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Piezoelectric Properties of Organic Compounds and Tissues

Własności piezoelektryczne związków organicznych i tkanek

Пьезоэлектрические свойства органических соединений и тканей

The effect of piezoelectricity occurs in anisotropic dielectric materials and it consists in the appearance of electric charges on the walls of the material during its deformation (direct piezoelectric effect) and during the extension or compression of the substance placed within an external electric field (converse piezoelectric effect). The direct piezoelectric effect was discovered in 1880 by Pierre and Jacques Curie when they investigated the influence of mechanical stress on pyroelectric properties of the crystals of quartz, tourmaline, Seignette salt and others. On the surface of the crystals which had been subjected to the action of external mechanical stresses they discovered electric charges and their magnitude was directly proportional to the exerted stresses. In 1881 Lippmann showed theoretically, and the Curie brothers confirmed experimentally, the occurrence of the converse piezoelectric phenomenon. Already the first experiments revealed the very significant properties of the piezoelectric effect. It was also found out that this effect occurred in crystals without the symmetry centre and that the piezoelectric coefficients were the same in both direct and converse effects.

ELEMENTS OF THE PIEZOELECTRIC EFFECT THEORY

The magnitude of the piezoelectric effect depends on the crystallographic directions within the crystal. A description of the piezoelectric phenomenon, taking into account crystal anisotropy, is obtained by means

of vector and tensor calculuses. This method makes it possible to include the dependence of the piezoelectric effect in a given direction on all the components of the electric field and deformation. The direct piezoelectric effect is described by a system of linear equations which determine the relations between the produced electric polarization P (vector) in the crystal, caused by the external mechanical stress δ (second-order tensor):

$$P_m = d_{mij}\, \delta_{ij} \qquad (m,\ i,\ j = 1,\ 2,\ 3) \tag{1}$$

Symbols 1, 2, 3 correspond to directions x, y, z.

The values of the components of the stress tensor, $\delta_{ij} = \dfrac{\Delta F_i}{\Delta S_j}$, depend on the values and directions of the external forces (ΔF) acting on particular surfaces (ΔS) of the element cut out of the crystal. Stresses δ_{ij} for $i = j$ are known as normal stresses, while those for $i \neq j$ — as shear stresses. Index i indicates the direction of the acting force while index j determines the direction perpendicular to the crystal wall subjected to the acting force. Coefficients d_{mij} combine the second-order tensor with the vector and in this way they form the third-order tensor (16); they are known as piezoelectric moduli (coefficients).

Equation (1) may also be developed into

$$P_1 = d_{111}\ \delta_{11} + d_{112}\ \delta_{12} + d_{113}\ \delta_{13} + d_{121}\ \delta_{21} + d_{122}\ \delta_{22} + d_{123}\ \delta_{23} + d_{131}\ \delta_{31} + d_{132}\ \delta_{32} + d_{133}\ \delta_{33} \tag{2}$$

Equations for the polarization components P_2 and P_3 may be developed analogically. Equation (2) indicates that the total number of piezoelectric moduli is 27. In most cases mechanical stresses do not cause a rotation of the crystal around the axis passing through its centre, which results in the dependence $\delta_{ij} = \delta_{ji}$. Owing to this, the number of the components of tensor δ_{ij} decreases to 6, while that of independent piezoelectric moduli — to 18. The converse piezoelectric effect is described by the following equation:

$$\eta_{ij} = d_{mij}\, E_m \qquad (m,\ i,\ j = 1,\ 2,\ 3)$$

where:

η_{ij} — denotes the tensor components of the crystal strain,

E_m — components of the intensity of the electric field.

The equations which describe piezoelectric properties of crystals may be simplified by substituting matrix calculus for the tensor calculus. The expression of piezoelectric moduli by a matrix calculus consists in describing them with two indexes instead of the three indexes of the tensor calculus. The manner of changing their expression is shown in the following few examples:

d_{111} (tensor)$=d_{11}$ (matrix), $d_{122}=d_{12}$, $d_{233}=d_{23}$, $d_{322}=d_{32}$, $d_{123}=d_{132}=1/2d_{14}$,
$$d_{213}=d_{231}=1/2d_{25}$$
The full matrix of the tensor of piezoelectric moduli has thus the form:

	δ_{11}	δ_{22}	δ_{33}	δ_{23}, δ_{32}	δ_{31}, δ_{13}	δ_{12}, δ_{21}
P_1	d_{11}	d_{12}	d_{13}	d_{14}	d_{15}	d_{16}
P_2	d_{21}	d_{22}	d_{23}	d_{24}	d_{25}	d_{26}
P_3	d_{31}	d_{32}	d_{33}	d_{34}	d_{35}	d_{36}

