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PIEZOELECTRIC EFFECT IN COMPOSITE IMPLANTS FOR REPLACEMENT OF BONY TISSUE

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We developed "IKVOBAN-U" composite polymer implants to replace defects in bony tissue and fill large bone cavities. The presence of piezoelectric properties in the developed implants whose parameters are close to those of biological objects is revealed. Tests carried out on animals and the use of model media showed that the piezoeffect is preserved after prolonged holding in these media.

Very high requirements are imposed on biocompatible polymer materials used as implants. The most important of these are biological inertness and the time of the retention of basic mechanical and physicochemical properties under conditions of the constant effect of the enzymatic system of a living organism. These problems are of special importance when compact bony tissue that carries a load is to be replaced. There is another poorly known aspect of the problem which should be taken into account when developing artificial materials intended for implantation. This is the property of natural electrical polarization of living systems.

It is known that any process in bone manifesting itself on a mechanical-deformation level is accompanied by the appearance of a difference in electric potentials [1]. For the first time, molecular notions about the essence of electrical phenomena in biological objects were advanced in the middle of the last century by E. Duboua-Raymon in his hypothesis known as the electromolecular theory [2]. More than 90% of living matter consists of polar molecules of proteins, nucleic acids, lipids, hydrocarbons, and water, i.e., the main mass of a living system is represented by bound electrical charges (dipoles). The basic idea of the Duboua-Raymon theory was that the dynamics of polar molecules was of paramount importance in biological electrogenesis. By the beginning of the 1970s, two fundamental facts were established: the presence of natural electric polarization of bound charges as a universal property of living matter and the presence of a quasiconstant bioelectric field. Due to this, living (and dead) biological objects possess piezo- and pyroelectric effects and peculiar architectonics of the axes of polarization in tissue [3]. An important feature of the piezoelectricity of living tissue is a higher value of their piezoelectric coefficient as compared with dehydrated dead tissue [4], and also the presence of this property in living tissue due to vital processes.

Bony tissue, which is a special form of connective tissue with calcified intercellular matter, is a living object, in which continuous internal destruction and restoration of biochemical and structural components occurs [5]. It also possesses pyro- and piezoelectric effects [6]. The energy accumulated by stressed bony tissue in the form of the fields of inherent stresses, when added to those appearing in the bone under physiologic loading, exerts a substantial effect on metabolic processes in bony tissue [7, 8].

The results of investigations of thermally stimulated depolarization of the bony tissue of higher animals point to the fact that the charge density of the bones (10^{-8} C/cm^2) is in order of magnitude comparable with the polarization reserve of good electret materials [9]. The authors of [10] proved experimentally that the electric fields of polymer electrets can exert a biological effect at the supermolecular and cellular levels under the conditions that actually exist in living tissue. Therefore, when selecting materials for endoprosthetics of human internal organs a great deal of attention is paid to polymer electrets. According to the available information [11], endoprostheses

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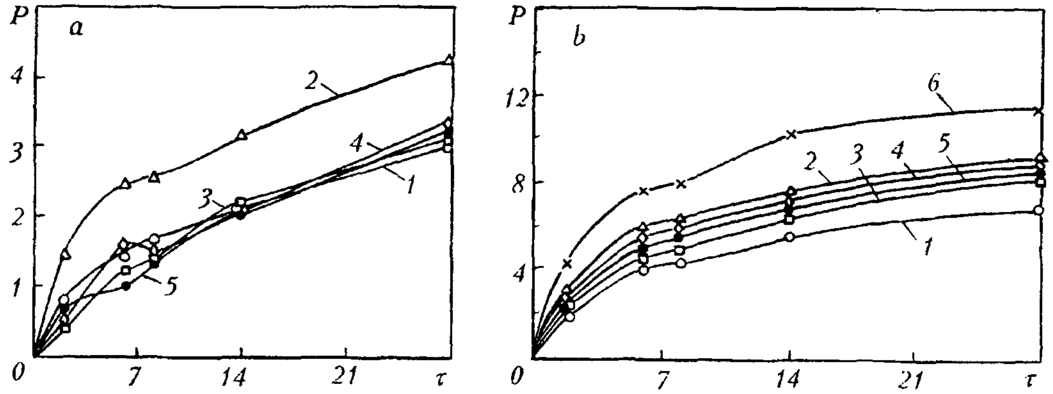

