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Piezoelectricity as a Fundamental Property of Wood

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Summary

The piezoelectric effect in wood, i.e. the occurrence of electric polarization under mechanical stress and also of mechanical strain in an electric field, was accounted for by considering the uniaxial orientation of cellulose crystallites in fibers and their monoclinic symmetry. A shear stress in one plane, including the grain direction, produced electrical polarization perpendicular to it. The value of the piezoelectric modulus for wood was approximately one twentieth of that of a quartz crystal.

The chemical treatments which transform the lattice structure from cellulose I to II or III, increased the piezoelectric modulus. However, gamma-ray irradiation up to a dose sufficiently high to decrease the molecular weight had only little influence on the piezoelectric modulus.

The variation with temperature of the phase angle between sinusoidal stress and polarization showed a maximum of advanced phase around room temperature and a maximum of delayed phase at about —100° C. Dielectric and viscoelastic measurements indicated that the former was caused by the dielectric loss due to water at a temperature above freezing and the latter by the viscoelastic loss due to local vibrations of cellulose molecules.

The piezoelectric polarization in wood can be utilized in technical problems such as the measurement of shock velocity in timber. The physiological meaning of the piezoelectrical effect in plants has not been investigated.

Zusammenfassung

Der piezoelektrische Effekt in Holz, d. h. das Auftreten einer elektrischen Polarisation unter mechanischer Spannung und ebenso das Auftreten mechanischer Verformungen in einem elektrischen Feld wird als Folgeerscheinung der einachsigen Orientierung der Cellulosekristallite in den Holzfasern und durch deren monokline Symmetrie erklärt. Es wurde beobachtet, daß eine Scherspannung in einer Ebene, welche in Faserrichtung liegt, eine elektrische Polarisation senkrecht dazu hervorruft. Die Größe des piezoelektrischen Moduls für Holz betrug etwa $\frac{1}{20}$ des piezoelektrischen Moduls eines Quarzkristalls.

Chemische Behandlungen, welche die Gitterstruktur der Cellulose I in diejenige von Cellulose II und III umformen, erhöhen gleichzeitig den piezoelektrischen Modul. Dagegen zeigte eine Behandlung mit γ-Strahlen selbst bis zu einer Dosisleistung, die ausreichte, um das Molekulargewicht zu erniedrigen, nur geringen Einfluß auf den piezoelektrischen Modul.

Die Temperaturabhängigkeit des Phasenwinkels zwischen einer S-förmig verlaufenden Spannung und der Polarisation zeigt ein Maximum der vorauseilenden Phase etwa bei Raumtemperatur und ein Maximum der nachlaufenden Phase bei etwa —100° C. Dielektrische und viskoelastische Messungen ließen erkennen, daß die Dielektrizität auf Grund dielektrischer Verluste von Wasser über 0° C zustande kommt und daß die Viskoelastizität durch viskoelastische Verluste auf Grund örtlicher Schwingungen von Cellulosemolekülen entsteht.

Die piezoelektrische Polarisation bei Holz kann für die Lösung technischer Probleme, wie z. B. bei der Messung der Schallgeschwindigkeit in Holz praktisch eingesetzt werden. Die physiologische Bedeutung des piezoelektrischen Effekts in lebenden Pflanzen ist bisher noch unbekannt.

Introduction

When mechanical stress is imposed on a certain type of crystal such as tourmaline or quartz, an electrical polarization is produced. This is called the direct piezoelectric effect. Conversely, when an electrical field is applied to the crystal, mechanical strain results. This is called the converse piezoelectric effect. Similar effects were found for wood around 1950, and the results of the succeeding investigations were summarized in a book entitled "Piezoelectric Properties of Wood" by Bazhenov [1960]. Galligan [1963, 1965] recently utilized the piezoelectric effect for a non-destructive test method of the strength of wood. The velocity of a shock wave through timber was determined by measuring the piezoelectric potential. From it the mechanical strength of the timber was estimated.

Fukada [1955] proved the existence of the converse piezoelectric effect in wood and continued his study on the piezoelectric properties [Fukada 1965]. He also found the piezoelectric effect in various kinds of polymers, including cellulose derivatives [Fukada, Date, Emura 1967], collagen [Fukada, Yasuda 1957, 1964] and synthetic polypeptides [Fukada, Date, Hirai 1966].