The above matrix makes it possible to understand the physical sense of individual piezoelectric moduli. Let us assume now that the crystal is subjected only to the action of the normal stress in the direction of axis z, that is, only $\delta_{23}\neq0$. We obtain then a system of equations: $P_1=d_{13}\,\delta_{33}$, $P_2=d_{23}\,\delta_{23}$, and $P_3=d_{33}\,\delta_{33}$. The value of d_{33} describes the longitudinal piezoelectric effect, that is, the polarization produced in the direction of the acting stress; values d_{13} and d_{23} describe the transversal effect, that is, the polarization produced perpendicularly to the stress. The nine coefficients on the right-hand side of the matrix determine crystal polarization in various directions produced by the action of shear stress.

The piezoelectric effect is most often described by giving the values of piezoelectric moduli d_{mij}. Choosing the dependences among other pairs of variables which characterize this effect (P_m, δ_{ij}, E_m, η_{ij}), we obtain four kinds of piezoelectric coefficients:

d_{mij} — which expresses polarization P_m as a function of stress δ_{ij} and of strain η_{ij} as a function of the intensity of the electric field E_m.

e_{mij} — which determines polarization P_m as a function of strain η_{ij} and stress δ_{ij} as a function of the intensity of the electric field E_m.

g_{mij} — which represents the intensity of the electric field E_m as a function of stress δ_{ij} and strain η_{ij} as a function of polarization P_m.

h_{mij} — which describes the intensity of the electric field E_m as a function of strain η_{ij} and stress δ_{ij} as a function of polarization P_m. Thus, the full set of equations describing the direct and converse piezoelectric effects is the following:

$$P_m = d_{mij}\,\delta_{ij} \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\text{3a}$$
$$\eta_{ij} = d_{mij}\,E_m$$
$$P_m = e_{mij}\,\eta_{ij} \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\text{3b}$$
$$\delta_{ij} = -e_{mij}\,E_m$$
$$E_m = -g_{mij}\,\delta_{ij} \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\text{3c}$$
$$\eta_{ij} = g_{mij}\,P_m$$
$$E_m = -h_{mij}\,\eta_{ij} \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\text{3d}$$
$$\delta_{ij} = -h_{mij}\,P_m$$

These relations may be illustrated diagrammatically by means of a scheme shown in Fig. 1.

dielectric
properties

elastic
properties
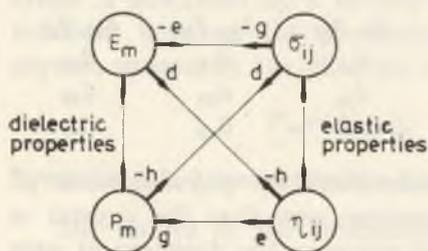
Fig. 1. Types of piezoelectric coefficients

The transformation of the reference system in respect to the symmetry element may produce a change in the signs of the coordinates of the system and thus also an accompanying change in the signs of the piezo-electric moduli. If a crystal has a symmetry centre, then the transformation of the reference system in respect to this centre will produce the following alteration in the coordinantes of this system:

$$x \rightarrow -x', \quad y \rightarrow -y', \quad z \rightarrow -z'$$

Applying these changes to the indexes of the piezoelectric moduli we obtain:

$$m \rightarrow -m, \quad i \rightarrow -i, \quad j \rightarrow -j,$$

whence, after the transfer of the sign resulting from the product of the indexes in individual components of tensor d_{mij} we obtain:

$$d_{mij} = -d'_{mij} \tag{4}$$

Equation (4) is fulfilled when the moduli occurring in it are equal to zero. Hence, it also indicates that all the piezoelectric moduli of the crystal with a symmetry centre are equal to zero, which has been experimentally confirmed. By the application of the method described above, that is, by the transformation in respect to other elements of crystal symmetry such as axes or surfaces, one may show the piezoelectric moduli of those crystals which are non-zero.

METHODS OF INVESTIGATING THE PIEZOELECTRIC EFFECT

The piezoelectric effect may be studied by static, quasi-static and dynamic methods [13, 20]. The static methods, based on the measurements of the electric charges produced by the application of stress to the sample

(direct effect) or on the measurement of the strain produced by an external electric field (converse effect), were first worked out by the Curie brothers and then further developed in the course of subsequent investigations. The electric charge is measured by a ballistic electrometer. Applying a reference capacitor, alternately turned on and off, one may also take measurements with other types of electrometers, for instance, with the tube electrometer. Studies on the crystal strain occurring in the converse piezoelectric effect employ interferential methods, capacitance method (measurement of the capacity change in plate capacitor with one plate connected to the crystal), or the piezoelectric method (the strain on the examined crystal produces a direct piezoelectric effect in another crystal).