Fig. 1. Kinetic curves of swelling of the composite implants IKVOBAN-U1 (a) and IKVOBAN-U2 (b) in a 2%-solution of citric acid (1), 3%-solution of lactic acid (2), 2% sodium hydrocarbonate (3), 0.4% isotonic solution of sodium chloride (4), a 1/5000 solution of furacillin (5), and a 0.4%-solution of potassium hydrophosphate (6).

made of polymer electrets that have an electric-potential distribution over the surface with a gradient of 01.–0.3 V/mm stimulate osteosynthesis and shorten the time needed for the regeneration of tissue.

At the Institute of General and Inorganic Chemistry (IGICh) of the National Academy of Sciences of Belarus, together with the Minsk State Medical Institute (MSMI), investigations are being carried out to develop and investigate biocompatible polymer composites for reconstructive maxillofacial surgery. Composite implants of different compositions (IKVOBAN-U1 and IKVOBAN-U2) have been developed for replacement of bone defects formed as a result of the removal of bony tissue and trauma, increasing the height of alveolar processes in the jaw, and arthroplasty of the mandibular joint [12].

The development is based on a fundamentally new approach to the formation of polymer compositions that are reinforced with element-containing fibers; it is based on regulation of the physicochemical processes occurring at the filler-polymer phase interface [13, 14]. Phosphorocarbonic fibers developed at the IGICh of the National Academy of Sciences of Belarus were used in the composite implants. The fibers were introduced into a binder as 5-mm-long pieces. Composite implants were obtained by compression moulding and free forming [15]. Preliminarily conditions were revealed under which one observes reactions of chemical interaction between the surfactant centers of the phosphorocarbonic fibers and the reactive groups of the binder that lead to the formation of an interphase layer with a supermolecular structure that differs from the structure of the fiber surface and from that in the volume of the composition. Due to the formation of a chemical bond on the phase interface and subsequent propagation of the reaction into the interstitial space of the fibers, a monolithic spatially sewn polymer structure is formed with rigidly bound and uniformly distributed, over the volume of the composition, phosphorus-containing fragments of the chain. This kind of monolith has high chemical stability against various aggresive media. In particular, in media that imitate the natural medium of implants, it swells only partially (Fig. 1). The strength of the bonds formed between heterophase components of the composition is also evidenced by the high stability of the implants developed against a heat shock under drastic conditions of thermocycling from the liquid nitrogen temperature to positive temperatures (above +100°C).

Since polymer implants must be as close as possible to living biological tissue to ensure normal vital activity of the organism, we, along with investigations of the physicochemical and biomedical properties of the materials developed, studied the possibility of the appearance of an electrical potential under the conditions of their deformation. We also investigated a biological object provided by a department of the MSMI (an allogene rib transplant). We determined the piezoelectric parameters by the method of static loading under conditions of uniaxial compression according State Standard GOST 12370-80. The essence of the method is the measurement of the charge that appears on the surface of a specimen on application (or removal) of static load [16]. The measuring system included a laboratory hydraulic press, a C8-13-type general-purpose oscillograph (storage), measuring electrodes, and dielectric insulation. Cylindrical specimens with a diameter of 10–15 mm and a height of from 2

TABLE 1. Basic Characteristics of IKVOBAN Polymer Implants after Holding in Model Media and Implantation Tests on Animals for 12 Months

Implant Medium	Medium	$\rho\cdot10^3$	$\nu\cdot10^3$	$Z_0\cdot10^6$	d	$\frac{K\cdot10^{-7}}{\sqrt{E}}$	$E\cdot10^{10}$	$\tau_r\cdot10^{-6}$
IKVOBAN-U1	Before implantation	1.46	2.28	3.33	$6.5\cdot10^{-15}$	0.02	0.76	1.84
IKVOBAN-U1	Femur of a guinea-pig	1.50	2.80	4.07	$1.0\cdot10^{-13}$	0.38	1.18	2.16
IKVOBAN-U2	Before implantation	1.36	2.30	3.14	$2.92\cdot10^{-15}$	0.009	0.72	78.6
IKVOBAN-U2	Femur of a guinea-pig	1.39	1.93	2.63	$8.95\cdot10^{-15}$	0.023	0.52	52.9
IKVOBAN-U2	3%-solution of lactic acid							
	Before loading	1.36	1.93	2.63	$1.72\cdot10^{-14}$	0.043	0.51	43.4
	Holding for 30 days	1.58	1.93	2.63	$3.68\cdot10^{-14}$	0.093	0.51	43.4
	After holding and drying	1.36	2.07	2.82	$3.13\cdot10^{-15}$	0.008	0.58	73.8
IKVOBAN-U2	0.4% isotonic solution of NaCl							
	Before loading	1.36	2.07	2.82	$5.35\cdot10^{-15}$	0.015	0.58	70.9
	Holding for 30 days	1.39	2.07	2.82	$1.1\cdot10^{-14}$	0.029	0.60	70.9
	After holding and drying	1.36	2.07	3.20	$1.2\cdot10^{-14}$	0.037	0.75	77.4