Fundamental Oberservations

The piezoelectric effect in wood may be observed as illustrated in Fig. 1. The z-axis represents the fiber direction in wood. If a shearing stress is applied as indicated by arrows, an electrical polarization takes place in the direction perpendicular to the plane of the stress. The sign of the value of polarization is reversed when the direction of shear is reversed.

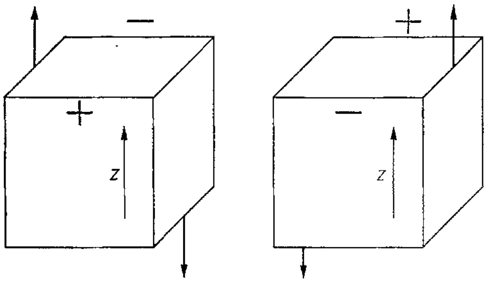

Fig. 1. General scheme to produce piezoelectric polarization in wood.

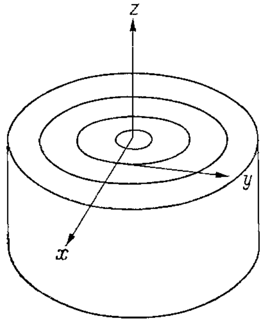

Fig. 2. Rectangular coordinates assigned to wood.

Rectangular coordinates are assigned to the wood structure with the z, x, and y axes representing the longitudinal, radial and tangential directions in a tree trunk respectively (Fig. 2). To study the anisotropy in the piezoelectric effect, a small circular disk was cut in the plane of the z-axis. Thin silver foils were attached as electrodes to both faces by the alcoholic solution of shellac. When one end of the disk was clamped and the opposite end given a sinusoidal oscillation, a sinusoidal electrical polarization was produced between the two electrodes, hence an alternating voltage could be detected between them. By changing the position of the clamps and rotating the disk, the anisotropy of piezoelectric effect was easily observed.

Because a shearing stress produces the largest effect, square plates, cut at an angle of 45° to grain direction, were used for the measurement of temperature variation of the piezoelectric modulus.

Fig. 3 shows the variation of piezoelectric polarization with the angle between directions of pressure and fiber orientation in a specimen of Oregon pine. These results were obtained by rotating the same circular specimen. An anisotropy was clearly observed. Separate measurements were possible on summerwood and springwood because the thickness of the plate was less than 1 mm. A greater effect was observed for summerwood due to its larger density. The dotted lines show the amount of mechanical deformation under constant stress, representing an elastic anisotropy.

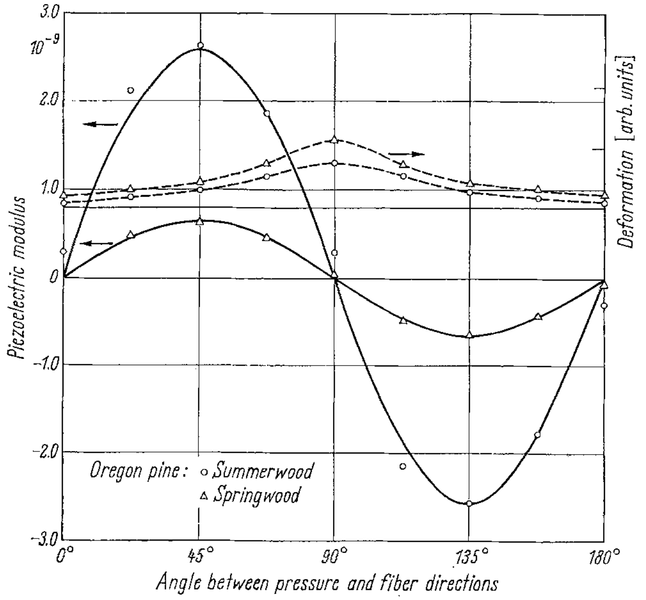

Fig. 3. Anisotropy in piezoelectric modulus and mechanical compliance for summerwood and springwood of Oregon pine.

