed induced piezoelectric stress coefficients as a function of the applied electric field. The unit slope of the experimental results plotted on logarithmic scales verifies the linearity of the induced effects. Polar materials, with large dielectric constant have larger proportionality constants as expected. Gelatin is displayed on the same graph, even though its major effect is almost entirely 90° out of phase with those of the synthetic polymers.

Fig. 3 shows a detailed comparison of the induced effects in hydrated gelatin and in a typical synthetic polymer polyvinyl chloride (PVC). The induced piezoelectricity in PVC at room temperature is almost entirely in phase with the applied stress at 20 Hz. The small positive imaginary coefficient d'' represents a delay in alignment of the electric dipoles in response to the applied stress. Ref. 1 treats in detail this electric field-induced piezoelectric effect in synthetic polymers, for which Eq. 8 was used to interpret the observations.

In contrast hydrated gelatin displays an induced piezoelectricity almost entirely 90° out of phase with the applied stress, d'' being negative and almost two orders of
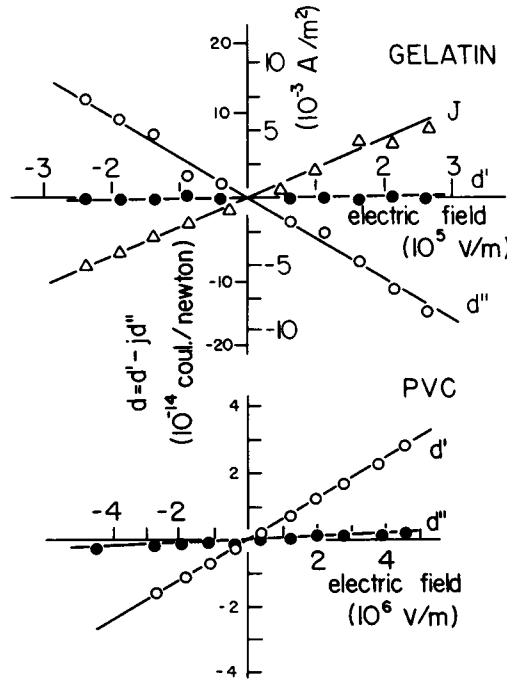

FIGURE 3 Comparison of the induced piezoelectricity in hydrated gelatin and in polyvinyl chloride (PVC) at 20 Hz and 20°C. d'' is proportional to the current density J in hydrated gelatin.
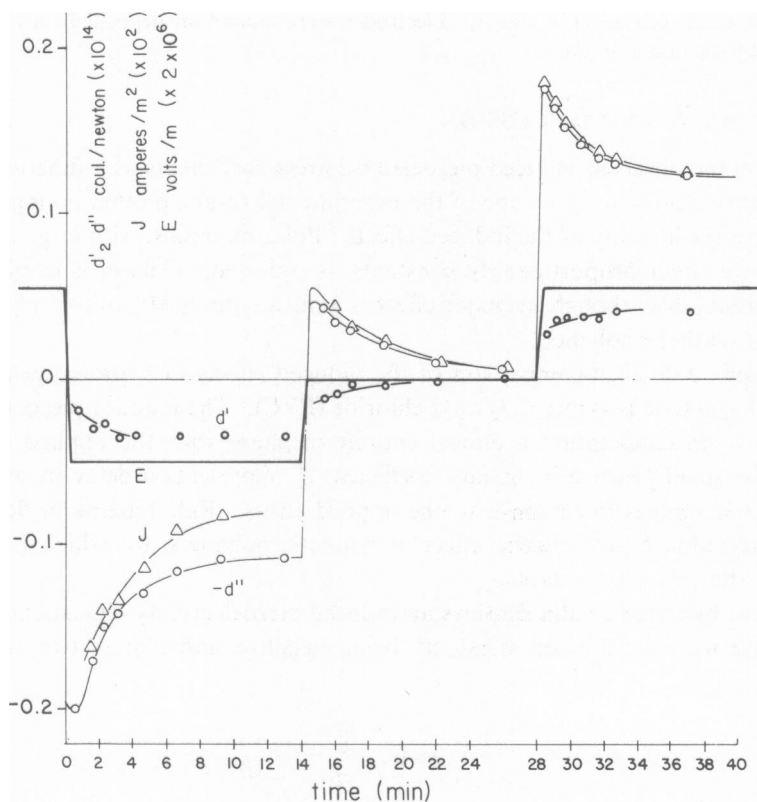
magnitude larger than d'. The real coefficient d' for hydrated gelatin and for PVC are observed approximately in the ratio of their dielectric constants. The negative value of d'' is consistent with Eq. 11 B and shows that $dp/ds < \rho$.