The quasi-static methods consist in applying stresses or electric fields which change with the acoustic frequency. Taking advantage of the capacitance method, one measures changes in the capacity of the condenser included as an element in the resonance circuit of the generator.

Still, in studies on the piezoelectric effect most common are the dynamic methods which consist in measuring the frequency of resonance vibrations of the samples cut out of piezoelectric crystals. The advantages of the dynamic methods include: great sensitivity resulting from the resonance character of the measurements, employment of precise electronic systems for the detection of the phenomenon, possibility of examining samples of relatively small dimensions and of high electric conductivity. The dynamic method generally concern the converse piezoelectric effect. The piezoelectric crystal is excited to vibrate by the electric field and it transforms some part of the electric field energy into the energy of mechanical vibrations; the relation between the value of the mechanical energy and that of the electric energy reaches its maximum with the resonance and the larger the piezoelectric modulus of the crystal, the greater the magnitude of the effect. The basic qualitative methods for the detection of piezoelectric resonance include: the effect of stabilizing the generator vibration at the frequency which corresponds to that of the natural vibrations of the piezo-crystal sample, and the effect of the change in the equilibrium of the bridge containing the piezoelectric element at the resonance frequency. The methods of series and parallel resonances are the basic quantitative methods for the investigations in the piezoelectric resonance [13, 20].

In piezoelectric substances placed within an alternating electric field there occurs a phase shift δ between mechanical vibrations and changes in the intensity of the electric field. This effect is quite convenient to be described by introducing complex piezoelectric moduli. The piezoelectric modulus d_{ij} is thus expressed as $d_{ij} = d'_{ij} - id''_{ij}$, where $d''_{ij}/d'_{ij} =$

$= \text{tg} \delta$. The introduction of a complex dielectric constant facilitates the analysis of the electric circuits substitute of piezoelectric substances since the calculations in a.c. circuits are principally carried out also on complex numbers [5].

Studies aiming at a determination of the numerical values of piezoelectric moduli are usually carried out on samples cut in the direction appropriately oriented in respect to crystallographic axes. The ways of cutting the sample and applying stress or external electric field depend on the type of piezoelectric moduli under examination [13]. Results of some measurements, mainly with the application of shear stress, may conveniently be presented within another reference system by carrying out a transformation of the original reference system through a transformation matrix formed of directional cosines [13, 16].

PIEZOELECTRIC PROPERTIES OF ORGANIC COMPOUNDS

The piezoelectric effect was discovered in industrial polymers (nylon, vinyl polychloride), synthetic polypeptides (poly-L-alanine, poly-γ-methyl-glutamate), biopolymers (nucleic acids, proteins), tissues (bone, tendon, cartilage, blood vessels, skin). Some exemplary values of the piezoelectric modulus d_{25} for several industrial polymers and synthetic polypeptides are set up in Tab. 1 [12]. The examination of the latter [8] was

Tab. 1. Piezoelectric constant of industrial polymers and synthetic polypeptides at room temperature

Polymer	d_{31} $[10^{-13} \text{ mV}^{-1}]$
Polyvinyl fluoride	67
Polyvinyl chloride	100
Nylon	5

Polypeptide	d_{25} $[10^{-13} \text{ mV}^{-1}]$
Poly-L-alanine	10
Poly-γ-methyl-L-glutamate (α)	20
Poly-β-benzyl-L-aspartate (α)	0.33

carried out in order to obtain some basis for an explanation of the piezoelectric effect mechanism in biopolymers. The apparatus for the studies on piezoelectricity had been designed in such a way as to allow a determination of all the four kinds of piezoelectric moduli d, e, g, h [12] (Fig. 2).