to 10 mm and strictly parallel planes were placed between the electrodes, and then the entire system was put under a hydraulic press. The area of the specimen to which a mechanical load was applied was smaller than the area of the electrodes. The load applied to the specimen (0.6–20 mPa) was removed suddenly at the start of the oscillograph sweep. The potential difference appearing on loading the specimen was determined from the number of divisions by which the electron beam of the oscillograph was deflected, with account for the attenuation factor. The time base of the oscillograph was within 0.5–1 division per second. The cathode-ray tube of the oscillograph operated in the storage regime. The oscillograph input for the signal was switched to the position of conductive coupling. The method is particularly attractive for determining charges in deformation of piezoelectric crystals that have a rather high conductivity, and it is convenient due to the possibility of observing and storing the entire dynamics of the piezoelectric effect, with allowance for residual polarization. Using the measuring system, we determined the piezoelectric parameters of the well-known piezoelectric material TsTs-19. The discrepancy of the results from those given in [17] does not exceed 5%.

The investigations showed that the IKVOBAN-U composites have a piezoelectric effect. The basic characteristics of the materials are presented in Table 1. Taking into consideration the complex but not yet completely understood structure of the carbon fibers themselves, it is difficult at the present time to draw final conclusions concerning the dominating factor that determines the piezoelectric properties and their changes under the conditions of the formation of carbon fiber composite implants. At the same time, the great deal of statistical material obtained and its comparative analysis with the data of physicochemical investigations of the compositions allow one to say the following. The form of the signal and the magnitude of the appearing charge depend on the ingredient composition (Fig. 2, curves 1 and 2), on the length of the fibers used in the compositions, and also on the means of formation and temperature-time regime of the processing of the compositions.

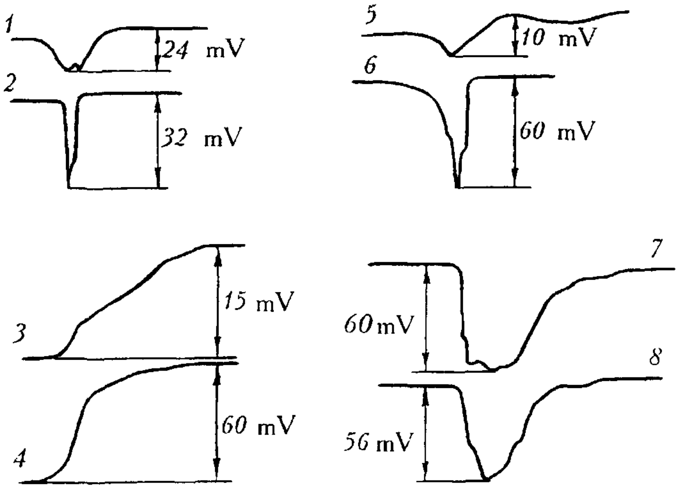

Fig. 2. Piezoelectric effect manifesting itself in deformation of the composite implants IKVOBAN-U1 (2) and IKVOVAN-U2 (1, 3-8) discretely reinforced with fibers of length ≈ 5 mm (3) and ≈ 1 mm (4) produced by the method of free formation (5) and under pressure (6) during heating under conditions of compression moulding (1) and subsequent additional thermal treatment (7). Static loading in the longitudinal (7) and normal (8) directions.