Fig. 3 shows the conduction current density in the gelatin at each applied electric field. The ratio E/J is the resistivity whose value was about 10^8 Ω-m.

The data shown in Figs. 2 and 3 are for constant applied electric fields. For step-function changes in electric field, current-induced piezoelectricity is observed because of the presence of isothermal polarization and depolarization currents dP/dt. Fig. 4 shows coefficients of induced piezoelectricity in gelatin following step function changes in the electric field. Polarization current and an ohmic conduction current are observed when the electric field is established, and a depolarization current is observed when the sample is subsequently short-circuited. The current-induced piezoelectricity d'' displays the same behavior as the current. The field-induced piezoelectric coefficient d' is evident in this sample of lower hydration. Each of these observed variables follows the relaxation of electric dipoles in the material, and observations of the decay constant at two temperatures determine an activation energy, a variation of

the well-known methods of using thermally stimulated discharge currents or low frequency dielectric constant measurements for this purpose.

CONCLUSIONS

The possible biological significance of current-induced piezoelectricity may be assessed by comparing it with intrinsic piezoelectricity, whose measurement and significance have been discussed in a well-referenced review by Fukada (4).

The intrinsic piezoelectric strain constant e_i has been measured for many biological macromolecules, usually in samples of low hydration. Physically, e_i is interpreted as a surface charge density per unit strain. Since strain frequencies in biological systems are usually smaller than the characteristic reciprocal time $1/\rho\epsilon$ in the piezoelectric material or in the adjoining tissues, a peak-to-peak current density $J = 2e_i\omega$ per unit strain is a common result of piezoelectric effects in vivo. Energy is supplied mechanically.

Eq. 11B, and our experimental demonstration of it in hydrated gelatin, shows that the strain modulated resistance causes similar peak-to-valley fluctuations in an average current density J_o supplied by some other energy source. One may compare the strain-produced current density in an intrinsically piezoelectric material with the strain-modulated current density in an amorphous material for equal strains at the same frequency. According to Eq. 11B the fluctuations in current in the two materials will be numerically comparable if $J_o \sim e_i\omega$.

Bone, whose piezoelectricity has now a recognized biological role, has a piezoelectric stress constant $d' = 2 \times 10^{-12}$ C/N when dry and probably about $d' = 6 \times 10^{-14}$ C/N in the natural state (5). This would correspond to a piezoelectric strain constant $e' = 1 \times 10^{-3}$ C/m^2, using a compliance of approximately 6×10^{-11} m^2/N (6). Thus, an amorphous texture carrying an average current density of 10^{-3} A/m^2 would exhibit current density fluctuations comparable to those produced by bone, for equal 1 Hz strains. Currents this size exist, for example in nerve membranes (7). The detection of these fluctuations in the average current could take place in systems where supply and demand of the current-carrying ion are almost equal, and small differences are critical.

Alternatively, where there are equal fluxes of ions of opposite sign across a membrane (no average current) there will be a strain-produced current density across the membrane owing to differing strain-dependent carrier drift velocities. Such an ion flux-induced piezoelectricity exactly resembles true piezoelectricity.

REFERENCES

1. ZIMMERMAN, R. L., C. SUCHICITAL, and E. FUKADA. 1975. Electric field-induced piezoelectricity in polymer film. *J. Appl. Polymer Sci.* **19**:1373.

2. NYE, J. F. 1964. Physical Properties of Crystals. Oxford University Press, London. 257.

3. PERLMAN, M. M. 1971. Thermal currents and the internal polarization in carnaúba was electrets. *J. Appl. Phys.* **42:**2645.

4. FUKADA, E. 1974. Piezoelectric properties of biological macromolecules. *Ad. Biophys.* **6:**121.

5. NETTO, T. G., and R. L. ZIMMERMAN. 1975. Effect of water on piezoelectricity in bone and collagen. *Biophys. J.* **15:**573.

6. REILLY, D. T., A. H. BURSTEIN, and V. H. FRANKEL. 1974. The elastic modulus for bone. *J. Biomech.* **7:**271.

7. HODGKIN, A. L., A. F. HUXLEY, and B. KATZ. 1952. Current-voltage relation in nerve. *J. Physiol.* **1b:**424.