The piezoelectric properties of organic compounds were examined by the quasi-static method by applying sinusoidal vibration of the frequency of $f = 10$ Hz and then measuring both real and imaginary parts of piezo-
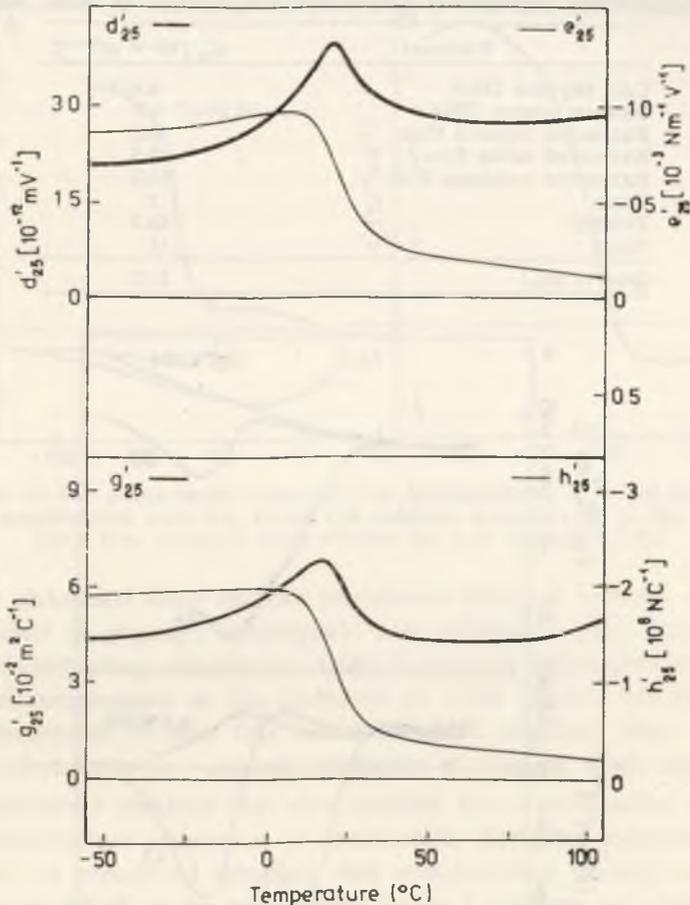
Fig. 2. The temperature dependence of the real part of the piezoelectric constants
for oriented poly-γ-benzyl-L-glutamate

electric moduli. All the values which characterize the piezoelectric effect
(equation 3) have been measured by the apparatus as determined voltages
registered by the recorder. The measuring chamber also made it possible
to take measurements at different temperatures and humidities, which
is most significant in the analysis of the piezoelectric effect in organic
compounds. By way of example, some results of these studies are pre-
sented in Tab. 2 and Figs. 3 and 4.

Many studies on the piezoelectric properties were carried out on
samples of DNA and its salts. F u k a d a and A n d o [11] reported re-
sults of measurements taken on dried films formed from ethanol solutions
of DNA. In order to obtain a desired orientation of the DNA molecules
the films were stretched in an appropriate direction. Measurements were

Tab. 2. Piezoelectric constant of dehydrated biopolymers at room temperature

Polymer	d_{25} [10^{-13} mV^{-1}]
Calf thymus DNA	0.017
Salmon sperm DNA	0.1
Extracted myosin film	0.1
Extracted actin film	0.5
Extracted collagen film	33.3
Bone	2
Tendon	23.3
Horn	18
Quartz (d_{11})	21.7
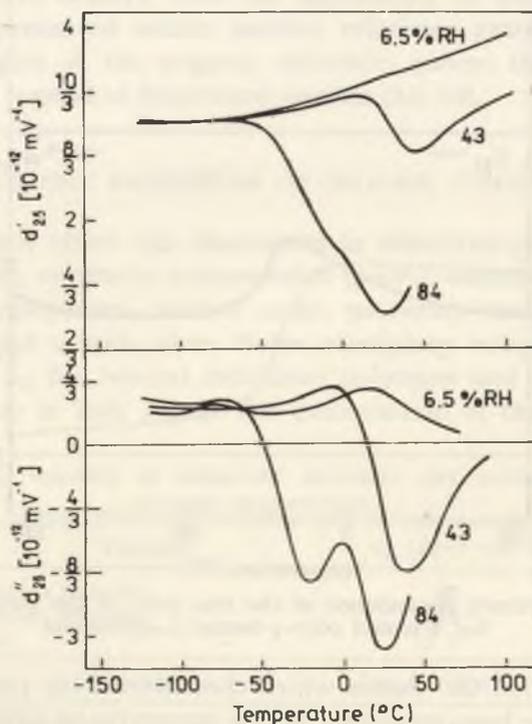
Fig. 3. The temperature dependence of the piezoelectric constant $d_{25} = d'_{25} -$ i d''_{25} for the oriented collagen tape equilibrated with 6.5, 43 and 84% relative humidity