Tensor Representation of the Piezoelectric Modulus

Relations between electrical polarization and mechanical stress are generally given by the following equations:

$$
\begin{aligned}
P_x &= d_{11}S_x + d_{12}S_y + d_{13}S_z + d_{14}S_{xy} + d_{15}S_{yz} + d_{16}S_{zx} \\
P_y &= d_{21}S_x + d_{22}S_y + d_{23}S_z + d_{24}S_{xy} + d_{25}S_{yz} + d_{26}S_{zx} \\
P_z &= d_{31}S_x + d_{32}S_y + d_{33}S_z + d_{34}S_{xy} + d_{35}S_{yz} + d_{36}S_{zx}
\end{aligned}
$$

where P_x, P_y, P_z represent the polarizations in x, y and z-directions, S_{yz}, S_{zx} and S_{xy} the shear stresses in yz, zx, and xy-planes, respectively. The piezoelectric modulus d_{ij} relates each component of polarization to each component of stress. In general, there are 18 components of d_{ij}'s and they are represented by a piezoelectric tensor as follows:

$$
\begin{array}{cccccc}
d_{11} & d_{12} & d_{13} & d_{14} & d_{15} & d_{16} \\
d_{21} & d_{22} & d_{23} & d_{24} & d_{25} & d_{26} \\
d_{31} & d_{32} & d_{33} & d_{34} & d_{35} & d_{36}
\end{array}
$$

By examination of the geometrical relationship between applied stress and the resulting polarization in wood, the piezoelectric tensor for wood has been determined as follows:

$$
\begin{array}{cccccc}
0 & 0 & 0 & d_{14} & 0 & 0 \\
0 & 0 & 0 & 0 & d_{25} & 0 \\
0 & 0 & 0 & 0 & 0 & 0.
\end{array}
$$

The modulus d_{14} means that shear stress in the yz-plane produces polarization in the x-direction, the modulus d_{25} means that shear stress in the zx-plane produces polarization in the y-direction. Experimentally their magnitudes are nearly the same and their signs are opposite. This fact makes evident that the piezoelectric effect is symmetrical about the z-axis.

It is known that cellulose is crystallized to a fairly large extent and that the unit cell of cellulose crystal belongs to monoclinic symmetry C_2. The piezoelectric tensor for a crystal is determined by the symmetry of the crystal lattice [CADY 1946].

The tensor for a crystal with the symmetry C_2 is

$$\begin{matrix} 0 & 0 & 0 & d_{14} & d_{15} & 0 \\ 0 & 0 & 0 & d_{24} & d_{25} & 0 \\ d_{31} & d_{32} & d_{33} & 0 & 0 & d_{36} \end{matrix}$$

where the z-axis is taken in the direction of the longitudinal axis of the molecules in the crystal. Eight components of the piezoelectric modulus should be finite.

The structure of wood composed of cellulose fibers is very complicated. However, in a first approximation, we assume that the fiber is composed of many numbers of cellulose crystallites, orientated in the same direction, that is the fiber axis, and that such fibers are regularly orientated parallel to the trunk axis. Fig. 4 illustrates the unaxial orientation of cellulose crystallites. The positive end of the z-axis of each crystallite is distributed at random in the axis of symmetry, that is, with the same probability for two opposite directions. The x-axis of each crystallite is distributed at random and uniformly in the plane perpendicular to the axis of symmetry. The piezoelectric modulus for such an assembled system of crystallites can be calculated by taking an average of the moduli of the crystallites. Then it turns out that only d_{14} and d_{25} are finite for the system and that the other moduli become zero due to cancellation of the effect. The values of d_{14} and d_{25} of the system are proportional to the mean value of d_{14} and d_{25} in the single crystal of cellulose. The coefficient of proportion is dependent on density, crystallinity, and degree of orientation.

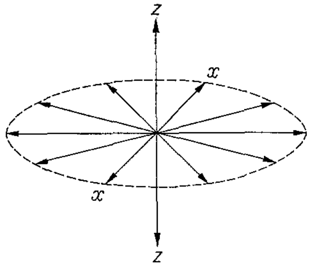

Fig. 4. Unaxial and non polar orientation of crystallites.

The piezoelectric tensor for such an assembly of unidirectionally orientated crystallites is:

$$\begin{matrix} 0 & 0 & 0 & d_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & -d_{14} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0. \end{matrix}$$

This tensor form is identical to that experimentally determined for wood.

It is known that cellulose fibrils twist spirally with a certain angle to the longitudinal axis of the cell. However, if the average is taken for the layers in which fibrils describe a spiral form in alternative directions, the form of the resultant tensor of piezoelectric modulus is the same as derived above.

Table 1 shows examples of the numerical values of the piezoelectric modulus obtained for wood and cellulosic fibers. Quartz crystals are a standard material for piezoelectric experiments. The modulus d_{14} of wood amounts to roughly one twentieth of the d_{11} modulus of quartz. The modulus was also determined from the converse piezoelectric effect by measuring the mechanical deformation in an electric field. The moduli derived from the direct effect and the converse effect agree well within experimental accuracy.