TABLE 2. Physical and Mechanical Properties of IKVOBAN-U2 Polymer-Composite Implants Depending on the Conditions of Formation

Characteristics	Propertties of compositions obtained by the method of	
	free formation	compression moulding
Density, kg/m^3	1160–1230	1400–1450
Porosity, %	22.5–24.5	12.5–15.9
Elastic modulus, N/m^2·10^{10}	0.71–0.84	0.76–1.2
Destructive strain on compression, mPa	63.4–72.0	80.0–137.0
Specific shock viscosity, kJ/m^2	8.1–8.9	9.3–12.0

According to the data of physicochemical investigations, the formation of composites under conditions of thermal compression moulding leads to a decrease in porosity and accordingly to an increase in the density of the composition and also to an increase in all of their physical-mechanical characteristics in comparison with the composites obtained under conditions of free forming (Table 2). An adequate dependence is also observed for the charge that appears on a specimen under loading (Fig. 2, curves 5 and 6). An increase in the time of thermal treatment of the compositions, especially in the case of additional hardening after compression, is not essential for increasing the charge on a specimen (Fig. 2, curves 1 and 7). As to the length of the fibers introduced into the compositions, according to the data obtained, it is preferable to use shorter fibers under all other comparable conditions of the production of composites (Fig. 2, curves 3 and 4). The latter can be explained by the possibility of a more uniform distribution of discrete fibers throughout the volume of the composition and by the resulting formation of a rather homogeneous structure of the composite. In these cases, specimens of the same composition obtained under the same conditions manifest isotropy of their piezoelectric properties: the contours of the sweeps and the magnitudes of the potential difference observed in uniaxial compression of specimens along and normal to the load applied in formation of the compositions coincide closely (Fig. 2, curves 7 and 8).

Numerous experiments made it possible to find conditions for the production of polymer composites under which there is virtually complete identity of the form of the signals that appear in composites and in living bony tissue in measurements in the direction of the main carrying load (Fig. 3, curves 2 and 3). In some compositions,

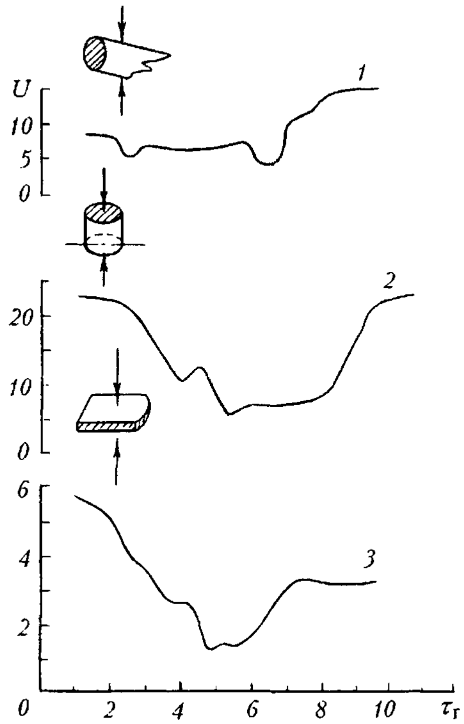

Fig. 3. Piezoelectric effect manifesting itself in uniaxial compression of bony tissue in the transverse (1) and longitudinal (2) directions (σ_{com} = 0.6 mPa) and composite implant IKVOBAN-U2 (3) (σ_{com} = 20 mPa).

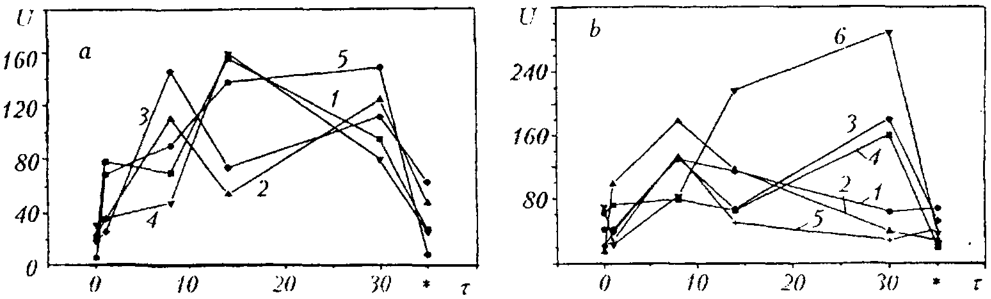

Fig. 4. Change in the electric potential on the surface of the polymer-carbon implants IKVOBAN-U1 (a) and IKVOBAN-U3 (b) on exposure to model media: a 0.4% isotonic solution of sodium chloride (1), 3%-solution of lactic acid (2), 2%-solution of citric acid (3), a 1/5000 solution of furacillin (4), 2%-solution of potassium hydrocarbonate (5), and 0.4%-solution of potassium hydrophosphate (6), (*), after removal and drying.

residual polarization is present, i.e., the composites display the property of mechanoelectrets. This is a rather important characteristic for the polymer implants obtained, since it is known that electrets usually feature an antithrombogenic property, which is preserved for a long time on multiple deformation.