then taken by applying sinusoidal shear stresses and recording the electric polarization together with the phase angle between the voltage and the stress. The piezoelectric modulus d_{14} ($d_{14} = d'_{14} -$ i d''_{14}) was determined. The obtained value of modulus d'_{14} was of the order of $0.3 \cdot 10^{-14}$ which, when compared with the d'_{14} value of proteins, was quite small, thus indicating low crystallinity of the DNA samples. In 1955 D u c h e s n e et al. [6] carried out measurements which determined the piezoelectric properties of NaDNA, RNA and nucleoproteins. Some years
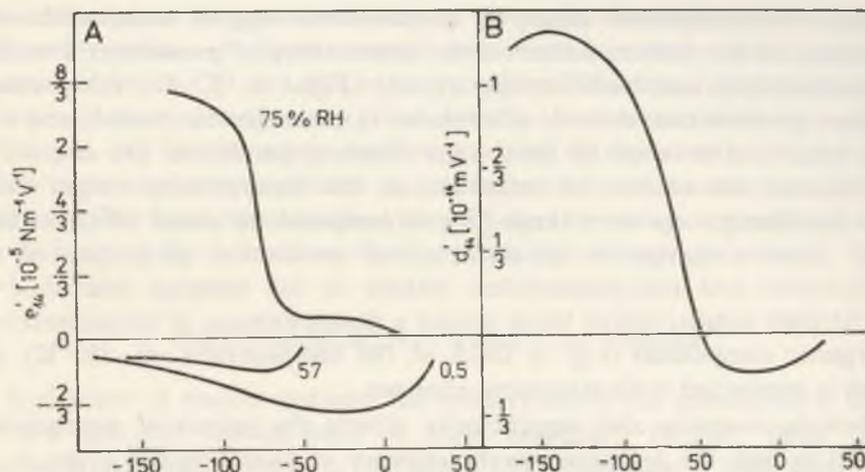
Fig. 4. Plots of the piezoelectric constants vs. temperature; A — for salmon sperm DNA film equilibrated with 0.5, 17 an 75% relative humidity, B — for calf thymus DNA film obtained from ethanol gel and elongated 1.6×

later they extended their studies to include DNA of various origins and such proteins as myosin, actomyosin and collagen. The measurements consisted in detecting absorption in the frequency interval of 33—35 MHz in samples compressed at the pressure of 7,000 N/cm². All the samples showed absorption within this interval which implied that conclusion that piezoelectricity is a general property of nucleic acids and proteins.

The resonance method was also applied for a qualitative determination of piezoelectric properties in aminoacids [21]. The experiments were carried out on powdered samples, and concentrated mainly on checking the L isomers which occur in proteins. Table 3 presents selected examples

Tab. 3. Comparison of experimental and theoretical piezoelectricity for amino-acids

Amino-acid	Theoretical piezoelectricity	Experimental piezoelectricity
L-alanine	+	+
L-asparagine H_2O	+	+
L-cysteine	+	+
L-glutamine	+	—
L-proline	+	+
L-valine	+	—

of some out of several scores of obtained results and their comparison with theoretical predictions based on crystallographic examinations which made it possible to determine elements of symmetry of a given compound; a majority of the experimental results reveals a fair agreement with the theoretical predictions.

Many measurements taken on piezoelectric organic compounds concentrated on the determination of the dependence of piezoelectric moduli on temperature and humidity [6, 11, 12] (Figs. 2, 3, 4). Temperature changes produce considerable alterations in piezoelectric moduli and may even lead to a reversal of their sign. These dependences are caused by the thermic movements of molecules in the temperature range where modulus changes are very large (Fig. 4, temperature about $50°C$) or they result from a change in the electric and mechanical properties of the piezoelectric and non-piezoelectric phases of the samples examined [6, 12]. At high temperatures there occurs a disappearance of piezoelectricity in organic compounds (e.g. in DNA at the temperature of $323°K$) [6], which is connected with structural changes.

Sample moisture also significantly affects the values of piezoelectric properties and the temperature dependence of these moduli (Figs. 3, 4). Among others, the effect of moisture was examined in collagen, keratin and DNA films. The effect is important in view of the possible occurrence of piezoelectricity in living organisms. In keratin and collagen the values of piezoelectric moduli decrease with increasing humidity [12]; in DNA films the humidity dependence of the moduli is slight at low levels of humidity but when the latter exceeds 60%, the value of the piezoelectric modulus greatly increases and its sign is reversed. Changes in keratin and collagen which occur at low humidity are explained by the effect of absorbed water on the electric and mechanical properties of the non-piezoelectric phase, while at high humidity they are accounted for by a change in the electric properties of the piezoelectric crystalline structures. The considerable increase in the values of the piezoelectric moduli in DNA samples at the humidity of 75% [12] indicates a basic increase in the ordering of the samples. This result is confirmed by X-ray examinations and absorption measurements at infra-red light, which revealed that the molecular structure of DNA becomes crystalline over the humidity level of the order of 60% and it is not so highly ordered below this level. At humidity level over 60% water molecules are absorbed by the bases and they stabilize the double DNA helix; in consequence, the dipoles of the bases containing CO and NH groups considerably increase the piezoelectric effect in DNA sample. The low values of modulus d_{14} discovered in dried DNA samples [11] confirm the above conclusions and they are also connected with the low crystallinity of the sample examined by X-rays.