Table 1. *Piezoelectric Modulus* (10^{-9} *c.g.s.e.s.u.*)

		Direct effect	Converse effect
Quartz	d_{11}	65	65
Maple	d_{14}	−2.6	−2.4
	d_{25}	2.8	1.6
Spruce	d_{14}	−5.0	−2.3
Ramie bundle	d_{14}	−8.1	−6.5
Rayon bundle	d_{14}	−0.8	−0.8

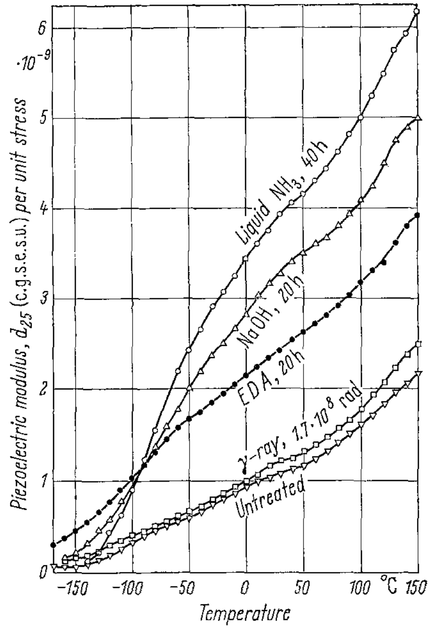

Fig. 5. Variation with temperature of piezoelectric modulus for Hinoki, treated by liquid ammonia sodium hydroxide, ethylene diamine, and gamma ray.

Piezoelectricity and Chemical Modification

Fig. 5 shows the temperature variation of the piezoelectric modulus for Hinoki (*Chamaecyparis obtusa*, Endl.). Over a range of temperature from −170° C to +150° C, the piezoelectric modulus increased with rising temperature, showing variations of the slope at some temperature levels. The treatment of specimens by liquid ammonia, sodium hydroxide and ethylene diamine increases the piezoelectric modulus remarkably. For example, after treatment by liquid ammonia, the modulus at room temperature was approx. three times as large as that observed on untreated wood. On the contrary, irradiation by gamma rays up to a dosage of 1.7×10^8 rad caused only a slight increase of the modulus.

After chemical treatments, the weight of the specimen decreased slightly and resulted in increased density by about 10 percent. However, this increase in effective density cannot explain the two or threefold increase of the piezoelectric modulus. *X*-ray diffraction spectroscopy on treated specimens showed a decrease in the crystallinity of cellulose by less than 10 percent. Neither can the change in crystallinity explain the increase of the piezoelectric modulus. X-ray diffraction spectra showed, however, that the crystal lattice of cellulose has been transformed from cellulose I of natural specimen to cellulose II when treated with sodium hydroxide, and cellulose III when treated with liquid ammonia or ethylene diamine.

Therefore, the increase of the piezoelectric modulus seems to be associated with modifications in the crystal lattice from cellulose I to cellulose II or III. It is well known that the state of hydrogen bonds is quite different in these modifications of cellulose crystals. The author assumes that the piezoelectric effect in cellulose is produced by the displacement or reorientation of dipoles in crystal lattice under external stress. The dipoles are most probably hydroxyl groups (OH) which cause hydrogen bondage inside the crystal lattice. After chemical treatment the crystal lattice is altered and the state of hydrogen bondage becomes entirely different. It appears that the stress-induced orientation of OH groups is much easier accomplished in cellulose II and III than in cellulose I.

It is known that the irradiation by gamma rays causes a degradation of cellulose molecules. At a dose of more than 100 Mrad, the degree of polymerization should have decreased appreciably. However, a decrease in molecular weight would not greatly influence the crystallization or the orientation of crystallites. If the piezoelectric effect is caused by the property of crystallites, the decrease in molecular weight should not much alter the piezoelectric effect.

It may be noticed from Fig. 5 that the slope of curves changes at certain temperatures. This suggests that the molecular motion of cellulose in the amorphous regions would influence the piezoelectric effect. The more detailed study of this problem is reported below.