We also studied the dynamics of the piezoelectric parameters on exposure of the polymer implants to media that imitate the natural medium: 2%-solution of citric acid, 3%-solution of lactic acid, a 0.4% isotonic solution of sodium chloride, 2%-solution of sodium hydrocarbonate, 0.4%-solution of K_2HPO_4, and also a 1/5000 solution of furacillin. The investigations showed that holding of implants in model media leads to changes in the form and magnitude of the signal; the potential difference increases substantially (Fig. 4), the area of sweeping is increased, and the electret state on exposure of composites to the media is preserved. A general tendency for an increase of the piezoelectric modulus and of the coefficient of electromechanical coupling also appears. After removal of the composites from the media and subsequent drying, the parameters do not return to their initial values (see Table

Fig. 5. Piezoelectric effect manifesting itself in the composites IKVOBAN-U2 before carrying out the implantation test (1), after removal from the organism of an animal (12 months) (2) and subsequent drying (3).

1). The changes observed can be explained by swelling of the composites in the model media, which leads to structural rearrangements on different microlevels. The kinetic curves of the swelling of the polymer implants IKVOBAN-U1 and IKVOBAN-U2 are presented in Fig. 1. It is seen that the process proceeds most intensely in the first days, then it slows down, and after 30–45 days the curves form a plateau. At the same time, the piezoelectric parameters of the composites are also stabilized.

Naturally, investigations with model media cannot represent the true picture of the behavior of an implant in a living organism. On introduction of composites into biological objects, processes of interaction of living and nonliving matter are certain to occur. As a result, a change in the surface potential of the implant introduced into the organism can be observed. Precisely this manifested itself in the investigations. An implantation test was run on animals. IKVOBAN-U1 and IKVOBAN-U2 were introduced into the muscle tissue of the femur of guinea-pigs and into the body or lower jaw of dogs. With the implantation test lasting for a year signs of a systematic effect were not recorded. The characteristics of the implants removed from the bodies of the animals are presented in Table 1. When comparing these characteristics with those obtained on exposure of implants to model media it is seen that an increase in the piezoelectric modulus and in the coefficient of electromechanical coupling is also observed, the impedance of the material and the elastic moduli change within the same ranges. The piezoelectric effect of the implants after their removed from a living organism is shown in Fig. 5. As is seen from the figure, the contour of the signal changes little. However, the potential difference increases by a factor of 4–5, but after holding in a drying cabinet the values are restored to their initial levels. Morphological investigations showed that a distinct connective tissue capsule is formed around the implanted materials, which indicates the high biocompatibility of the polymer composites developed.

It should be noted in conclusion that the biocompatibility of polymer implants is a concept that includes a wide range of mechanical, physicochemical, and biophysical aspects of the interaction of a polymer composite with living tissue. The data obtained in the course of investigations are as yet of a statistical character. At the same time, the problem of the manifestation of a bioelectret state in processes of vital activity and the prospects for its practical use are given much attention at present. Therefore, the revealed fact that the polymer-composite materials IKVOBAN-U possess a piezoelectric effect, which relates to one of the fundamental properties in the structural organization of living systems, represents a very timely and self-sustained aspect of the problem of implantation of artificial materials which requires deep and thorough investigation.

NOTATION

P, degree of swelling, %; τ, time of holding in media, days; ρ, density, kg/m^3; v, speed of ultrasound, m/sec; Z_0, wave resistence, N·sec/m^3; d, piesomodulus, C/N; K, coefficient of electromechanical coupling; E, elastic modulus, N/m^2; τ_r, time of dielectric relaxation, sec; U, difference of potentials, mV; σ_{com}, strength limit in compression, mPa.

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