The origin of piezoelectricity in organic compounds and biopolymers is ascribed to the mechanical movement of charged groups within the crystal or within the molecules. The piezoelectricity of DNA is regarded as caused by a change in the arrangement of the polar groups of their

bases. The cause of piezoelectricity in polymers is sought in the stress-
-induced rotation of dipols around asymmetric carbon atoms, e.g. the
rotation of dipols CO and NH in polypeptides. The interrelation observed
between piezoelectricity and optical activity further confirms this expla-
nation [12, 21]. In fibrous molecules, such as collagen, cellulose, keratin,
which form single-axis systems due to transverse bonds, the piezoelectric
effect results from the translocation of electric charges connected with
the turning of the transverse bonds, probably of hydrogen bonds.

THE PIEZOELECTRIC EFFECT IN TISSUES

A number of results indicate the occurrence of the piezoelectric effect
in hard and soft tissues, such as bone, cartilage, tendon, skin, blood
vessels, muscles. Experiments confirmed the occurrence of both direct and
converse effects and in several cases piezoelectric moduli were de-
termined. It turned out that the occurrence of the effect was basically
connected with the presence of proteins of fibrous structure, e.g. of
collagen.

The first remark about the existence of the piezoelectric effect in
tissues was reported in 1941 by M a r t i n [15] who observed electric
polarization in a boundle of hair and wool subjected to mechanical stress.
The greatest number of measurements concerning the piezoelectric effect
in tissues was taken from bones. Histological, radiographic and electron
microscopy examinations revealed a highly ordered structure of bone in
which the most significant element is the parallel arrangement of collagen
fibres. In 1957 and 1964 there appeared reports by F u k a d a and Y a-
s u d a [7] who presented results of measurements of the piezoelectric
effect in dried femur bone of man and ox and who determined the piezo-
electric modulus d_{14} there. In 1963 Shamos et al. discovered by the static
method the occurrence of the piezoelectric effect in dried bone samples
taken from various anatomic parts [18]. Even more interesting are the
results of experiments carried out on wet bones since these are the con-
ditions similar to those of bones *in vivo*. Anderson and Eriksson made
measurements of the piezoelectric effect d for dried and wet bones taken
from bovine femur and placed in such a way that axis 3 was directed
along the bone axis [2]. A matrix of piezoelectric moduli d is presented
below as calculated for dried samples in the units of $1/3 \cdot 10^{-12}$ mV^{-1}=
$= 10^{-8}$ c.g.s.; the calculations take into account the transformation of the
coordinates by the angle of $10°$, which corresponds to the angle formed
by collagen fibres and the longitudinal bone axis:

$$d_{11} = +0.740 \qquad d_{12} = 0.035 \qquad d_{13} = -0.662$$
$$d_{21} = -1.368 \qquad d_{22} = 0.000 \qquad d_{23} = +1.368$$
$$d_{31} = +0.079 \qquad d_{32} = +0.197 \qquad d_{33} = +0.380$$

These results are comparable to those obtained by Fukada for pure collagen, which confirms the basic role of this protein played in the piezoelectric properties of the bone. For a wet bone, maintained in Ringer solution, the values of piezoelectric moduli d were larger and they depended on the pH values of the solution. Some exemplary results obtained for bone kept in Ringer solution are shown by the tensor of absolute values of piezoelectric moduli below:

$$
\begin{array}{ccc}
0.54 & 6.70 & 1.33 \\
8.90 & 1.12 & 0.96 \\
28.00 & 11.50 & 2.50
\end{array}
$$

Reinish and Nowick examined the piezoelectric properties of bone as a function of the sample moisture by applying a sinusoidally alternating force in the frequency range of 3.2—5.6 MHz [17]. They determined the piezoelectric moduli d_{14} and d_{31} for samples taken from human femur bone, measuring the direct and converse piezoelectric effects (Fig. 5).
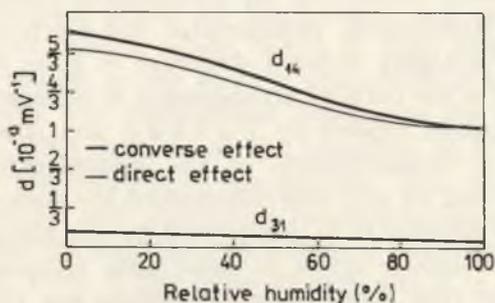
Fig. 5. Piezoelectric coefficients of bone as a function of relative humidity measured at 5600 Hz