Temperature Dispersion of Complex Piezoelectric Modulus

Fundamental equations of piezoelectricity are expressed as follows:

$$\begin{aligned} P &= dS + \eta E \\ \gamma &= JS + dE. \end{aligned}$$

When a stress S is given to a substance, a polarization P is produced. At the same time, an electric field E is also caused by the polarization of the substance. The coefficient d is called the piezoelectric modulus and η the electric susceptibility. The converse effect is shown by the second equation. A mechanical strain γ is produced by an applied electric field E and is accompanied by a stress S. The coefficient J is termed the mechanical compliance. The coefficient d for the converse effect is the same as that for the direct effect. If the condition is made that $E = 0$, then, by an experimental procedure, the modulus d can be determined as a ratio of polarization P to stress S.

Since polymeric substances possess a viscoelastic property, it must be anticipated that when stress is applied, electrical polarization does not appear instantly, but arises gradually with time. Therefore, the author treated the piezoelectric modulus as a complex quantity and determined the phase lag between stress and polarization as well as the absolute value of the modulus.

Fig. 6 represents stress and polarization in a vector diagram. The polarization is delayed behind the stress by an angle δ_d. The component of polarization in phase with the stress represents the real part of modulus d' and the component of polarization 90 degrees out of phase with the stress the imaginary part of modulus d''. The ratio of d'' to d' may be expressed as the tangent of δ_d. These relationships are very similar to those encountered with the complex mechanical compliance and the complex dielectric constant.

Fig. 7 shows the variations with temperature of the absolute value of the piezoelectric modulus and of the phase angle between stress and polarization as

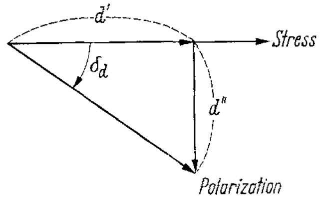

Fig. 6. Vector representation of stress S and polarization P.
$P/S = d^* = d' - j d''$; $\tan \delta_d = d''/d'$.

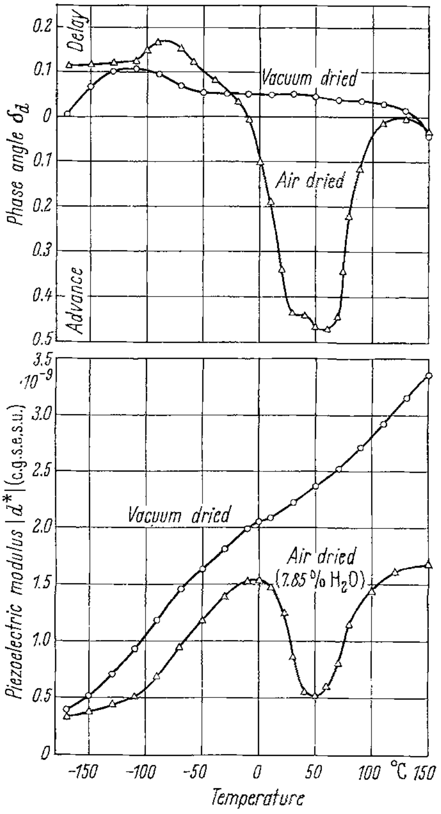

Fig. 7.

Fig. 7. Variation with temperature of absolute value of piezoelectric modulus $|d^*|$ and phase angle between stress and polarization δ_d for Hinoki treated by liquid ammonia.

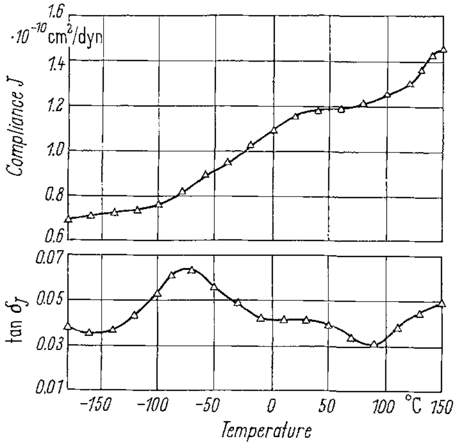

Fig. 8. Variation with temperature of dynamic elastic compliance J and loss tangent $\tan \delta_J$ for air-dried Hinoki treated by liquid ammonia.