The values of the moduli obtained for the direct effect proved the same as those obtained for the converse effect and they both decreased with increasing moisture of the sample (as opposed to those in report [2]). The value of modulus d_{14} is of the order of 10^{-12} mV^{-1} and it is greater by one order of magnitude than the value of modulus d_{31}. Marino and Becker measured the piezoelectric effect in bone and tendon in their physiological conditions of humidity but at a non-physiological temperature ($-25°$C) [14]. The freezing of the sample facilitated the measurements since it eliminated high electric conductivity of water which poses serious difficulties in measuring the piezoelectric effect. The measure-

ments of the converse piezoelectric effect revealed that frozen tendon and bone were piezoelectric. The hydration and freezing of the samples reduced the value of the measured modulus d_{14} for bone making it almost twice as small ($d_{14}=1.8 \cdot 10^{-13}$ mV^{-1} for dry bone at temperature $+24°$C, and $d_{14}=0.97 \cdot 10^{-13}$ mV^{-1} for wet bone at temperature $-25°$C). The structure of collagen is very stable and that is why, the authors expressed the opinion that temperature rise to physiological values could not cause changes drastic enough to eliminate the piezoelectric properties.

Some of the papers deal with the influence of the stream potential on the results of piezoelectric measurements in wet bone samples. In bone between collagen fibres there are pores which can be penetrated by water solutions during the deformation of the bone, thus producing stream potentials. The basic property of the stream potential is its pH dependence. Anderson and Eriksson found this dependence of obtained results on pH [2] and they concluded that the potential measured at the deformation of collagen itself was exclusively the stream potential, and when measured at the deformation of the bone it should be largely ascribed to the stream potential. The presence of hydroxyapatite which, besides collagen, is the other basic component of bone, changes the conditions of water absorption by collagen and thus it preserves then a less symmetrical form, revealing piezoelectric properties even in the hydrated state. Some later works, however, based on precise resonance measurements [14, 17], did not confirm this significant role of the stream potential, indicating the fact that hydrated bone samples showed purely piezoelectric properties.

Fukada and Hara observed the piezoelectric effect in such tissues as trachea, intestines, ligament, aorta and vena [9]. The measurements were taken by the quasi-static method at the frequency of 20 Hz on dried, cylindrical samples. The values of the piezoelectric moduli d_{14} changed from that of the order of 10^{-14} mV^{-1} for intestine and trachea to that of 10^{-13} mV^{-1} for ligament. They stated anisotropy of piezoelectric moduli, that is, the dependence of their values on the direction of applied force (Fig. 6) and the decrease in the values of the moduli after drying the samples.
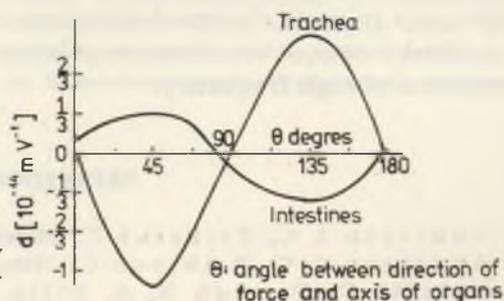
Fig. 6. Anisotropy of piezoelectricity in dehydrated trachea and intestines

Anisotropy indicates the ordered arrangement of piezoelectric fibers of elastin and collagen in examined tissues. The obtained results also implied (Fig. 6) that collagen fibers had a different direction of arrangement in intestine (axial) than in trachea (circumferal); this conclusion is in keeping with the data obtained from anatomic examinations. The piezoelectric effect was also discovered in the muscles [10] by measuring the values of modulus d_{14} (the maximum value $0.4 \cdot 10^{-12}$ mV^{-1}) and proving its anisotropy. The examined muscles consisted mostly of the fibres of actin and myosin which implied the conclusion that these proteins were piezoelectric; still, their piezoelectric modulus is by several times smaller than that of dried collagen ($2 . 10^{-12}$ mV^{-1}).

The piezoelectric effect was also found in human skin, jaw bone, dentin, while tooth enamel was lacking that property [19]. This finding seems to confirm the conclusion that piezoelectric properties of biological structure are connected with the presence of oriented proteins of fibrous structure occurring in tissues.