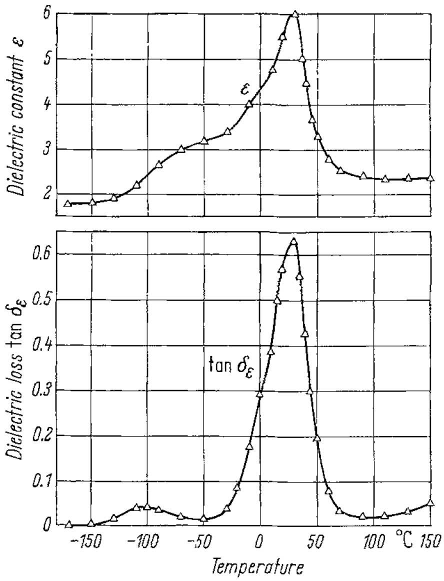

Fig. 9. Variation with temperature of dielectric constant ε and dielectric loss $\tan \delta_\varepsilon$ for air-dried Hinoki treated by liquid ammonia.

measured on a liquid ammonia treated specimen of Hinoki at a frequency of 30 c/s. When the specimen was completely dried in vacuum, the piezoelectric modulus increases with temperature as also indicated in Fig. 5 and the angle of phase lag showed two broad maxima at about —100° C and at room temperature. When the specimen was air-dried and contained about 10 percent moisture, the piezoelectric modulus decreased at room temperature and showed a minimum at about 50° C. The phase angle was delayed at lower temperatures and showed a maximum around —100 °C. At room temperature, the phase angle advanced and showed a maximum. The advance of the phase angle means that the phase of sinusoidally varying polarization proceeds beyond the phase of sinusoidal mechanical stress. This corresponds to a situation in which a stress is applied statically and kept constant and a then resulting piezoelectric polarization relaxes gradually with time from an initial value.

What was the cause that these two peaks of phase angle occurred at —100° C and at room temperature ? Because piezoelectric properties are closely related to elastic and dielectric properties, the viscoelastic loss and the dielectric loss for the same specimen was investigated.

Fig. 8 shows the dynamic elastic compliance and the loss tangent as functions of temperature and measured at about 500 c/s. A maximum occurred at about —100° C for elastic loss. The peak value and the temperature of this maximum correspond closely to those of the piezoelectric loss maximum at low temperature. Therefore, it may be concluded that the maximum of piezoelectric loss at low temperature is caused by a mechanical relaxation in cellulose molecules in the amorphous regions. This relaxation seems to be associated with torsional vibrations of cellulose molecules. A pronounced maximum for the elastic loss around room temperature was not observed.

Fig. 9 shows the temperature variation of dielectric constant and dielectric loss measured at 50 c/s for the same specimen. At low temperature, a small maximum occurred, corresponding to the peak of the mechanical loss due to the rotational vibration of cellulose molecules. At room temperature, the dielectric constant suddenly dropped with a rise in temperature, which indicated the desorption of moisture due to heating. At the same temperature range, a large maximum of dielectric loss was observed which was caused by the leakage conductance of water at a temperature above freezing and its disappearance with drying. The peak value of the dielectric loss corresponded just to that of the piezoelectric loss at room temperature. Therefore, it can be concluded that the minimum of the piezoelectric phase angle at room temperature was caused by the dielectric loss due to moisture. Thus piezoelectric dispersion or absorption with temperature was closely associated with elastic and dielectric relaxations. This should point to a new approach for investigating molecular motion and molecular structure in wood.

Prospects of Piezoelectric Polymers

In order to obtain a view of future prospects for the study of piezoelectricity in wood, a brief account on the piezoelectric effect in polymers other than cellulose should be of interest. The piezoelectric effect has been found in a variety of substances, for example, in bone, cellulose acetate, silk, tendon, and synthetic polypeptides. Bone and tendon which consist mainly of collagen molecules produce a piezoelectric polarization inside the living body when subjected to a mechanical force [FUKADA, YASUDA 1957, 1964; SHAMOS, LAVINE 1963, 1967; BASSETT, BECKER 1962]. Orthopedists have found that when a weak current flows continuously through bone, its growth is accelerated along the path of the current. Therefore, they assume that the piezoelectric effect produced in a bone should have some influence upon its growth mechanism [BASSETT, BECKER 1964; BASSETT 1965]. It seems that investigations of the physiological meaning of piezoelectric properties of cellulose in plant are not being conducted.

Recently the author found that the piezoelectric modulus in thin films of polymethyl-glutamate is twice or thrice as large as that of a quartz crystal. This substance is a simple model compound for proteins and is easily synthesized. A microphone utilizing a thin film of polymethyl-glutamate as a mechano-electric transducer showed a sensitivity and performance similar to ordinary dynamic microphones.

It is hoped that the piezoelectric effects of polymers including wood cellulose which have not been widely investigated so far, would provide many attractive topics for research in the near future.

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