Interest in the studies on the piezoelectric properties of tissues even increased after the discovery of several facts showing that the electric field affects the development of bone and that the healing of bone fractures may be stimulated electrically [3, 4]. It is supposed that local electric fields, created by charges on the surface of bone under stress, may influence the orientation and distribution of ions and polarized molecules. They even consider a possibility of piezoelectricity occurring at the reaction of touch, of piezoelectric properties of cell membranes, and of the important role of piezoelectricity in forming clots at damaged blood vessels [19].

The estimation of the magnitude of the piezoelectric voltage produced in a blood vessel in the functioning organism gives the value of $3 \cdot 10^{-9}$ V with the assumed pulse frequency of 1 Hz [9]. Such voltage corresponds to the intensity of th current of $3 \cdot 10^{-12}$ A between the two surfaces of blood vessel walls. The current of such a small intensity reveals no physiological effects. The electric current induced piezoelectrically may reach the intensity of the micro-ampere order and of physiological significance only in some abnormal situations such as, for instance, the rupture of a blood vessel, when there may occur great stresses or periodical deformations of high frequency.

REFERENCES

1. A n d e r s o n J. C., E r i k s s o n C.: Nature 218, 166 (1968).
2. A n d e r s o n J. C., E r i k s s o n C.: Nature 227, 491 (1970).
3. B a s s e t t C., P a w l u k R. J., P i l l a A. A.: Science 184, 575 (1974).

4. B e c k e r R. O.: Nature 235, 109 (1972).
5. C h e ł k o w s k i A.: Fizyka dielektryków, PWN, Warszawa 1979.
6. D u c h e s n e J., D e p i r e u x J., B e r t i n c h a m p s A., C o r n e t N., v a n d e r K a a J. M.: Nature 188, 405 (1960).
7. F u k a d a E., Y a s u d a I.: Jap. J. Appl. Phys. 3, 117 (1964).
8. F u k a d a E., D a t e M., H i r a i N.: Nature 211, 1079 (1966).
9. F u k a d a E., H a r a K.: J. Phys. Soc. Jap. 26, 777 (1969).
10. F u k a d a E., U e d a H.: Jap. J. Appl. Phys. 9, 844 (1970).
11. F u k a d a E., A n d o Y.: J. Polymer Sci. 10, 565 (1972).
12. F u k a d a E.: Ann. N. Y. Acad. Sci. 238, 7 (1974).
13. K r a j e w s k i T.: Własności piezoelektryczne kryształów, in: Zagadnienia fizyki dielektryków, WKŁ, Warszawa 1970.
14. M a r i n o A. A., B e c k e r R. O.: Nature 253, 627 (1975).
15. M a r t i n A. J. P.: Proc. Phys. Soc. 53, 186 (1941).
16. N y e J. F.: Własności fizyczne kryształów, PWN, Warszawa 1962.
17. R e i n i s h G. B., N o w i c k A. S.: Nature 253, 626 (1975).
18. S h a m o s M. H., L a v i n e L. S., S h a m o s M. I.: Nature 197, 81 (1963).
19. S h a m o s M. H., L a v i n e L. S.: Nature 213, 267 (1967).
20. S m o l e ń s k i G. A., K r a j n i k N. N.: Ferroelektryki i antyferroelektryki, PWN, Warszawa 1971.
21. V a s i l e s c u D., C o r n i l l o n R., M a l l e t G.: Nature 225, 635 (1970).

STRESZCZENIE

Artykuł zawiera przegląd badań eksperymentalnych i teoretycznych dotyczących piezoelektrycznych własności związków organicznych (DNA, polipeptydy, aminokwasy, białka) i tkanek (kość, ścięgno, skóra, naczynia krwionośne, tchawica). Omówiono rodzaje współczynników (modułów) piezoelektrycznych i sposoby ich wyznaczania oraz przedyskutowano niektóre możliwości wyjaśnienia piezoelektryczności związków organicznych i tkanek. Przedstawiono wpływ temperatury i wilgotności na zmianę modułów piezoelektrycznych.

РЕЗЮМЕ

В работе произведен обзор экспериментальных и теоретических исследований пьезоэлектрических свойств органических соединений (ДНК, полипептиды, аминокислоты, белки) и тканей (кость, сухожилие, кровеносные сосуды, дыхательное горло). Представлены значения пьезоэлектрических коэффициентов (модулов) и методы их измерения. Обсуждаются также некоторые идеи объясняющие пьезоэлектричество органических соединений и тканей. Рассмотрено влияние температуры и влажности на изменения пьезоэлектрических модулов.